

ABSTRACT

Title of Dissertation: ELECTRIFIED HIGH-TEMPERATURE
MANUFACTURING AND APPLICATIONS
IN ENVIRONMENTAL SCIENCE

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Engineering

High temperature processes hold great potential for material and chemical manufacturing. On the one hand, high temperature can help overcome energy barriers and thus effectively convert precursors to desired products. On the other hand, high temperature can also boost the reaction rate and improve synthesis efficiency. Recent development of electrified high temperature technologies by our group further revealed the important role played by non-equilibrium conditions on nanomaterial and chemical syntheses. For example, Joule-heating of carbon-based materials through a programmable electrical signal can offer spatial and temporal temperature profiles, which can be used to manipulate the chemical reaction pathways. For another example, tunable heating duration and quenching rates can be used to achieve a range of compositions and structures of nanoparticles. In this dissertation, two specific applications of the electrified high temperature technology will be explored, including: (1) Thermal shock synthesis of multi-

elemental nanoparticles as selective and stable catalysts; and (2) Efficient biomass upgrading via pulsed electrical heating.

Supported nanoparticle (NP) catalysts are widely used for various reactions. However, it remains challenging to synthesize high quality NPs with accurate morphology and structure control. In this part of the research, NP catalysts with morphology or structural design were prepared by high temperature thermal shock methods. Ultra-small and high-loading carbon supported Pt₃Ni NPs: Strong electrostatic effect was introduced between metal salts and carbon particles that can largely improve anchoring and dispersion of the precursors, thereby achieving high NP loading (40 wt%) as well as small NP size and good distribution (1.66 ± 0.56 nm). This method is not only limited to bimetallic NPs synthesis or NPs on carbon black but can be extended to a range of NP compositions on various substrate materials, thus providing a general strategy for developing ultrafine and high-loading NPs as electrocatalysts for various reactions.

Sustainable aviation fuels (SAFs) are essential to meet future air travel demand while reducing the carbon footprint. Among many potential feedstocks to produce SAFs, lignin stands out as it is an abundant and renewable aromatic biopolymer that is usually treated as a waste material from the paper industry. However, converting lignin to SAFs by conventional thermochemical processes has been challenging due to poor control on the reaction pathway which leads to undesired product distribution. In this study, a programmed electrified heating method was designed and used to break down large lignin molecule to small aromatic molecules with targeted product distribution. A controlled heating step offers sufficient energy input to break down lignin molecules to smaller fragments without excessive secondary reactions toward undesired species such as coke. The lignin thermal decomposition products were evaluated as

potential precursor for SAFs generation. This process can be further extended to process other biomass materials such as algae and sawdust to value-added chemicals.

ELECTRIFIED HIGH-TEMPERATURE MANUFACTURING AND
APPLICATIONS IN ENVIRONMENTAL SCIENCE

by

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Dedication

To my parents, who support all my choices without holding back.

To my late grandfather, who inspired me to live an adventurous life.

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Chapter 1: Introduction

1.1 High-temperature manufacturing and challenges

1.1 Introduction of high-entropy alloys (HEAs)

A new alloying method to form single-phase solid solution alloys of five or more principal elements with near-equi-molar compositions was first introduced independently by two research groups in 2004 and the concept of high-entropy alloys (HEAs) was proposed by Yeh *et al*¹. In general, there are two definitions of HEAs based on either entropy or compositions. The following is the brief introduction of the two definitions. (1) Entropy-based definition. The total mixing entropy of the HEA solid solution system is the sum (see Equation (1)) of configurational entropy (ΔS_{mix}^{conf}), vibrational entropy (ΔS_{mix}^{vib}), magnetic dipole entropy (ΔS_{mix}^{mag}), and the electronic randomness entropy (ΔS_{mix}^{elec})². For an equimolar alloy system, in which the mixing entropy is dominated by the configurational entropy, the ΔS_{mix}^{conf} is calculated based on the relationship between entropy and complexion by Equation (2) below:

$$\Delta S_{mix} = \Delta S_{mix}^{conf} + \Delta S_{mix}^{vib} + \Delta S_{mix}^{mag} + \Delta S_{mix}^{elec} \quad (1)$$

$$\Delta S_{mix} = \Delta S_{mix}^{conf} = -R \sum_{i=1}^n c_i \ln(c_i) = -R \sum_n \frac{1}{n} \ln \frac{1}{n} = R \ln(n) \quad (2)$$

$$T_m \Delta S_f = \Delta H_f \quad (3) \quad \Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \quad (4)$$

n is the number of elements, c_i is the concentration of component i and R is the gas constant, 8.314 J/K·mol. Figure 1.1(a) is a graphic demonstration of Equation (2), and it is obvious that the configurational entropy increases as the number of elements in the system increases. The Gibbs free energy of the transformation process from

intermetallic compounds to single phase solid solution is described by Equation (4). To determine the configurational entropy at high temperature for enthalpy compensation, the enthalpy of the mixing process needs to be properly estimated. Based on Richards' rule, the entropy change per mole from solid to liquid during melting, ΔS_f , is about one gas constant R for metals. And the enthalpy change or latent heat per mole, ΔH_f , can be correlated with ΔS_f by the Equation (3). ΔH_f is about one twelfth the energy required to destroy all bonds in the solid, a mixing entropy of R per mole in an alloy state would be sufficient to decrease the mixing Gibbs free energy by an amount of RT at high temperatures³. Configurational entropy of a ternary equimolar alloy is slightly higher than $1R$ and that of a quinary alloy is higher than R by 61%. Thus, it is reasonable to consider that $1.5R$ is large enough to compete with mixing enthalpy, and R and $1.5R$ are set as the border lines for medium-entropy and high-entropy alloys as shown in Figure 1.1(b)³. (1) Composition-based definition. A broader definitional is that HEAs are alloys containing at least five principal elements, each having the atomic percentage between 5% and 35% and the atomic percentage of each minor element, if any, is less than 5%³.

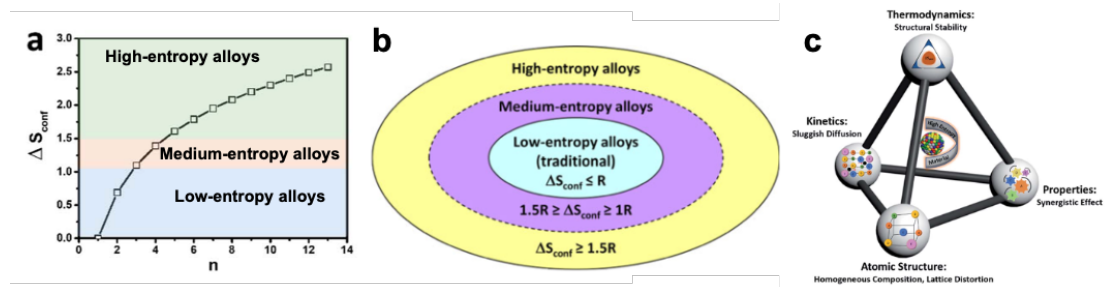


Figure 1.1 (a) Effect of equimolar number on the mixing entropy of the system. (b) Definition of low-, medium-, high-entropy alloys based on configurational entropy. (c) Schematic of the four effects of HEAs.

Unlike conventional alloys, HEAs have a complicated composition of five or more principal elements and a solid-solution phases stabilized by their significantly high entropy of mixing compared to intermetallic compounds, especially at high temperatures. The co-existence of multiple principal elements in HEAs leads to complicated microstructures and various potential properties⁴. The four core properties can be summarized in (Figure 1(c)): (1) High-entropy effect. This is the main property of HEAs as implied by the name. Thermodynamically, the high-entropy effect could interfere with complex phase transformation and enhance the formation of a simpler solid solution phase structure³. (2) Lattice distortion. In a microstructure level, the crystal lattice of HEAs is composed of atoms with different sizes randomly occupying lattice sites. These slightly unbalanced sites of the lattice and random positions of atoms lead to severe lattice distortion⁴. (3) Sluggish diffusion. The lattice distortion of HEAs would delay atomic movement and replacements, and results in another effect called sluggish diffusion that could also slow down phase transformation kinetically⁴. (4) Cocktail effect. Under the influences of all three prementioned effects, HEAs have excess quantities of properties than predicted due to the mixture and this is called the cocktail effect³. The synergetic mixture of elements in HEAs gives them excellent features and potentials for multiple functional materials applications⁴.

During early years, the development of HEA materials were mainly focused on bulk materials with nanocrystalline or amorphous microstructures. Recently, high-entropy nanoparticles (HEA NPs) synthesis has been gaining more and more interests due to their beneficial properties in the nanoscale. HEA NPs could offer large surface

area with a broad range of catalytically active sites⁵. Moreover, the incorporation of multiple elements can decrease the noble metal composition that leads to high material utilization efficiency⁶. Another main advantage of HEA NPs over bimetallic or trimetallic nanoparticles is the maximization of configurational entropy, which endows the resultant materials with extraordinary physicochemical and mechanical properties, such as promising resistance to wear, oxidation and corrosion, remarkable temperature strength, and excellent stability⁷⁸⁹. However, combining multiple metal elements into one well-designed nanostructured phase is not an easy task¹⁰. Therefore, enormous efforts to develop synthetic strategies for the fabrication of HEA NPs have been made over the past few years.

1.2 Synthesis methods of HEAs NPs

The properties of functional HEA NPs materials, such as size, distribution, composition, and crystallinity are highly dependent on the synthesis strategies and experimental conditions¹¹. The fabrication method of HEA NPs can be categorized into two groups, top-down and bottom-up approaches⁵. (1) Top-down approaches. This approach utilizes energy sources, such as mechanical, chemical, thermal or laser irradiation to break down solids to smaller fragments or particles¹² with a size distribution of about 1 μm to 100 nm. The most commonly used techniques are mechanical alloying (ball milling and arc melting), dealloying, laser ablation, and photolithography¹³¹⁴¹⁵. The top-down approaches are simple, usually only have few steps, but limited in particle morphology control, defective surface and composition loss¹⁶. (2) Bottom-up approaches. HEA NPs synthesis using the bottom-up approach is

based on the interaction of precursor atoms or some molecular species through chemical reactions and then condensed to form either amorphous or crystalline nanoparticles¹⁷. Wet chemistry synthesis, co-deposition from metal precursors (sputter-deposition, electrodeposition, and magnetron co-sputtering), and single-source precursor strategies (sol-gel auto-combustion and pyrolysis) are some of the bottom-up approaches to fabricate HEA NPs¹⁸¹⁹²⁰²¹. These methods provide good abilities to compositional design and particle morphology control and are capable of synthesizing particles with size down to 0.1 nm¹².

1.3 High-temperature Shock Method and Radiation Heating

Previous HEA nanomaterial synthesis is usually limited by multi-elemental mixing, structural control for complexed compositional design. Our group recently reported a carbothermal shock (CTS) method for HEA NPs synthesis (Figure 1.2(a), Science 2018)¹⁸. This method utilizes a flash heating step and a following rapid cooling step (temperature of $\sim 2000\text{K}$, shock duration of $\sim 55\text{ms}$) of metal precursors on carbon support to enable multi-elemental mixing while facilitates kinetic control to prevent the nanoparticles from agglomeration. Therefore, we were able to synthesize single-phase solid-solution nanoparticles up to eight dissimilar elements. This method developed a general strategy of multi-elemental material synthesis and provides insight of chemistry and structural control over HEA synthesis and design. Our studies on HEA and high-entropy oxide nanoparticles (HEO NPs) for highly stable ammonia oxidation and methane combustion were published on Science¹⁸ and Nature Catalysis, respectively²². The CTS method requires current to pass through the carbon substrate and initiate Joule

heating. To extend the application of this shock method to synthesizing high-entropy nanomaterials on more diverse and commercialized substrates with high-throughput capability, an indirect shock method called radiation heating was designed and explored. Radiation heating utilizes energy radiated from a heater, which serves as both heat source and large-scale production platform. Figure 1.2(b) demonstrates a schematic model of radiative heating process. It would largely expand our capability to apply the HEA nanoparticles on various carbon materials, including carbon black, carbon nanotubes, graphene, wood or even other insulating substrate materials such as silica or Al_2O_3 . The capability of incorporating HEAs with multiple types of substrates empowers them great potential in different catalytic applications.

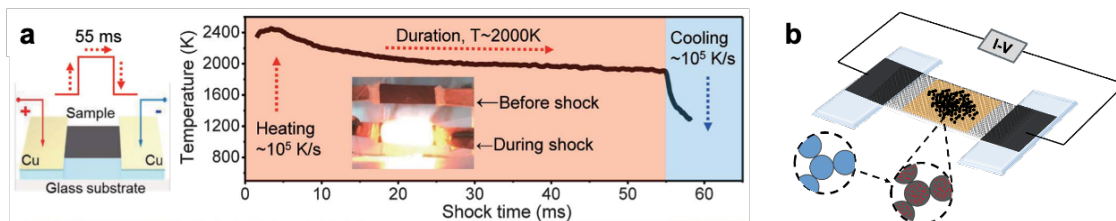


Figure 1.2 (a) Sample preparation and the temporal evolution of the temperature during the 55-ms thermal shock.¹⁸ **(b)** Schematic illustration of the radiation heating set-up.

1.4 Applications of HEAs

The excellent mechanical properties, activity, and durability of HEA materials have made them widely investigated and applied in many engineering fields, including environmental protection, gas storage and sensing, energy storage, electromagnetic wave absorption, radiation protection, superconducting materials, shape memory alloys and catalysts materials². Specifically, in the catalysis fields, HEAs have attracted increasing attention in different types of catalytic reactions. In thermal catalysis, HEAs

demonstrated good performance in ammonia oxidation²³, ammonia decomposition¹⁸ and CO oxidation²⁴. HEA-based nanomaterials are also utilized for various electrode reactions in fuel cells, such as electrocatalysts for the cathodic reduction of oxygen (oxygen reduction reaction (ORR))²⁵ in different electrolyte media and for anodic oxidation of fuels, including methanol oxidation reaction (MOR)²⁶, ethanol oxidation reaction (EOR)²⁷, and formic acid oxidation reaction (FAOR)²⁸. In addition, HEA nanomaterials have been developed as electrocatalyst for water-splitting (hydrogen evolution reaction (HER))²⁹ and oxygen evolution reaction (OER))²⁴ and selective CO₂ reduction reaction (CO₂RR)³⁰.

1.2 Existing plastics recycling method

The disposal of plastic waste presents significant ecological and environmental challenges. The accumulation of plastic waste, particularly single-use plastics, has become a pervasive problem, with negative impacts on wildlife, ecosystems, and human health. Plastic waste can persist in the environment for centuries, resulting in the contamination of waterways, soil, and air. In recent years, the recycling of plastic waste has been promoted as a solution to mitigate these challenges. However, the effective recycling of plastic waste remains a complex and costly process, often hindered by technical limitations, economic factors, and inadequate infrastructure. Furthermore, the scale of plastic waste production continues to grow, with global plastic production projected to increase significantly in the coming years. This trend, coupled with the inadequate waste management infrastructure in many parts of the world, underscores the urgent need for alternative strategies to address the ecological

and environmental challenges posed by plastic waste. Efforts to reduce plastic waste, such as implementing policies to limit the production and use of single-use plastics, promoting sustainable design and production practices, and investing in alternative materials and waste management systems, are essential to address this pressing issue. The development and adoption of innovative solutions that prioritize environmental sustainability and ecological integrity are critical to ensure a healthier and more sustainable future.

Current plastic recycling and/or upcycling techniques include mechanical recycling, chemical recycling, and energy recovery methods. Mechanical recycling (under heating but without reaction) involves a series of processes such as collection and sorting, size reduction, cleaning and drying, and extrusion and pelletizing, which convert waste plastics into pellets that can be used to create new products. However, mechanical recycling of plastics can only produce low-end and low-value products. Thermochemical recycling (under heat and with reaction), on the other hand, breaks down waste plastics into their constituent monomers or valuable chemicals through methods such as pyrolysis, gasification, and depolymerization, which can be used to synthesize new polymers or serve as feedstocks for other chemical industries. In particular, plastic waste can be converted into liquid fuels such as gasoline, jet fuel, and diesel, which hold great economic incentive. Nevertheless, conventional thermochemical approaches suffer from poor product selectivity due to lack of control on the reaction pathway and low system durability due to coking, catalyst degradation, and side reactions.

Similar to synthetic polymers (e.g., plastics), natural macromolecules such as lignin and cellulose can also be used as feedstocks to produce useful chemicals thermochemically. For example, lignin can be used as feedstock to produce sustainable aviation fuels (SAFs) with targeted aromatic motifs, it is also abundant in natural and usually treated as a waste material from the paper industry (only 2% for chemical production). However, converting lignin to SAFs by conventional thermochemical processes has been challenging due to poor control on the reaction pathway which leads to undesired product distribution and low selectivity.

1.3 Summary and motivation

Both Propane dehydrogenation (PDH) and ORR catalysis faces critical challenges such as poor stability during prolonged operations as well as high catalyst cost due to the heavy use of noble metal platinum. It is therefore crucial to develop catalysts that are cheaper, active, and stable. HEA nanoparticles exhibit features including high surface absorption sites density, entropy-stabilization effect, and tunable compositions, together enabling good catalysis activity and enhanced stability to resist oxidation and degradation. However, there lacks an efficient and scalable method for HEA nanoparticles synthesis with large elemental numbers and uniform mixing.

High-entropy alloy (HEA) nanoparticles hold a great potential in catalysis and energy storage applications. Highly diverse surface absorption sites and entropy-promoted stability of HEA nanoparticles make them the potential platform to resolve the stability issue and push the activity boundaries of PDH and ORR. I propose to design and synthesize HEA nanoparticles using a radiation heating method, and to screen HEA nanoparticle candidates for high performance PDH and ORR catalysis.

Specifically, I aim to achieve four major goals: i) developing a viable synthesis strategy for HEA nanoparticles through a new shock method (for scaling-up synthesis) and explore the optimal parameters; ii) characterizing the nanoparticle morphology, compositional distribution and crystalline structure to understand the synthesis-structure relationship; iii) evaluating catalysis performance and stability to screen promising HEA NPs candidates (composition and structure design) for highly active and stable PDH and ORR catalysis.

There is a large amount of plastic waste ending up in the ocean every year, threatening wildlife, and harming biodiversity. Furthermore, microplastics and plastic microfibers have been found in the air and municipal drinking water, posing health and ecological concerns. Common but highly unsustainable methods of removing plastic waste include burning or landfilling, with the former being extremely carbon-heavy and air-polluting, whereas the latter can cause long-term damage to the environment. Alternatively, many thermoplastics can be recycled through mechanical processing into low-end but useful materials. However, mechanical plastic-recycling approaches often suffer from limited product value. To continue using plastics, it is imperative to develop efficient plastic recycling and upcycling strategies to ensure a sustainable future.

Recently, thermochemical plastic decomposition has emerged as a promising route for converting plastic waste into value-added chemicals. Among the numerous thermochemical plastic-decomposition pathways, selective depolymerization to monomers holds great economic incentive, as the generated monomers can be reused in subsequent polymerization reactions for another product life cycle or as chemical feedstocks for other processes¹. Although a few plastics that have relatively low ceiling

temperatures can be readily depolymerized through conventional thermochemical methods such as pyrolysis (for example, poly(methyl methacrylate) and polystyrene), most polyolefins and polyesters cannot be converted to their monomers with high selectivity, as conventional approaches lack precise control of the reaction progress. This is because of the complex physicochemical transformations of reactants and intermediate products (for example, melting, vaporization, decomposition etc.), as well as the severe competing side reactions to the depolymerization pathway during continuous heating of the plastic, which lead to a range of products beyond the monomer (for example, gases, condensable hydrocarbons, aromatics etc.). To solve this problem, conventional thermochemical processes often use catalysts to enhance the product selectivity. However, catalysts are prone to performance degradation and provide limited improvement of the depolymerization selectivity. For example, the pyrolysis of PP typically features a monomer yield of only about 10% without catalysts and < 25% using optimized catalysts. In another example, the pyrolysis of PET leads to various aromatic species, often with < 25% yield to the 1,4-benzenedicarboxylic acid monomer.

Chapter 2: Experimental Setup and Characterization

3.1 Materials preparation

Carbon nanofibers (CNF) preparation: Polyacrylonitrile (PAN) was purchased from Sigma-Aldrich and dissolved in dimethylformamide (DMF) to form an 8%wt solution and stirred at 60 °C for 12 hours. The resulting transparent solution was electrospun at a voltage of 10 kV, a spinning distance of 15 cm and a feeding rate of 1 ml/hour. The electrospun nanofibers were collected by a rotation drum at a speed of 80 rpm. The PAN nanofibers were then stabilized at 260 °C for 2 hours in the air and carbonized at 600 °C in an argon protected atmosphere.

Preparation of CNF: CNF was prepared by electrospinning of PAN with a concentration of 8 wt% in DMF at a voltage of 10kV, with a spinning distance of 15cm and a rate of 1 mL/h. The as-spun nanofibers were collected by a rotation drum at a speed of 80 rpm, stabilized at 260 °C for 5 h in the air, and then carbonized at 800 °C in an argon protected atmosphere for 2 h to obtain CNF.

Preparation of precursor salt supported on CNF: For aqueous precursor solutions, the metal salt precursor solution was drop onto the CNF strips (0.01 mol/L for each element), and the CNF strips were placed under vacuum for 30 minutes, and then transferred to a 60°C oven to dry. For ethanol-based precursor solutions, the mixed solutions (0.05/n mol/L for each element, where n is the total number of elements) were

directly dropped onto the suspended CNF film with a loading of $\sim 120 \mu\text{L}/\text{cm}^2$ and left to dry at room temperature.

Preparation of power-like substrate with metal salts: The single salt solution (usually 0.05 M) was prepared by dissolving precursor salts in ethanol. Then precursor solution was obtained by mixing the single salt solution by the designed composition of the target alloy product. The substrate materials were grounded to fine powder to achieve good distribution in the precursor solution as well as even loading of the precursor salt (especially for silica substrate with a relatively large grain size). Then the mixed solution was added into substrate powder with a targeted loading amount, and then mixed under ultrasound for 0.5 hr. After the homogenous mixture was obtained, the mixture was carefully freeze-dried and ground to power. Then the precursor loaded powder was transferred to an Ar filled glovebox for high-temperature treatment.

Materials preparation of the programmable electrified heating: (1) Heater and reactor preparation: Carbon felt (AvCarb G280A, AvCarb G475 and AvCarb G650A, soft graphite battery felt) was purchased from the Fuel Cell Store. Before use, the carbon felt was thoroughly washed with acetone and then dried under vacuum overnight at 80°C . It was further purged in argon atmosphere for 1 h before use to remove any trapped moisture and oxygen in the porous material. The carbon felt was later cut into different dimensions (width, length, height) for different application purpose, such as heaters or reactors. (2) Reservoir design: The reservoir container was used to hold the reactant (such as polymer pellets, plastics, or other biomass reactants). The reservoir is

made of inert titanium foil and the size of the titanium container is designed to match with the reactor. (3) Reactant preparation: Reactant like PP (isotactic, average M_w about 580,000, average M_n approximately 166,000) and PET (granular) were purchased from Sigma-Aldrich. They were used as purchased or pressed to fit the height of the reservoir container. Commodity plastic products, including PP bags and PET water bottles, were purchased from Amazon and shredded into small piece for later use. (4) Loading reactant directly to the heater: The lignin powder was dissolved in ammonia solution (or other organic/aqueous solutions depending on the type of lignin or other precursor used in the reaction). Then the precursor solution was dropped onto the carbon felt strip followed by drying in the air and in the freeze dry machine consecutively.

3.2 High temperature setup and process

There were two major high-temperature heating setup studied in the research, including the thermal shock process to synthesis NPs on various substrates, and the electrified heating setup for the pyrolysis of reactants like biomass or plastics.

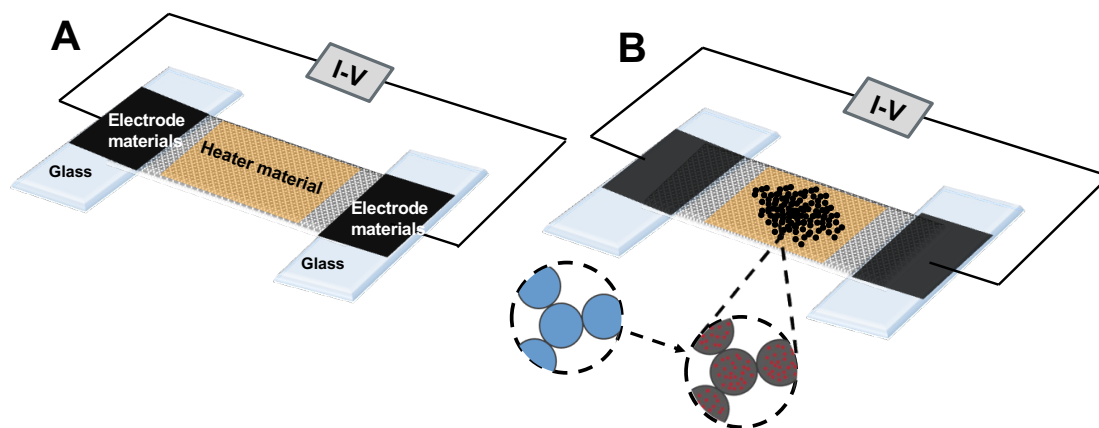


Figure 2.1. Schematic of setup for **A** Thermal shock and **B** Radiation heating.

The thermal shock setup is displayed in Figure 2.1A. The Joule heating was generated and controlled by an electric field to the set temperatures with at a controllable rate and duration. The heater materials were connected to electrodes and suspended on a glass substrate to avoid the thermal damage during the Joule heating process. The heaters are usually carbon materials like CNFs, carbon papers, and carbon felts, so they could serve as substrate materials for the NPs synthesized by the process. Metal precursors were pre-loaded on the heater materials, and heaters were heated to a high temperature in an argon protected atmosphere or vacuum. A Keithley 2400 source meter was used as an input power source for current below 1 A or power below 20 W. A higher power source (Volteq HY6020EX) was used for current up to 20 A or 60W. The external current source was programmed “sweep function” with adjustable amplitude and duration. Typically, there are three rates of 5 ms, 55 ms, and 505 ms for the synthesis of NPs.

To extend the application of this thermal shock method to synthesizing high-entropy nanomaterials on more diverse and commercialized substrates with high-throughput capability, an indirect shock method called radiation heating was designed and explored. Radiation heating utilizes energy radiated from a heater, which serves as both heat source and large-scale production platform. Figure 2.1B demonstrates a schematic model of radiative heating process. The heater size was typically scaled around 1.5*5 cm and the pre-loaded substrate with metal salt precursor were evenly spread as a thin layer on the heater. After the shock process, the NPs-loaded substrate powder would be scraped off and new batch of precursor-substrate could be reapplied onto the heater. It would largely expand our capability to apply the HEA nanoparticles

on various carbon materials, including carbon black, carbon nanotubes, graphene, wood or even other insulating substrate materials such as silica or Al_2O_3 .

The electrified heating setup is shown in the Figure 2.2. In Figure 2.2A, the core reaction system is demonstrated, showing the reactor layer was placed under the heater in soft contact (that is, without external pressure) and placed on top of the titanium reservoir used to hold the plastic reactant and the resulting melt during heating. The size of the titanium container matched that of the reactor, or it could be adjusted to other scale if needed. In another case, there would only be a single heater system once the reactants could be loaded on the felt heater without using any containers (Figure 2.2B, lower photo).

Both ends of the carbon felt heater were wrapped with copper foil, which were then connected to the power supply through alumina-covered copper wires and alligator clips (Figure 2.2B, upper photo). The gaps between the copper wire and alumina tube were filled with thermoset epoxy (Gorilla). Finally, the assembled reaction system, including the heater layer, reactor layer and reactant reservoir, was placed in a flow reaction system made of a quartz tube (1/2 in. outer diameter, 10.5 mm inner diameter for the small-scale reaction system, QSI). The quartz tube was sealed with two Ultra-Torr tee fittings (Swagelok). The ports of the Ultra-Torr fittings were used for the electrical wires and gas flow. Overview of the setup is shown in the Figure 2.2C. Control over the temperature was achieved through a solid-state relay device (DC input and DC output, maximum current 25 A, Omega), a high-accuracy sourcemeter (Keithley, Model 2400) and a power supply (75 V, 20 A, Volteq) connected to the top carbon felt heater layer.

The temperature range, heating duration and heating frequency can be programmed by adjusting the settings of the power supply and the sourcemeter. Experiments under continuous heating were conducted using a constant power input by the power supply, without the need for the sourcemeter and the relay device. In a typical electrical pulsed heating process, the heating duration can be programmed through the sourcemeter by setting a certain time within one period (for example, 1.10 s) as ‘power on’ (for example, 0.11 s, power on) by applying the power and setting the remaining time as ‘power off’ (for example, 0.99 s, power off) by removing the power. The peak temperature was controlled by the power input (that is, the applied voltage to the heater) from the power supply.

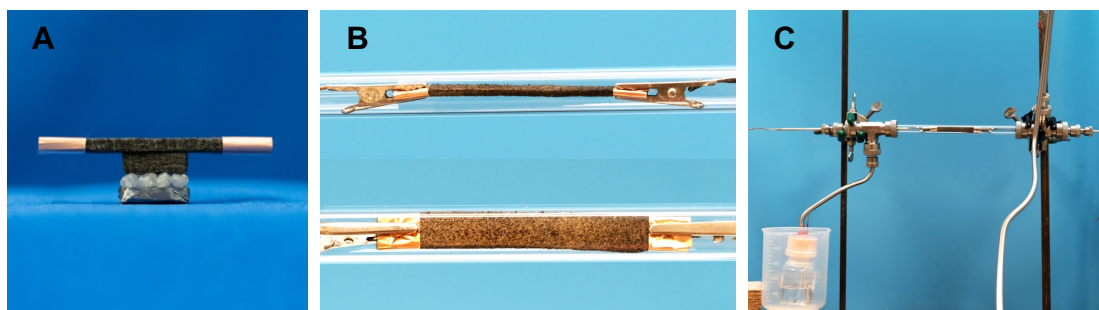


Figure 2.2. Photos of setup for **A** Reaction system consists of heater, reactor, and container filled with plastic reactants. **B** Single heater reaction system and connecting reaction system to the circuit. **C** Assembled reaction system placed in the flow reaction system made of a quartz tube sealed with two Ultra-Torr tee fittings (Swagelok).

3.3 Temperature measurement

Temperature mapping of the heater and reactor was performed by an infrared camera VarioCAM HDx head 600 (7.5 - 14 μm) with a resolution of 640×480 infrared

pixels using a standard lens (20 mm). The VarioCAM camera has an infrared image rate of 30 Hz in full frame and can measure the temperature in the range -40 - 1700 °C with an accuracy of $\pm 2\%$. During the measurement, the VarioCAM camera was placed 10 cm away from the heater and reactor.

3.4 Characterization and measurements

High-resolution TEM: The microstructure and morphology of the prepared samples was observed by a scanning electron microscope (SEM) (Hitachi SU-70 FEG- SEM at 10 kV) and transmission electron microscopes (TEM) (JEOL 2100F FEG TEM/STEM operated at 200 kV, and JEOL TEM/STEM ARM 200CF equipped with high angle annular dark field (HAAD-F) and annular bright field (ABF) detectors). A 22 mrad probe convergence angle was used to perform STEM imaging. HAADF detector in the JEOL 2100 FEG TEM with 90 mrad inner-detector angle was utilized to obtain the Z-contrast atomic-resolution images. For EDS data collection, an Oxford X-max 100TLE windowless X-ray detector was utilized. The average particle size and distribution were determined by ImageJ software using at least three microscopy images per sample.

Other characterizations: Raman spectra were characterized by Horiba Jobin-Yvon with laser wavelength 532 nm and the integration time 4 seconds repeated for 4 times. A diffractometer (D8 Advance, Bruker, Karlsruhe, Germany) was used with Cu K α radiation to collect the XRD spectra of materials. An AXIS 165 spectrometer (Kratos, Manchester, UK) was used to determine the XPS spectra of materials. The mass

loading of nanoparticles on substrate was measured by thermogravimetric analysis (Discovery SDT 650, TA Instruments). UV-vis spectra for aqueous solutions were recorded in a SHIMADAZU UV-3400 i Plus spectrometer in the 500-900 range and using an optical length of 0.2 cm. pH values of aqueous solutions were measured by sartorius pHBasic+ pH meter. Zeta-potential of was determined using the Zetasizer Nano ZS90 equipment.

Electrochemical Measurement: The catalyst ink for HER test was prepared by 1mg carbon-supported NPs dispersed in 200 μL mixed solution of Nafion, water, and isopropanol (1:50:150), and then sonicated for 30 min. 15 μL ink was dropped onto the 0.196 cm^2 glassy carbon disk, and then dried at room temperature for 2h. The three-electrode system was used for the test on an electrochemical workstation (VMP-300, Bio-Logic) with a rotator (Pine Instruments). The obtained film on the glassy carbon disk was used as the working electrode. A graphite and an Ag/AgCl (saturated KCl) electrode were used as the counter electrode and reference electrode, respectively. The electrolyte was 0.5 M H_2SO_4 aqueous solution. The activity of the catalyst was evaluated by linear sweep voltammetry from 0 to -0.6 V (vs RHE) with a scan rate of 2 mV/s.

This chapter included general experimental methods, characterizations, and measurements used in the study, and specific research methods for each project will be demonstrated in the following chapters. Other characterizations and measurements not mentioned here will be described in detail in the corresponding chapters.

Chapter 3: Synthesis of unary, binary, and high-entropy nanoparticles by high-temperature thermal shock

4.1 Carbon-supported NPs and applications in electrocatalysis

Oxygen reduction reaction (ORR) catalysis faces critical challenges such as poor stability during prolonged operations as well as high catalyst cost due to the heavy use of noble metal platinum. High-entropy alloy (HEA) nanoparticles potentially offers high activity due to the synergistic effect through elemental mixing, superior stability due to the entropy-stabilization effect, and tunable compositions that can facilitate materials screening and optimization. Additionally, through alloying multiple elements, the noble metal loading can be effectively reduced while maintaining a comparable or achieving an even better activity. These merits together promise good ORR activity such as high current densities and low overpotentials, as well as high stability to resist oxidation and leaching. However, due to the great complexity of composition, structure, electronic state etc. of the HEA nanoparticles, their design and characterization are of great difficulty. While rational design and deep mechanistic understanding can enormously expedite the development of the HEA nanoparticles toward high-performance catalysts, there lacks an effective approach to tailor the large material space. Compared to the conventional trial and error to study HEA nanoparticles, data science-based methodologies can potentially resolve this issue. To this end, this project aims to develop highly efficient ORR catalyst based on HEA nanoparticles through data-science guided materials discovery.

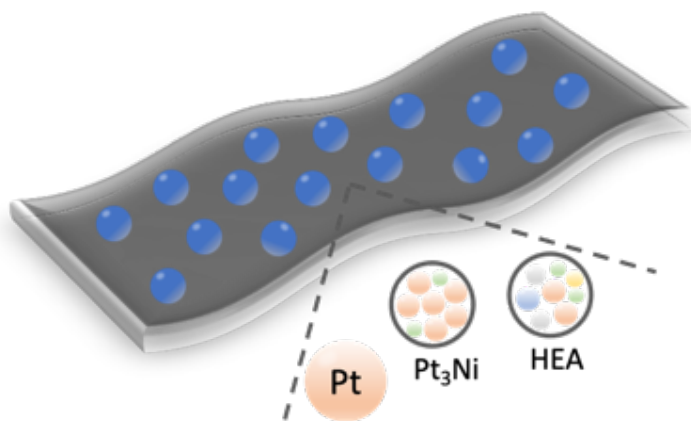


Figure 3.1. Schematic of well-dispersed NPs on carbon black, including Pt, Pt₃Ni and HEA nanoparticles.

4.1.1 Synthesis process of HEA nanoparticles

The radiation heating was employed for the scalable synthesis of single, binary and HEA NPs on the carbon black substrate. In a typical process, the precursor salts including $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, were dissolved in ethanol separately to form 0.05 M solution. Then the salt solutions were mixed by the designed composition and loading to obtain the precursor solutions. Ketjen carbon black was then added to the precursor solution and was kept under ultrasound for 1h. After the homogenous mixture was obtained, the mixture was carefully freeze-dried and ground to powder. Then the precursor loaded powder was transferred to an Ar filled glovebox for high-temperature treatment. A 1.5×5 cm carbon nanotube (CNT) film heater was applied as the radiation heater, which serves as both heating element as well as large-scale production platform to process and collect the product. To synthesize the HEA nanoparticles, the salt precursor mixture on carbon black were treated by thermal shock around 800-1200 °C for 0.5

second. The thermal shock was applied to the heater using an external Keithley 2425 Sourcemeter as the power source to generate the desired temperature and to control the heating duration.

4.1.2 High-loading and well-dispersed nanoparticles on carbon black

Pt is a widely used and benchmark catalyst for ORR. In addition, Pt/Ni, Pt/Co, and Pt/Fe alloys have also shown good ORR catalytic activity in the literature. In this regard, we designed the HEA composition based on Pt, Ni, Co and Fe as basic compositional element, meanwhile bringing in Mn, Cu to form the high-entropy alloy structure and further increase the stability by increasing entropy. We synthesized Pt, Pt₃Ni and HEA (Pt₅NiCoFeMnCu) NPs with up to 40 wt% catalyst loading on Ketjen carbon black substrate (Figure 3.2). TEM images (Figure 3.2A-B, D-E, G-H) present the well-distributed nanoparticles on the carbon substrate. All samples have average particle sizes around 8 nm with a narrow size distribution.

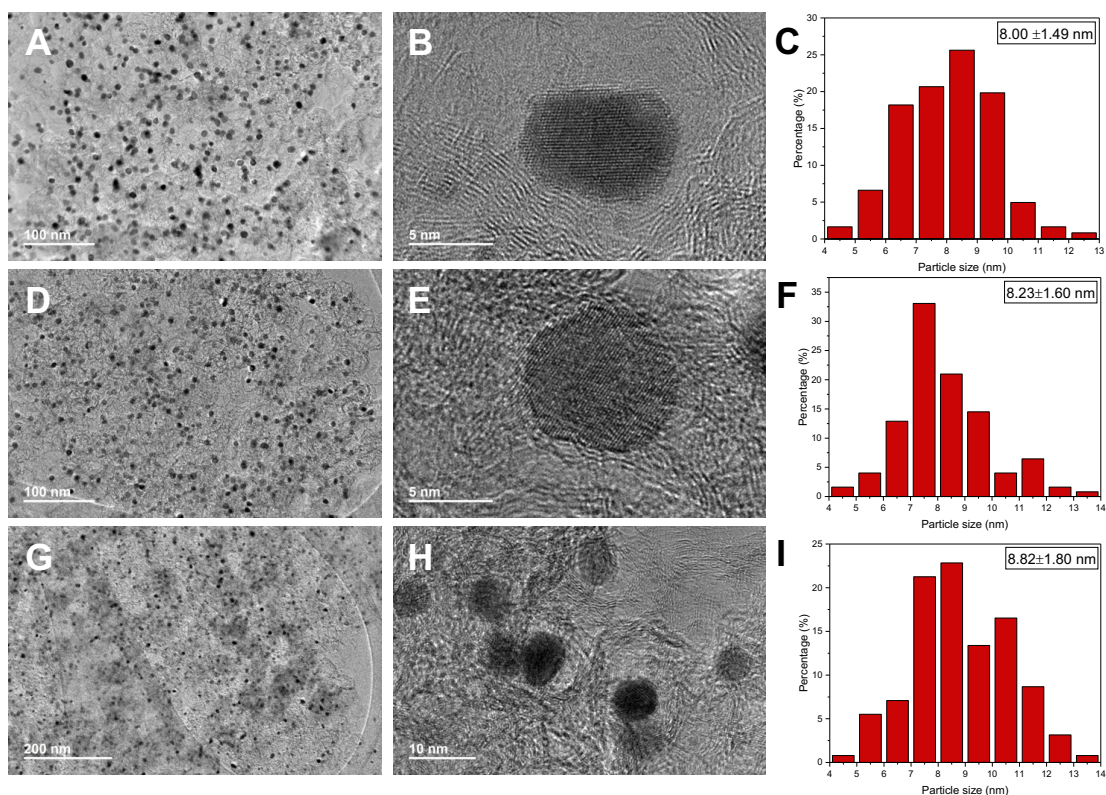


Figure 3.2. **A, B** TEM images of Pt NPs loaded on carbon black. **D, E** TEM images of Pt₃Ni binary NPs loaded on carbon black. **G, H** TEM images of HEA (Pt₅MnFeNiCoCu) nanoparticles loaded on carbon black. **C, F, I** Particle size distribution maps of Pt, Pt₃Ni binary and HEA (Pt₅MnFeNiCoCu) NPs loaded on carbon black.

The XRD patterns (Figure 3.3) indicate fcc structure for unary, binary and HEA samples without noticeable phase segregation. The slight right shift of (111) peak in Pt₃Ni and HEA samples can be ascribed to the transition metal incorporation. These results suggest successful and versatile synthesis of high-loading metal and alloy nanoparticles with elemental numbers up to 6 via our radiation heating approach.

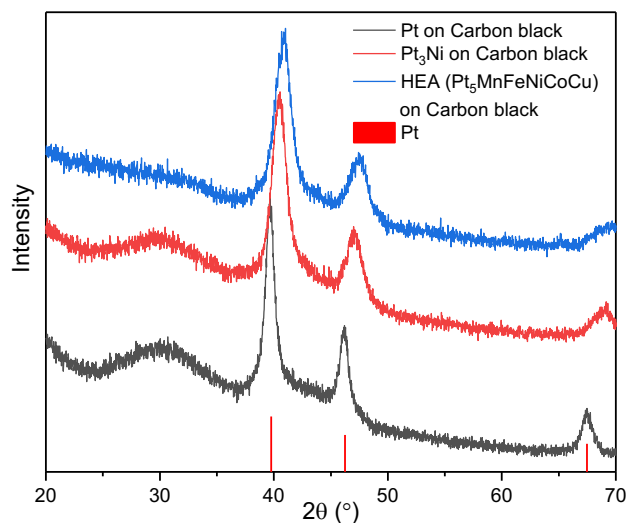


Figure 3.3. XRD patterns of Pt, Pt_3Ni binary and HEA nanoparticles loaded on carbon black.

4.1.3 Effect of temperature control on particle morphology

Peak temperature plays a key role in the thermal shock method. Figure 3.4A shows Pt NPs loaded on carbon black synthesized by radiation heating with relatively lower temperature (500 °C). The Pt nanoclusters have a mean value and standard deviation of 3.32 and 0.62 nm, respectively (Figure 3.4B). In comparison, the sizes for Pt NPs are of 8.00 ± 1.49 nm (Figure 3.3A-C), indicating that thermal shock at higher temperature can induce Pt nanoparticles with large size anchored on the carbon black. This effect can be explained by the increasing energy provided by the heater that promotes small particle fusion, as well as the decreasing number of defects on the carbon surface that inhibits particle fission.

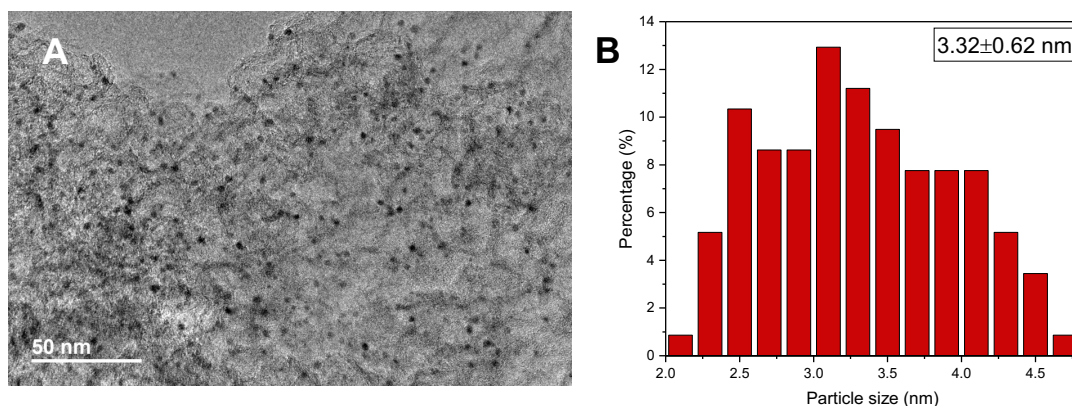


Figure 3.4. **A** TEM images of Pt NPs loaded on carbon black synthesized under 500 °C (Lower than regular synthesis temperature). **B** Particle size distribution maps of Pt NPs loaded on carbon black synthesized under 500 °C.

4.1.4 Loading effect on particle morphology

To explore the loading effect on particle morphology in the shock method, experiments were designed to synthesize HEA nanoparticles with various loading from 10 wt% to 40 wt% (based on the mass of Pt over carbon black) and studied the corresponding TEM images to identify the highest possible loading for obtaining nanoparticles with good quality. Figure 3.5A-D demonstrate the trend of size and distribution by varying catalyst loading. Higher loading leads to larger particle size and distribution. Particle size increases from ~5 nm, ~10 nm to more than 20 nm when particle loading increases from 10 wt% to 40 wt% (Pt). Lowering the loading of NPs would allow the precursors to distribute uniformly throughout the substrate, thus leads smaller size and better dispersion.

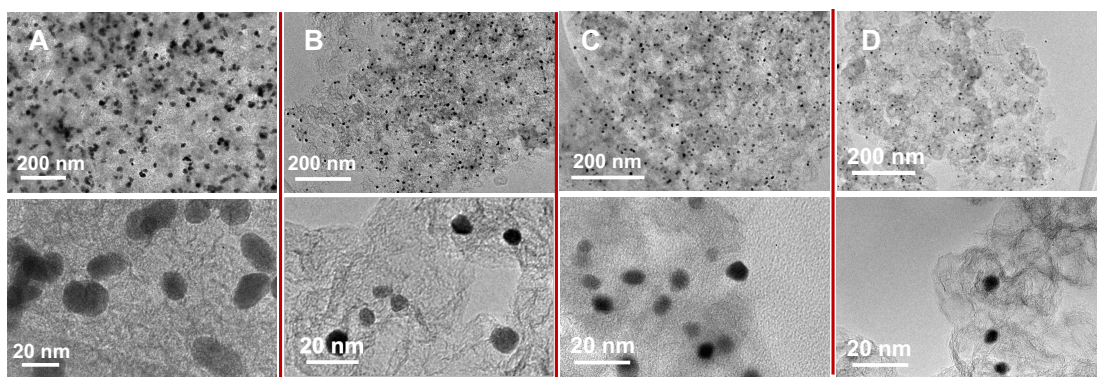


Figure 3.5. A-D TEM images of HEA ($\text{Pt}_5(\text{NiCoFeCu})_{1.25}$) nanoparticles with Pt loading of 40, 30, 20 and 10 wt% on carbon black substrate.

4.1.5 Composition design and control of HEA NPs

In the design of functional HEA NPs, chemical composition is as critical as the particle morphology. Transition chloride metal salts usually have higher decomposition temperature compared to noble metal salts (close to 1000K, as shown in Figure 3.6A). Due to the high partial pressure under high temperatures (Figure 3.6B), the loading of transition metals is usually compromised during shock method. We designated several measures to tailor this issue, including adding more transition metal precursor to compensate the volatilization loss, increasing the rate of thermal shock, and creating a closed environment for the synthesis to shift the equilibrium. We are also capable of synthesizing various HEA compositions, such as $\text{Pt}_5(\text{NiCoFeCu})_{1.25}$ and $\text{Pt}_5\text{IrNiCoFeCu}$. However, precise composition tailoring needs to be calibrated when design and synthesise a new HEA composition.

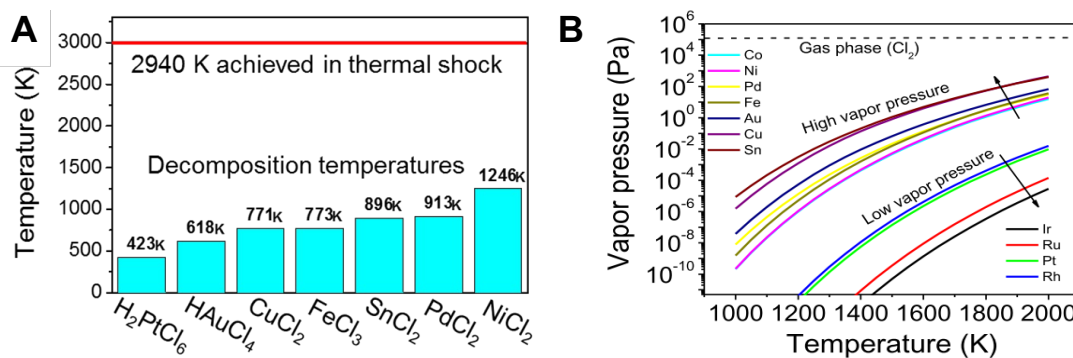


Figure 3.6. **A** Decomposition temperatures of different metal precursor salts³¹. **B** Graph of Vapor pressure vs temperature relations for different metal salts¹⁸.

In summary, by tuning various parameters of the shock method synthesis process, we can obtain good control over particle morphology and chemical composition, which laid a solid foundation for design functional HEA catalysts for different reactions.

4.1.6 Addressing the carbon coating issue on NPs

Defected and amorphous carbon from the substrate would evaporate under the high temperature of the shock process and generate carbon atmosphere. It would later redeposit in the fast-cooling step and could negatively affect the particle quality as they can form a carbonaceous coating layer (Figure 3.7A) onto the surface of the particles to block the catalytic active sites. Figure 3.7B illustrates the carbon coating layer formation process.

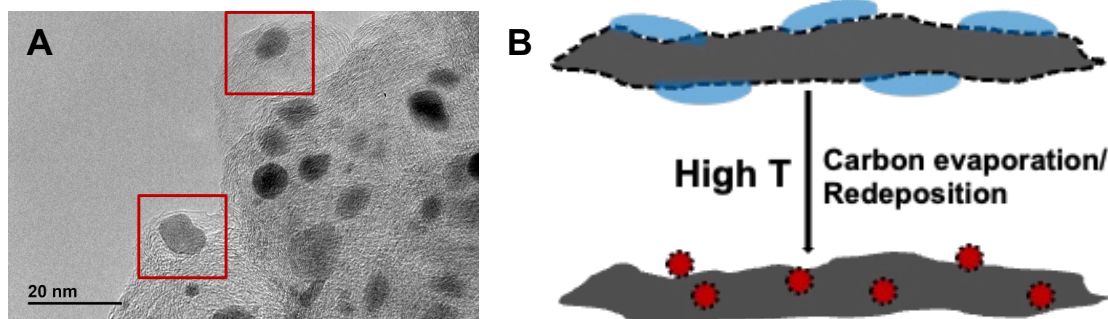


Figure 3.7. **A** TEM images of HEA ($\text{Pt}_5(\text{NiCoFeCu})_{1.25}$) NPs synthesized by radiation shock method with a layer carbon coating layer on the substrate. **B** Schematic of the carbon coating formation mechanism during the shock process.

Substrate	Sonication time	Temperature/ $^{\circ}\text{C}$	Shock duration/s	Batch size	Substrate treatment
Ketjen CB	5 min	~ 1000	~ 0.5	small	1h $> 1000^{\circ}\text{C}$

Table 4.1 Experimental details of the carbon-coating free treatment.

There were several strategies developed to resolve this issue, including reduction of the amorphous carbon, preservation of the crystalline structure, and avoiding organic contaminants (treatment details are summarized in Table 4.1).

Adjusting the device design: We replaced the previous silver glue and copper tape used on thermal shock synthesis with graphite plates as the electrical connection to minimize the organic solvent decomposition under high temperatures. Heater material adjustment: We applied carbon material with higher crystallinity such as CNT film to avoid amorphous carbon evaporation and redeposition onto the particle surface. Pre-crystallization heat treatment of carbon black: We pre-heated carbon black in glovebox

under 1000C for 1h to increase the crystallinity of carbon substrate surface. This strategy can prevent amorphous carbon evaporation under high temperature and redeposition on the NPs. Sonication time decrease: We decreased the sonication time of carbon black dispersion in precursor solutions from, 1h to 10min. This strategy also serves to preserve the carbon of the substrate surface. Other strategies: Other than the major methods listed above, smaller synthesis batch, lower synthesis temperature, and more precise temperature control can also help to prevent the carbon coating formation.

Precursor composition (atomic%)	Substrate	Loading	Method	Temperature
Pt ₅ (FeNiCoCu) _{1.25}	Carbon black	~30 wt % Pt/CB	Radiative heating	~1000 °C
Pt ₅ (IrFeNiCoCu)	Carbon black	~30 wt % Pt/CB	Radiative heating	~1000 °C

Table 4.2 Sample information of the NPs synthesized by radiation heating with a carbon-coating free treatment.

With aforementioned strategies, HEA NPs synthesized by the shock method were characterized and the TEM figures in Figure 3.8. The sample information of NPs is summarized in Table 4.2. The overall morphology of the NPs is shown in Figure 3.8A and Figure 3.8D with an average size around 10 nm and narrow distribution. Furthermore, morphology of single particles was characterized by HRTEM. It shows that NPs sitting on top of the porous carbon substrate with good single crystal structure. However, it is hard to identify surface is carbon-free or not since the particles are on

the carbon substrate (Figure 3.8B and Figure 3.8E). In Figure 3.8C and Figure 3.8F, the particles at the edge of the substrate were identified with no carbon substrate underneath, and there were no carbon-coating layer observed. The new HEA NPs will be further characterized and tested for ORR catalysis. It is promising that the carbon-free HEA NPs catalysts will have better ORR performance and reveal the real nature of the HEA NPs catalysts in electrochemical catalysis.

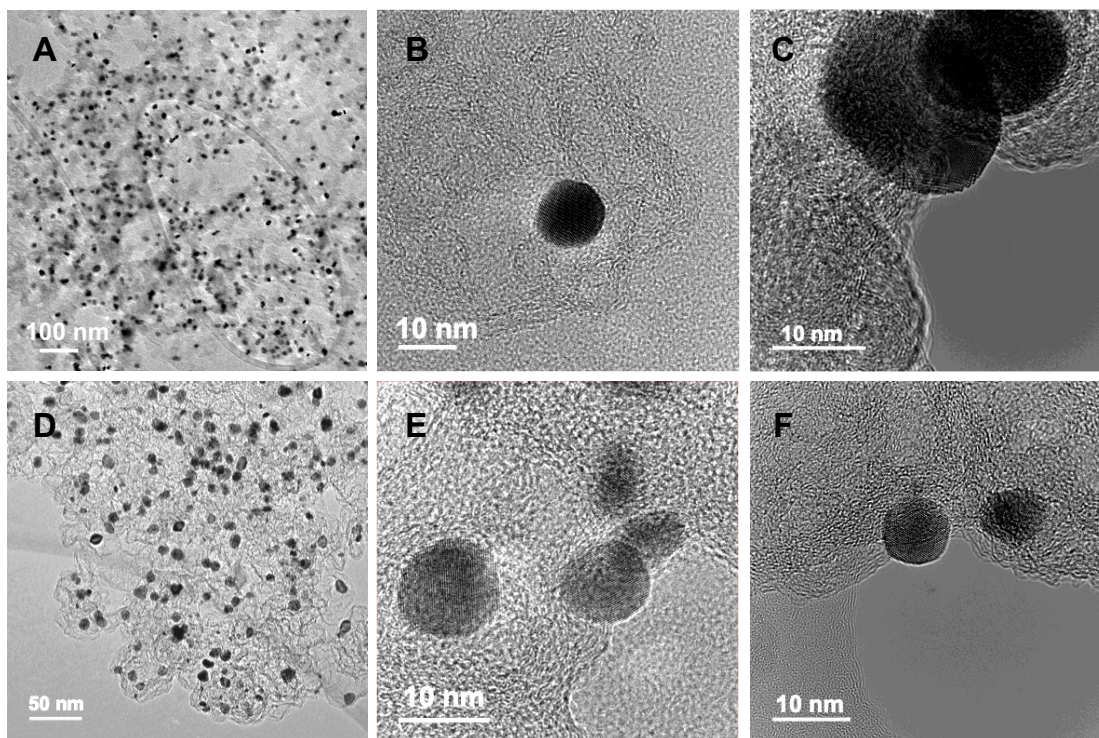


Figure 3.8. A TEM image of large area morphology of the HEA ($\text{Pt}_5(\text{FeNiCoCu})_{1.25}$) NPs loaded on carbon black. B, C HRTEM images of HEA ($\text{Pt}_5(\text{FeNiCoCu})_{1.25}$) NPs on top of the carbon substrate and on the edge of the substrate showing clean carbon-free surface. D TEM image of large area morphology of the HEA ($\text{Pt}_5(\text{FeNiCoCuIr})$) NPs loaded on carbon black. E, F HRTEM images of HEA ($\text{Pt}_5(\text{FeNiCoCuIr})$) NPs on top of the carbon substrate and on the edge of the substrate showing clean carbon-free surface.

4.1.7 Preliminary ORR performance data

ORR Evaluation and Screening: The goal is to evaluate the ORR catalysis performance of HEA nanoparticles and screen optimal candidates for highly active and stable ORR catalysts. Cyclic voltammograms will be used to measure the position and current densities of oxygen reduction peak. Together with the limiting current density and half-wave potential obtained by linear sweep voltammograms, I will systematically evaluate the activity of ORR catalysis for a range of compositions and structures. The Tafel analysis will be used to understand the reaction mechanism. The long-term stability of catalysts will be tested using chronoamperometry at a certain voltage. The proposed screening strategy consists of three steps: activity screening, stability evaluation, and a new composition design of combination of the previous promising candidates on elemental level by high-entropy synthesis. During the process, I will explore the process-structure-performance relationship of HEA nanoparticles with the help of data science tools such as machine learning, and hopefully to establish a database for future HEA studies.

4.2 Pt Atom in High-entropy Alloy Nanoparticles as a Single Atom Catalyst

Propane is one of the most important chemical feedstocks. In industry, nonoxidative propane dehydrogenation (PDH) is a key technology to produce propylene as a widely used chemical for a series of downstream industrial synthetic processes. Commercially, both Pt (Oleflex and steam-activated reforming (STAR) processes) and chromium oxide-based (Catofin process) catalysts are utilized in the process³². This endothermic reaction operates at a relatively high temperature (550° to 700°C) and atmospheric pressure to increase the equilibrium conversion³³. Under harsh operation conditions, conventional catalysts suffer from limited selectivity and catalyst

deactivation due to coke formation on the catalyst surface, particle sintering and component loss³⁴³⁵. In comparison, nanostructured catalysts potentially enable better performance by regulating the local structure of catalytic ensembles and electronic structures. Herein, we utilize the radiation heating approach as a facile method to develop novel PDH catalysts, featuring multi-elemental and HEA nanoparticles with versatile surface sites and entropy-induced stability as schematically shown in Figure 3.9.

Pt ensembles are known to catalyze the side reactions of Propane dehydrogenation (PDH) such as hydrogenolysis, C-C cracking, and coking that are structure-sensitive and cause rapid catalysts deactivation. Breaking the Pt ensembles is a common strategy to avoid coking and increase the catalyst operation lifetime. Single-atom alloys (SAAs), consist of a reactive dopant metal atomically dispersed in other metal hosts, are good candidates for this design purpose. By diluting Pt sites in other excess metals such as Cu or Sn, the coke formation during PDH could be successfully suppressed while maintaining good performance at the same time. However, SAAs catalysts usually lack sufficient thermal stability, and the active single sites tend to aggregate at high temperature (PDH typically over 600 °C). Sintered Pt sites will catalyze side reactions of PDH and irreversibly deactivate the catalysts. To this end, it is imperative to develop a thermally stable SAA catalyst is important for high-temperature PDH catalysis.

In this project, we report a single-atom high-entropy alloy (SA-HEA) catalysts that isolate Pt as single-sites in high-entropy alloy (HEA) lattices. Unlike conventional alloys, HEAs are consisted of five or more principal elements mixed in a solid-solution

phases. These materials are stabilized by their high entropy nature compared to intermetallic compounds, especially at high temperatures. In the SA-HEA, we combined seven promotor elements, including Sn, Co, Cu, Ga and In along with the active composition Pt to form a solid solution structure. Promoters such as Sn, Co, Cu, Ga and In can be alloyed with Pt and have been studied as PDH catalysts for improved selectivity and suppressed catalyst deactivation. Other than contributing to the thermal stability by increasing mixing entropy, the promoters also modify the catalytic properties of Pt and disperse the Pt into single atoms on the catalyst surface. Dispersed Pt single sites can still catalyze C-H bond cleavage, while the structure-sensitive C-C bond cleavage and deep dehydrogenation could be suppressed.

With this design strategy, we prepared SA-HEA catalyst with electronically enriched, geometrically dispersed and entropy stabilized Pt single site that is coke-resistant and thermochemically stable (Figure 3.9).

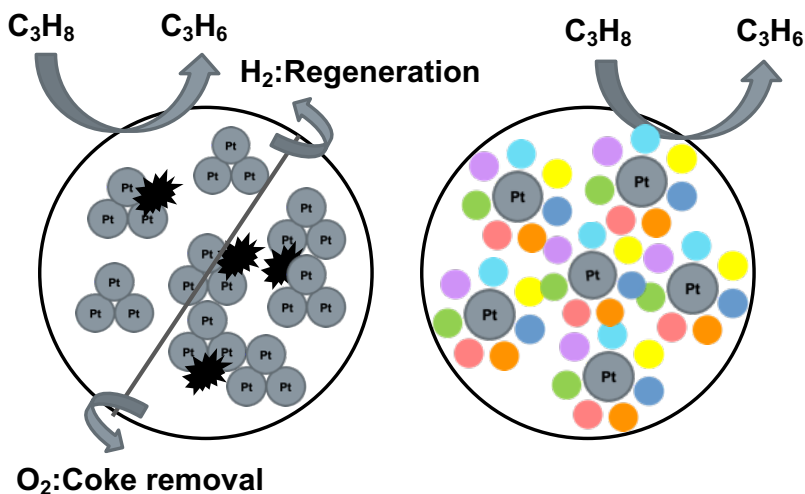


Figure 3.9. Schematics demonstrating the Pt Atom in High-entropy alloy as a stable single atom catalyst.

4.2.1 Synthesis of Pt, Binary and HEA NPs on Silica

Flexible substrate choice is the key advantage of synthesizing HEA nanoparticles via radiation heating. Our previous experience on carbon black laid a solid foundation for us to explore this method on ceramic materials such as silica. The synthesis method is similar to using carbon black as the substrate, where we conducted precursor loading, freeze-drying, thermal shock heating, and product collection process. We dissolve the precursor salts including $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{VCl}_4 \cdot 2\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CrCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ in ethanol separately to form 0.05 M solution and then mix them by the designed composition and loading to obtain the precursor solutions. Due to the nature of ceramic substrate, the silica (Davisil 636) powder (Figure 3.10A) was pre-grounded (Figure 3.10B) before the loading process to ensure uniform precursor dispersion. It shows porous nanostructure under SEM in the Figure 3.10C. Pre-grounded silica was then added to the precursor solution and was kept under ultrasound for 1h. After the homogenous mixture was obtained, the mixture was carefully freeze-dried and ground to power. Then the precursor loaded powder was transferred to an Ar filled glovebox for high-temperature treatment. A 1.5×5 cm carbon nanotube (CNT) film heater was applied as the radiation heater, which serves as both heating element as well as large-scale production platform to process and collect the product. To synthesize the HEA nanoparticles, the salt precursor mixture on silica were treated by thermal shock around 1000K for 0.5 second. The thermal shock was applied to the heater using an external Keithley 2425 Sourcemeter as the power source to generate the desired temperature and to control the heating duration.

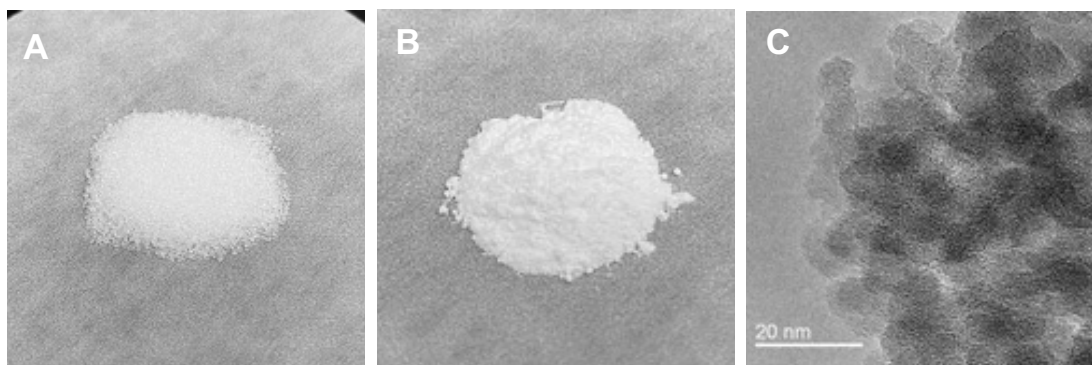


Figure 3.10. Photos of **A** Pristine silica substrate (Davisil 636). **B** Grounded silica substrate. **C** SEM image showing the nanostructure of the grounded silica substrate.

Uniformly loaded Pt NPs with size of ~ 3 nm on Davisil 636 silica as shown in Figure 3.11A, B. The catalyst loading was designed to be 3 wt% for geometrically dispersing the active sites. XRD pattern demonstrates a FCC structure without observable phase segregation (Figure 3.11C).

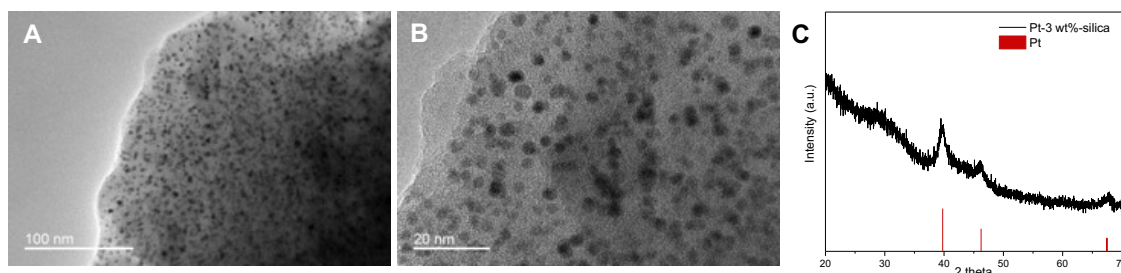


Figure 3.11. **A, B** TEM image of Pt NPs on Davisil 636 silica. **C** XRD pattern of Pt and NPs on Davisil 636 silica.

Binary Pt_3Ni NPs could also be achieved by the radiation heating process with a catalyst loading of 3 wt%. The particles were geometrically dispersed on the substrate (Figure 3.12A, B). The particle size distribution is shown in Figure 3.11C of 2.36 ± 0.4

nm. XRD pattern in Figure 3.11D also demonstrates a FCC structure without observable phase segregation.

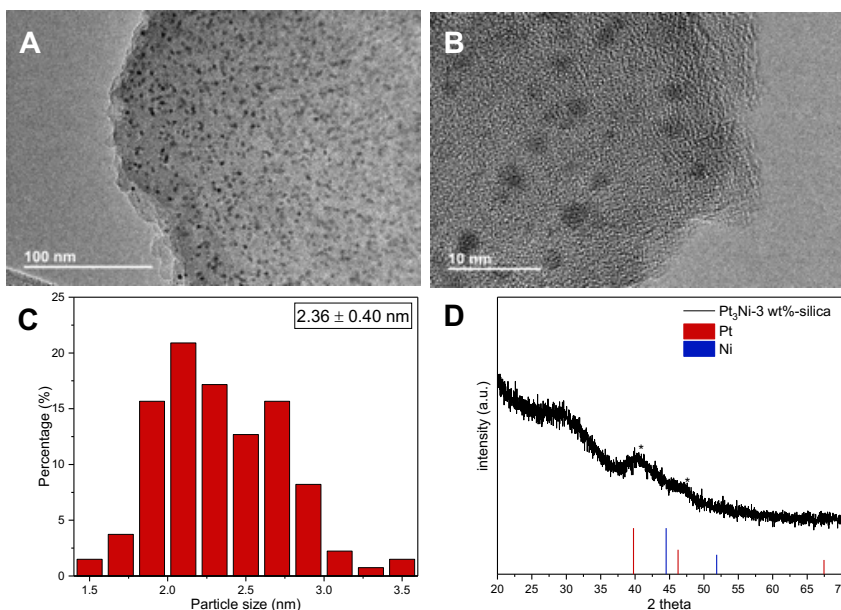


Figure 3.12. **A, B** TEM image of Pt₃Ni NPs on Davisil 636 silica. **C** Particle size distribution map of Pt₃Ni NPs on Davisil 636 silica. **D** XRD pattern of Pt₃Ni NPs on Davisil 636 silica.

Another binary composition was explored to achieve better catalytic performance potentially. PtV has a high melting temperature, which makes it a good candidate for high temperature operation with anti-sintering resistance. However, the material is difficult to be synthesized by traditional method. On the other side, radiation heating provides enough energy for the alloying of Pt and V while the short synthesis time ensures elemental mixing without further phase separation. Composition control of PtV binary NPs could also be achieved with different Pt/V by adjusting the precursor salt ratio. TEM images (Figure 3.13A, B) show that the NPs evenly distributed on the

silica substrate and have an average size around 3 nm with a narrow distribution. EDX analysis demonstrates successful incorporation of V and Pt in the NPs with designed composition of Pt/V = 2: 3 (atomic ratio). In addition to the morphological and compositional analysis, we used XRD to confirm the single phase fcc structures without phase separation (Figure 3.13D).

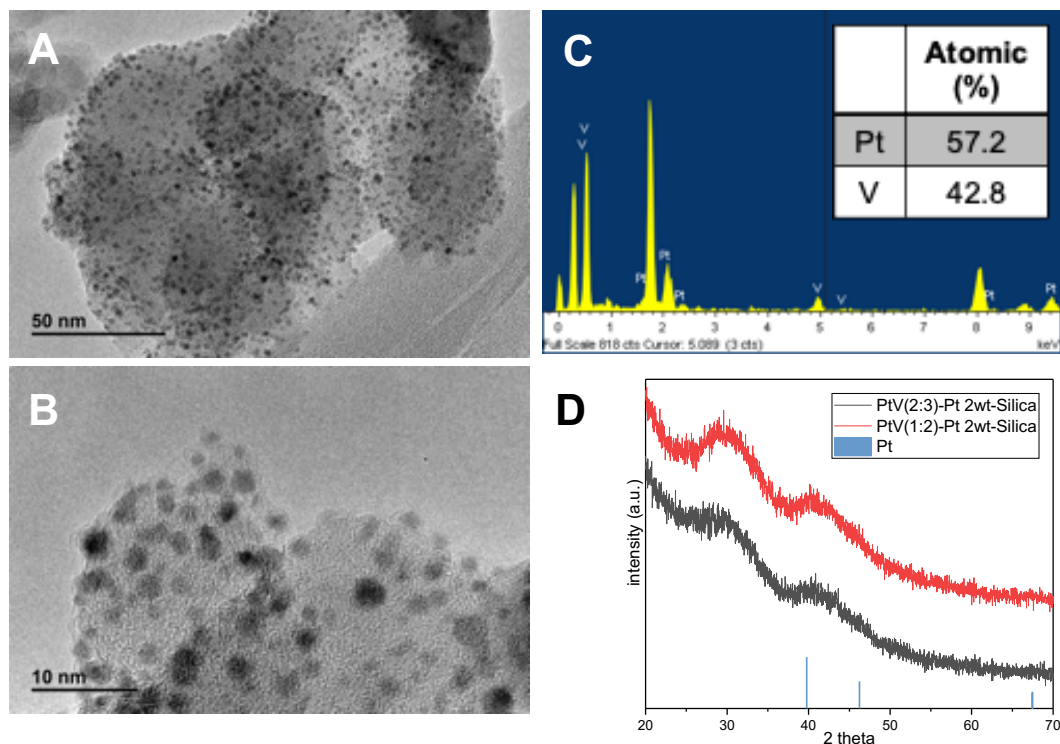


Figure 3.13. **A, B** TEM images of PtV NPs on Davisil 636 silica. **C** TEM EDX analysis of the PtV NPs on Davisil 636 silica. **D** XRD patterns of PtV (P:V = 2:3 and 1:2) on Davisil 636 silica.

After obtained experiences on synthesizing Pt and binary alloy NPs by radiation heating, HEA NPs loaded on silica with different Pt compositions were designed and synthesized. V,Cr,Co,Sn,Cu,In and Ga were chosen as promoter elements due to their

binary alloys with Pt have been well investigated and proven good performance for PDH. For the eight elemental HEA composition referred as 8-HEA, the precursor composition is designed as Pt(VSnCrCoSnGaIn) with a loading of Pt 2wt% over silica. TEM images (Figure 3.14A-F) show that all 8-HEA NPs (Pt compositions from 38, 15 to 7 atomic%) have a size range around 3-5 nm and evenly distributed across the substrate. EDX analysis demonstrate successful incorporation of all elements in the NPs. More importantly, it confirmed that the Pt composition in the HEA design is adjustable and composition as low as 7 atomic% could be achieved with a good particle morphology (Figure 3.14G-I). It laid a solid ground for later study to further dilute the Pt atoms in the HEA NPs.

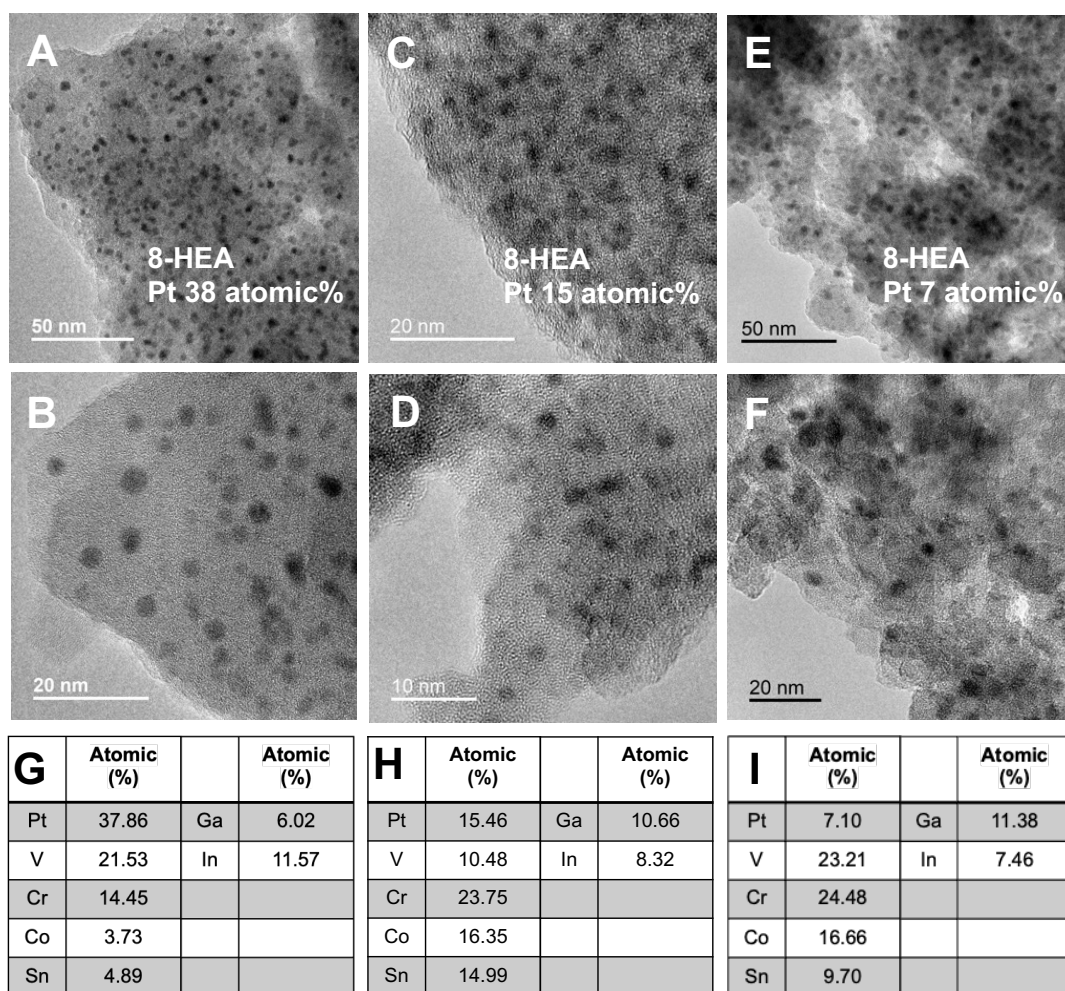


Figure 3.14. **A, B** TEM images of 8-HEA (Pt 38 atomic%) NPs on Davisil 636 silica. **C, D** TEM images of 8-HEA (Pt 15 atomic%) NPs on Davisil 636 silica. **E, F** TEM images of 8-HEA (Pt 7 atomic%) NPs on Davisil 636 silica. **G-I** EDX analysis of 8-HEA NPs with Pt composition of 38, 15, 7 atomic% in HEA on Davisil 636 silica.

4.2.2 Pt Atom in High-entropy Alloy Nanoparticles

The precursor salts including $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ were dissolved in ethanol separately to form 0.05 M solution and then mix them by the designed

composition and loading to obtain the precursor solutions. Due to the nature of ceramic substrate, the silica (Davisil 636) powder was pre-grounded before the loading process to ensure uniform precursor dispersion. Pre-grounded silica was then added to the precursor solution and was kept under ultrasound for 1h. After the homogenous mixture was obtained, the mixture was carefully freeze-dried and ground to power. Then the precursor loaded powder was transferred to an Ar filled glovebox for high-temperature treatment. A 1.5×5 cm carbon nanotube (CNT) film heater was applied as the radiation heater, which serves as both heating element as well as large-scale production platform to process and collect the product. To synthesize the HEA nanoparticles, the salt precursor mixture on silica were treated by thermal shock around 1000K for 0.5 s.

Silica supported six elemental HEA Pt single-atom NPs (SA-6HEA) were prepared by the high-temperature shock method with a low Pt loading of 0.25 wt% on silica. In the Z-contrast HAADF image (Figure 3.15A, B), bright spots in the particles can be interpreted as Pt atoms. Pt atom can be directly seen in the particles, isolated from the rest of the elements. EDX mapping in Figure 3.15C also shows good mixing of elements and good distribution without aggregation. However, silica substrate is not stable enough under the electron beam for clear images to showcase the single Pt site in a HEA nanoparticle.

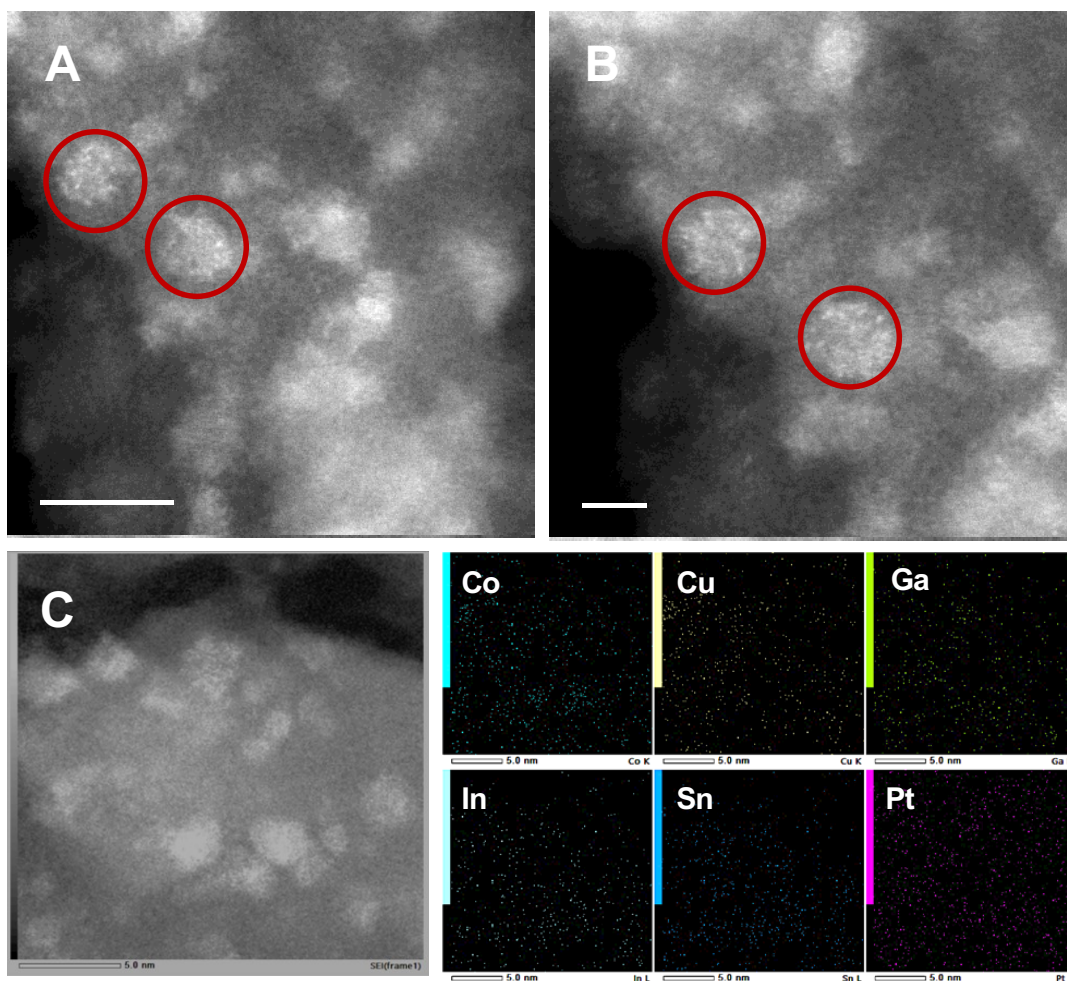


Figure 3.15. Morphology of SA-HEA nanoparticles on silica. **A, B** HAADF-STEM image of SA-HEA nanoparticles with loading of 0.25 wt%. **C** EDX mapping of elemental distribution of SA-HEA nanoparticles with loading of 0.25 wt%.

In this stage of the research, HEA NPs with Pt single site structure were successfully synthesized by screening composition and loading. Optimizing the protocol for TEM characterization demonstrating the single-atom Pt structure are in progress. In the next step, the potential performance of this material for PDH catalysis application will be further explored.

4.2.3 Sintering stability of HEA NPs on silica

Pt-based NPs sintering during the operation at high temperature is one of the causes of poor catalysis stability of PDH, which requires short-term regeneration of the catalysts. HEA NPs are synthesized under higher temperature than the PDH operation temperature and are stabilized by the high entropy. The more elements are incorporated in the HEA NPs, the higher chance they have anti-sintering stability during the catalysis process. We designed an experiment to demonstrate anti-sintering stability of HEA NPs. The NPs were sintered under oxidation cycle and a reduction cycle, mimicking the real regeneration cycle in the PDH operations, and the detailed conditions are listed in the Table 4.3 (Upper rows: mild conditions; Lower rows: severe conditions).

Procedure	Atmosphere	Temperature/C	Duration/h
Oxidation	Air	400	1
Reduction	H ₂ /Ar	550	1
Procedure	Atmosphere	Temperature/C	Duration/h
Oxidation	Air	550	1
Reduction	H ₂ /Ar	750	1

Table 4.3 Experimental details of sintering resistance test.

PtSn NPs synthesized by impregnation method on Davisil 636 silica was the control group for the sintering resistance test. It is widely used in industry as PDH catalyst and well-studied in research. The pristine PtSn NPs was characterized by TEM and the morphology are shown in Figure 3.16A, B. The particle size is estimated to be

3.43 $\pm$ 0.91 nm in Figure 3.16C and TEM EDX analysis confirmed the elemental composition of PtSn. The particle morphology after the sintering test is shown in Figure 3.16D, E, with an increased particle size and distribution to 5.00 $\pm$ 1.88 nm (Figure 3.16F). The PtSn NPs clearly sintered in the test, showing growth in particle size and doubling the distribution. Larger particle size and sintered active sites would lead to lower activity and catalyst stability in long operation.

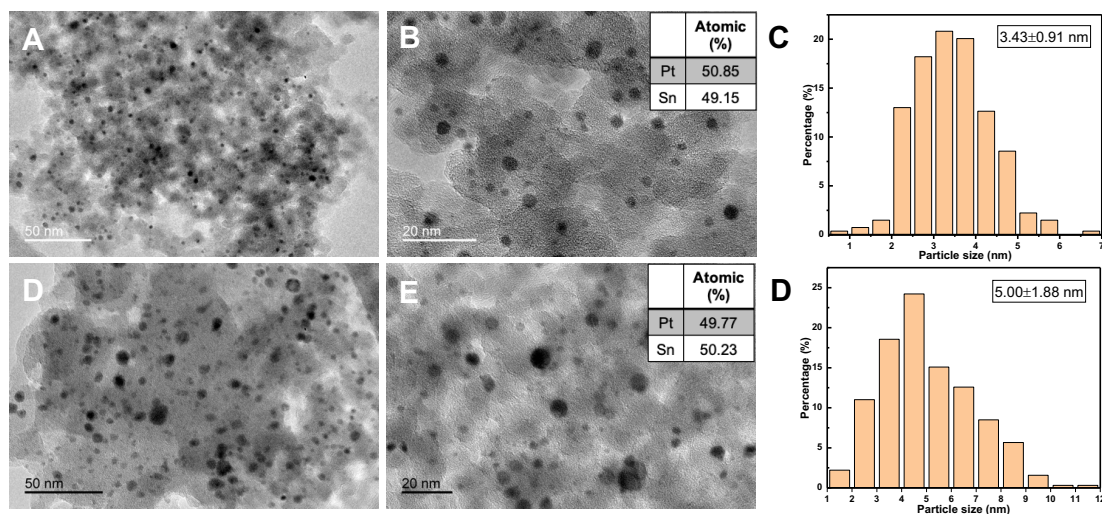


Figure 3.16. A, B TEM images of PtSn NPs synthesized by impregnation method on Davisil 636 silica before sintering resistance test and C particle size distribution. D, E TEM images of PtSn NPs synthesized by impregnation method on Davisil 636 silica after sintering resistance test and F particle size distribution.

Similar sintering resistance test were carried out on the 8-HEA (Pt 38 atomic%) NPs synthesized by radiation heating method on Davisil 636 silica. By comparing the TEM figures of the 8-HEA NPs before (Figure 3.17A, B) and after (Figure 3.17D, E and Figure 3.17G, H) the sintering experiment, we can conclude that morphology the NPs are identical, and the 8-HEA NPs have good anti-sintering stability under the PDH

operation conditions. The particle size and distribution were slightly increased as the sintering conditions became more severe (Figure 3.17C-F), but the growth was much smaller compared to the sintering of PtSn NPs under the similar conditions.

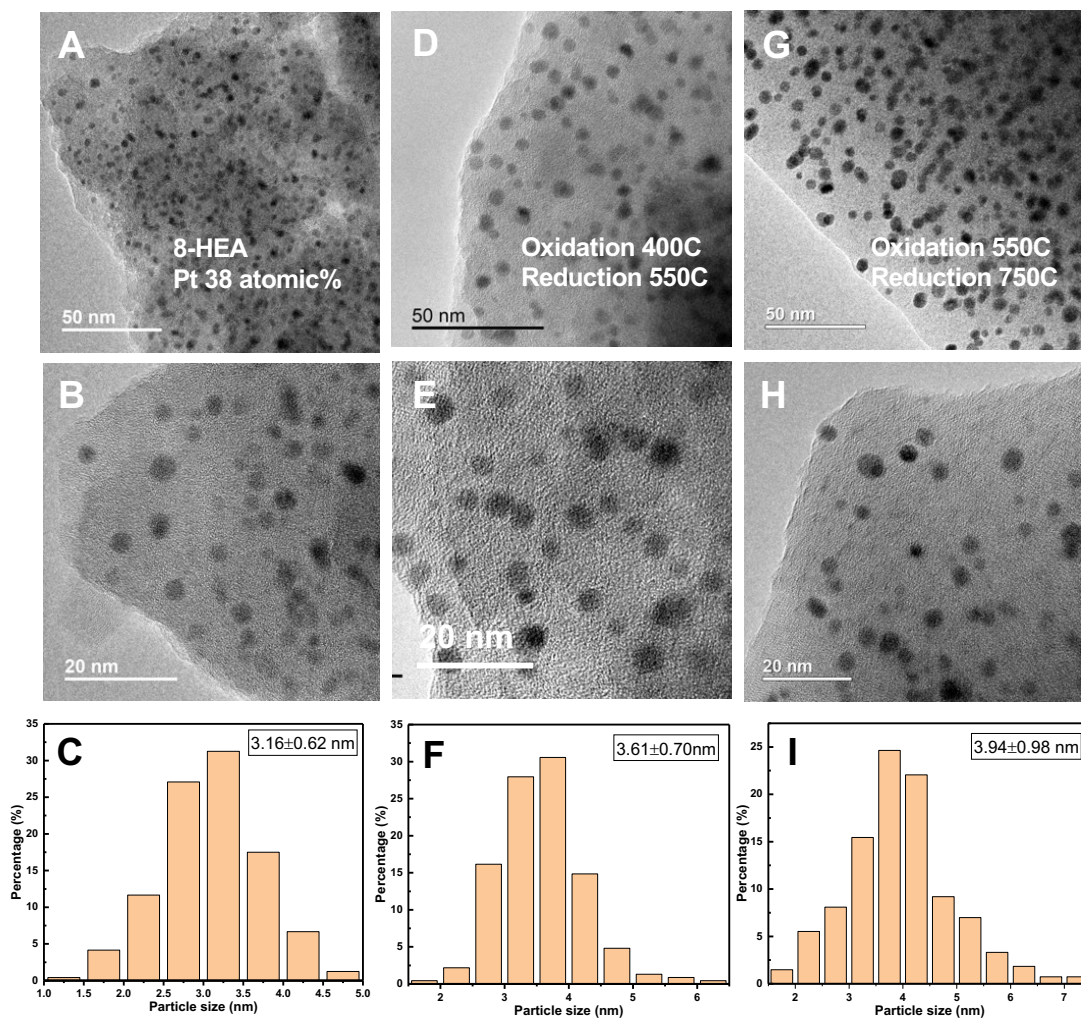


Figure 3.17. A, B TEM images of 8-HEA (Pt 38 atomic%) NPs synthesized by radiation heating method on Davisil 636 silica before sintering resistance test and C particle size distribution. D, E TEM images of 8-HEA (Pt 38 atomic%) NPs synthesized by radiation heating method on Davisil 636 silica after sintering resistance test (upper rows) and F particle size distribution. G, H TEM images of 8-HEA (Pt 38

atomic%) NPs synthesized by radiation heating method on Davisil 636 silica after sintering resistance test (lower rows) and **I** particle size distribution.

By comparing the TEM figures of the SA-HEA NPs before (Figure 3.18A, B) and after (Figure 3.18D, E) the sintering experiment, we can conclude that morphology the NPs are identical, and the SA-HEA NPs also have good anti-sintering stability under the PDH operation conditions.

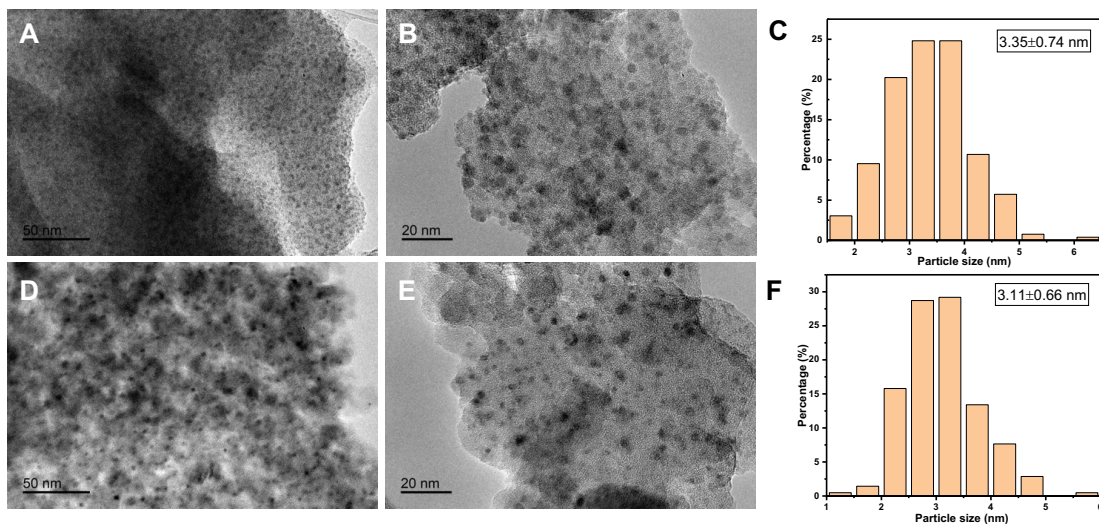


Figure 3.18. A, B TEM images of SA-6HEA (Pt 0.25 wt%) NPs synthesized by radiation heating method on Davisil 636 silica before sintering resistance test and C particle size distribution. D, E TEM images of SA-6HEA (Pt 0.25 wt%) NPs synthesized by radiation heating method on Davisil 636 silica after sintering resistance test (lower rows) and F particle size distribution.

4.2.4 PDH conversion and selectivity

Both Pt and binary NPs on silica synthesized by radiation heating showed promising PDH performance. The reaction was carried out at 550 °C, and the catalysts showed 80%, 90% selectivity at 30% conversion rate for Pt and PtV accordingly. For the multi-elemental catalysts, we even obtained 95% selectivity at 40% conversion rate (results tested by collaborator, Miller group, Purdue University). The catalysis performance of HEA NPs will be carried out in the future and we believe that they have the potential to yield higher selectivity.

4.3 Binary, ternary, and HEA NPs as ammonia decomposition catalyst

Ammonia is a promising liquid fuel for hydrogen storage medium. But its large-scale application is limited by the need for precious metal ruthenium (Ru) as catalyst to decompose ammonia. Due to the scarcity and high cost of this precious metal, research efforts have been turned to alloys of earth-abundant elements^{5–9}. Bimetallic Co-Mo has been shown to be promising for ammonia decomposition, as rationalized by the computational interpolation of adsorption properties on the alloy surfaces with mixed sites^{9,10}. However, the ability to functionally tune and catalytic activity of Co-Mo catalysts are largely constrained by the large miscibility gap present in the phase diagram of this binary alloy (Figure 3.19), and the experimental studies have primarily been limited to the catalysts with elemental ratio of Co/Mo around 1:1^{11–15}. It is crucial to bridge this gap for both fundamental understanding of alloy catalysts and practical improvement of the performance of earth-abundant materials in energy-conversion systems.

With the thermal shock method, over five metals could be incorporated into a single solid-solution phase, driven by the entropy effect. In the HEA solid solution structure, miscible Co-Mo bimetallic structures could be achieved with robust tuning of surface adsorption properties, and the continuous varying of alloy composition (Co/Mo ratio). By breaking the immiscibility limitation, a comprehensive and systematic study of the structure property-catalytic performance relationship can be studied. The robust tunability of alloy composition and surface adsorption property on the HEA NPs would also indicate great potential in composition screening for their implementation in practical reactors with the catalytic performance optimized under various reaction conditions.

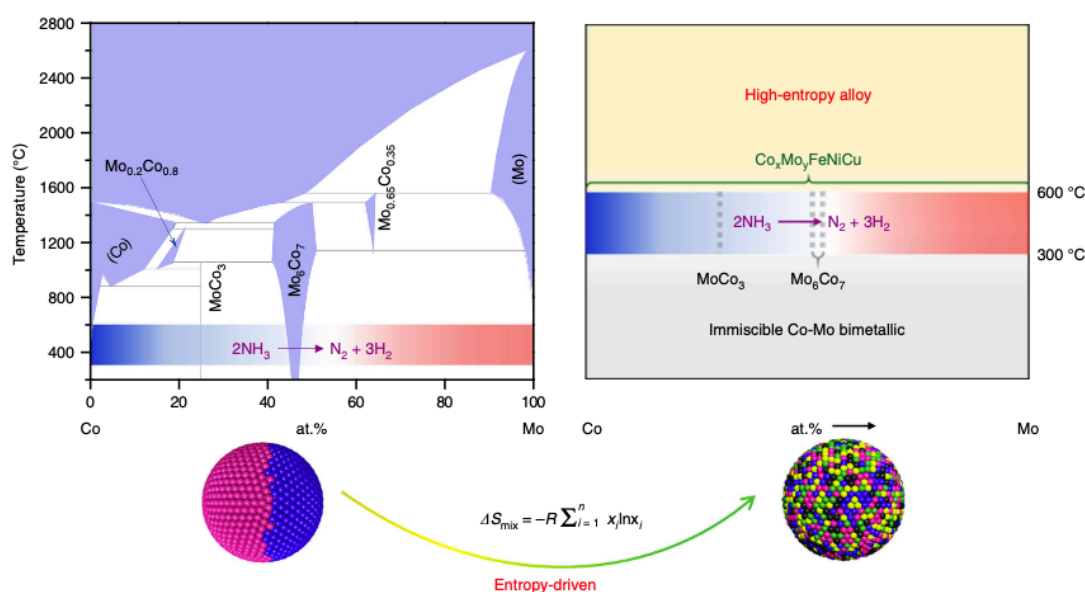


Figure 3.19. HEA catalysts breaking the miscibility limitation of conventional binary alloys. The phase diagram of bimetallic Co-Mo (left) is reprinted from Wang et al³⁷.

Figure 3.20 demonstrates the preliminary results on synthesis the CoMo NPs on the carbon felt substrates. Carbon felt was chosen as the substrate material due to its

commercial availability and porous structure. Carbon felt was prepared as stripes and pre-loaded with CoMo precursor salts (Figure 3.20A) and connected to the circuit in an Ar-filled glovebox (Figure 3.20B). In the thermal shock process, the carbon felt would serve both as heater and substrate. After the shock process, CoMo NPs were formed onto the fibers of the carbon felt and was characterized by SEM. Figure 3.20C, D demonstrate the morphology of CoMo-3 wt% NPs. The NPs are evenly distributed on the fiber and were estimated of an average size around 50 nm. For the CoMo-10 wt% NPs (Figure 3.20E, F) synthesized by a similar process, the particle morphology was less optimal due to the relatively high loading. Higher loading of the precursor salts usually would lead to a non-uniformly coating of the precursor salt in between the carbon felt networks. Under the fast shock process, the densified spots of precursor salts would tend to form large and irregular-shaped particles.

In the future study, a two-step shock process will be studied to improve the particle morphology of the CoMo and CoMo-HEA NPs. The purpose of the two-step shock process is to re-disperse the precursor salts on the carbon felt networks before the actual synthesis step. A lower temperature will be employed in the first step to melt and mix the Co and Mo precursor salts while a higher temperature will be used in the following step to decompose the precursor salt and enabling particle alloying. Furthermore, an optimized shock profile will be applied to the synthesis of CoMo-HEA and other HEA compositions.

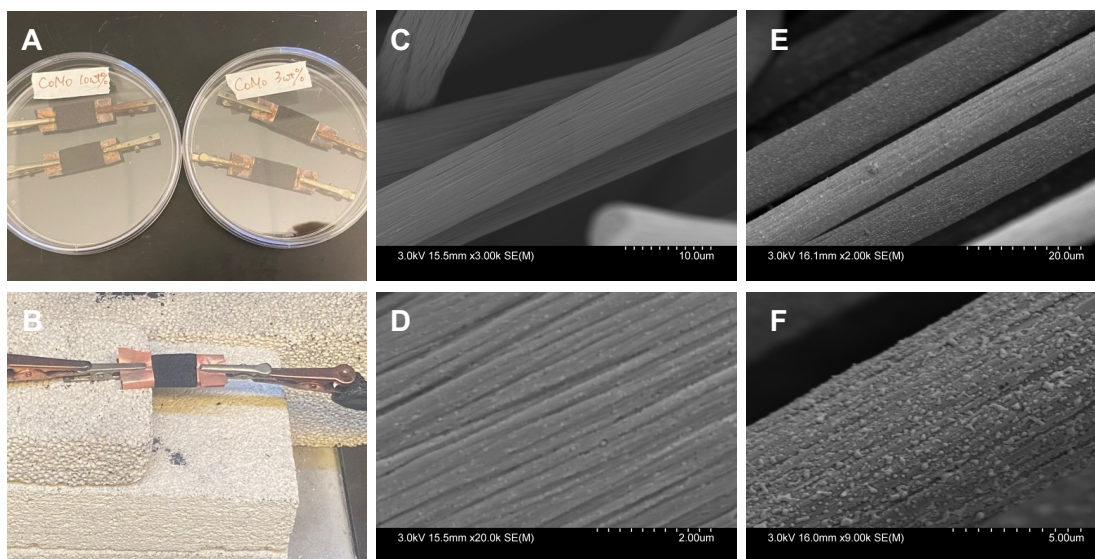


Figure 3.20. Photos of the **A** precursor salt loaded carbon felt stripes and **B** precursor salt loaded carbon felt stripe connected to the circuit. **C**, **D** SEM images of the CoMo-3 wt% NPs loaded on the carbon felt fiber networks. **E**, **F** SEM images of the CoMo-10 wt% NPs loaded on the carbon felt fiber networks.

Chapter 4: Carbon-Supported, High-Loading, Ultra-Small Pt₃Ni Nanoparticles via Tuning the Surface Electrostatic Effect*

Abstract

Carbon-supported nanoparticles (NPs) are widely used as catalysts in fuel cells and electrolyzers. While it is well known that NPs with smaller size and higher loading often lead to better catalytic activity, they remain challenging to synthesize due to the weak control over the surface properties of the support. Herein, A facile approach to synthesize carbon-supported, high-loading, and ultra-small Pt₃Ni NPs via applying thermal shock on strongly interacted carbon support with metal salt is reported. Specifically, sodium citrate is introduced into the precursor solution and substrate mixture, which induces strong electrostatic effect between metal salts and carbon particles that markedly improves precursor anchoring and dispersion, thereby achieving high particle loading as well as small size and distribution. As a proof-of-concept, the synthesis of Pt₃Ni NPs supported on carbon black with particle size of 1.56 ± 0.36 nm at 30 wt% loading and 1.66 ± 0.56 nm at 40 wt% loading is reported, where the sizes are among the smallest while the loadings are among the highest in the literature. This approach can be readily extended to many compositions and substrates, with tunable particle size and loading, thereby substantially expanding the synthesis space for NP catalysts in various electrochemical applications.

* The results in this chapter have been published: Li, S.; Xie, H.; Dong, Q.; Jing, S.; Li, T.; Xu, L.; Hu, L. Synthesizing Carbon-Supported, High-Loading, Ultra-Small Pt₃Ni Nanoparticles via Tuning the Surface Electrostatic Effect. *Small Structures* **2023**, 4 (1), 2200176. ³⁸

6.1 Introduction

Highly dispersed nanoparticles (NPs) on the carbon supports are attractive electrocatalysts for a range of applications such as fuel cells and electrolyzers³⁹⁴⁰⁴¹⁴²⁴³⁴⁴⁴⁵⁴⁶⁴⁷. For practical considerations, NPs with smaller size and higher loading are highly desired for improving the areal activity (e.g., current density) of the formed electrode⁴². However, from the synthesis viewpoint, there is often a tradeoff between the NP quality (size, size distribution, uniformity, etc.) and NP loading. This is because the carbon support has limited sites (e.g., defects) to anchor NPs, which limits the ultimate NP loading density⁴⁸. In addition, as most syntheses require adding the metal salt precursors through wet impregnation, the loading density of the metal cations is also determined by the surface electrostatic force by the carbon support, which is often limited as well⁴⁹. Due to these reasons, increasing the NP loading typically results in wider NP size distribution, larger NP sizes than desired, and even NP agglomeration that can severely undermine the catalytic performance. Given the sprout of electrochemical technologies for energy conversion and storage, it is urgent to develop new synthetic approaches to fabricate carbon-supported, high-loading, and high-quality NP electrocatalysts⁴².

To this end, substantial efforts have been dedicated to improving the NP loading on the carbon supports while maintaining optimal NP size and distribution⁴². For example, colloidal synthesis has been proven to successfully gain composition and size control for Pt₃Ni NPs using ligands and capping agents⁴⁰⁵⁰. However, the active sites on the surface would be partially covered by the adding agents, thus hinder the electron transport, and suppress the catalytic performance⁴⁰⁵⁰. In the impregnation method,

reducing of temperature by carbonyl complex process and water-in-oil micro-emulsion method can help to prevent the particle agglomeration and synthesize small size NPs but still limited in the loading and composition control⁵¹⁵². Moreover, the aforementioned methods usually involve with multi-step fabrication procedures containing particle synthesis and additional combination with support. Such process can easily cause afterwards particle growth, agglomeration, composition loss and lose attachment with supporting substrate, which usually requires extra immobilization treatment. Also, compared to specially fabricated substrate, it would be beneficial to synthesize NPs on commercial, scalable, and feasible substrate materials, like CB⁵³⁵⁴⁵⁵. To date, there still lacks an effective method that can precisely tune the interaction between metal salt precursor and the carbon support, thereby achieving high NP loading with desired NP size and distribution.

In this study, we report a facile method for the synthesis of high-quality, carbon-supported, high-loading, and ultra-small NPs. Our approach is based on tuning the electrostatic interaction between metal salts and carbon particles via introducing sodium citrate as a stabilizing agent into the precursor solution and carbon support mixture, which markedly improves precursor anchoring and dispersion. Then, a thermal shock process is conducted following the impregnation, resulting in high NP loading as well as small NP size and distribution¹⁸²⁵²²⁵⁶. As a proof-of-concept, we chose Pt₃Ni bimetallic NPs as a model system credit to the large body of literature reports on Pt-based bimetallic NP catalysts and their great promises in electrochemical catalytic reactions⁵⁷⁵⁸⁵⁹⁶⁰. We revealed the mechanism behind the citrate-assisted and charge-enhanced process and screened optimal experimental parameters. By tuning the

electrostatic effect using sodium citrate, we demonstrate the synthesis of Pt₃Ni bimetallic NPs supported on Ketjen carbon black at 30 wt% and 40 wt% loading, with NP size of 1.56 ± 0.36 nm and 1.66 ± 0.56 nm respectively. Notably, the NP size and distribution at such high loadings are among the best in the literature. Additionally, the Pt₃Ni bimetallic NPs show excellent dispersion on the Ketjen carbon black support without agglomeration. This approach can be readily transferred to other NP compositions such as Pt₃Co and other supports such as CNF with tunable size and loading, thereby largely expanding the synthesis scope of NP catalysts. These high-quality, carbon-supported, high-loading, and ultra-small NPs hold great potential as highly active catalysts for a variety of electrochemical devices (Figure 4.14).

6.2 Results and discussion

Figure 4.1A schematically demonstrates the critical roles sodium citrate stabilizing agent plays in the precursor loading process using Pt₃Ni as a model system. First, the sodium citrate, together with the metal precursor H₂PtCl₆ dissolved in DI water, creates a buffering system with an optimal and stable pH value. Under the weak acidic condition, the citrate and proton-citrate species surround and stabilize the Ni²⁺ in the precursor solution and form negatively charged complexes. The appropriate pH condition in the precursor solution also helps the protonation of the CB surface to a positively charged surface and generates of strong electrostatic interaction between the carbon support and negatively charged ions in the precursor solution. In this way, the metal salt precursor can form a uniform coating over the carbon support even with high loading.

Figure 4.1B compares the precursor impregnation process with and without the sodium citrate stabilizing agent. The first step in Figure 4.1B represents the precursor loading process. Without sodium citrate in the system, precursor salts tend to randomly distribute over the support and form aggregation after freeze drying. In the case with sodium citrate, we prepared a precursor solution of sodium citrate, metal precursor salt H_2PtCl_6 and NiCl_2 with molar ratio of 3:1 in DI water and mix the precursor solution with CB under ultrasound until they form a homogenous slurry (See the Experimental Section for details). The presence of citrate anions improves the loading process that leads to a layer of uniform precursor coating over the support. The precursor-loaded material was transferred onto the heater, a stripe of carbon nanotube film that was connected to a homemade sample holder⁶¹⁶². By applying different currents through the heater for radiative Joule-heating, the Pt_3Ni NPs are formed and anchored onto the support (See the Experimental Section for details).

From a mechanistic viewpoint, a uniform coating of precursors undergoes more simultaneous decomposition reaction, followed by even nucleation of the NPs, leading to good dispersion. Notably, the rapid heating and cooling rates as well as the short shock duration of the radiative Joule heating also help to prevent agglomeration and ripening of the NPs. On the contrary, unevenly coated precursor tends to form large nucleus on the concentrated area and thus generating broad NP size distribution and even NP agglomeration. The ultra-small and evenly distributed NPs on carbon black with high loading offer increased surface area/ volume ratio and active sites density for various applications.

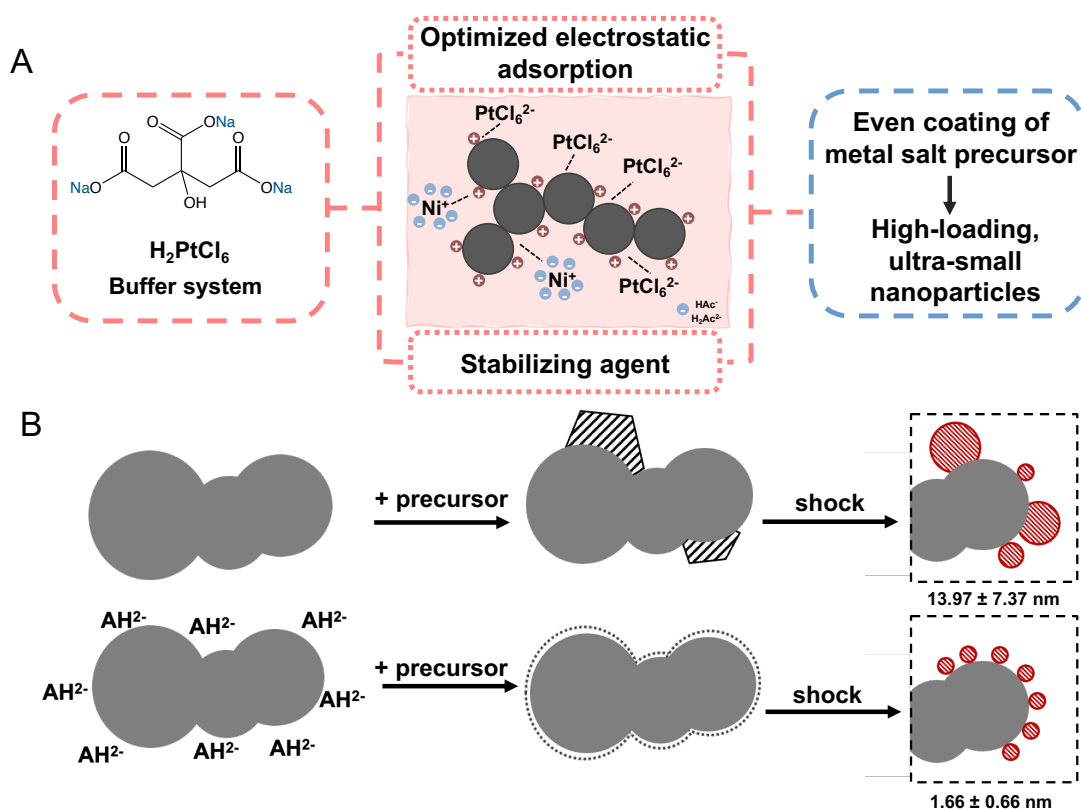


Figure 4.1. The working principle of citrate-assisted synthesis of ultrasmall Pt_3Ni NPs.

(A) Schematic showing the roles played by sodium citrate in the precursor loading process. (B) Schematic comparison of the precursor loading process with and without citrate anions.

The citrate-assisted precursor loading process is illustrated in Figure 4.2A and 6.2B, showing the precursor solution with CB support and the slurry mixture after sonication, respectively. The citrate containing precursor solution demonstrate good liquid-solid interaction and can form a well-mixed slurry with CB under sonication without excess liquid. We conduct a series of characterizations to better understand the role of sodium citrate in the precursor loading process. For studying the difference of surface defects between pristine CB and citrate treated CB, an investigation was

conducted by Raman spectroscopy on different CB samples. The Raman spectra of CB and citrate-treated CB are shown in Figure 4.5. After treated with citrate, the I_D/I_G value slightly increased from 1.29 (CB) to 1.31 (citrate-CB) indicating an increase in oxygen-containing functional groups on the carbon surface. The increased amount of surface oxygen-containing groups by the incorporation of sodium citrate should induce strong interaction between precursor salts and CB support, which is the foundation to allow precursor salt to evenly distribute on the support.

To further support the argument that citrate improves the uniformity of precursor loading on CB, we characterize the surface morphology of the precursor loaded CB supports with and without the citrate treatment. The SEM images shown in Figure 4.2C reveal a layered, coarse, and spotted CB surface with precursor loading but without citrate, showing a certain level of precursor aggregation. In contrast, the SEM images shown in Figure 4.2D demonstrate a much more uniform precursor salt coating on CB assisted by citrate. Note that the SEM samples are used as prepared without further treatment in order to preserve the surface morphology, which to some extent undermines the image quality. Nevertheless, the stark comparison between Figure 4.2C and 2D reveals the critical effect of sodium citrate to improve the dispersion of precursor salts. Such effect can also be seen in other carbon supports such as CNF as shown in the Figure S3. Precursor salt coating presents a smooth and even layer on CNF assisted by citrate while accumulate to chunks and clusters without the citrate treatment. We further conduct elemental mapping (Figure 4.2E) on the citrate treated CB support with precursor salts, where we observe uniform distributions of both Pt and Ni on the CB surface. The homogenous coating of metal salt precursors on the

carbon support laid the foundation toward forming evenly distributed and ultra-small NPs also with a narrow size distribution.

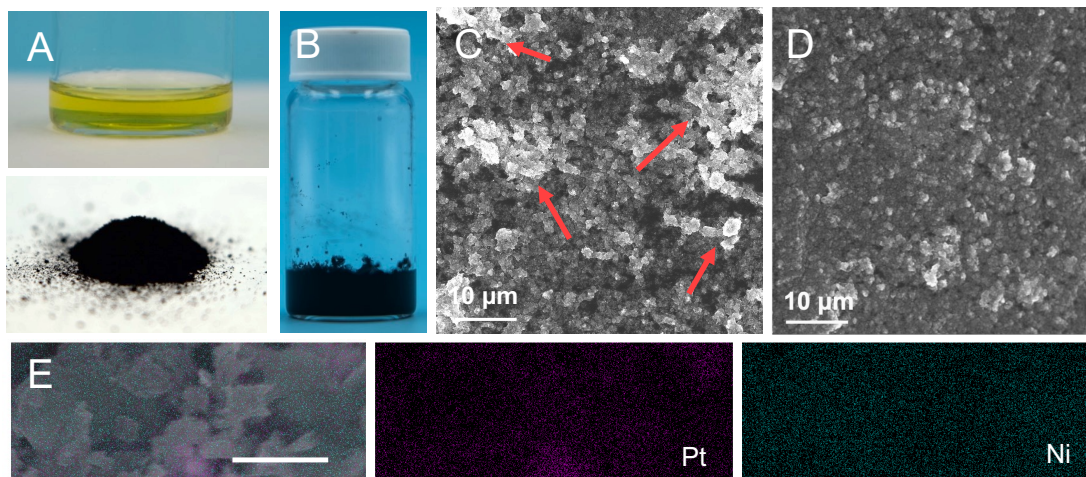


Figure 4.2. Precursor preparation and loading processes. (A) Digital images of the precursor solution and the CB support. (B) Digital image of the slurry mixture of precursor solution and CB support after sonication. (C) SEM image showing the uneven precursor coating on CB without the sodium citrate treatment (Precursor salt aggregation regions are pointed out by arrows). (D) SEM image showing the uniform precursor coating on CB with the sodium citrate treatment. (E) Elemental maps of Pt and Ni on the CB support, demonstrating uniform coating of both precursor salts (Scale bar: 10 μm).

After thermal shock via radiative Joule heating, we loaded Pt_3Ni NPs on the CB support. We compare the particle size and distribution of non-citrate and citrate-assisted Pt_3Ni NPs with 30 wt% (Figure 4.3A and 6.3B) and 40 wt% (Figure 4.3C and 6.3D) loadings using transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). Note that these loadings are at a practical level for most

electrochemical energy conversion and storage devices such as alcohol fuel cells and electrolyzers, which is challenging for conventional methods to have fine control on the NP size and distribution. Figure 4.3A and 6.3B compares the morphology of the Pt₃Ni NPs at 30 wt% loading prepared without and with the citrate during the precursor loading process, respectively. The NPs present broad size distribution and large particle size in general without citrate (Figure 4.3E), which translates to a mean value and standard deviation of 8.81 ± 3.57 nm. For citrate-assisted Pt₃Ni NPs, we observed ultra-small particle size and narrow size distribution of 1.56 ± 0.56 nm (Figure 4.3F), indicating much improved NP dispersion and size control. As we further increase the loading to 40 wt% (Figure 4.3C and 6.3D), we can still obtain ultrafine Pt₃Ni NPs with the help of citrate while those without citrate treatment remain agglomerated with broad size distribution. Without the citrate, the Pt₃Ni NPs showed a 13.97 ± 7.37 nm NP size (Figure 4.3G). In comparison, with the citrate treatment, the Pt₃Ni NPs showed a 1.66 ± 0.56 nm NP size at 40 wt% loading, which is only slightly larger than that at 30 wt%. The elemental composition is further confirmed by the TEM-EDX as shown in Table 6.2 and 6.3. The nominal loadings of Pt₃Ni NPs are also confirmed by thermal gravimetric analysis as shown in Table 6.4 and Figure 4.11.

Powder X-ray diffraction (XRD) was conducted to study the crystal structures of the obtained carbon-supported NPs samples, as shown in Figure 4.8. All samples are in Pt₃Ni alloy phase and present a fcc crystalline structure without impurity phases or phase segregation. The diffraction peaks of all synthesized Pt₃Ni NPs tend to move toward higher 2θ values from the pure Pt standard (JCPDS 87-0642) because of the lattice difference between Ni ($a_{\text{Ni}} = 3.524$ Å) and Pt ($a_{\text{Pt}} = 3.923$ Å). These evidences

indicate the successful alloying of Pt and Ni during the conversion from precursor salt to metal alloy NPs via the thermal shock process. Notably, the Pt₃Ni NPs (black line) synthesized without citrate treatment at both 30 wt% (Figure 4.7A) and 40 wt% loadings (Figure 4.7B) show a sharp peak, indicating relatively larger NP size, which is in consistence with the TEM observation. In comparison, the Pt₃Ni NPs (red line) synthesized with the citrate treatment presents boarder diffraction peaks, which are consistent with their ultra-small size and narrow distribution as observed under TEM.

To demonstrate the adaptability of this method, we also successfully synthesized Pt₃Ni NPs on CNF and Pt₃Co NPs on CB, where we achieved similar improvements in particle size and distribution with the citrate-assisted loading process (Figure 4.9). These results show that our approach can be extended to various alloy compositions and substrate choices.

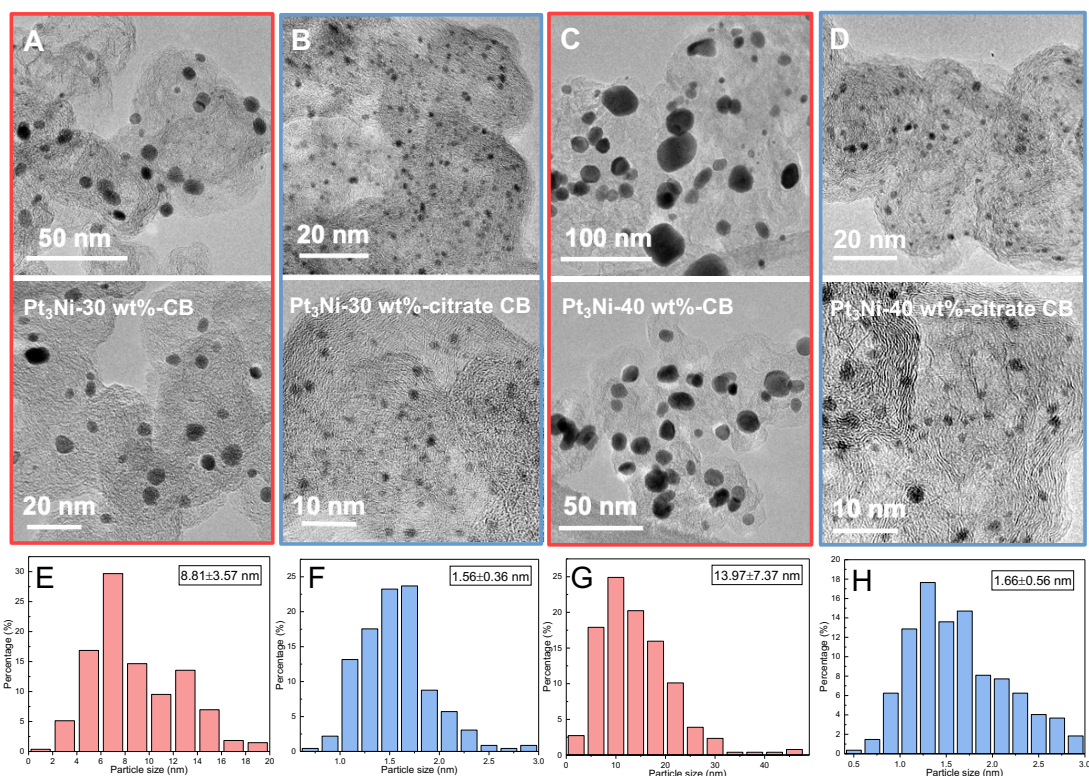


Figure 4.3. Morphology of the Pt₃Ni-CB samples prepared under different conditions. (A) and (B) TEM images of Pt₃Ni-30 wt%-CB and Pt₃Ni-30 wt%-citrate CB. (C) and (D) TEM images of Pt₃Ni-40 wt%-CB and Pt₃Ni-40 wt%-citrate CB. (E-H) Size distribution histograms of Pt₃Ni-30 wt%-CB, Pt₃Ni-30 wt%-citrate CB, Pt₃Ni-40 wt%-CB, and Pt₃Ni-40 wt%-citrate CB.

To understand the mechanism behind this citrate assisted method to synthesize ultra-small NPs, we adjusted the pH value of the citrate-precursor solution and study its effect on the NP size and distribution. In general, sodium citrate and H₂PtCl₆ together form a buffer solution and can stay stable during the preparation process. Without the citrate, the pH value of the precursor solution drops in the range of 0-1, while the pH value of the citrate-containing precursor solution is about 5-6. We used

1M HCl solution to adjust the pH value of the citrate-containing precursor solution (while keeping the same amount of citrate used in the solutions) to 0-1 and 2-3. We also include a control sample with ethanol being the solvent as compared to aqueous precursor solutions. These precursor solutions were then applied to the same loading, followed by an identical thermal shock procedure to synthesize Pt₃Ni NPs. Figure 4.4A show the trend of particle size and distribution as a function of precursor solution and their pH value. The Pt₃Ni NPs prepared in ethanol showed the largest particle size and relatively broad size distribution. The particle size and distribution decrease as the incorporation of citrate and increase of pH value of the precursor solution, which means the presence of citrate and appropriate pH value are both crucial for obtaining fine size.

In general, citrate undergoes a three-step hydrolysis in aqueous solution, in which the dominant species is different in different pH ranges⁶³. As shown in Figure 4.4B, H₃A is the major component in strong acid while in weak acid condition, the dominant species are HA²⁻ and H₂A⁻. HA²⁻ and H₂A⁻ would substitute the H₂O in Ni (H₂O)₆²⁺ complex and form negatively charged complexes as pH value increases from strong acid to weak acid conditions. The UV spectrum confirm this trend in Figure 4.4C. As the pH value increases, the absorption peak of Ni²⁺ complexes around 700 nm wavelength in the solution shows a blue shift, indicating the substitution of citrate species of H₂O^{64,65}. Figure 4.4E demonstrates the citrate-assisted and charge-enhanced mechanism in detail. In the aqueous precursor solution, the CB surfaces are protonated to different levels depending on the pH value⁶⁶. In weak acid solution, the CB surfaces are positively charged⁶⁷, which is confirmed by a surface zeta-potential of 6.6 eV (Figure 4.4D). Both negatively charged Ni-citrate complexes and PtCl₆²⁻ ions are

absorbed to the positively charged CB surface due to strong electrostatic interactions and would form a uniform layer of coating on CB, leading to ultra-small NPs with narrow size distribution. In strong acid solution, however, the CB surfaces are fully positively charged with extra protons in the solution. The $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ ions in the solution are repulsive from the carbon surface and the extra protons in the solution may also hinder the interaction between PtCl_6^{2-} and the CB surface. The precursor salts are not in a favorable position to interact with the CB surface, in which case they would tend to form uneven coating on the surface. Lastly, when ethanol is used as the solvent, there should be the weakest interaction between the CB surface and precursor salt ions, leading to large particle size and distribution.

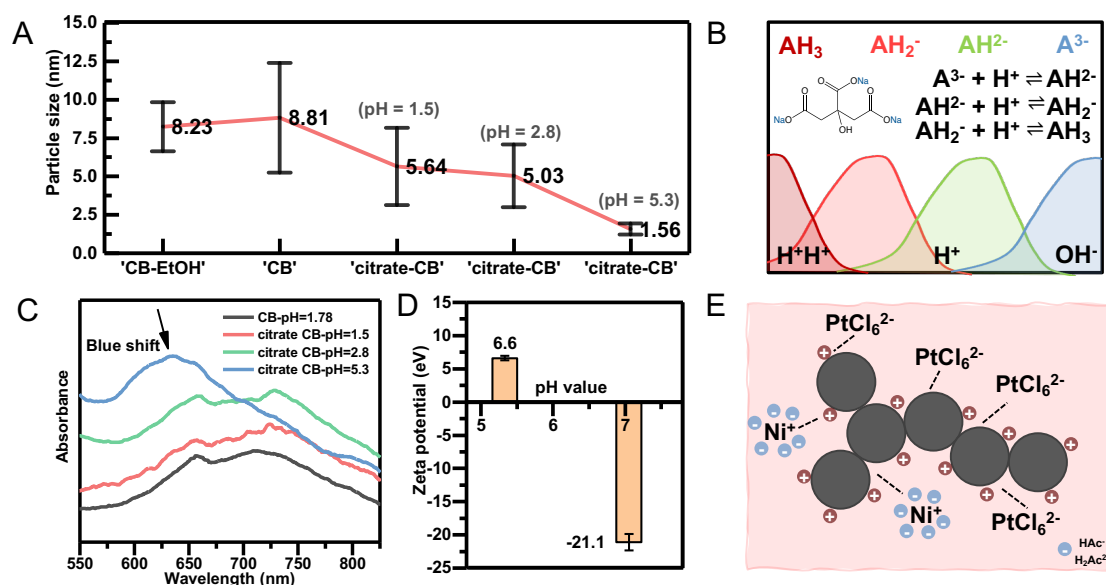


Figure 4.4. Mechanistic exploration of the role of citrate. (A) Particle size and distribution trends vs pH value of different precursor solutions. (B) Chemical structure of sodium citrate, three-step hydrolysis of sodium citrate and schematic illustration of different citrate species in different pH ranges. (C) UV absorption spectrum of Ni^{2+} in

sodium citrate solution of different pH values. (D) Zeta potentials of CB in DI water and weak acid solution. (E) Schematics illustration of citrate-assisted and charge-enhanced mechanism on precursor loading process.

6.3 Conclusion

In summary, we have designed a facile synthesis approach of ultra-small and high-loading NPs on carbon substrate via tuning the surface electrostatic effect. We employed sodium citrate in the precursor loading process as a modifier, stabilizing the precursor ions and buffer in the precursor solution to achieve an optimal acidity that leads to desired surface charge of the carbon surface. Via tuning this electrostatic effect, the interaction between the CB surface and precursor salt ions is largely improved, which results in uniform precursor coating thus high NPs quality. We use this method to achieve ultrafine Pt₃Ni NPs on carbon black as a proof-of-concept with high particle loading of 30 wt% and 40 wt%. We obtained ultrafine Pt₃Ni NPs with 1.56 ± 0.36 nm in size at 30 wt% and 1.66 ± 0.56 nm in size at 40 wt%, which are nearly 10 nm smaller compared to Pt₃Ni NPs prepared without the citrate in the precursor loading process. These NP sizes at such high loadings are among the smallest among the literature reports. We note that this method is not only limited in bimetallic NPs synthesis or NPs on carbon black but can be extended to a range of NP compositions on various substrate materials, thus providing a general strategy for developing ultrafine and high-loading NPs as electrocatalysts for various reactions.

6.4 Experimental

Materials

Commercial carbon black (Ketjen black EC-400JD) was chosen as the substrate to support Pt₃Ni and Pt₃Co NPs. Polyacrylonitrile (PAN, M_w = 860 000), dimethylformamide (DMF), H₂PtCl₆·xH₂O, NiCl₂·6H₂O, CoCl₂·6H₂O, 1M HCl solution and sodium citrate tetrahydrate are purchased from Sigma Aldrich.

Synthesis of Pt₃Ni NPs supported on CB

Preparation of precursor solutions: The single salt solution (0.05 M) was prepared by dissolving precursor salts in ethanol. Then Pt₃Ni precursor solution was obtained by mixing the single salt solution by the designed composition of Pt:Ni = 3:1.

Preparation of Pt₃Ni NPs: The mixed solution was added into carbon black with a targeted loading concentration, and then mixed under ultrasound for 0.5 hr. After the homogenous mixture was obtained, the mixture was carefully freeze-dried and ground to power. Then the precursor loaded powder was transferred to an Ar filled glovebox for high-temperature treatment. A 1.5×5 cm carbon nanotube (CNT) film heater was applied as the radiation heater, which serves as both heating element as well as large-scale production platform to process and collect the product. To synthesize the Pt₃Ni NPs, the salt precursor mixture and carbon black were treated by thermal shock at 1000 K for 0.5 second. The thermal shock was applied to the heater using an external StarPower DC Power Supply as the source to generate the desired temperature and to control the heating duration.

Pt₃Co NPs supported on CB were prepared by a similar method as the Pt₃Ni NPs.

Synthesis of Pt₃Ni NPs supported on CNF

Preparation of CNF: CNF was prepared by electrospinning of PAN with a concentration of 8 wt% in DMF at a voltage of 10kV, with a spinning distance of 15cm and a rate of 1 mL/h. The as-spun nanofibers were collected by a rotation drum at a speed of 80 rpm, stabilized at 260 °C for 5 h in the air, and then carbonized at 800 °C in an argon protected atmosphere for 2 h to obtain CNF.

Preparation of Pt₃Ni NPs supported on CNF: The metal salt precursor solution was drop onto the CNF strips and further dried under room temperature to prepare precursor loaded CNF strips. Then the precursor load CNF strips was transferred to an Ar-filled glovebox and connected to Cu electrodes by silver paste. The thermal shock was directly applied to the CNF stripe using an external Keithley 2425 SourceMeter to generate the desired temperature and to control the heating duration.

Characterization

Transmission electron microscopy (TEM; JEM-2100, JEOL, Tokyo, Japan) was used to reveal the morphology of Pt₃Ni nanoparticles, and their elemental analysis were achieved using energy dispersive spectroscopy (EDS; X-MaxN-100TLE, Oxford Instruments, Oxford, UK). A diffractometer (D8 Advance, Bruker, Karlsruhe, Germany) was used with Cu K α radiation to collect the XRD spectra of the Pt₃Ni nanoparticles supported on CB at room temperature. An AXIS 165 spectrometer (Kratos, Manchester, UK) was used to determine the XPS spectra of carbon black, citrate processed carbon black and Pt₃Ni nanoparticles. Raman characterization was conducted on a Horiba Jobin Yvon using a 532 nm solid-state laser with a 4 s integration time for 4 repeated measurements. The mass loading of Pt₃Ni nanoparticles on CB was measured by thermogravimetric analysis (Discovery SDT 650, TA

Instruments). UV-vis spectra for aqueous solutions were recorded in a SHIMADAZU UV-3400 i Plus spectrometer in the 500-900 range and using an optical length of 0.2 cm. pH values of aqueous solutions were measured by sartorius pHBasic+ pH meter. Zeta-potential of CB in DI water and weak acid solution was determined using the Zetasizer Nano ZS90 equipment.

Electrochemical Measurement

The catalyst ink for HER test was prepared by 1 mg carbon-supported Pt₃Ni NPs dispersed in 200 μ L mixed solution of Nafion, water, and isopropanol (1:50:150), and then sonicated for 30 min. 15 μ L ink was dropped onto the 0.196 cm² glassy carbon disk, and then dried at room temperature for 2h. The three-electrode system was used for the test on an electrochemical workstation (VMP-300, Bio-Logic) with a rotator (Pine Instruments). The obtained film on the glassy carbon disk was used as the working electrode. A graphite and an Ag/AgCl (saturated KCl) electrode were used as the counter electrode and reference electrode, respectively. The electrolyte was 0.5 M H₂SO₄ aqueous solution. The activity of the catalyst was evaluated by linear sweep voltammetry from 0 to -0.6 V (vs RHE) with a scan rate of 2 mV/s.

6.5 Supporting materials

Sample	Loading (wt%)	Solvent	pH	Substrate and loading method
Pt ₃ Ni-CB	30	EtOH	-	Ketjen carbon black
Pt ₃ Ni-CB	30	DI water	1.78	
Pt ₃ Ni-citrate CB	30	DI water	1.51	Ketjen carbon black; Prepared with Sodium Citrate in the precursor solution
Pt ₃ Ni-citrate CB	30	DI water	2.77	
Pt ₃ Ni-citrate CB	30	DI water	5.33	
Pt ₃ Ni-citrate CB	40	DI water	5.26	

Table 6.1. Synthesis parameters (loading, solvent and actual pH value) of different Pt₃Ni/CB samples.

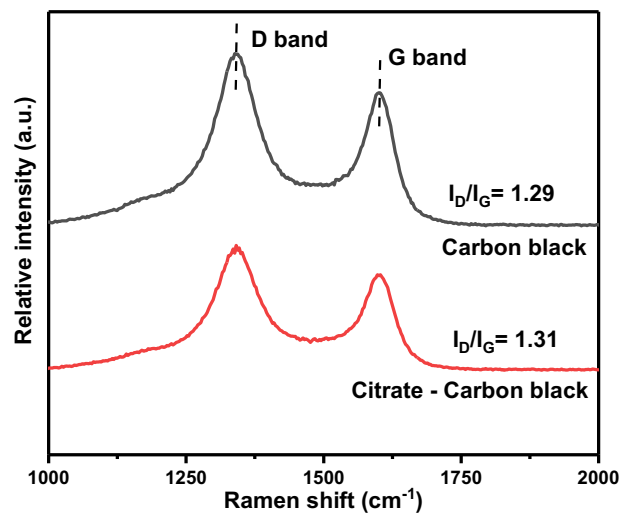


Figure 4.5. Raman spectra of CB and citrate-processed CB.

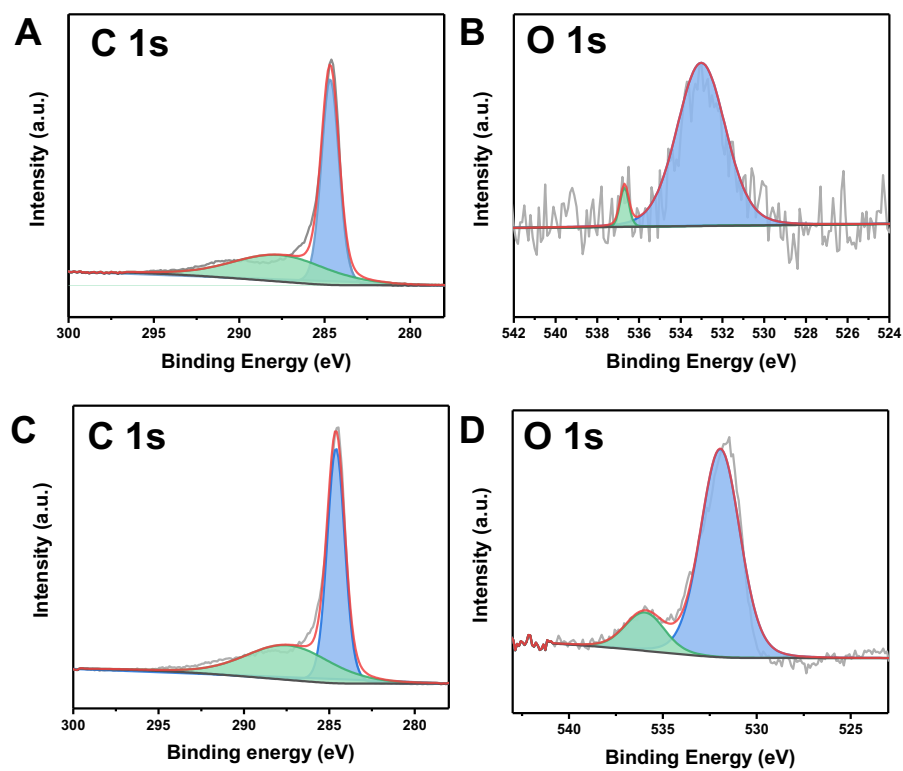


Figure 4.6. XPS spectra of (A) C 1s and (B) O 1s for Ketjen carbon black and (C) C 1s and (D) O 1s for citrate-processed carbon black.

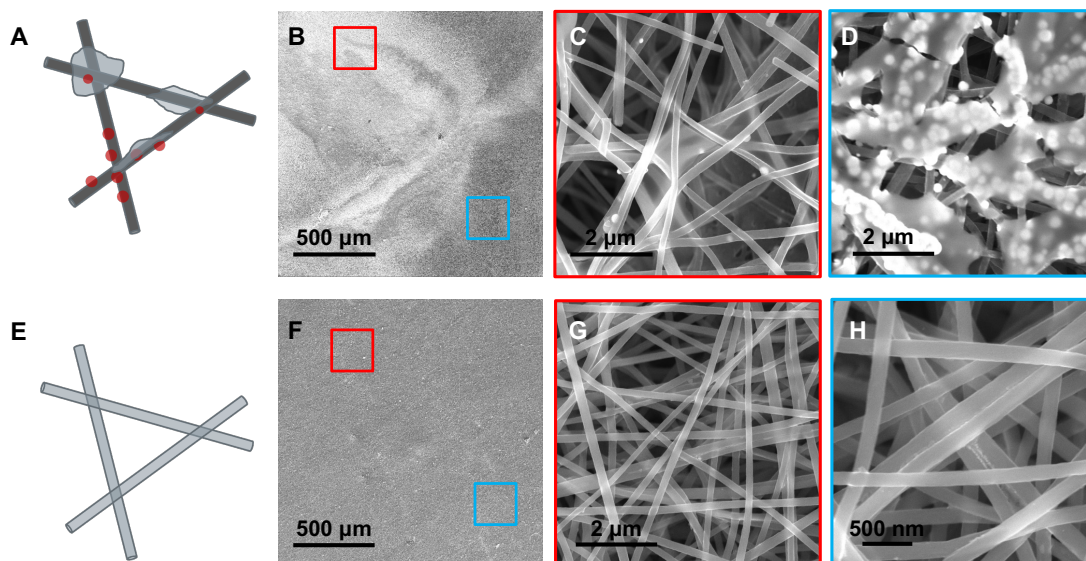


Figure 4.7. Precursor preparation and loading processes on CNF. (A) and (E) Schematics of the precursor coating on the CNF support without and with the sodium citrate treatment. (B)-(D) SEM image showing the uneven precursor coating on CNF without the sodium citrate treatment on different scale (Images of zoom-in area shown in same color squares respectively). (F)-(H) SEM image showing the uniform precursor coating on CNF with the sodium citrate treatment.

Element	Pt	Ni
Atomic ratio/ %	74.08	25.92
	78.61	21.39
	80.86	19.14

Table 6.2. Elemental analysis by TEM EDX for Pt₃Ni-30 wt%- citrate CB sample.

Element	Pt	Ni
Atomic ratio/ %	80.84	19.16
	79.91	19.09
	81.57	18.43

Table 6.3. Elemental analysis by TEM EDX for Pt₃Ni-40 wt%-citrate CB sample.

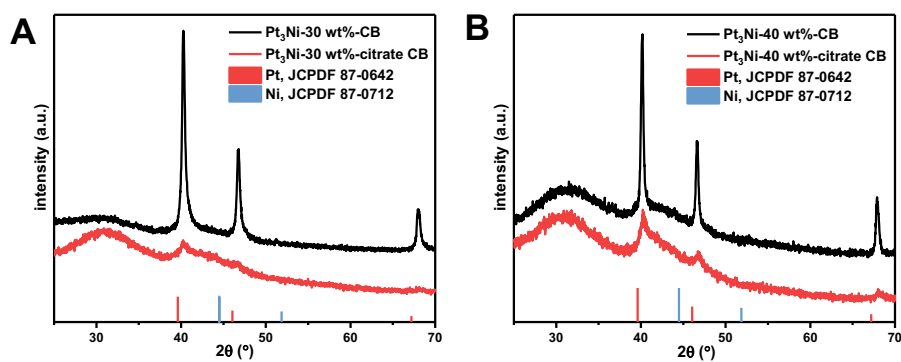


Figure 4.8. (A) XRD patterns of Pt₃Ni-30 wt%-CB and Pt₃Ni-30 wt%-citrate CB. (B) XRD patterns of Pt₃Ni-40 wt%-CB and Pt₃Ni-40 wt%-citrate CB.

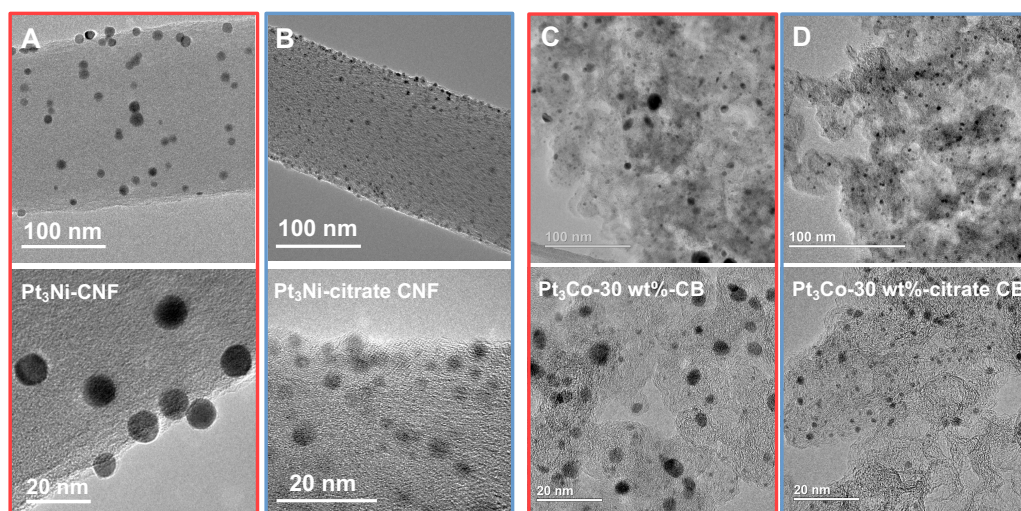


Figure 4.9. (A) and (B) TEM images of Pt₃Ni-CNF and Pt₃Ni-citrate CNF. (C) and (D) TEM images of Pt₃Co-30 wt%-CB and Pt₃Co-30 wt%-citrate CB.

Element	Pt	Ni
Atomic ratio/ %	71.52	28.48
	73.20	26.80
	75.08	24.92

Table 6.4. Elemental analysis by TEM EDX for Pt₃Co-30 wt%- citrate CB sample.

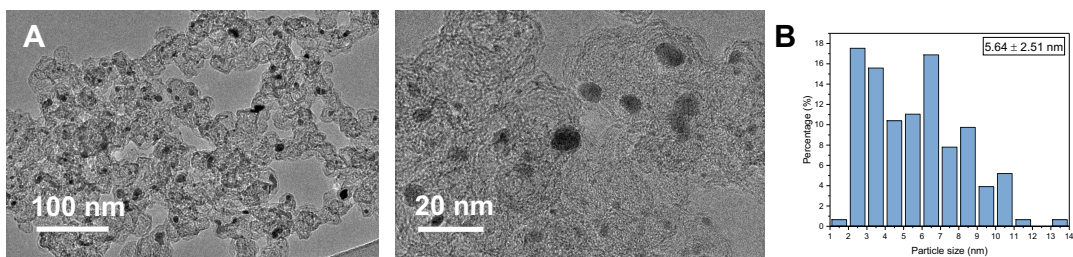


Figure 4.10. (A) TEM images of Pt₃Ni-30 wt%-citrate CB (pH=1.6) sample and (B) particle size distribution.

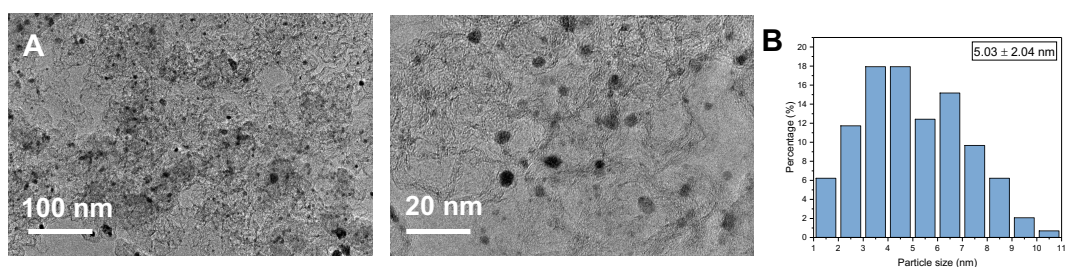


Figure 4.11. (A) TEM images of Pt₃Ni-30 wt%-citrate CB (pH=2.8) sample and (B) particle size distribution.

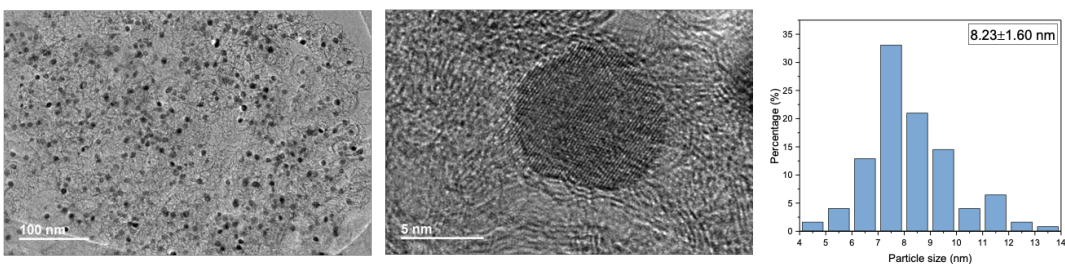


Figure 4.12. (A) TEM images of Pt₃Ni-30 wt%-EtOH sample and (B) particle size distribution.

Sample	Precursor loading (Pt ₃ Ni/ substrate (wt%))	TGA Residue (wt%)	NPs loading (Pt ₃ Ni/ substrate (wt%))
Pt ₃ Ni-citrate CB	30	32	47
Pt ₃ Ni-citrate CB	40	38	61

Table 6.5. TGA analysis data of Pt₃Ni-30 wt%-citrate CB and Pt₃Ni-40 wt%-citrate CB sample.

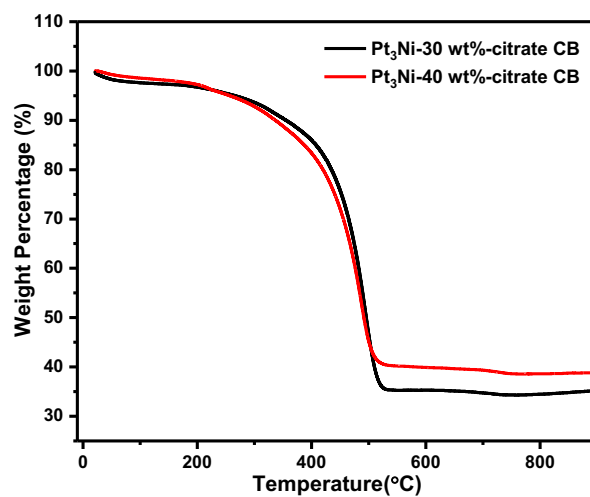


Figure 4.13. TGA curve of Pt₃Ni-30 wt%-citrate CB and Pt₃Ni-40 wt%-citrate CB sample.

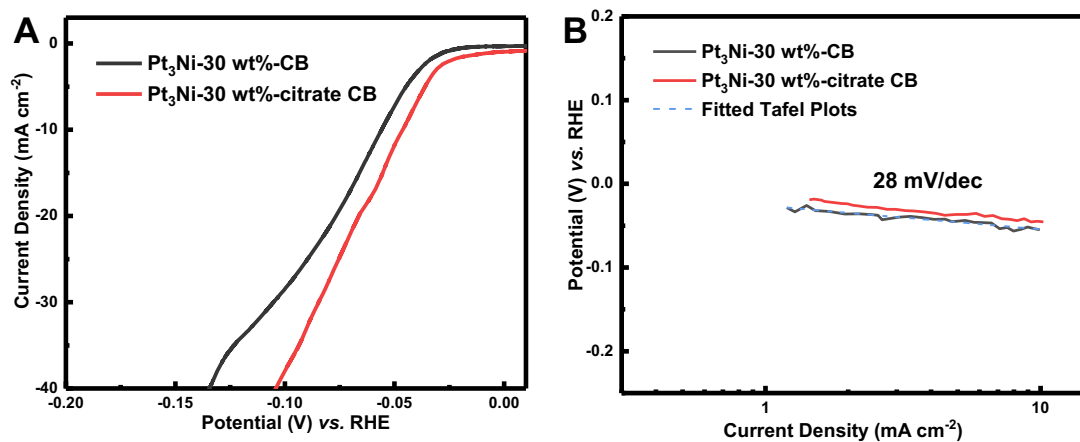


Figure 4.14. The electrocatalytic performance of Pt₃Ni-CB samples prepared under different conditions. (A) The linear sweep voltammetry in 0.5 M H₂SO₄ with a scan rate of 2 mV s⁻¹. (B) Fitted (blue dashed line) and observed Tafel plots under the same condition.

Chapter 5: Dispersed Ru in a Multielement Alloy Catalyst for Highly Selective Electrochemical Nitrate to Ammonia Conversion*

Abstract

Electrochemical reduction of nitrate to ammonia (NH_3) converts an environmental pollutant to a critical nutrient. However, current electrochemical nitrate reduction operations based on monometallic and bimetallic catalysts are limited in NH_3 selectivity and catalyst stability, especially in acidic environments. Meanwhile, catalysts with dispersed active sites generally exhibit a higher atomic utilization and distinct activity. Herein, we report a multielement alloy nanoparticle catalyst with dispersed Ru (Ru-MEA) with other synergistic components (Cu, Pd, Pt). Density functional theory elucidated the synergy effect of Ru-MEA than Ru, where a better reactivity (NH_3 partial current density of -50.8 mA cm^{-2}) and high NH_3 faradaic efficiency (93.5%) is achieved in industrially relevant acidic wastewater. In addition, the Ru-MEA catalyst showed good stability (e.g., 19.0% decay in FE_{NH_3} in three hours). This work provides a potential systematic and efficient catalyst discovery process that integrates a data-guided catalyst design and novel catalyst synthesis for a range of applications.

* The results in this chapter have been published: Yang, M.; Li, B.; Li, S.; Dong, Q.; Huang, Z.; Zheng, S.; Fang, Y.; Zhou, G.; Chen, X.; Zhu, X.; Li, T.; Chi, M.; Wang, G.; Hu, L.; Ren, Z. J. Highly Selective Electrochemical Nitrate to Ammonia Conversion by Dispersed Ru in a Multielement Alloy Catalyst. *Nano Lett.* **2023**, 23 (16), 7733–7742. ⁶⁸

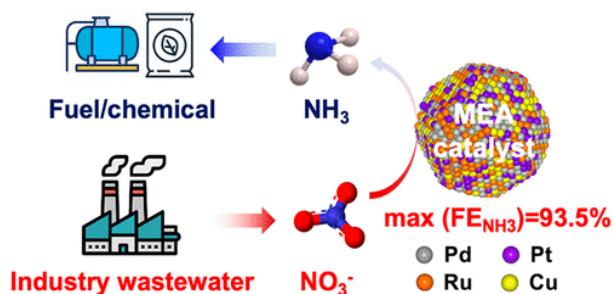


Figure 5.1. Schematics of the electrochemical reduction of nitrate to ammonia pathway and MEA catalyst design.

7.1 Introduction

The global nitrogen (N) cycle has been largely altered by human activities in the past century, resulting in severe energy and environmental problems⁶⁹⁷⁰. In the N cycle, nitrate (NO_3^-) is a major contaminant from industrial effluents and is typically converted to N_2 gas through biological denitrification (Figure 5.2a)⁷¹⁷². This process is not economically efficient and is associated with potent greenhouse gas nitrous oxide (N_2O) emissions^{7374,7576}. However, many of these liquid wastes (e.g., fertilizer, ammunition, metal pickling, and nuclear industries) are acidic at their source of generation due to the consumption of nitric acid and have very low biodegradability; thus, chemical addition or pretreatment is necessary for NO_3^- removal and^{77–80}. Ammonia (NH_3) is another critical component of the cycle and an essential fertilizer and chemical feedstock. NH_3 is mostly synthesized using N_2 and H_2 by the energy-intensive Haber Bosch process, which accounts for 1.8% of global energy consumption and 1.4% of global CO_2 emissions⁸¹. During utilization, the NH_3 is generally oxidized to NO_3^- , and decades of overfertilization and releases of these nitrogen pollutants in the water body have been a major cause of eutrophication, biodiversity loss, and N_2O

emissions. Therefore, rather than finishing the N cycle via N_2 using high cost of energy and chemicals, a shortcut reduction directly from NO_3^- to NH_3 holds the promise to reduce nitrogen pollution while producing green and distributed NH_3 (Figure 5.2a)⁸²⁸³⁸⁴.

To catalyze electrochemical NO_3^- reduction (ENR), a range of monometallic catalysts made by transition metals such as Ru, Rh, Pt, Pd, Ti, Cu⁸⁵⁸⁶⁸⁷, and bimetallic catalysts such as Pd-Cu⁸⁸, Pt-Ir²⁰, Pt-Pd⁸⁹, Pt-Ru⁹⁰, Cu-Ni have been extensively studied. However, monometallic catalysts generally exhibit low ENR activity since the single metal site is incapable of accommodating multiple reaction intermediate steps. Compared to monometallic materials, bimetallic alloy catalysts often show enhanced performance (i.e., activity and selectivity), but these catalysts are still limited in their product selectivity and long-term stability since the lack of compositional tunability and limited synergy. Metal-free catalysts, such as graphite felt, amorphous graphene, and active-carbon fiber paper⁹¹, are potential alternatives, particularly suitable for operating under extreme conditions (e.g., acidic environment) due to their strong corrosion resistance, wide operation potential range, and comparable selectivity. However, metal-free catalysts still face some major barriers in achieving competitive reaction efficiencies compared with metal catalysts. In the case of metallic catalysts, compared with bulk structures, dispersing transition metal atoms into isolated sites exhibit extraordinary advantages, such as higher atomic utilization, enhanced activity, and high selectivity. However, this generally requires advanced fabrication methods, is difficult to extend to all metal species, and is immature for binary and ternary compositions³⁴. More importantly, among the catalysts studied to date, few candidates have shown satisfying ENR activity nor high NH_3 faradaic efficiency (FE_{NH_3}) in acidic

conditions ($FE_{\text{NH}_3} = 78\%$, $i_{\text{NH}_3} = 22 \text{ mA cm}^{-2}$ on Ti foil⁹²), which are industrially relevant. On the one hand, some high-strength NO_3^- waste streams from industry are in acidic environments (pH 2-3) at their source of generation.⁹³ On the other hand, conducting ENR in acidic conditions promises better practicality, where acidic electrolyte enables the use of proton-exchange membranes to permit higher current densities. Therefore, developing highly efficient catalysts to enable ENR under acidic conditions becomes an imperative task.

7.2 Results and discussion

In this study, we report the first multielement alloy (MEA) nanoparticles (NPs) with dispersed Ru atoms (Ru-MEA) for highly selective and stable ENR to NH_3 in industrially relevant-acidic wastewater conditions. The Ru-MEA catalyst is developed upon the benchmark Ru catalyst, where an additional synergy effect is achieved by dispersing Ru with other metals to form alloy NPs. Cu is selected to mix with Ru due to its activity for NO_3^- reduction and to potentially reduce Ru usage. However, Ru and Cu are conventionally immiscible even above the melting point according to their wide miscibility gaps in the phase diagrams⁹⁴⁹⁵⁹⁶. Pt and Pd are added to realize the homogeneous alloying between Ru and Cu. Besides, synergies in bimetallic catalysts such as RuPt, PtCu, PtPd, and PdCu have been widely studied⁹⁷⁹⁸⁹⁹¹⁰⁰. Therefore, the addition of Pt and Pd not only serves as the “glue” to overcome the immiscibility between Ru and Cu and form MEA but also further enhances the reaction activity (Figure 5.2b). Using thermal shock, we are able to synthesize Ru-MEA NPs in a solid solution state in a simple manner and achieve homogeneous Ru dispersion. In Ru-MEA, the uniform mixing of Ru, Pd, Pt, and Cu has the potential to create numerous favorable

surface binding sites. The interactions between adjacent elements could modify their coordination environment and electronic environments, allowing for the fine-tuning of adsorption energies suitable for various intermediate species in the ENR reaction.⁴⁹ Density functional theory (DFT) assisted by machine learning (ML) proved that the Ru site in the Ru-MEA benefited from a synergistic effect based on the free energy diagram, with the rate-limiting energy of 0.17 V vs -0.36 on Ru, resulting in enhanced ENR activity. By investigating the electrocatalytic behavior of Ru-MEA under different NO_3^- concentrations and applied potentials, the Ru-MEA NP catalyst exhibits a high NH_3 partial current density (i_{NH_3}) of -50.8 mA cm^{-2} (vs 26.8 mA cm^{-2} by Ru) and a record-high NH_3 FE_{NH_3} of 93.5% in an acidic condition relevant to industrial runoff in a flow cell reactor. In addition, under 3 h of continuous operation, the Ru-MEA showed only 19.0% decay in FE_{NH_3} , much better than Ru (31.7% decay). This study paves the way toward developing next-generation electrocatalysts by combining novel synthesis and data-guided material designs for a range of applications.

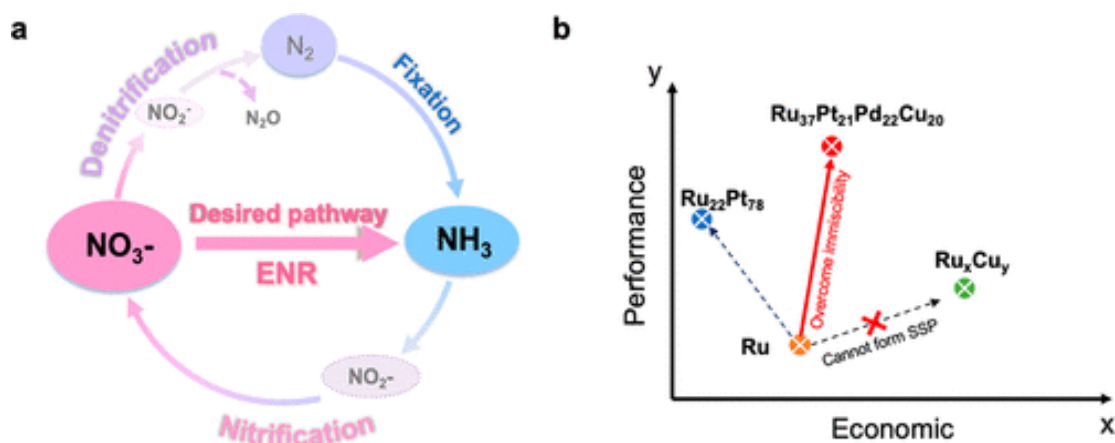


Figure 5.2. **a.** Schematic diagram of the traditional nitrogen conversion cycle consisting of nitrification, denitrification, and N_2 fixation (greyed), and the reported direct electrocatalytic NO_3^- reduction (ENR) to NH_3 in this work. **b.** Design principle

of MEA NP ($\text{Ru}_{37}\text{Pt}_{21}\text{Pd}_{22}\text{Cu}_{20}$) catalyst based on a benchmark Ru catalyst, where SSP indicates a solid solution phase.

The Ru-MEA NP catalyst was first synthesized on carbon paper substrates using a high-temperature thermal shock method (see the experimental section).⁴⁸ The high-temperature shock (1200 K) leads to fast and complete decomposition of the precursor salts. Meanwhile, the short heating duration (~55 ms) along with the fast heating/cooling rates ensure the formation of a solid solution with a homogeneous elemental mixing state. Based on the composition screening calculations (Figures S1 and S2, Notes S1 and S2), the proposed Ru-MEA NPs should have a uniform dispersing of Ru with the Pt, Pd, and Cu metal elements, to form a cuboctahedron particle. In addition to the Ru-MEA NPs, monometallic NPs (Ru, Cu, Pd, Pt) control samples were prepared using the same method (Figures S3-S5, Note S3).

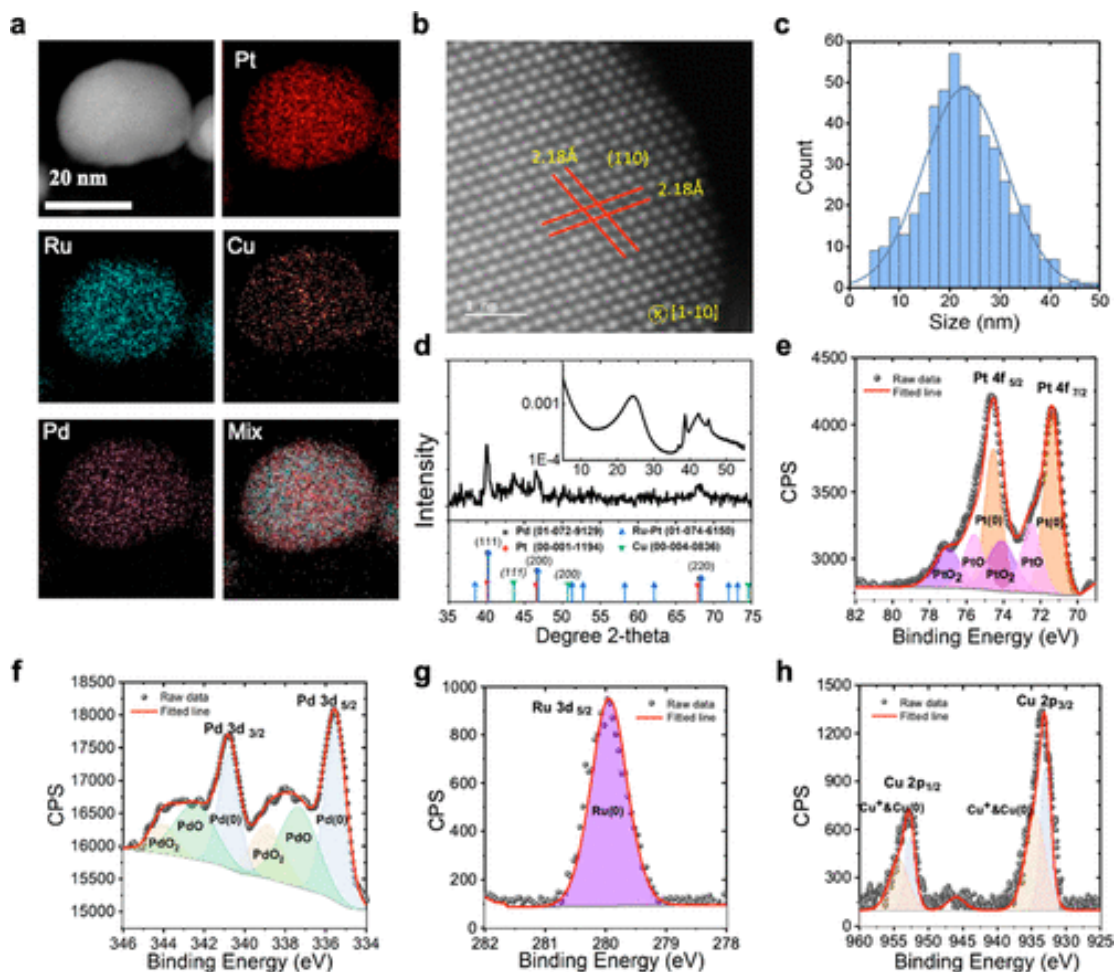


Figure 5.3. Characterization of the Ru-MEA NPs: **a.** STEM elemental maps for Ru-MEA NPs. **b.** HAADF image. **c.** Catalysts' size distribution was generated from the SEM spectrum and the fitted normal distribution (details in Supporting Information). **d.** XRD pattern and SAXS data of Ru-MEA with labeled phases corresponding to reference standards of Pd/Pt/RuPt and Cu (italic). XPS core level scan of each component in Ru-MEA NPs: **e.** Pt 4f, **(f)** Pd 3d, **(g)** Ru 3d_{5/2}, **(h)** Cu 2p.

A suite of characterizations was carried out to determine the structures of synthesized Ru-MEA NPs (see the experimental section). According to scanning transmission electron microscopy (STEM) energy-dispersive X-ray spectroscopy

(EDX) (Figure 5.3a), no phase or elemental segregation was observed in the Ru-MEA NPs. The four constituent elements were uniformly distributed. The high-angle annular dark-field (HAADF) image (Figure 5.3b) further revealed the formation of a face-centered-cubic (fcc) crystalline structure of the Ru-MEA NPs. The pristine carbon paper and synthesized Ru-MEA on carbon paper were compared using scanning electron microscope (SEM) (Figure S6). The mean radius of Ru-MEA NPs on carbon paper was identified as approximately 22.8 nm (Figure 5.3c) from a low magnification (10 000 $\times$) SEM (Figure S7). Moreover, the crystal structure identified from the powder X-ray diffraction (XRD) pattern (Figure 5.3d) confirmed the fcc structure, and small-angle X-ray scattering (SAXS) corresponded well with the XRD data. For Ru-MEA NPs synthesized with equally mixed precursor solutions, the bulk composition was determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The atomic ratio of Ru, Pt, Pd, and Cu was found to be 37%, 21%, 22%, and 20%, respectively. Additionally, the average atomic ratio at the surface or subsurface of Ru-MEA was characterized using X-ray photoelectron spectroscopy (XPS) and SEM-EDX based on three parallel samples (Table S1). This composition of MEA NPs is utilized for the following electrocatalytic tests. In addition, the valence states of the constituent elements were investigated by using XPS (Figure S8, Figures 6.3e-h). The three peaks of Pt 4f_{7/2} at about 71.35, 72.49, and 74.13 eV shown in Figure 5.3e show the oxidation of Pt. Figure 5.3f shows that Pd 3d_{5/2} was formed by Pd (0) 3d_{5/2}, PdO 3d_{5/2}, and PdO₂ 3d_{5/2} at 335.52, 337.32, and 338.88 eV, respectively. Figure 5.3g shows the Ru (0) 3d 5/2 peak centered at 279.94 eV. Cu 2p_{3/2} spectrum (Figure 5.3h) showed peaks at 933 and 934.52 eV, agreeing with the Cu (I) and Cu (0) oxidation states, along with

a weak satellite peak at 945.94 eV, which indicates the valence state of +1. Note that the minor oxide components are likely due to surface oxidation of the NPs after synthesis.⁵⁰ Details of the XPS peak fitting parameters are summarized in Table S2.

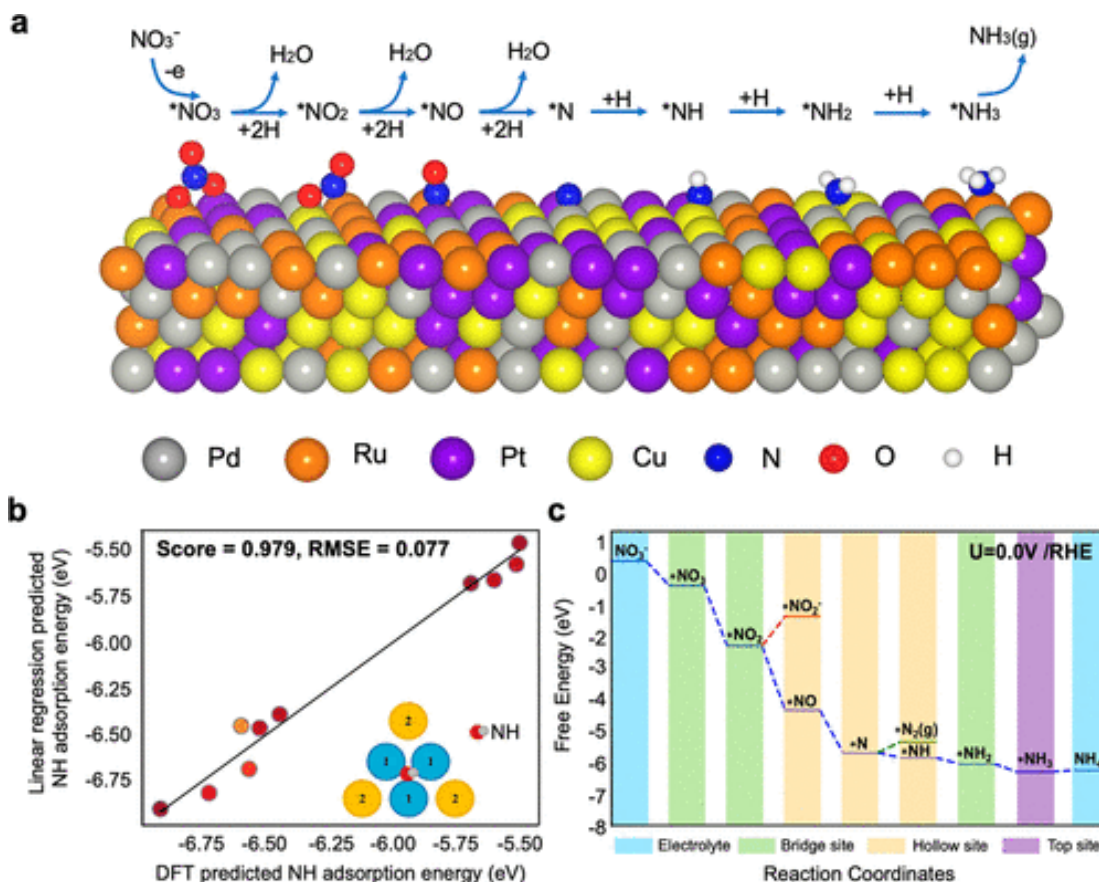


Figure 5.4. **a.** Proposed NO_3^- reduction reaction pathway to NH_3 on the RuPtPdCu (111) surface. In the figure, the gray, orange, purple, yellow, blue, red, and white balls represent Pd, Ru, Pt, Cu, N, O, and H atoms, respectively. **b.** DFT predicted the adsorption energy as compared to the adsorption energy predicted by the linear regression model, which links the local chemical environment of the surface sites and NH adsorption energy. The inset shows that an NH is adsorbed on a surface site on RuPtPdCu (111) containing the three nearest neighboring metal atoms (i.e., the blue balls marked with “1”) and three second-neighboring metal atoms (i.e., the yellow balls

marked with “2”). **c.** Predicted free energy evolution for NO_3^- to NH_3 (blue line), NO_2^- (red line), and N_2 (green line). In this figure, the NO_3^- reduction intermediates highlighted by the blue shadow are dispersed in the electrolyte, and the NO_3^- reduction intermediates highlighted by the green, orange, and purple shadows are adsorbed on a bridge site, hollow site, and top site on RuPtPdCu (111), respectively.

We performed first-principles DFT calculations to predict if the Ru-MEA could improve the activity for ENR compared to pure Ru. Due to its low energy (Note S4), we first investigated herein the ENR reaction activity on the RuPtPdCu (111) surface from Ru-MEA with an established atomistic structure shown in Figure S9. For ENR on Ru-MEA, we examined an eight-electron pathway as shown in Figure 5.4a, where NO_3^- will be first adsorbed on the metal surface, followed by reduction of the adsorbed NO_3^- to sequentially form NO_2 , NO , and $\text{N}^{101102103}$. Finally, the formed N will be further protonated to form NH , NH_2 , and the final product NH_3 . Figure S10 shows the optimized adsorption configurations of all possible ENR intermediates on RuPtPdCu (111) surface, which agrees well with that on the unary hexagonal close packed (hcp) Ru (0001) (Figure S11) and fcc Cu (111) surface.⁸² To efficiently analyze all the possible chemical species in Ru-MEA, we then applied a linear regression to correlate the DFT calculated adsorption energies for various chemical species involved in ENR on RuPtPdCu (111) with the chemical environments of the active sites (Figure 5.4b, Figure S12, and Note S5), with all fitting scores higher than 0.90. Table S3 shows that NO_3^- -reduction species are favorable to be adsorbed on the Ru atom of the RuPtPdCu (111) surface, as compared to the Cu, Pt, and Pd atoms, which proved our purpose of

dispersing Ru in MEA components. This finding also reveals that the NO_3^- reduction will predominantly occur on the site containing at least one Ru atom on the RuPtPdCu (111) surface. Consequently, we believe that ENR will proceed on the Ru- MEA surface with the chemical environment having one Ru atom on the first neighboring site and random atom distribution on other neighboring sites, as shown in Figure S13. It is also inferred that the Ru-MEA catalyst should exhibit a similar ENR selectivity to metallic hcp Ru (0001), agreeing well with our observations (Figure 5.5) and previous reports. To elaborate on the reaction mechanism and understand how synergistic function works on Ru-MEA NPs, we further applied DFT to calculate the free energy evolution for ENR to NO_2^- , N_2 , and NH_3 on both RuPtPdCu (111) and Ru (0001) surface using the computational hydrogen electrode method¹⁰⁴. In Figure 5.4c, the desorption of $^*\text{NO}_2$ requires a higher energy barrier than that of NO_2^- deoxidation, revealing that NO_2^- is a minor product of NO_3^- reduction on the RuPtPdCu (111) surface. Similarly, we predict that N is more energetically favorable to be protonated to form NH than dimerization of N to N_2 . Therefore, the NH_3 product on Ru-MEA is predicted to be boosted via an eight-electron NO_3^- reduction reaction pathway. The limiting potential for ENR of Ru-MEA is predicted to be 0.17 V on the RuPtPdCu (111) surface with the corresponding rate-determining step being the protonation of N to form NH. The metallic hcp Ru (0001) surface shows a lower limiting potential of -0.36 eV to promote NO_3^- reduction (Figure S14). This finding explains why Ru-MEA exhibits a higher ENR activity than the unary Ru catalyst. In addition, we examined the activity of competitive hydrogen evolution reaction (HER) to gauge ENR selectivity on Ru-MEA (Figure S15 and Note S6). By comparing the difference between the limiting

potentials for ENR and HER (denoted as $U_L(\text{ENR}) - U_L(\text{HER})$) on RuPtPdCu (111) (0.56 eV) and hcp Ru (0001) (0.07 eV), RuPtPdCu (111) is predicted to have a higher selectivity toward ENR. In conclusion, our DFT calculations predict enhanced selectivity of the Ru-MEA NPs catalyst for ENR.

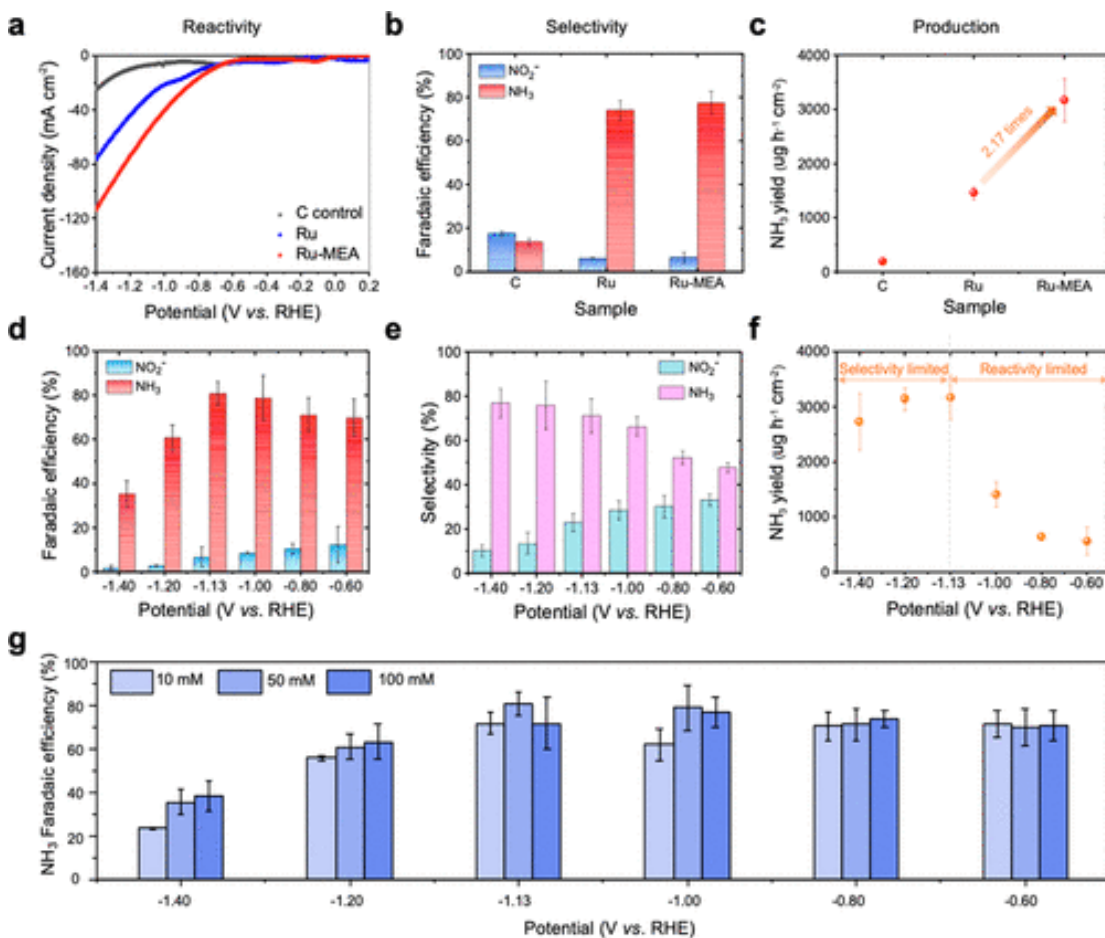


Figure 5.5. Key performance comparisons among different catalysts (C control, Ru, and Ru-MEA) in 0.5 M Na₂SO₄ containing 50 mM NO₃⁻, pH 2.5: **a.** Linear sweep voltammetry (scan rate 5 mV s⁻¹). **b.** FE NO₂⁻ and FE_{NH₃} at -1.13 V vs RHE. **c.** NH₃ yield (g h⁻¹ cm⁻²) at -1.13 V vs RHE. Electrocatalytic performance of Ru-MEA in 0.5 M Na₂SO₄ containing 50 mM NaNO₃, pH 2.5 at different applied potentials: **d.** FE_{NH₃}. **e.** Selectivity toward NH₃ and NO₂⁻. **f.** NH₃ yield (g h⁻¹ cm⁻²). Error bars indicate the

standard deviation of the FE calculation from at least three independent samples. **g.** FE_{NH_3} of Ru-MEA catalyst with varying applied potentials and NO_3^- concentrations (10, 50, and 100 mM NO_3^-) in moderate acidic media (pH 2.5).

The ENR activities of catalysts were investigated in a standard H-type cell with three electrodes (see Methods for details). An acidic electrolyte (pH 2.5) with 50 mM NO_3^- that mimics the industrial-level wastewater was selected for electrochemical measurements. The Ru-MEA catalyst showed a current density nearly 1.54 times higher than Ru (-63.7 mA cm^{-2} vs -41.4 mA cm^{-2}) at -1.13 V vs RHE (Figure 5.5a). Such an enhanced current density reflects higher ENR activity of Ru-MEA over Ru, consistent with DFT prediction. Ru-MEA increased the electrochemical surface areas (ECSA) than Ru (Figure S16 and Note S7), which has a positive effect on ENR activity. Notably, Ru-MEA features the highest activity among all catalyst compositions studied (Figure S17). In addition to the current density, the FE_{NH_3} from monometallic catalysts (Cu, Pt, and Pd) was compared at a fixed potential (-1.13 V vs RHE). As a result, Ru exhibited the highest NO_3^- conversion rate and FE_{NH_3} . It should be noted that even though the Cu-based catalyst was reported to show high selectivity toward NH_3 in neutral medium, the unary Ru catalyst was measured to show higher NH_3 selectivity than the unary Cu catalyst at an electrode potential of -1.13 V vs RHE in acid medium, agreeing well with our DFT prediction (Figure S19 and Note S8). In addition, Cu and Pd significantly contribute to enhancing the reaction activity, while the inclusion of Pt further improves the ENR activity of RuPdCu. Among all catalysts studied, the Ru-MEA catalyst showed the best FE_{NH_3} of $79.8 \pm 5.8\%$ (Figure 5.5b), which is also

record-high among literature reports. Pure Ru also exhibited a comparable FE_{NH_3} of $71.9 \pm 2.6\%$, representing its intrinsic good NH_3 selectivity. As a result of enhanced current density and FE_{NH_3} , the Ru-MEA catalyst doubled the NH_3 yield ($3171.0 \mu g h^{-1} cm^{-2}$) compared to pure Ru ($1461.2 \mu g h^{-1} cm^{-2}$) (Figure 5.5c), which proved the DFT calculation that ENR is promoted on Ru-MEA surface with the chemical environment having one Ru atom on the first neighboring site and random atom distribution on other neighboring sites.

We then investigated the FE_{NH_3} of Ru-MEA with varying applied potentials. For ENR in 50 mM NO_3^- (Figure 5.5d), with decreasing applied potentials, the FE_{NH_3} first increased and then gradually decreased. For applied potential between -0.60 V and -1.13 V vs RHE, the FE_{NH_3} increased as the reduction was promoted, while NO_2^- and other intermediate species were reduced into NH_3 . The measured optimized potential was at -1.13 V vs RHE, exhibiting a FE_{NH_3} of $79.8\% \pm 5.8\%$. When the applied potential was further reduced, the effect of competing hydrogen evolution reaction (HER) became more significant, thus reducing FE_{NH_3} ¹⁰⁵. As the potential decreased, the selectivity of NH_3 increased and the selectivity of the toxic byproduct NO_2^- decreased accordingly (Figure 5.5e). At the optimum condition (-1.13 V vs RHE), the NH_3 selectivity was 71.15%, and selectivity toward NO_2^- was approximately 23.07%, the reaction consistent with first-order kinetics (Figure S20 and Note S9).

ENR performance on Ru-MEA was also investigated with different NO_3^- concentrations. In addition to 50 mM NO_3^- , 10 mM and 100 mM NO_3^- were considered to cover the range of other types of NO_3^- -containing wastewater at the source of

generation, such as textile wastewater and nuclear industry^{106,107,108}. NO_3^- reduction was hindered by competition reaction, mainly HER, especially for low NO_3^- concentration; however, a proton is necessary for the NO_3^- reduction. At 10 mM NO_3^- , the FE_{NH_3} went through a peak with applied potential since mass transport of NO_3^- becomes the limiting factor, even for more negative potentials (Figure S21). This trend can be further proved with higher NO_3^- concentration (Figures S22-23), and when there is more NO_3^- available in the electrolyte, mass transport becomes less limiting for the NO_3^- reduction reaction. However, the higher FE_{NH_3} at high NO_3^- concentrations (100 mM NO_3^-) compared to 50 mM NO_3^- under more negative potential is most likely due to the competitive adsorption of protons with the NO_3^- ion (Figure 5.5g) considering the Ru site is preferred for both NO_3^- and $^*\text{H}$ species (Table S3). In addition, overall $\text{FE}_{\text{NO}_2^-}$ increased with a higher initial NO_3^- concentration, contributing to further NO_2^- degradation. Since the availability of active sites mainly limits reaction kinetics, NO_2^- reduction is understandably less efficient than NO_3^- reduction due to the lack of active adsorption sites for NO_2^- and available $^*\text{H}$ on adjacent sites, leading to NO_2^- desorption and accumulation in the electrolyte. Lastly, when considering the ENR performance at a specific NO_3^- concentration, the FE_{NH_3} was found to increase with more negative applied potential due to the enhanced reducing power, which has a higher impact on ENR compared to that on HER. When applied potential became more negative, the HER became dominant, which was observed by the increasing FE_{H_2} in Figures S21-23.

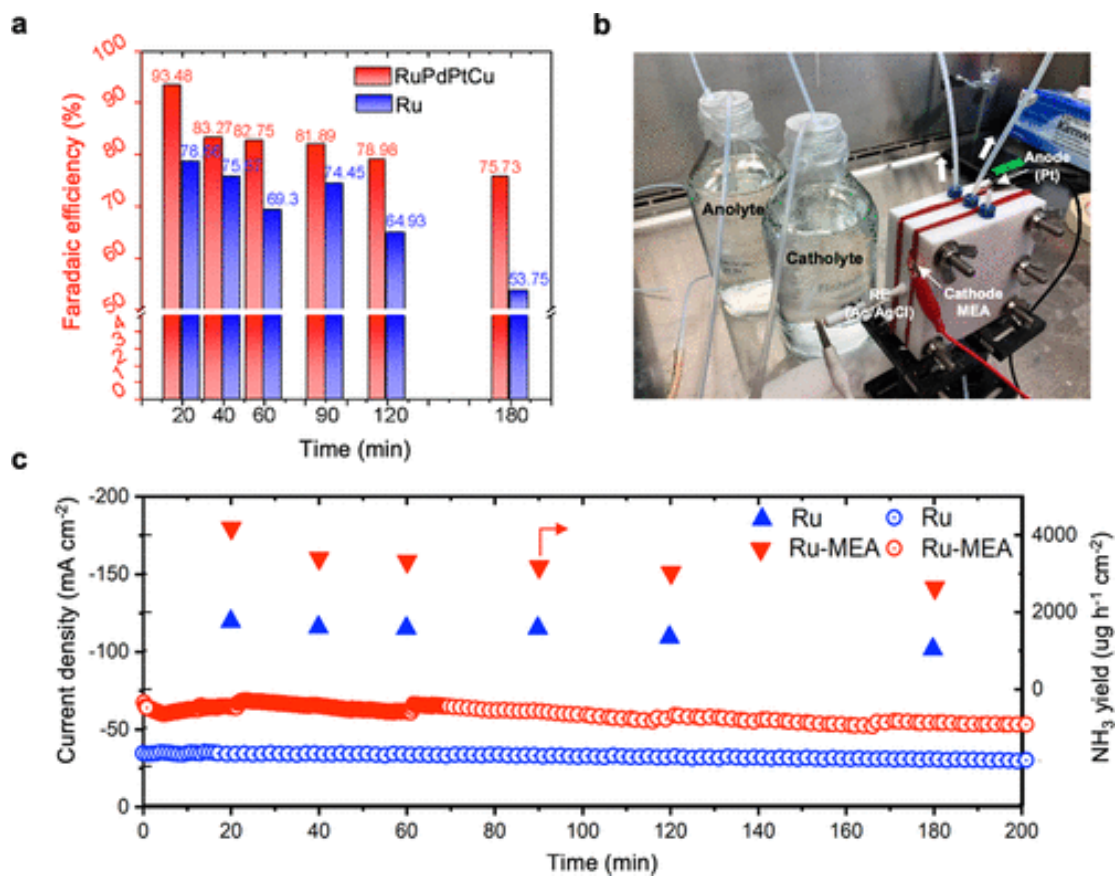


Figure 5.6. Stability test of Ru and Ru-MEA using a flow cell with fresh electrolyte (50 mM NO_3^- in 0.5 M Na_2SO_4 , pH 2.5), at -1.13 V vs. RHE, detailed design of the flow cell is in Figure S30: **a.** F_{NH_3} of Ru and Ru-MEA. The F_{NH_3} of Ru-MEA remains above 75% for the 200 min test, whereas the F_{NH_3} at 20 min is 93.5%. **b.** Photo of the electrocatalytic flow cell. **c.** Current density (mA cm^{-2}) and NH_3 yield ($\text{ug h}^{-1} \text{cm}^{-2}$) of Ru and Ru-MEA.

We compared the electrochemical stability of Ru and Ru-MEA catalysts using chronoamperometry (CA) at -1.13 V vs RHE with 50 mM NO_3^- in a flow cell (Methods, Figure 5.6b, Figure S30). For Ru, the initial F_{NH_3} was at an average of 74.5% for the first hour with an NH_3 partial current density (i_{NH_3}) of 24.2 mA cm^{-2} . However, the

performance decayed over time and dropped to 53.8% at around 180 min, followed by a further decline in the following hours (Figure 4a). In contrast, the Ru-MEA catalyst demonstrated a much higher FE_{NH_3} at 93.5% in the first 20 min. Though the FE_{NH_3} also slightly decreased in the following hours, the value remained high and relatively stable (75.7%) until 180 min (Figure 5.6a), along with a high i_{NH_3} of 42.8 mA cm⁻² (Figure 5.6c). Tables S4 and S5 summarize the up-to-date reported highest FE_{NH_3} under the different conditions, where our Ru-MEA catalyst stands out. The decline in FE_{NH_3} may be caused by several factors. For example, metal corrosion and leaching may cause catalyst composition change and affect sample performance, which has been reported and is hard to avoid^{109–111}. Material poisoning caused by strong adsorption energy between active sites and intermediates may cause temporary or permanent loss of reaction sites for ENR. Particle aggregation and nanostructure change will also cause an irreversible change of catalysts' morphology. To understand these effects, we characterized the surface elemental composition (Figures S24-25), catalyst morphology (Figures S26-27), and crystal structure (Figure S28) of Ru-MEA after a 4 h stability test. While the crystal structure and the composition remained relatively stable, we observed a notable decrease in the number of NPs on the carbon paper surface (e.g., 169 to 107, Figure S27), suggesting detachment issues. We further utilized ICP-MS to analyze the electrolyte after the test (details in the Supporting Information), and the results revealed a loss of 12.8 wt % of Cu and 6.8 wt % of Ru in the initial catalyst during the ENR process. The losses of Cu and Ru were also shown by the SEM-EDX analysis of the catalysts after the stability test (Table S6). Direct NO_3^- reduction in an acidic environment has historically been a challenging process

due to catalyst leaching issues. Therefore, to enhance the stability of catalysts, we incorporated a binder of 20 wt.% Nafion. With the binder, we observed that the current density changed by less than 8% within 3 h, vs 16.8% without the binder (Figure S29). Nevertheless, this Ru-MEA catalyst design for the first time enables highly selective ENR to NH_3 in acidic solutions with record-high FE_{NH_3} and better stability compared to benchmark Ru catalysts.

7.3 Conclusion

This study for the first time reported a MEA NP catalyst designed for efficient ENR toward NH_3 with dispersed Ru sites and synergy between Ru and Pd, Pt, and Cu. A simple thermal shock method achieved solid-solution-level mixing of Ru in the MEA NPs. DFT assisted by ML predicted the enhanced ENR activity and NH_3 selectivity on Ru-MEA NPs compared to the benchmark Ru catalyst, exploiting the synergistic effect of the components to provide optimized multistep NO_3^- reduction energy. The resulting Ru-MEA NP catalyst exhibits record high FE_{NH_3} in acidic conditions among existing catalysts and superior stability compared with the Ru. This work demonstrated a rational catalyst discovery pathway by integrating novel synthesis and DFT-guided design toward a range of applications related to sustainability. In future studies, the critical masses of Pt and Pd need to be optimized and the composition of the designed MEA could be extended to economically more viable components (e.g., non-noble metals). In addition, considering the cost of catalysts and pretreatment of acidic wastewater, a thorough techno-economic analysis would be necessary to ensure a practical and economically viable solution for treating acidic wastewater. It needs to be acknowledged that the catalyst loading for this study is relatively lower (2 wt %) than

existing studies; with a potential improvement of the catalyst loading, the NH_3 yield has the potential for a significant increment to satisfy the practical requirements. In addition, Ru-MEA must be tested in real NO_3^- -containing wastewater with various coexisting components.

Author Contributions

M.Y., B.L., and S.L. contributed equally to this work. M.Y., L.H., G.W., and Z.J.R. conceived the design of the project and initiated the project. S.L. is in charge of catalyst design and synthesis. M.Y. performed most of the material characterization and electrochemical measurements. M.Y. performed SEM and XPS measurements and data analysis. Z.H. performed TEM measurements and data analysis. S.Z. performed XRD measurements and data analysis. All electrochemical data were collected, analyzed, and interpreted by M.Y. and Q.D. G.Z. performed the stability test. B.L. performed the DFT calculations. Y.F. performed the machine learning model predictions. All authors contributed to discussions.

7.4 Experimental

Preparation of MEA NPs catalysts

In this study, 1 cm $\times$ 2 cm carbon papers (CP) (Freudenberg H23) were used as the substrate to load the MEA NP catalyst for electrochemical measurements. Precursor salts including $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, $\text{PdCl}_2 \cdot x\text{H}_2\text{O}$, $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, and CuCl_2 were purchased from Sigma Aldrich. The precursor salts were first dissolved in ethanol to form precursor solutions with a concentration of 0.05 M. For a single salt precursor, the

solution was then evenly drop-casted on the CP substrate with a total catalyst loading of ~2 wt.%, which was then dried in air at 60 °C. For MEA samples, the equally mixed precursor solutions (resulting in a 0.05/n M concentration for each element, where n is the number of elements) were drop-casted onto the substrate. In addition to carbon paper, carbon nanofiber (CNF) was utilized as the substrate for the Transmission electron microscopy (TEM) characterizations due to its thinness for more clear views of the structure and elemental distribution of the MEA NPs. CNF substrates are formed from the carbonization of electrospun polyacrylonitrile (PAN, Sigma Aldrich) fibers. In a typical process, PAN was dissolved in dimethylformamide (DMF, Sigma Aldrich) to form a solution of 8 wt.%. Then the electrospinning was operated using a voltage of 15 kV, with a spinning distance of 10 cm, and a feed rate of 1 mL h⁻¹. The resulting electrospun fibers were collected on a rotating drum (speed of 80 rpm) and separated. For carbonization, the electrospun fibers were first stabilized at 533 K for 5 h in air and then carbonized at 1073 K for 2h in Ar to form CNF. The NPs loaded on carbon substrates were synthesized via the high- temperature thermal shock method.³ A ~55 ms electrical pulse and a peak temperature of ~1200 K carried out in Ar were used for the NPs studied in this work. A 1.5×5 cm CNT film was applied as the radiation heater via Joule-heating. The thermal shock process was applied to the heater using an external Starpower DC power supply and a Keithley 2425 sourcemeter to generate desired pulse heating duration and temperature.

Sample characterization

Scanning electron microscope (SEM) was conducted on a Quanta 200 FEG Environmental-SEM. TEM, high-resolution TEM, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and STEM-EDS mapping were performed on probe-corrected JOEL NEOARM electron microscopes at an accelerating voltage of 80kV. X-ray photoelectron spectroscopy (XPS) data were collected using a ThermoFisher K-alpha XPS/UPS equipped with a monochromatic Al K-alpha x-ray source at 15 kV. All XPS measurements were collected using slot (30-400 μm spot size) collimation and hybrid lens mode without using a charge neutralizer during acquisition. Survey scans were collected with a 1.0 eV step size and a 160 eV pass energy, followed by high-resolution scans with a step size of 0.1 eV, and a 20 eV pass energy. All XPS spectra were shifted to the binding energy of the carbon 1s (assigned to 284.8 eV) to compensate for any offset during measurements. The resulting XPS spectra were fitted using Avantage software to estimate the chemical state and nature of the catalysts. All fittings followed a self-consistent method like our previous publication.^{4,5} X-ray powder diffraction (XRD) data were collected using a Bruker D8 Discover X-ray diffractometer using a Cu K α source ($\lambda = 0.154178$ nm). Small-angle X-ray scattering (SAXS) data were tested using Xenocs Xeuss 3.0, where $q = 4\pi\sin\theta/\lambda$, $\lambda = 1.54189$ Å. The bulk composition of Ru-MEA was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Thermo Scientific iCAP RQ ICP-MS.⁶ The samples were operated in the standard (STD) mode with 1550 W plasma power and a carrier flow of 1.1L min⁻¹ nebulizer gas. The characterization of particle size from SEM images is a and can provide about the morphology and structure of nanomaterials. In this case, the nanoparticles on the carbon fiber were identified and

measured using ImageJ software, which is a widely used image processing software.⁷ After summarizing the nanoparticle size data, a histogram was generated to visualize the distribution of particle sizes. A was then fitted to the histogram, and the mean and standard deviation were calculated.

Chapter 6: Depolymerization of Plastics by means of Electrified Spatiotemporal Heating*

Abstract

Depolymerization is a promising strategy for recycling waste plastic into constituent monomers for subsequent repolymerization¹¹³. However, many commodity plastics cannot be selectively depolymerized using conventional thermochemical approaches, as it is difficult to control the reaction progress and pathway. Although catalysts can improve the selectivity, they are susceptible to performance degradation¹¹⁴. Here we present a catalyst-free, far-from-equilibrium thermochemical depolymerization method that can generate monomers from commodity plastics (polypropylene (PP) and poly(ethylene terephthalate) (PET)) by means of pyrolysis. This selective depolymerization process is realized by two features: (1) a spatial temperature gradient and (2) a temporal heating profile. The spatial temperature gradient is achieved using a bilayer structure of porous carbon felt, in which the top electrically heated layer generates and conducts heat down to the underlying reactor layer and plastic. The resulting temperature gradient promotes continuous melting, wicking, vaporization, and reaction of the plastic as it encounters the increasing temperature traversing the bilayer, enabling a high degree of depolymerization. Meanwhile, pulsing the electrical current through the top heater layer generates a temporal heating profile that features

* The results in this chapter have been published: Dong, Q.; Lele, A. D.; Zhao, X.; Li, S.; Cheng, S.; Wang, Y.; Cui, M.; Guo, M.; Brozena, A. H.; Lin, Y.; Li, T.; Xu, L.; Qi, A.; Kevrekidis, I. G.; Mei, J.; Pan, X.; Liu, D.; Ju, Y.; Hu, L. Depolymerization of Plastics by Means of Electrified Spatiotemporal Heating. *Nature* **2023**, 616 (7957), 488–494. ¹¹²

periodic high peak temperatures (for example, about 600 °C) to enable depolymerization, yet the transient heating duration (for example, 0.11 s) can suppress unwanted side reactions. Using this approach, we depolymerized PP and PET to their monomers with yields of about 36% and about 43%, respectively. Overall, this electrified spatiotemporal heating (STH) approach potentially offers a solution to the global plastic waste problem.

8.1 Introduction

There is a large amount of plastic waste ending up in the ocean every year, threatening wildlife, and harming biodiversity¹¹⁵. Furthermore, microplastics and plastic microfibers have been found in the air and municipal drinking water, posing health and ecological concerns¹¹⁶. Common but highly unsustainable methods of removing plastic waste include burning or landfilling, with the former being extremely carbon-heavy and air-polluting, whereas the latter can cause long-term damage to the environment. Alternatively, many thermoplastics can be recycled through mechanical processing into low-end but useful materials¹¹⁷. However, mechanical plastic-recycling approaches often suffer from limited product value. To continue using plastics, it is imperative to develop efficient plastic recycling and upcycling strategies to ensure a sustainable future¹¹⁸.

Recently, thermochemical plastic decomposition has emerged as a promising route for converting plastic waste into value-added chemicals^{119–122}. Among the numerous thermochemical plastic-decomposition pathways, selective depolymerization to monomers holds great economic incentive, as the generated monomers can be reused in subsequent polymerization reactions for another product

life cycle or as chemical feedstocks for other processes¹¹³. Although a few plastics that have relatively low ceiling temperatures can be readily depolymerized through conventional thermochemical methods such as pyrolysis (for example, poly(methyl methacrylate) and polystyrene)^{123,124}, most polyolefins and polyesters cannot be converted to their monomers with high selectivity, as conventional approaches lack precise control of the reaction progress. This is because of the complex physicochemical transformations of reactants and intermediate products (for example, melting, vaporization, decomposition etc.)^{119,125}, as well as the severe competing side reactions to the depolymerization pathway during continuous heating of the plastic, which lead to a range of products beyond the monomer (for example, gases, condensable hydrocarbons, aromatics etc.). To solve this problem, conventional thermochemical processes often use catalysts to enhance the product selectivity. However, catalysts are prone to performance degradation and provide limited improvement of the depolymerization selectivity^{117,120}. For example, the pyrolysis of PP typically features a monomer yield of only about 10% without catalysts and < 25% using optimized catalysts^{126,126–129}. In another example, the pyrolysis of PET leads to various aromatic species, often with < 25% yield to the 1,4-benzenedicarboxylic acid monomer^{124,130,131}.

8.2 Results and discussion

Here we demonstrate a catalyst-free and far-from-equilibrium depolymerization process based on electrified STH, which can control the reaction progress and pathway to convert commodity plastics to monomers with high yields. In this process, a bilayer of porous carbon felt is placed in contact above a reservoir of

solid plastic reactant (Figure 6.1a). We then apply a pulsed electrical current to the top carbon heater layer, which generates heat that conducts to the bottom carbon reactor layer and the underlying plastic reactant, forming a vertically distributed spatial temperature gradient. This temperature gradient causes the plastic to melt in the reservoir and continuously wick upwards through the porous fiber network of the bottom carbon reactor layer by means of capillary forces (Figure 6.1a). Decomposition of the plastic occurs as the liquid polymer experiences sufficiently high temperatures while gradually moving upwards. As the temperature increases, volatile species enter the gas phase (for example, $C_{<20}$ at about 350 °C (ref. ¹³)), continue to diffuse through the porous structure and interact with higher sections of the reactor layer, as well as the top carbon heater layer for further cracking (Figure 6.1a). In these regions, the rapid heating pulses (for example, high heating rate $>10^3$ °C s⁻¹, T_{peak} up to about 600 °C for PP and about 1050 °C for PET) provide sufficient energy to break the C-C or C-O bonds that connect the monomer fragments. Meanwhile, the transient heating duration (for example, 0.11 s) in each pulse cycle potentially reduces the energy cost compared with the operation using continuous heating¹³² and, more importantly, prevents the reaction from approaching chemical equilibrium that would otherwise result in the formation of a large amount of undesired side products (for example, methane, aromatics¹¹⁹) through random C-C bond breaking, dehydrogenation, C-C bond coupling, aromatization etc. These processes have higher energy requirements and/or longer reaction timescales^{133–135}, which should be slowed down more intensively compared with the monomer formation process by the rapid cooling (for example, cooling rate >120 °C s⁻¹) after a transient heating duration (for example, 0.11 s) in each

pulse cycle, resulting in a high monomer selectivity. Also, the continuous melting, wicking, vaporization, and reaction process within the bilayer structure allows the intermediate products (that is, shorter polymers and oligomers in the liquid and gas phases) to gradually diffuse up through the porous scaffold and experience multiple heating pulses during the increased residence time, thereby reaching a high degree of depolymerization and an improved monomer yield.

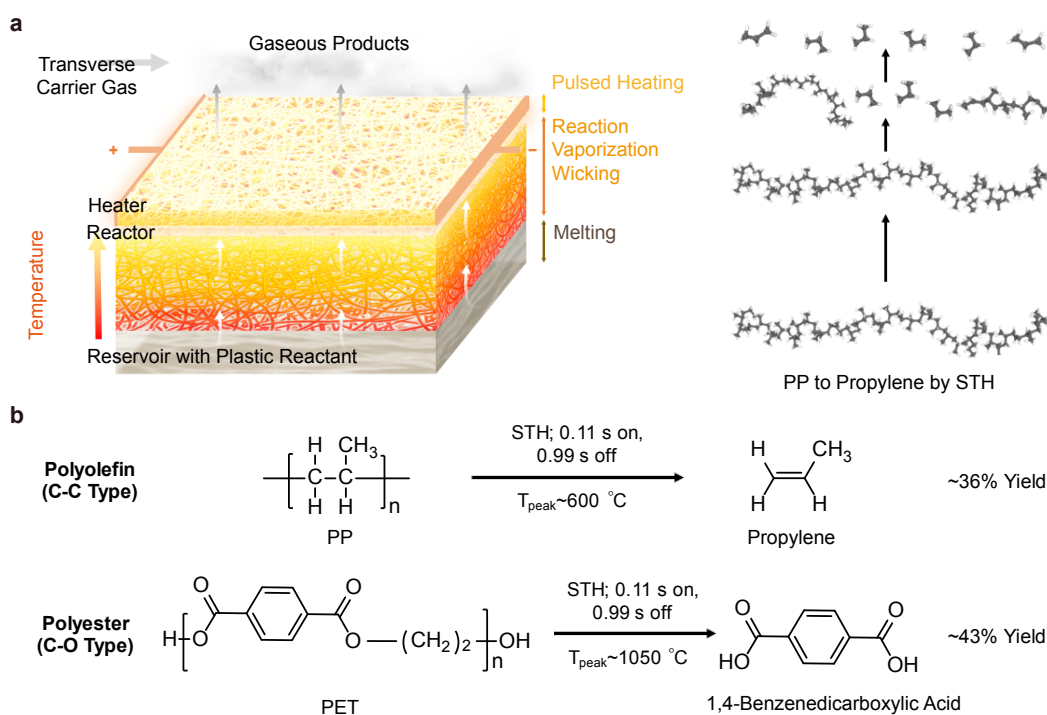


Figure 6.1. The working principle of the electrified STH approach. **a.** Schematic demonstrating the STH process in the bilayer configuration and the molecular transformation from polymer to monomer using PP as a model plastic. **b.** The depolymerization reactions of PP (as a model polyolefin) and PET (as a model polyester) to their monomers by STH, with yields of about 36% and about 43%, respectively, using a non-optimized pulsed heating program of 0.11 s power on and

0.99 s power off in every pulse cycle. T_{peak} refers to the peak temperature of the periodic pulse cycles in a temporal heating profile.

Taking advantage of both the spatial and temporal heating effects, we used the electrified STH approach to depolymerize PP and PET as model polyolefin and polyester plastics, respectively, which feature C-C and C-O backbones (Figure 6.1b). The yields from polymer to monomer by means of pyrolysis of PP and PET using STH were about 36% and about 43%, respectively, which are considerably higher compared with conventional thermochemical methods^{124,126–131}. Note that our approach does not require any catalysts, as STH not only offers high selectivity by controlling the reaction progress and pathway but also creates periodic high temperatures (for example, about 600 °C every 0.11 s for the pyrolysis of PP) to enable rapid bond activation and thus a high instantaneous reaction rate. We further show that the electrified STH process exhibits good scalability on the laboratory scale and can potentially be operated in a continuous mode using renewable electricity with reduced CO₂ emissions compared with conventional techniques. Overall, this electrified STH process holds great potential for improving the sustainability of commodity plastics.

We first explore this electrified STH approach using PP as a model commodity plastic, as it holds one of the largest market shares among all synthetic polymers¹²⁰. The selective depolymerization of PP to its monomer propylene (C₃H₆) has proved to be challenging owing to the difficulty in controlling the reaction progress and pathway by conventional methods, which often leads to a variety of products of different carbon numbers^{126–129}. In a typical process, we assembled a STH system by laminating two

layers of porous carbon felt (heater layer: $25 \times 9 \times 2.3$ mm; reactor layer: $13 \times 6 \times 4.7$ mm), which were placed on top of a small reservoir that contained the solid PP reactant. This structure was housed in a quartz tube (10.5 mm inner diameter) that featured inlet and outlet ports for inert argon carrier gas flow as well as electrical wiring to connect the top carbon heater layer to a power source using Cu electrodes (Figure 6.2a and Figure 6.4; see Experimental for details). Applying a repeated electrical pulse to the top carbon heater layer (Figure 6.2b) creates a transient Joule heating effect (Figure 6.4) that we suggest would produce a vertical temperature gradient between the top and bottom surfaces of the reactor layer. The temperature gradient should promote the continuous melting, wicking, vaporization, and reaction of the polymer as it moves up through the bilayer carbon felt structure (Figure 6.2c). Note that we fabricated the top heater layer using a thinner piece of carbon felt (about 2.3 mm) to reduce the thermal inertia and thereby providing rapid heating and cooling rates, whereas the bottom carbon reactor layer was thicker (about 4.7 mm) to enable gradual wicking of polymer melt and diffusion of volatile intermediate species for an increased residence time.

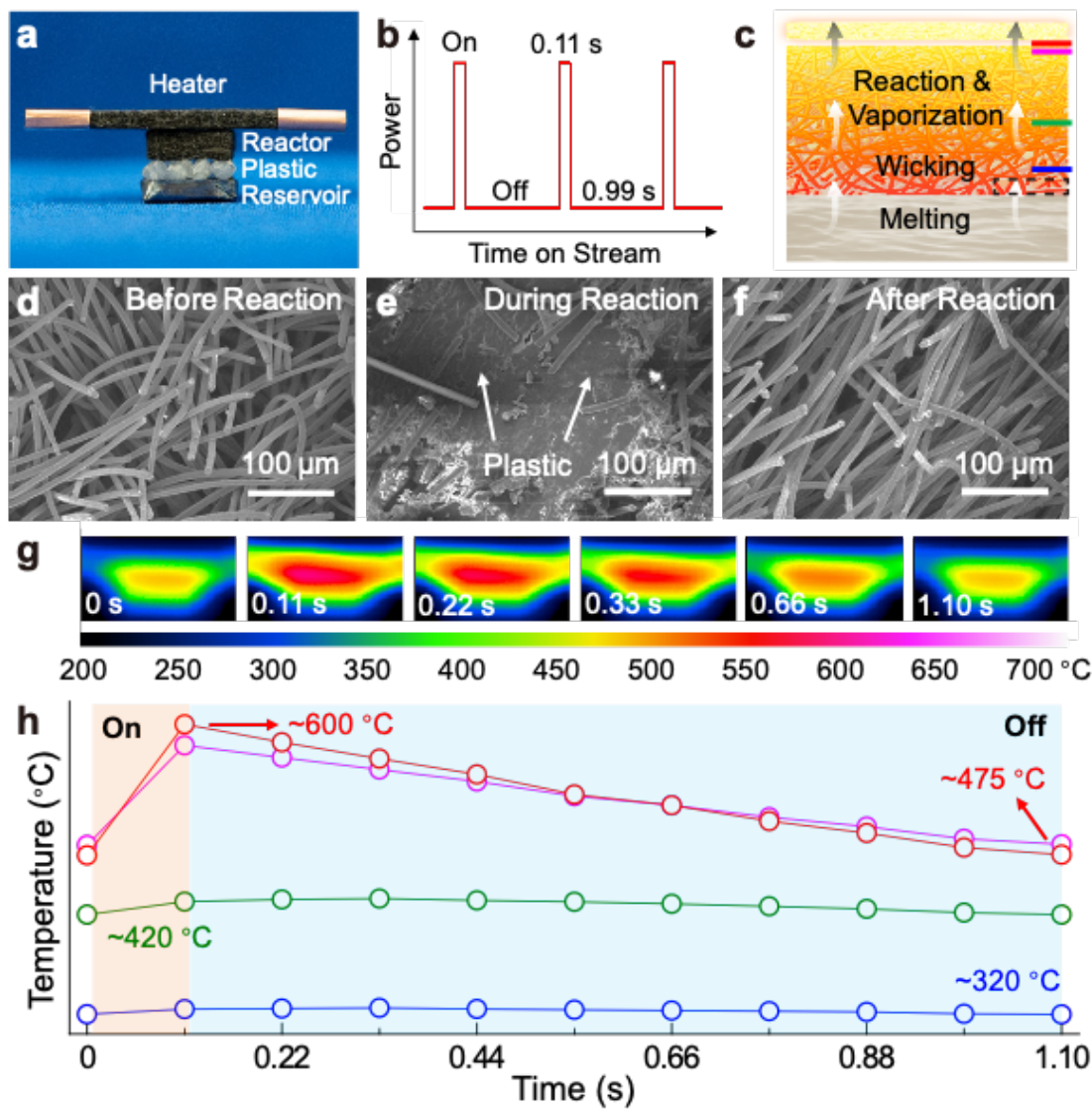


Figure 6.2. The porous carbon felt bilayer of the STH system and its depolymerization process by means of pulsed electrical heating. **a.** The STH system is assembled from a porous carbon felt ‘heater layer’ that is placed in soft contact on top of a carbon felt ‘reactor layer’. The reactor layer then rests on top of the plastic reactant (PP beads shown here), which is contained within an inert reservoir. Note that in this picture the PP beads are intentionally stacked above rather than inside the reservoir only for demonstrating the assembly of the setup. For STH operations, the PP beads are placed

inside the reservoir. For heating, an electric current is passed through the top heater layer by means of the copper electrodes, whereas the bottom reactor layer is non-electrified. **b.** The periodic pulsed electrical signal applied to the STH system. **c.** Schematic of the STH system during pulsed electrical heating. The red, pink, green and blue lines indicate where the temperature profiles were measured for Figure 6.2g,h. The dashed black box indicates where the SEM images were taken for Figure 6.2d-f. **d.** SEM image showing the bottom region of the pristine reactor layer. **e.** SEM image showing the infiltration of the plastic melt into the bottom region of the reactor layer within 5 min of STH operation (power on for 0.11 s at about 22 V, power off for 0.99 s). **f.** SEM image showing the bottom region of the reactor after 35 min of STH operation. **g.** Temperature maps of the heater and reactor layers at various time points during one heating/cooling cycle of 1.10 s total (power on for 0.11 s at about 22 V, power off for 0.99 s), measured in a lab-built argon-filled environmental chamber. **h.** The temporal temperature profiles at four representative positions of the STH system, in which the red, pink, green and blue curves correspond to the red, pink, green and blue positions shown in **c**. The light-orange region indicates ‘power on’, whereas the light-blue region indicates ‘power off’. Scale bars in **d-f**, 100 μm .

To demonstrate the STH process, we placed 0.1 g of PP in the reactant reservoir and applied about 22 V to the top heater layer for 0.11 s, followed by 0.99 s of the power turned off. We repeated this electrical pulse cycle for 35 min, at which point all of the PP had reacted from the reservoir. Using scanning electron microscopy (SEM), we observed the wicking of the plastic melt through the bottom of the reactor layer by stopping the batch STH reaction at certain time points. The porous reactor layer is

composed of a network of carbon fibers (Figure 6.2d), which gradually became filled by the plastic melt within 5 min of pulsed electrical heating (Figure 6.2e and Figure 6.5). After 35 min, the reactor layer once again returned to its original state, with almost no solid residue or solid-phase product observed (Figure 6.2f). Also, there was negligible difference in the total weight of the bilayer carbon felts and reservoir before the loading of PP and after 35 min of the batch STH reaction. These results indicate the complete pyrolysis of the plastic and insubstantial coke formation through the applied pulsed electrical heating. Note that the fibers in the carbon felt do not need to be loaded with catalysts to conduct the reaction (although some catalytic residues may remain from the plastic reactant in the previous polymerization processes). This makes the electrified STH approach unsusceptible to catalyst degradation, enabling the durability and reusability of the system.

To understand the heating process, we used an infrared camera to measure the temperature distribution at the outer surface of the two carbon felt layers. As the quartz tube wall blocks the infrared signal, we mimicked the configuration of the STH system by placing the bilayer structure in an argon-filled lab-built environmental chamber with an opening to allow the infrared signal to transmit to the infrared camera (see Experimental section for details). On the basis of the temperature distribution maps acquired with the environmental chamber (Figure 6.2g), we extracted four temperature profiles at representative vertical positions (labelled in Figure 6.2c) of the bilayer structure within a period of 1.10 s (that is, one pulse cycle, power on for 0.11 s at about 22 V, power off for 0.99 s; Figure 6.2h). The interfacial region between the heater and reactor layers seems to have the highest peak temperature (T_{peak}). After turning the

power on for 0.11 s, the temperature in this region (red trace, Figure 6.2h) quickly rises to about 600 °C then drops back to about 475 °C within 0.99 s after removing the power input to complete the power on/off cycle, corresponding to a heating rate of $> 10^3$ °C s⁻¹ and a cooling rate of about 126 °C s⁻¹. Note that the temperature ranges at the interfacial region between the heater and reactor layers (red trace) and at the top section of the reactor layer (pink trace) are much higher than the temperature (about 420 °C) at which PP starts to show apparent weight loss (Figure 6.14), suggesting that the polymer vaporization and reaction processes readily occur below these regions. Unlike these top sections, the middle and bottom sections (green and blue traces) of the reactor layer exhibit much milder temperature variation (< 35 °C) within one power on/off cycle, probably because the top section of the reactor layer absorbs most of the radiative heat flux from the heater. These results indicate that the reactants near the top regions of the reactor layer and in the heater layer are subjected to pulsed heating, whereas those near the bottom of the reactor undergo almost continuous heating at nearly constant temperatures. These four temperature profiles also demonstrate a vertically distributed temperature gradient from 475 to 600 °C (top) to about 320 °C (bottom). Note that this temperature measurement setup using an environmental chamber offers better spatial resolution to differentiate the heater and reactor layers; however, the surrounding environment of the carbon felt bilayer (that is, the walls of the environmental chamber) is slightly different from that in the quartz tube used for the real STH operation. To corroborate the environmental-chamber measurements, we also measured the temperature of the bilayer using a customized quartz tube (10.5 mm inner diameter) with a smaller opening on the tube wall for transmitting the infrared signal,

which should provide better consistency with the real STH system, although at lower spatial resolution owing to the limited opening size on the tube wall (Figure 6.6a). The measurement using the customized quartz tube shows almost identical temporal temperature profiles to those shown in Figure 6.2h, suggesting the accuracy and robustness of the lab-built environmental chamber for conducting the temperature measurements (Figure 6.6b,c).

Note that the role played by the bilayer structure is critical for STH as it creates the temperature gradient that ensures a continuous melting, wicking, vaporization, and reaction process. If instead of a heater/reactor bilayer design we were to use a single carbon layer to heat the entire plastic melt in the container, there would be no temperature gradient to promote the wicking effect, resulting in poor control of the reaction progress (Figure 6.15). Also, the gradual wicking and diffusion of the reactants through the porous reactor layer allow the intermediate products to have increased residence times and thereby experience more heating pulses compared with the operation using a single heater layer, which should improve the degree of depolymerization and the monomer yield.

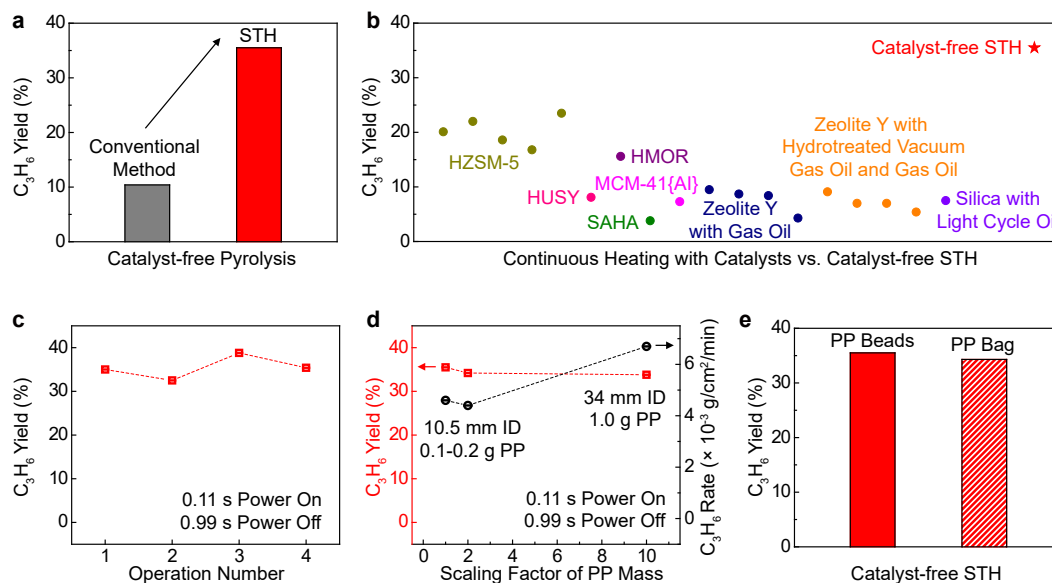


Figure 6.3. The depolymerization performance of the STH approach using PP as a model plastic. **a.** Comparison of the C_3H_6 monomer yield between our work using STH under far-from-equilibrium conditions and a literature report using catalyst-free pyrolysis by furnace heating under near-equilibrium conditions. **b.** Comparison of the C_3H_6 monomer yield between our work using STH and literature reports using different catalysts, reaction media and/or processes. **c.** The C_3H_6 monomer yield of four consecutive PP pyrolysis batch reactions using STH. **d.** The C_3H_6 monomer yield and production rate as a function of the reaction scale. The scaling factor is based on the PP mass feed, with the initial scale of 0.1 g PP defined as 1. **e.** The C_3H_6 monomer yield by STH using PP beads and a commercial PP bag. All STH processes used a program of 0.11 s on, 0.99 s off and $T_{peak} \approx 600$ °C. The data shown in this figure are listed in Tables 7.1 and 7.2. ID, inner diameter.

We used gas chromatography with flame ionization detection (GC-FID) to quantify the yield of various species (for example, CH_4 , C_2H_4 , C_3H_6 etc.) in the argon carrier gas collected downstream during the PP pyrolysis batch reaction (Figure 6.7). After applying a typical pulsed heating program (power on for 0.11 s at about 22 V, power off for 0.99 s, one power on/off cycle for 1.10 s; total operation time 35 min) to 0.1 g of PP beads, we achieved a high C_3H_6 monomer yield of $35.5\% \pm 6.2\%$ (Figure 6.3a and Table 7.1), with most of the C_3H_6 monomer obtained in the first 10 min. This yield by the catalyst-free STH process, despite being non-optimized, is already much higher compared with values reported in the literature through catalyst-free pyrolysis of PP¹²⁸ (for example, about 10%; Figure 6.3a). Also, the C_3H_6 monomer yield by STH is among the highest compared with the literature even using optimized catalysts and processes, including fast pyrolysis methods that can reduce side reactions by controlling timescales in seconds^{126–129} (typically $< 25\%$; Figure 6.3b and Table 7.1). Note that, compared with such fast pyrolysis methods, our STH approach adds a new dimension of tunability, featuring transient heating durations of milliseconds provided by the heater, which can potentially be combined with existing fast pyrolysis techniques towards even more favorable synthesis outcomes^{119,136}.

To explore the reaction pathway of the PP pyrolysis and understand the role played by STH, we performed reactive molecular dynamics by ReaxFF, which simulated a spatially and temporally homogeneous reactor^{137,138}. The simulation of the reaction process from the starting polymeric molecules to the near-equilibrium products was conducted at 1527 °C, which was selected to be higher than the operation temperature of STH to extract the complete reaction progress within a reasonable

simulation time (that is, <1 year)^{139,140}. Figure 6.8a-d shows a series of representative zoomed-in images of the simulated space to demonstrate the molecular-level transformation of the polymer as it is heated over time (from 0 to around 100 ns). The PP molecules first crack into smaller polymeric species, oligomers, and monomer fragments (at roughly 5.5 ns), which then dehydrogenate, recombine, and gradually form larger and unsaturated species (at about 28 ns and about 100 ns). We plotted the number of monomers as a function of the simulated reaction time (up to about 100 ns) and found that the number quickly peaks at approximately 5.5 ns, then continues to decrease over time (Figure 6.8e). Meanwhile, the number of H₂ molecules increases throughout the simulated reaction time frame, indicating that the dehydrogenation side reaction (C-H bond breaking) occurs continuously. These results indicate that a transient heating duration (the closer to the timescale of the highest monomer number the better) by the temporal heating profile is useful in terms of achieving high monomer selectivity while reducing side products (for example, methane, aromatics and so on^{119,125}) whose formation processes have longer timescales. Note that, although continuous heating with long timescales could lead to unwanted side reactions, long residence times are found to promote the formation of gaseous products including the desired monomer (for example, methane, ethylene, acetylene, C₃H₆ monomers) from plastic pyrolysis owing to the increased degrees of depolymerization and cracking^{141,142}. Therefore, the bilayer design with a spatial temperature gradient is critical in terms of exerting increased residence times and thus multiple heating pulses to the reactant and intermediate products by means of a gradual melting, wicking, vaporization, and

reaction process to improve the monomer yield, meanwhile allowing the temporal heating profile to help reduce side reactions in each heating/cooling cycle.

Increasing the heating rate is also known to improve the plastic pyrolysis yield to gaseous products, including monomers. Given that the heating rate of the STH carbon heater is much higher than in conventional devices (for example, $>10^3\text{ }^\circ\text{C s}^{-1}$ versus $0.33\text{ }^\circ\text{C s}^{-1}$ (ref. 18)), we conducted a control experiment to isolate the effect of the heating rate by placing a single carbon heater layer beneath a reservoir containing 0.1 g of PP beads. This setup allowed us to remove both the spatial temperature gradient as well as the temporal heating profile and focus solely on the impact of the heating rate. With rapid temperature ramping ($>10^3\text{ }^\circ\text{C s}^{-1}$, that same as in the STH process) followed by an isothermal hold (that is, continuous heating) at $600\text{ }^\circ\text{C}$ (equal to the highest T_{peak} in STH) for 35 min, we obtained a C_3H_6 monomer yield of just $16.7\% \pm 6\%$. This result suggests that the fast-heating rate by STH has a relatively minor role on the improvement of the monomer yield compared with the spatial temperature gradient and the temporal heating profile.

Next, we explored the practicality of the STH approach. We found that the STH system demonstrates good reusability over consecutive operations with consistently high C_3H_6 monomer yields close to 36% (Figure 6.3c). We then studied the scalability of the STH approach on the laboratory scale to investigate its potential for practical depolymerization of plastics. As the STH reaction requires a vertical temperature gradient, which confines the potential thickness of the heater and reactor layers, scaling the STH process should depend more on the surface area (that is, width $\times$ length) of the bilayers than their volume. Therefore, to scale the reaction, we first increased both the

mass of the PP feed and the surface area of the bilayer structure twofold (PP: 0.2 g; heater: $50 \times 9 \times 2.3$ mm; reactor: $26 \times 6 \times 4.7$ mm; Table 7.3), as well as the power input (from about 22 V to about 32 V) to obtain a comparable temperature profile (for example, T_{peak} , heating and cooling durations). The resulting C_3H_6 monomer yield was 34.2%— comparable with the yield measured at the initial scale of 0.1 g PP feed (Figure 6.3d). The average C_3H_6 production rates were also comparable at these two scales (that is, $4.6 \times 10^{-3} \text{ g cm}^{-2} \text{ min}^{-1}$ and $4.4 \times 10^{-3} \text{ g cm}^{-2} \text{ min}^{-1}$ for 0.1 g and 0.2 g of PP feed, respectively; Figure 6.3d), with most of the C_3H_6 monomers obtained in the first 10 min during the 35-min batch reactions. To further scale up the process, we then fabricated a larger STH system (Figure 6.8), in which the heater and reactor layers were housed in a larger quartz tube of 34 mm inner diameter, translating to a more than ten times larger cross-sectional area compared with that of the smaller-scale reaction system (Table 7.3), enabling a corresponding increase of the PP feed up to tenfold (from 0.1 g to 1.0 g). With this system and by increasing the surface area of the heater and reactor layers, as well as the applied voltage to maintain the temperature profile (heater layer: $100 \times 18 \times 2.3$ mm; reactor layer: $35 \times 12 \times 4.7$ mm; 40 V), we were still able to obtain a high C_3H_6 monomer yield of 33.8%, which is comparable with the values measured using the smaller-scale STH system (Figure 6.3d). The PP was also fully reacted after 35 min, with most of the C_3H_6 monomer detected in the first 12 min. Notably, the average C_3H_6 production rate increased from $4.4\text{--}4.6 \times 10^{-3} \text{ g cm}^{-2} \text{ min}^{-1}$ to $6.7 \times 10^{-3} \text{ g cm}^{-2} \text{ min}^{-1}$ by increasing the size of the quartz tube. This is probably because of the reduced surface area to volume ratio of the larger quartz tube, which

improves heat transfer and reduces heat loss of the system. Overall, these results showcase the potential of scaling up the STH approach for practical applications. Last, to demonstrate the utility of this STH approach for commodity plastics, we conducted the pyrolysis of a commercial PP-based product (that is, a PP bag) by applying a typical pulsed heating program (power on for 0.11 s at about 22 V, power off for 0.99 s, one power on/off cycle for 1.10 s; total operation time: 35 min) with the smaller-scale STH system. Despite having additives such as plasticizers, antioxidants, stabilizers etc. in the PP bag, we still achieved a high C_3H_6 monomer yield of $34.3\% \pm 7.5\%$ (Figure 6.3e), comparable with that from the pyrolysis of PP beads using STH under identical operation conditions ($35.5\% \pm 6.2\%$).

As well as depolymerizing PP as a representative polyolefin, we also applied the electrified STH approach to depolymerize PET as a representative polyester, which has been widely used as plastics but also as fabrics. To depolymerize PET, we used the STH system to apply a higher T_{peak} compared with PP, given the higher melting point of PET (about 250 °C versus about 160 °C for PP). As a non-optimized, proof-of-concept demonstration, we used a power on (heating) duration of 0.11 s at about 26 V and a power off (cooling) duration of 0.99 s applied to the top carbon heater layer to generate the highest T_{peak} of about 1050 °C throughout the bilayer structure (Figure 6.10). By increasing the temperature of the heater, the temperature at the bottom of the reactor increases accordingly, which helps ensure good fluidity of the reactant for effective and continuous wicking through the bottom porous carbon reactor layer. Our qualitative product analysis of the depolymerized PET by gas chromatography-mass spectrometry (GC-MS; Figure 6.11 and Table 7.4) showed a monomer yield (that is,

relative abundance of 1,4-benzenedicarboxylic acid) of up to about 43%, along with roughly 6% monomer-like product (that is, relative abundance of 1,4-benzenedicarboxylic acid, 1-ethenyl ester), for a total of about 49%. This monomer yield is among the highest compared with the literature of conventional thermochemical methods such as pyrolysis (for example, < 25%)^{124,130,131}. The monomer of 1,4-benzenedicarboxylic acid is probably formed on the basis of a β -CH hydrogen transfer mechanism¹⁴³ during PET pyrolysis in inert environments, which is supported by the presence of 1,4-benzenedicarboxylic acid, 1-ethenyl ester in the liquid-phase products (Table 7.4) and acetylene in the gas-phase products (Figure 6.12). Similarly, when we applied the same process to a commercial PET plastic bottle, we obtained a roughly 45% total yield of 1,4-benzenedicarboxylic acid and 1,4-benzenedicarboxylic acid, 1-ethenyl ester, which is close to the approximately 49% total yield of the monomer and monomer-like species from the PET pellets under the same operation conditions.

Besides the broad reactant scope (that is, polyolefins and polyesters) and improved monomer yield, the STH approach also features good potential for continuous processing instead of being conducted in batch reactions. For example, Figure 6.13 shows a proposed prototype for a plastic depolymerization process based on the same STH bilayer design along with commercially available tools. In this process, solid plastic waste would be mechanically shredded into smaller pieces, which are easier to melt. These pieces would then be dropped into a reservoir kept above the melting temperature to form a liquid. The plastic melt would then fill the reservoir, come into contact with the reactor layer of the bilayer structure and undergo the

depolymerization process to produce monomers with high selectivity and yield. Finally, the products would be collected above the bilayer region for further separation and storage. We note that the carbon heater in the STH system can be powered by renewable electricity, whereas the melting of plastic waste can potentially be achieved using renewable energy sources, such as concentrated solar light, making the whole system more energy-efficient, environmentally benign, and sustainable with reduced CO₂ emissions.

8.3 Conclusion and discussion

In this work, we demonstrate a catalyst-free and far-from-equilibrium electrified STH approach that can selectively depolymerize representative commodity polyolefins (PP) and polyesters (PET) to their monomers at high yields by means of pyrolysis, which offers a promising route for recycling plastic waste. Using a bilayer porous carbon felt structure, we implement a continuous plastic melting, wicking, vaporization, and reaction process through pulsed electrical heating. The resulting spatial temperature gradient in the bilayer structure enables a high degree of depolymerization by implementing long residence times on the reactant and intermediates. Meanwhile, the temporal heating profile potentially suppresses the formation of side products and secondary reactions by applying a short heating duration (that is, 0.11 s) in every pulse cycle. We also explored the scalability of the STH approach on the laboratory scale by increasing the surface area of the bilayer, which allowed us to increase the PP mass feed tenfold without compromising the monomer yield, showing the potential of this approach for practical applications.

Note that the monomer yield of the PP and PET pyrolysis reactions by STH described here has not been optimized. To further improve the reaction outcome, the material properties of the reactor layer (for example, pore shape, pore size and distribution, surface energy etc.) could be modified to enhance the plastic melt wicking and gas diffusion processes. Furthermore, unlike continuous heating, the electrified STH process can be controlled by varying the input power and the on/off timescale in milliseconds, enabling us to tune the heating duration, frequency, and heating pulse temperature, as well as the temperature distribution in the reactor layer, to optimize the product yield and reduce the energy cost. As we move beyond lab-scale and proof-of-concept demonstrations towards truly large-scale and continuous reactors, data-driven machine learning algorithms (for example, Bayesian optimization of the temperature profile) can also help determine the reaction parameters to optimize the yield tailored to a particular feedstock and desired product¹⁴⁴. As well as its good performance and potentially better tunability compared with conventional thermochemical methods, the electrified STH approach could be further integrated with commercially available tools for continuous operation using renewable energy sources for higher energy efficiency and reduced CO₂ emissions³⁷. Overall, this electrified STH approach holds great potential for converting a range of plastics, biomass and other supramolecules towards the sustainable, energy-efficient, and scalable manufacturing of value-added chemicals.

Author contributions

L.H. and Q.D. conceived the concept and designed the STH approach. L.H. and Q.D. designed the reactors, with input from S.C. and Y.L. Q.D., S.L., M.G., M.C., T.L. and

A.Q. collected the experimental data. X.Z. conducted the temperature measurement, with help from Q.D. and S.L. A.D.L. and Y.J. conducted the molecular dynamics simulations. S.C. and D.L. analysed the gaseous products. Y.W. and X.P. analysed the liquid products. I.G.K. and J.M. helped with the data analysis and improved the manuscript. L.X. helped with the writing and figure design. L.H., Q.D. and A.H.B. collectively wrote the paper, with input from all authors. L.H. and Y.J. supervised the project. All authors discussed the results and contributed to the final manuscript.

8.4 Experimental

Materials

PP (isotactic, average M_W about 580,000, average M_n approximately 166,000) and PET (granular) were purchased from Sigma-Aldrich. Commodity plastic products, including PP bags and PET water bottles, were purchased from Amazon. Solvents, including tetrahydrofuran (HPLC grade) and acetone (>99.9%), were purchased from Sigma-Aldrich. Gases including argon, CH_4 , C_2H_4 and C_3H_6 (>99.9%) were purchased from Airgas. Carbon felt (AvCarb G280A, AvCarb G475 and AvCarb G650A, soft graphite battery felt) was purchased from the Fuel Cell Store. Before use, the carbon felt was thoroughly washed with acetone and then dried under vacuum overnight at 80 °C. It was further purged in argon atmosphere for 1 h before use to remove any trapped moisture and oxygen in the porous material. Multipurpose 110 copper sheets (99.9%, 0.002 in. thick) and multipurpose 110 copper wire (99.9%, 0.04 in. diameter) were obtained from McMaster-Carr. Alligator clips made of stainless steel were purchased from Amazon. All the materials used as electrical connections were cleaned with acetone and dried under vacuum before assembling the STH system. Alumina

ceramic tubes (99.8%, 0.125 in. outer diameter and 0.062 in. inner diameter, maximum temperature 1950 °C) were acquired from Omega for covering the copper wires. Quartz tubes were purchased from QSI (1/2 in. outer diameter, 10.5 mm inner diameter) and Technical Glass Products, Inc. (39 mm outer diameter, 34 mm inner diameter). The J-B Weld HI-TEMP RTV silicone gasket maker and sealant was purchased from Amazon.

STH operation

The dimensions of the carbon felt heater (exposed region) and reactor, and the flow rate of the argon carrier gas are listed in Supplementary Table 3 for various scales. Both ends of the carbon felt heater were wrapped with copper foil, which were then connected to the power supply through alumina-covered copper wires and alligator clips. The gaps between the copper wire and alumina tube were filled with thermoset epoxy (Gorilla). The reactor layer was placed under the heater in soft contact (that is, without external pressure) and placed on top of a reservoir made of inert titanium foil. The reservoir container was used to hold the plastic reactant and the resulting melt during heating. The size of the titanium container matched that of the reactor. Note that, as the temperature of the reservoir during STH operation is much lower than the reaction temperature, according to the infrared camera heat maps (Figure 6.2g), negligible chemical reaction will occur in the reservoir. Finally, the assembled STH system, including the heater layer, reactor layer and reactant reservoir, was placed in a flow reaction system made of a quartz tube (1/2 in. outer diameter, 10.5 mm inner diameter for the small-scale reaction system, QSI; or 39 mm outer diameter, 34 mm inner diameter for the larger-scale reaction system, Technical Glass Products, Inc.). For

the small-scale reaction system, the quartz tube was sealed with two Ultra-Torr tee fittings (Swagelok). For the larger-scale STH system, the quartz tube was sealed with sealant (J-B Weld HI-TEMP RTV Silicone Gasket Maker and Sealant) and attached to customized stainless-steel fittings (Figure 6.8). The ports of the Ultra-Torr fittings were used for the electrical wires and gas flow. Control over the temperature was achieved through a solid-state relay device (DC input and DC output, maximum current 25 A, Omega), a high-accuracy sourcemeter (Keithley, Model 2400) and a power supply (75 V, 20 A, Volteq) connected to the top carbon felt heater layer.

The temperature range, heating duration and heating frequency can be programmed by adjusting the settings of the power supply and the sourcemeter. Control experiments under continuous heating were conducted using a constant power input by the power supply, without the need for the sourcemeter and the relay device. In a typical STH operation with electrical pulsed heating, the heating duration can be programmed through the sourcemeter by setting a certain time within one period (for example, 1.10 s) as ‘power on’ (for example, 0.11 s, power on) by applying the power and setting the remaining time as ‘power off’ (for example, 0.99 s, power off) by removing the power. The peak temperature was controlled by the power input (that is, the applied voltage to the heater) from the power supply. In a typical experiment, 0.1 - 1.0 g of PP beads or about 0.2 g of PET pellets were used as the starting material. For PP bags and PET water bottles, the starting materials were cut into small pieces to fit into the reservoir.

Product detection in the gas phase

Gas products were detected and quantitatively measured by GC-FID (Agilent, Model 6890N). The gas sample was collected at the exit of the reaction system using a SupelInert multilayer foil gas sampling bag (0.6 liters for the small-scale STH system and 5.0 liters for the larger-scale STH system; Extended Data Figure 3, inset). Fifty-microliter gas samples were then extracted from the gas bag using a gas-tight syringe (50 μ l, Hamilton 1705) and injected into the injection ports of the FID. A thermal conductivity detector was used to quantify an internal standard gas (argon) to ensure the consistency of each injection. The column connected to the FID was a GS-GasPro (Agilent). The column connected to the thermal conductivity detector was a ShinCarbon ST packed column (Restek). Standard gases of CH₄, C₂H₄ and C₃H₆ were injected to calibrate the GC-FID peak areas.

Product detection in the liquid phase

Liquid products were detected and qualitatively measured by GC-MS analysis. The depolymerization products in the liquid phase were in part collected with the carrier gas downstream in an acetone-filled vial. The remainder of the products was condensed in the quartz tube, which was rinsed off using acetone and combined with the downstream products. The acetone solution was filtered through a 0.45- μ m syringe filter before injecting into the GC-MS. We used a Shimadzu GCMS-QP2010S system with an Rtx-5MS column (30 m $\times$ 0.25 mm, length $\times$ inner diameter, with 0.25 μ m film thickness). The products from PET depolymerization were silylated to improve the sample volatility. In a typical measurement, 400 μ l of the sample was mixed and reacted with 100 μ l *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) at room temperature

overnight. Helium was used as the carrier gas, with a flow rate of 1.27 ml min^{-1} . The GC oven temperature was programmed from $50 \text{ }^{\circ}\text{C}$ (5 min) to $150 \text{ }^{\circ}\text{C}$ at a heating rate of $10 \text{ }^{\circ}\text{C min}^{-1}$, from $150 \text{ }^{\circ}\text{C}$ to $220 \text{ }^{\circ}\text{C}$ at $5 \text{ }^{\circ}\text{C min}^{-1}$ and from $220 \text{ }^{\circ}\text{C}$ to $300 \text{ }^{\circ}\text{C}$ (10 min) at $10 \text{ }^{\circ}\text{C min}^{-1}$. The injector temperature was set at $280 \text{ }^{\circ}\text{C}$ in split mode, with a split ratio of 5:1. The MS detector was operated in electron impact ionization mode, with the ion source temperature set at $230 \text{ }^{\circ}\text{C}$. The scanning ion range was set between m/z 35 and 600. Qualitative analysis was performed using GCMS Postrun Analysis software. The products were identified on the basis of the NIST08 and NIST08s libraries and the percentages of the peaks were calculated from the total ion chromatogram peak area.

Determining the product yield

For determining the product yield of PP pyrolysis, the GC-FID peak areas of CH_4 , C_2H_4 and C_3H_6 (the main gaseous products from PP pyrolysis in this study by either STH or continuous heating) were quantitatively calibrated by injecting known amounts of standard gases. On the basis of the measured peak areas, the mass of each gaseous product from a batch reaction can be derived. The product yield is then calculated by dividing the mass of the product of interest by the feed mass of PP. Standard deviation is calculated with a value of $n \geq 3$.

The product yield (that is, relative abundance) of PET pyrolysis was qualitatively estimated on the basis of the GC-MS peak area percentages of the liquid-phase products after 55 min of reaction. This method follows the common practice in the literature when quantifying a specific product in a complex mixture^{38,39}. Note that

minimal solid (< 1%) or gaseous products (< 5%) were detected after the PET pyrolysis by STH. About 0.2 g of PET can be fully decomposed after 55 min (that is, approximately 100% conversion).

Determining the average C_3H_6 production rate

The average C_3H_6 production rate was calculated by dividing the produced mass of C_3H_6 by the surface area of the reactor layer and the reaction time used to collect the C_3H_6 product during the batch reactions. Note that the C_3H_6 production rate changes over time. The values shown in Figure 6.3d are the average reaction rates corresponding to the time used to collect most of the C_3H_6 product for all scales (that is, 10 min for a scaling factor of 1 or 2 and 12 min for a scaling factor of 10).

Temperature acquisition

Temperature mapping of the heater and reactor was performed by an infrared camera VarioCAM HDx head 600 (7.5 - 14 μm) with a resolution of 640×480 infrared pixels using a standard lens (20 mm). The VarioCAM camera has an infrared image rate of 30 Hz in full frame and can measure the temperature in the range -40 - 1700 $^{\circ}C$ with an accuracy of $\pm 2\%$. During the measurement, the VarioCAM camera was placed 10 cm away from the heater and reactor.

To estimate the temporal temperature profile, we first built a home-made model setup to mimic the real STH system, which was housed in an environmental chamber ($23 \times 13 \times 8$ cm) composed of thin aluminum siding and a side opening (10×4 cm) for the infrared signal to pass through to the camera. The chamber was continuously

purged with argon to remove air through one inlet and outlet. We placed the carbon felt bilayer structure along with the PP reactant inside the environmental chamber, applied the same electrical signal used in the real STH system and measured the temperature profile. This result is shown in Figure 6.2g,h, as it features good spatial resolution to differentiate the heater and reactor layers.

To acquire potentially better temperature accuracy, the temporal temperature profile of the bilayer structure during STH operation was also measured by the infrared camera using a customized quartz tube with a smaller opening on the tube wall (about 7×14 mm), which was created to allow the infrared signal to pass through to the camera. Argon protecting gas was purged to the surrounding environment to avoid air leaking into the quartz tube. We placed the bilayer structure with the PP reactant inside the customized quartz tube, applied the same electrical signal used in the real STH system and measured the temperature profile, the results of which are shown in Figure 6.6. This setup offers better temperature-measurement accuracy because it best resembles the real STH system, except for the small opening on the side of the quartz tube. However, this small opening and the background noise produced by the quartz tube reduces the spatial resolution for differentiating the position of the heater and reactor layers.

Note that both measurements were conducted in a relatively open space (quartz tube with a small opening or in the environmental chamber with a large opening) rather than in a closed quartz tube as in the real STH operation, therefore it is necessary to estimate the error caused by this factor. To do so, we further measured the temperature of the outer surface of the quartz tube (1/2 in. outer diameter, 10.5 mm inner diameter,

QSI) during real STH operations (0.11 s power on, 0.99 s power off, about 22 V). The outer surface of the quartz tube showed a nearly constant temperature of about 145 °C. Because the heating program and power input to the carbon heater and reactor layers in the quartz tube with a small opening or in the environmental chamber are the same as those in the intact quartz tube, assuming that the energy loss to the surroundings in the real STH system is equal to that in the systems used for the temperature measurement, the measured surface temperature of the carbon heater and reactor layers can be roughly corrected as:

in which T_C and T_M are the corrected and measured surface temperatures of the carbon heater and reactor layers in the quartz tube with the small opening, respectively, and T_{ambient} and T_{tube} are the ambient temperature (20 °C) and quartz tube temperature (145 °C) during the STH operation. On the basis of this estimate, the error of the temperature measurement should be < 24 °C for both setups. Note that this error becomes smaller at higher temperatures and larger at lower temperatures (for example, error = 6 °C at 700 °C, error = 9 °C at 600 °C, error = 24 °C at 340 °C).

Material characterization

SEM was conducted using a JEOL 6340F microscope operated at an accelerating voltage of 10 - 20 kV. The SEM images were taken from the selected region shown in Figure 6.2c. The SEM image with infiltrated reactants corresponds to the morphology of the bottom region of the reactor layer within 5 min of the STH operation using PP as a model material (0.11 s power on, 0.99 s power off, about 22 V). Thermogravimetric

analysis was conducted using a Discovery SDT 650 instrument from room temperature to 1000 °C in nitrogen, with a ramping rate of 5 °C min⁻¹.

Molecular dynamics simulations

The molecular dynamics simulation results presented in this work were performed at constant amount of substance (N), volume (V) and temperature (T) using ReaxFF^{138,140} reactive molecular dynamics code as a part of the LAMMPS software suite^{145,146}. The CHON-2019 ReaxFF parameters set¹⁴⁷ was used in this work to perform reactive classical molecular dynamics simulations, which has been previously used in polymer simulations^{148,149,138}. The ReaxFF reactive-force-field-based molecular dynamics is a computational tool for atomistic-scale simulations of complex reactive systems. The ReaxFF reactive force field is trained using quantum mechanics data. A bond-order formalism is used to describe reactive events through the ReaxFF potential. This allows ReaxFF to describe bond formation and breaking. ReaxFF can model much larger simulation systems (thousands of atoms) over relatively long simulation times (more than 100 ns in this work) compared with quantum-mechanics-based methods because of its lower computational cost. This makes ReaxFF a suitable tool to model complex reactive systems such as PP pyrolysis. Furthermore, any chemical intuition is not required to determine possible reactions before performing the simulations.

The ReaxFF method uses a bond-order concept¹⁵⁰ to describe reactive events. The bond order is calculated on the basis of the interatomic distance using an expression that contains the single, double and triple bond-order contributions. ReaxFF allows bond formation and bond breaking by updating the bond order at every iteration.

van der Waals and Coulomb interactions, which are non-bonded interactions¹³⁸, are calculated between every atomic pair independently from the bonded interactions. The energy of each atom governs the dynamics of the system by the following equation:

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{val}} + E_{\text{tor}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}$$

In the above equation, E_{bond} (bond energy), E_{over} (overcoordination penalty energy), E_{under} (undercoordination penalty energy), E_{lp} (lone pair energy), E_{val} (valence angle energy) and E_{tor} (torsion angle energy) are bond-order-dependent terms. E_{vdWaals} (van der Waals energy) and E_{Coulomb} (Coulomb energy) are non-bonded terms. A more detailed description can be found in previous ReaxFF-related literature^{138c}. The principles and applications of the ReaxFF method have also been discussed in recent literature¹⁵¹.

The CHON-2019 ReaxFF parameters set¹⁴⁷ was used in this work to perform reactive classical molecular dynamics simulations. The overall simulation methodology can be described as follows: first, energy minimization was performed on all the molecular structures. The energy-minimized polymer structures are then used to randomly fill a periodic simulation box. This simulation system is then energy-minimized at 0 K and equilibrated. The equilibration temperature is chosen such that no reactions were taking place during equilibration. The equilibrated system is then used to perform the final simulations. The Nosé-Hoover thermostat¹⁵⁰ was used to control the simulation temperature. A damping constant of 100 fs was used for the simulation temperature thermostating. The simulations time step was chosen to be 0.1

fs following previous work¹⁴⁰. A cubic ($88.5 \times 88.5 \times 88.5 \text{ \AA}$) simulation box was filled with 20 randomly placed polymers. Each PP polymer was constructed with 40 monomers. The number density of species formed throughout the simulation time was identified to perform the analysis presented in Extended Data Figure 4, which was performed at 1527 °C.

We calculated the general uncertainties for these simulations by averaging the results of several simulations. A different initial geometry was used in each of these simulations. Ten periodic simulation boxes randomly filled with 20 PP polymer molecules as described above were used to generate these initial geometries. The average number density of these ten simulations is used to determine the statistical uncertainty of the simulations. The major product number density uncertainty was up to 10%.

8.5 Supporting materials

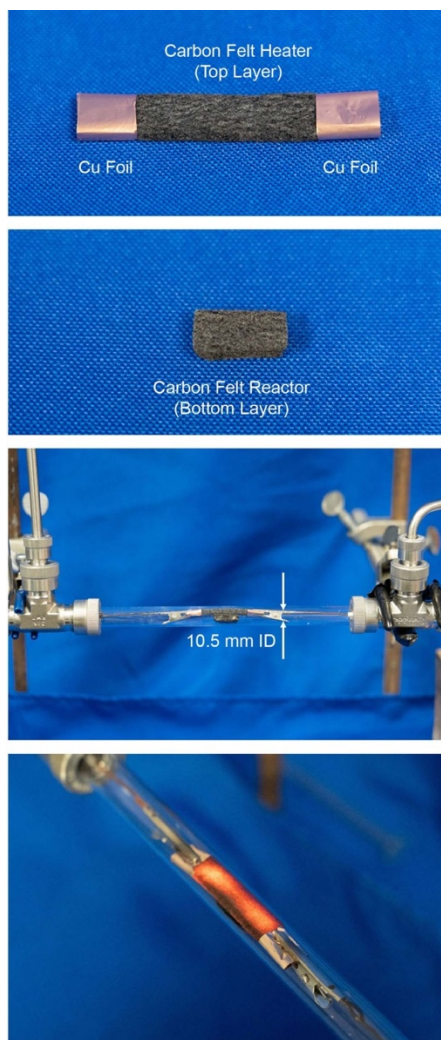


Figure 6.4. The assembly of the STH system. A thinner layer of carbon felt (about 2.3 mm) is used as the top heater layer. The two ends of the top heater layer are wrapped with Cu foil electrodes for Joule heating. The top and bottom layers are placed in soft contact (without external pressure) for the STH process. A quartz tube with 10.5 mm inner diameter was used to contain the carbon bilayer structure and the reactant reservoir. The bottom image shows the heater layer exhibiting a bright orange color as we apply an electrical current through the top heater layer, demonstrating its Joule-heating capabilities.

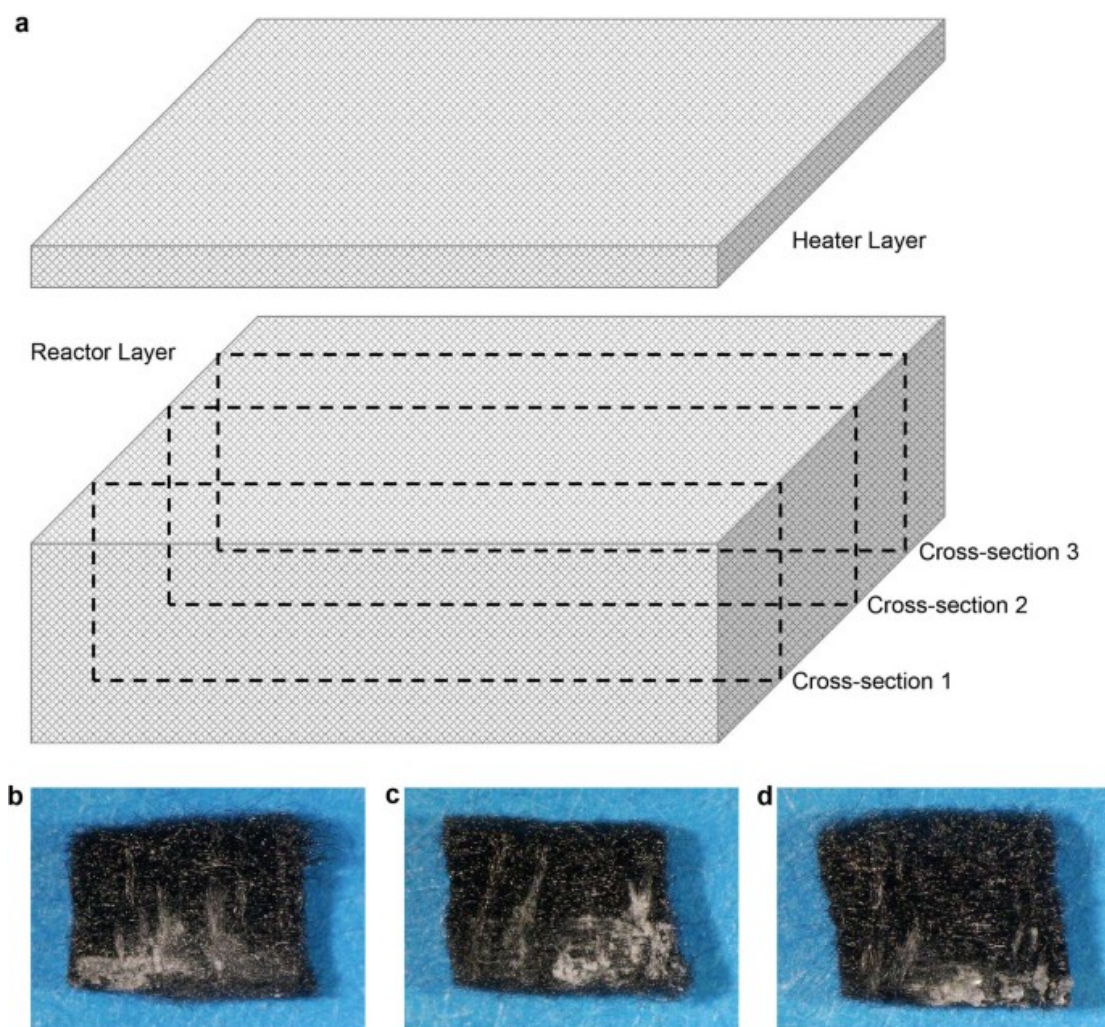


Figure 6.5. Characterization of the wicked PP melt. **a.** Schematic showing the position of the cross-sections cut from the reactor layer after STH operation for about 6 min (0.11 s power on at about 22 V, 0.99 s power off; small-scale reaction system). **b-d.** Representative optical microscopy images showing the wicking of PP in the reactor layer. The images correspond to the cross-sections shown in **a**. The white species are wicked plastic melt. The black objects are the cut pieces of the porous reactor layer with cross-sections facing out.

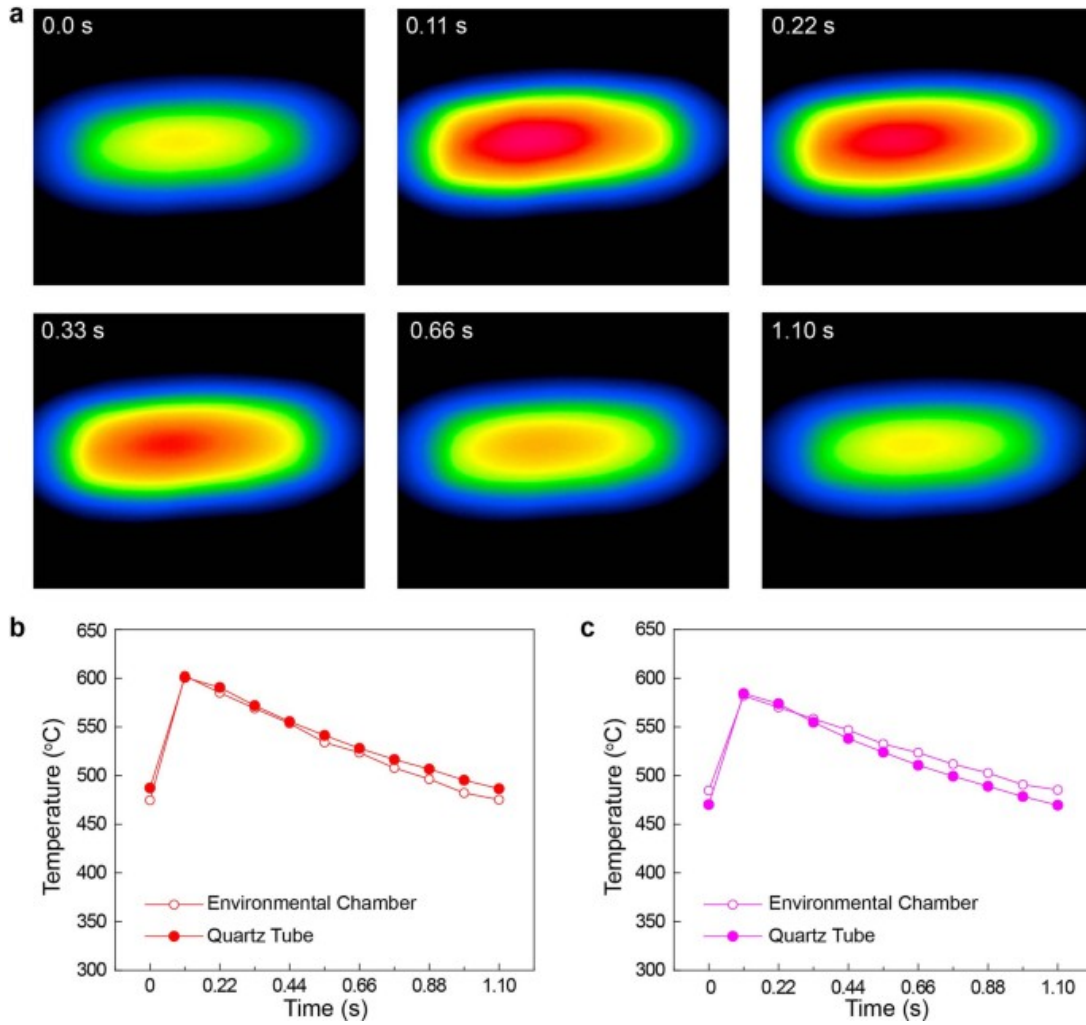


Figure 6.6. Temperature measurement using the customized quartz tube with a small opening. **a.** Temperature maps of the heater and reactor layers at various time points during one heating cycle of 1.10 s (power on time: 0.11 s at about 22 V; power off time: 0.99 s), measured in the customized quartz tube with a small opening (about 7×14 mm) on the tube wall. The temperature scale is the same that as shown in Figure 2g. This temperature measurement features better accuracy, as the bilayer structure is housed in a quartz tube setup similar to the real STH process but has lower spatial resolution because of the limited size of the opening on the quartz tube wall and background noise from the quartz tube for differentiating the position of the heater and

reactor layers compared with the measurement using the environmental chamber. **b.** Comparing the temporal temperature profiles measured using the lab-built environmental chamber and the customized quartz tube at the position labelled in red as shown in Figure 2c. **c.** Comparing the temporal temperature profiles measured using the lab-built environmental chamber and the customized quartz tube at the position labelled in pink as shown in Figure 2c.

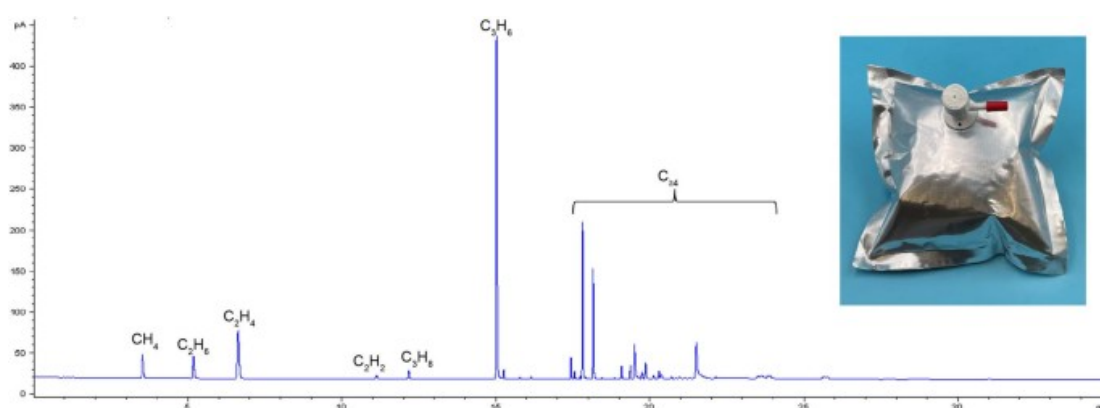


Figure 6.7. A typical gas chromatograph of the PP pyrolysis products by STH (0.11 s power on at about 22 V and 0.99 s power off). Inset, the gas bag used to collect the reaction products in the gas phase, which is connected downstream in the STH system.

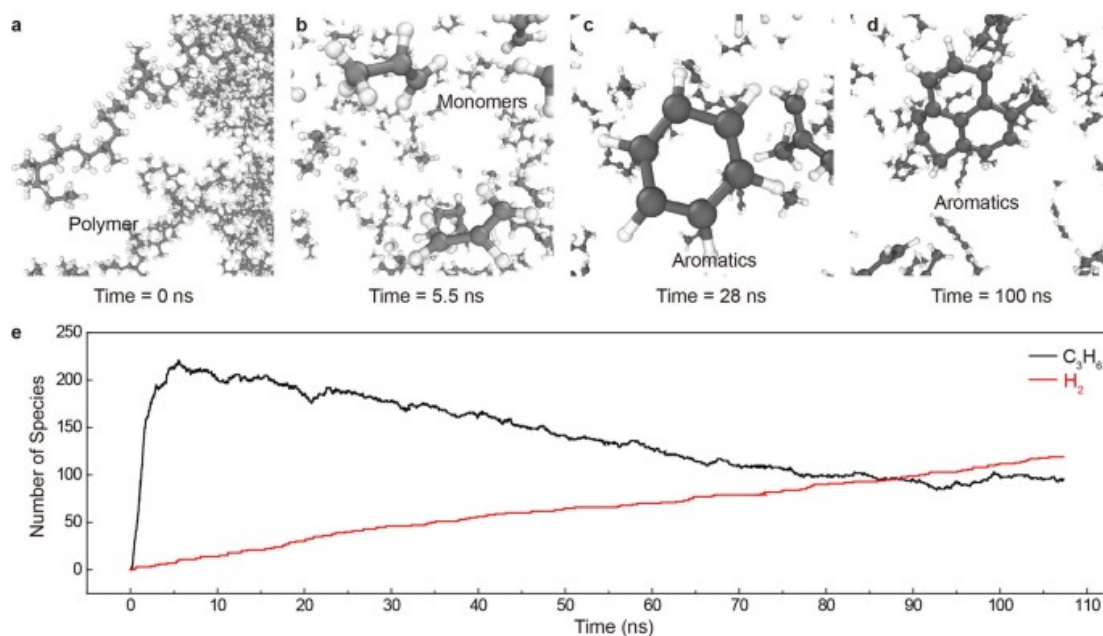


Figure 6.8. Reactive molecular dynamics simulations of PP pyrolysis at 1,527 °C. **a-d.**

A series of representative images of the simulated space, showing the transition from PP (0 ns; **a**) to a large number of C_3H_6 monomers (about 5.5 ns; **b**), and then to various aromatic species (about 28 - 100 ns; **c** and **d**) owing to dehydrogenation and aromatization under extended continuous heating. **e**, The counts of C_3H_6 and H_2 molecules throughout the simulated reaction time frame. The number of C_3H_6 monomers reaches a peak concentration within a short period of time (about 5.5 ns), followed by a gradual drop owing to dehydrogenation, C-C bond coupling, aromatization etc., whereas the number of H_2 molecules continues increasing as the reaction approaches chemical equilibrium.

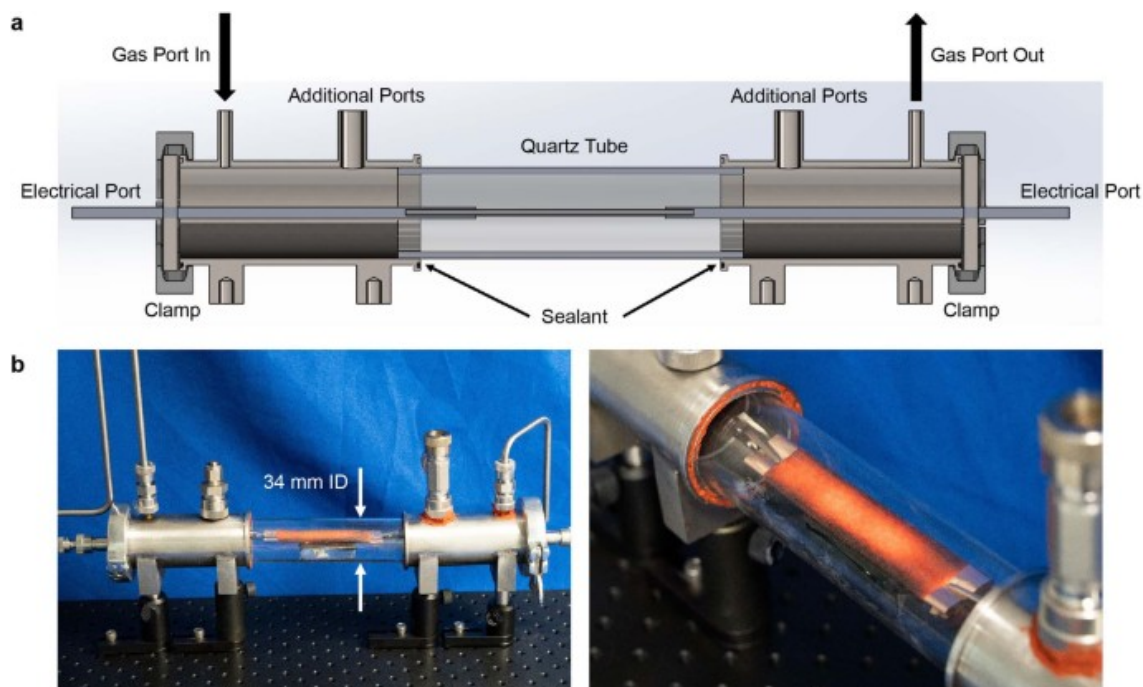


Figure 6.9 The larger-scale STH system. Schematic (a) and images (b) of the large-scale STH system. A quartz tube with 34 mm inner diameter was used to contain the carbon bilayer structure and reactant reservoir. This system allowed us to react up to 1.0 g of PP material within 35 min in a batch mode.

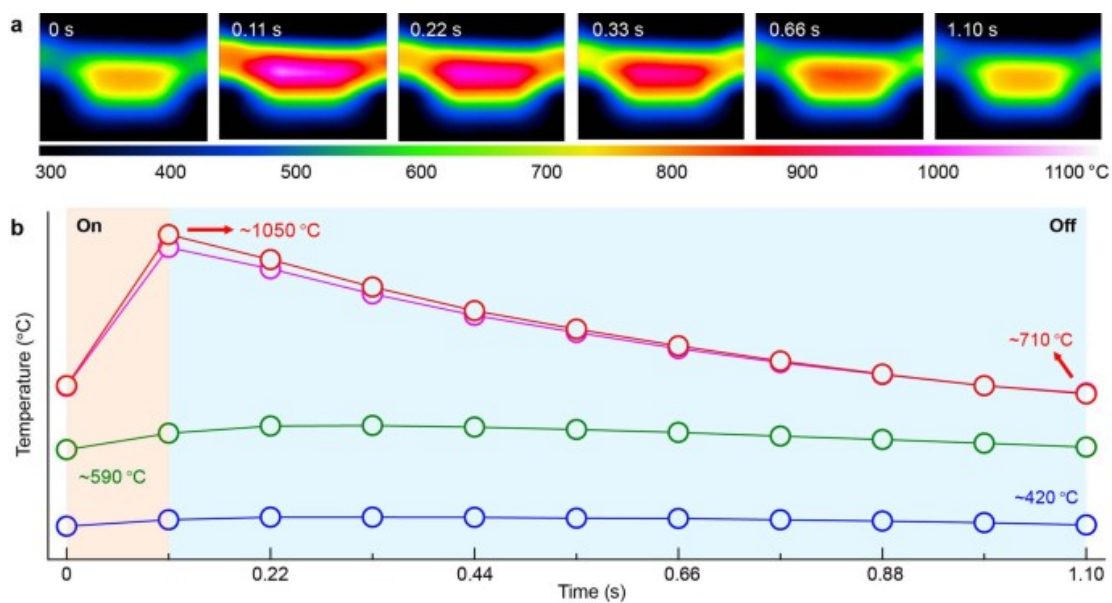


Figure 6.10. Temperature measurement during the PET depolymerization by STH. **a.** Temperature maps of the heater and reactor layers at various time points during one heating cycle of 1.10 s (power on time: 0.11 s at about 26 V; power off time: 0.99 s). **b.** The temporal heating profiles of the four representative positions shown in Figure 2c. The orange region indicates power on, whereas the blue region indicates power off.

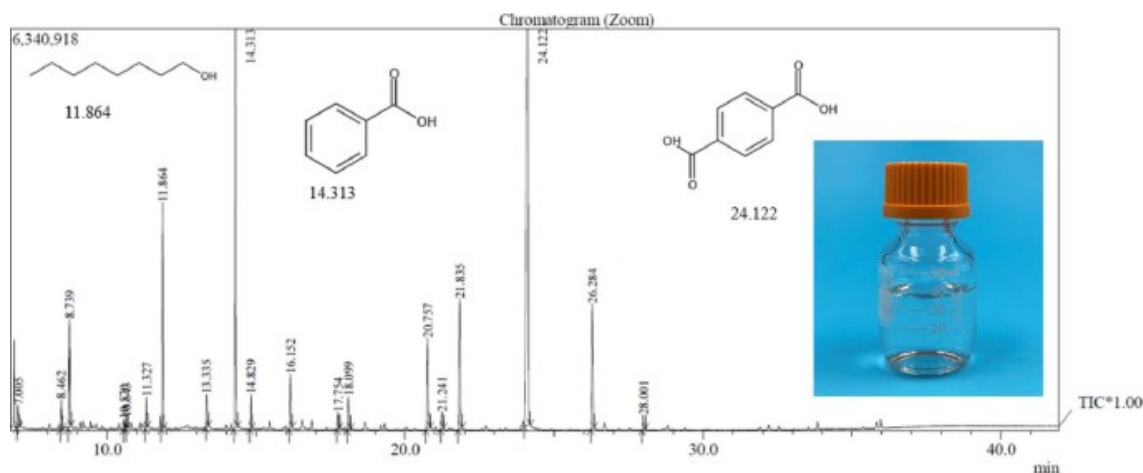


Figure 6.11. Gas chromatograph by GC-MS of the liquid products from PET pyrolysis by means of STH using a heating duration of 0.11 s at about 26 V in a period of 1.10 s. Inset, digital image showing the collected products (about 2 wt% in acetone) after three batches of the STH process with PET. A fraction of the products was collected downstream with the carrier gas. The rest of the products condensed in the quartz tube, which was rinsed off using acetone and combined with the downstream products.

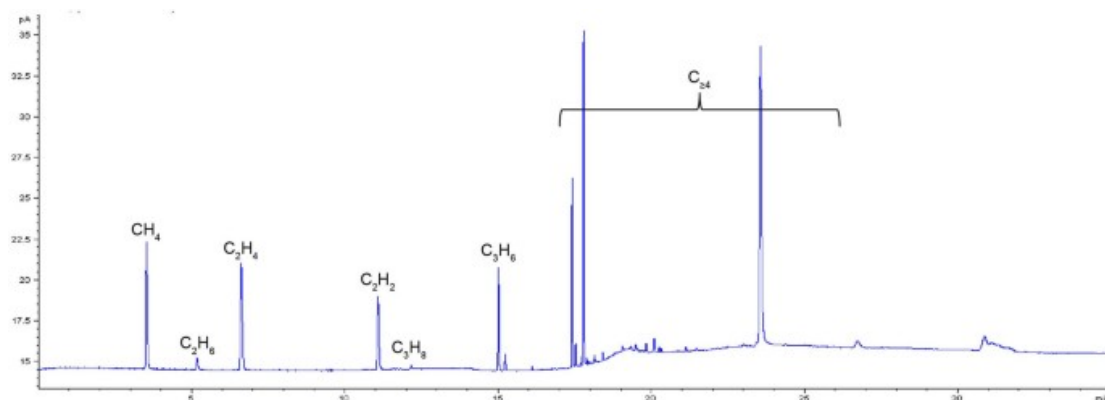


Figure 6.12. A typical gas chromatograph by GC-FID of the gaseous products from the STH process with PET using a heating duration of 0.11 s at about 26 V in a period of 1.10 s. Acetylene is observed as one of the gaseous products, which is consistent with the β -CH hydrogen-transfer mechanism³⁵. Note that acetylene is prone to secondary reactions, therefore the measured content does not directly reflect the total amount of acetylene produced along with the formation of 1,4-benzenedicarboxylic acid.

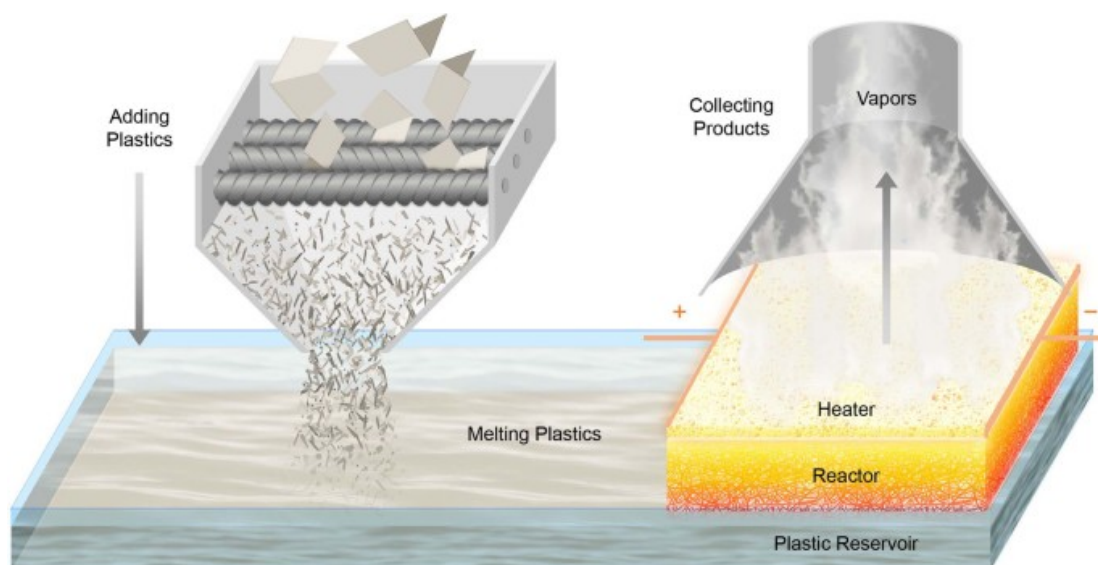


Figure 6.13. A prototype design of a continuous STH process that involves melting, wicking, vaporization, and reaction, along with pulsed electrical heating for recycling commodity plastics such as polyolefins and polyesters. The recycling system integrates commercially available tools and materials, demonstrating the potential practicality of the STH approach.

Table 7.1. The yield (or selectivity) of PP depolymerization in our work (using the electrified STH approach under far-from-equilibrium conditions) compared to literature reports.

Reaction Conditions or Catalyst	Yield or Selectivity (%)	Refs.
HZSM-5	20.1	16
HZSM-5	22	16
HZSM-5	18.6	16
HZSM-5	16.8	16
HZSM-5	23.5	15
HUSY	8.1	15
HMOR	15.6	15
SAHA	3.8	15
MCM-41{Al}	7.3	15
Zeolite Y with gas oil	9.5	17
Zeolite Y with gas oil	8.7	17
Zeolite Y with gas oil	8.4	17
Zeolite Y with gas oil	4.3	17
Zeolite Y with hydrotreated vacuum gas oil + gas oil	9.1	17
Zeolite Y with hydrotreated vacuum gas oil + gas oil	7	17
Zeolite Y with hydrotreated vacuum gas oil + gas oil	7	17
Zeolite Y with hydrotreated vacuum gas oil + gas oil	5.4	17
Silica with light cycle oil	7.5	19
Non-catalytic	10.4	18
Electrified STH	35.5	This work

Table 7.2. The yield of PP depolymerization under various reaction conditions reported in this work. The uncertainty values of the monomer yield denote standard deviation for $n \geq 3$. See the Experimental section for detailed calculations about the uncertainty value of the peak temperature.

Reaction Conditions	Monomer Yield (%)	Figure
STH, 0.11 s on, 0.99 s off, $T_{\text{peak}} = 600 \pm 9$ °C, PP beads, 0.1 g	35.5 ± 6.2	3a, b, d, e
Continuous heating, single heater layer placed underneath the reactant reservoir, $T = 600 \pm 9$ °C, PP beads, 0.1 g	16.7 ± 6.0	Control Experiment
STH, 0.11 s on, 0.99 s off, $T_{\text{peak}} = 600 \pm 9$ °C, PP beads, operation #1, 0.1 g	35.0	3c
STH, 0.11 s on, 0.99 s off, $T_{\text{peak}} = 600 \pm 9$ °C, PP beads, operation #2, 0.1 g	32.5	3c
STH, 0.11 s on, 0.99 s off, $T_{\text{peak}} = 600 \pm 9$ °C, PP beads, operation #3, 0.1 g	38.8	3c
STH, 0.11 s on, 0.99 s off, $T_{\text{peak}} = 600 \pm 9$ °C, PP beads, operation #4, 0.1 g	35.4	3c
STH, 0.11 s on, 0.99 s off, $T_{\text{peak}} = 600 \pm 9$ °C, PP beads, 0.2 g	34.2	3d
STH, 0.11 s on, 0.99 s off, $T_{\text{peak}} = 600 \pm 9$ °C, PP beads, 1.0 g	33.8	3d
STH, 0.11 s on, 0.99 s off, $T_{\text{peak}} = 600 \pm 9$ °C, commercial PP bag, 0.03 g	34.3 ± 7.5	3e

Table 7.3. Parameters used for the STH operation for different scales of the reaction system and masses of the PP reactant. The scaling factor is based on the PP mass feed, with the initial scale of 0.1 g defined as 1.

Scaling Factor	Carbon Felt Heater Layer			Carbon Felt Reactor Layer			Average Voltage/V	Flow Rate/sccm
	L/mm	W/mm	H/mm	L/mm	W/mm	H/mm		
1 (0.1 g)	25	9	2.3±0.1	13	6	4.7	22	100
2 (0.2 g)	50	9	2.3±0.1	26	6	4.7	32	100
10 (1.0 g)	100	18	2.3±0.1	35	12	4.7	40	1400*

The flow rate was scaled based on the estimated increase of the system's effective cross-sectional area (i.e., the cross-sectional area of the quartz tube minus the area occupied by the reaction unit, including the carbon felt bilayer structure, the reservoir, and the electrical connections).

Table 7.4. GC-MS product analysis of the PET pyrolysis reaction by STH using a 0.11 s heating duration at ~26 V in a period of 1.10 s.

Retention Time (min)	Chemical Name	Area (%)
7.005	Styrene	0.91
8.793	2-Hydroxy-acetic acid	3.46
10.570	4-Hydroxy-4-methyl- 2-pentanone	0.39
10.643	Indene	0.42
11.327	Oxanilic acid	0.85
11.864	Octyl alcohol	6.55
13.335	Azulene	1.55
14.313	Benzoic acid	19.57
14.829	Glycerol	0.94
16.152	2-Methyl- benzoic acid	2.07
17.754	4-Ethylbenzoic acid, methyl ester	0.63
18.099	3-Phenyl- 2-propenoic acid	1.47
20.757	1,2,3-Benzenetricarboxylic acid, trimethyl ester	4.32
21.241	1,4-Benzenedicarboxylic acid, monomethyl ester	0.80
21.835	1,4-Benzenedicarboxylic acid, 1-ethenyl ester	6.16
24.122	1,4-Benzenedicarboxylic acid	42.99
26.284	1,2-Benzenedicarboxylic acid, monoethyl ester	6.17
28.001	Fenbufen	0.75

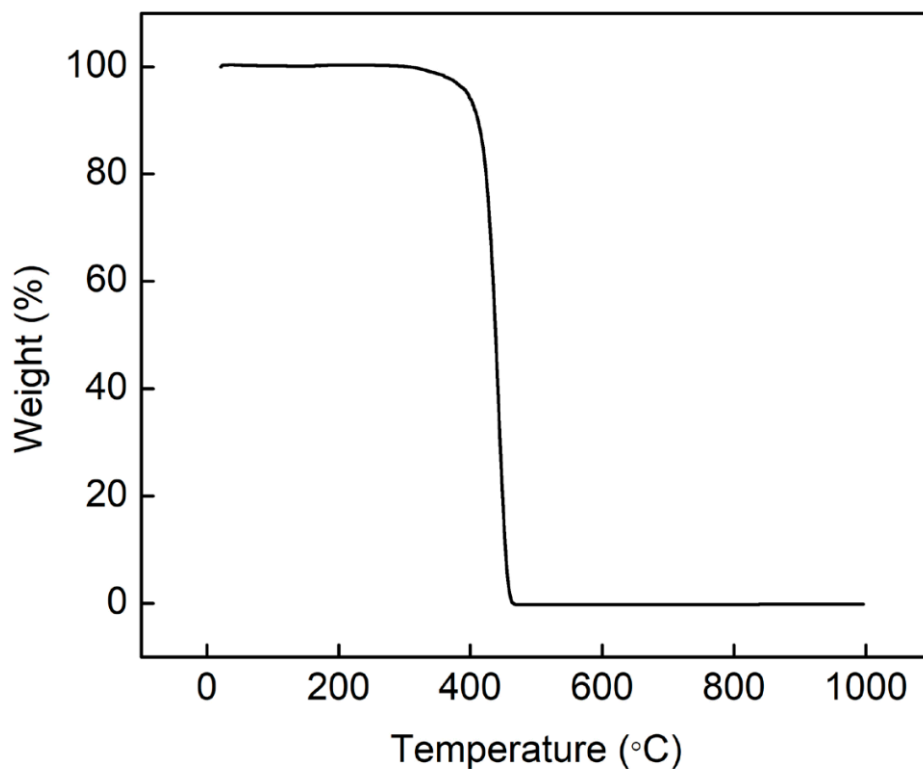


Figure 6.14 Thermal gravimetric analysis of the PP starting material.

Thermogravimetric analysis was conducted using a Discovery SDT 650 instrument from room temperature to 1000 °C with a ramping rate of 5 °C/min. PP displays apparent weight loss at ~420 °C (Supplementary Figure 1), suggesting that volatile species start to form at this temperature.

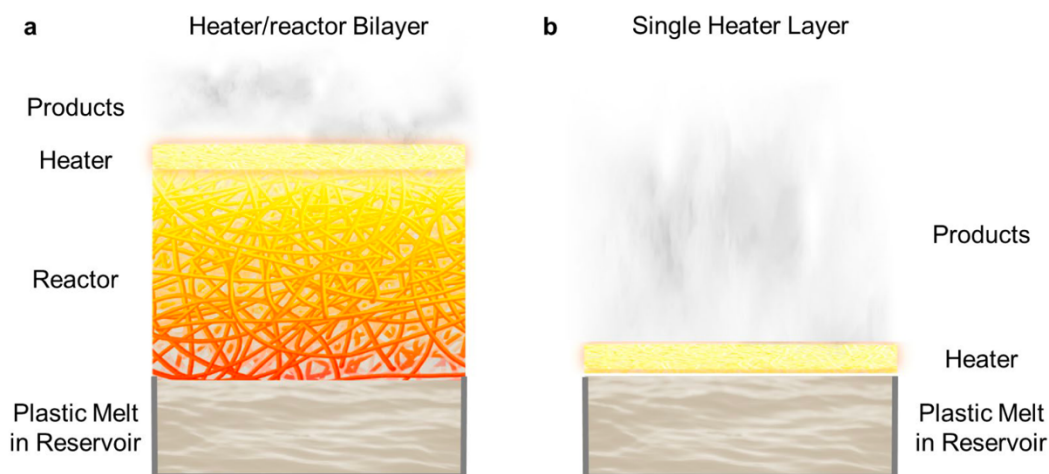


Figure 6.15 Schematic comparing (a) the reaction setup using the heater/reactor bilayer structure and (b) the setup using a single heater layer structure (i.e., without the reactor layer).

The role played by the bilayer structure is critical for STH as it creates a temperature gradient that ensures a continuous melting, wicking, vaporization, and reaction process (Figure 6.15a). If instead of a heater/reactor bilayer design we were to use a single carbon layer to heat the entire plastic melt in the container (Figure 6.15b), there would be no temperature gradient to promote the wicking effect. In this case, the single heater layer would primarily heat the reactant directly within the reservoir, where the thermal inertia of the large volume of the reactant would prevent the temperature profile of the material (e.g., heating and cooling rate, timescale) from closely following that of the heater, resulting in poor control of the reaction progress. In comparison, the temperature gradient produced by the heater/reactor bilayer structure promotes the plastic wicking mechanism, which gradually and continuously supplies small amounts

of reactant into the pores of the reaction zone. As the wicked reactant in these pores has lower mass and therefore lower heat capacity, the temperature profile of the wicked reactant can better synchronize with that of the heater, which can allow us to more accurately control the reaction pathway of the reactant. Additionally, the gradual wicking and diffusion of the reactants through the porous reactor layer allow the intermediate products to have longer residence times and thereby experiencing more heating pulses compared to the operation using single heater layer, which should increase the degree of depolymerization and the monomer yield.

Chapter 7: Lignin Upgrading to Jet-range Aromatics by Convection-assisted Electrified Heating

8.1 Introduction

Decreasing amount of crude oil, combined with increasing world populations and concerns about global carbon footprint, has led to increased demand in alternative sustainable energy sources such as solar, hydro, wind, and biomass. While many efforts were invested in developing battery technology, fuel cells and long-distance electricity transportation, aviation industry remains challenging to meet future air travel demand while reducing the carbon footprint. Sustainable energy sources are limited in the aviation industry compared to stationary and mobile energy users. Devices like lithium batteries or solar panels are hard to scale up and not compatible with the current aircraft design. Thus, airplanes still require liquid fuel with high energy density and other crucial properties, including low freezing point, turbine-compatible combustion characteristics, high degrees of consistency, and low levels of contaminants. The aviation industry is and will remain sensitive to fossil fuel supply and price as well as concerns about long-term climate change influence.

A major issue in the commercialization of sustainable aviation fuels (SAFs) is the need to ensure the same physical and chemical properties as petroleum aviation fuels. Current technical specifications states that renewable/synthetic aviation fuels be blended with conventional fuels such that the blend contains no more than 50 vol% renewable fuel. A minimum aromatics content of 8 vol% is required in the blended fuels. Studies have found that adding target aromatic compounds to renewable aviation fuels would make it possible to produce a 100% synthetic aviation fuel because low

molecular weight alkyl-benzenes, such as di- and tri-methylbenzene, ethyl-benzene, and iso-propyl-benzene, would significantly reduce the soot formation upon combustion in airplane engines.

Similar to synthetic polymers (e.g., plastics), natural macromolecules such as lignin and cellulose can also be used as feedstocks to produce useful chemicals thermochemically. For example, lignin can be used as feedstock to produce sustainable aviation fuels (SAFs) with targeted aromatic motifs, it is also abundant in natural and usually treated as a waste material from the paper industry (only 2% for chemical production). However, converting lignin to SAFs by conventional thermochemical processes has been challenging due to poor control on the reaction pathway which leads to undesired product distribution and low selectivity.

8.2 Results and discussion

In this section, we focus on plastics and natural molecules without fluidity. We used lignin as a material example and designed a programmed fast heating and quenching method to break down large lignin molecule to small aromatic molecules with targeted product distribution. A controlled heating step offers sufficient energy input to break down lignin molecules to smaller fragments while the fast quenching prevents excessive secondary reactions toward undesired species such as coke. The lignin thermal decomposition products were evaluated as potential precursor for SAFs generation. This process can be further extended to process other biomass materials such as algae and sawdust to value-added chemicals.

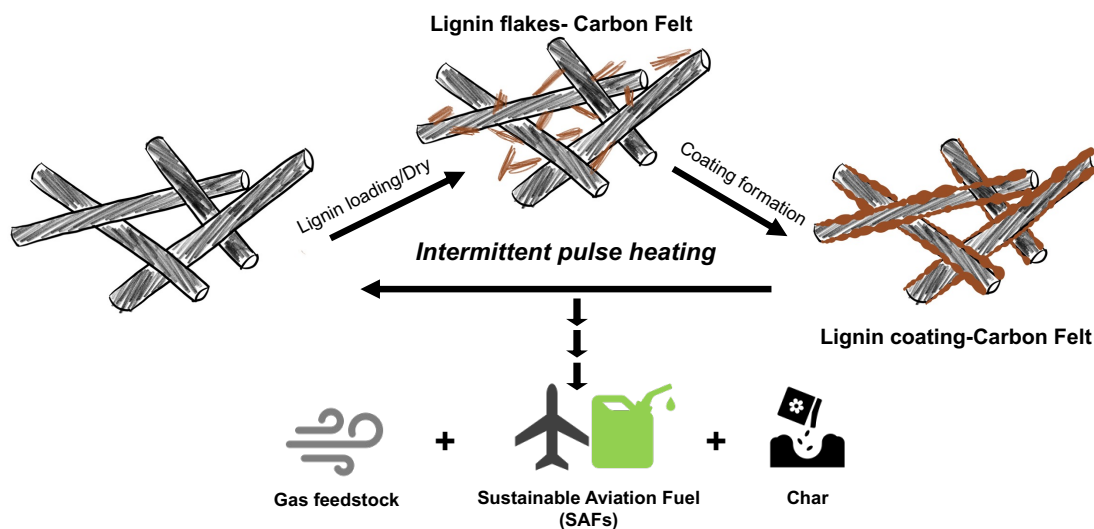


Figure 7.1. Schematics of the sustainable lignin upgrading process.

The method consists of 3 steps of operations as shown in Figure 7.1, including lignin loading, lignin coating formation, and pulse/product collection. Porous carbon felt serves as both electricity induced heater as well as network substrate to support lignin. Carbon felt is recyclable and can be used for continuous operation throughout the process. To load lignin power, we dissolved lignin in ammonia solution (or other organic/aqueous solutions depending on the type of lignin used) and dropped it onto the carbon felt strip followed by drying in the air and freeze drying consecutively (Figure 7.5). Then, the lignin-loaded carbon felt strip would be connected to the circuit in an Ar-flowed sealed quartz tube. A container with acetone was connected to the downstream of the quartz tube to absorb volatile (The setup is demonstrated in Figure 7.7). The second step is to transform loosely attached lignin powder to a thin layer of lignin coating over each carbon fiber to ensure efficient contact between the heater and lignin as well as prevent lignin loss from thermal concussion. We applied a relatively

low and continuous current through the heater in this step to around 150 °C in this step, which is about the glass transition temperature of most types of lignin. The successful process of lignin coating formation was verified by the SEM images of the lignin-carbon felt networks at different stages. In the Figure 7.3C, there is a clear trend of pristine carbon felt networks, lignin flakes-carbon felt networks, and lignin coating-carbon felt networks after initial low-temperature heating step. The SEM EDX mapping of O and C also confirms the formation of lignin over the carbon felt fiber. The shape of O map matches (from lignin) with the morphology of the lignin coating layer. When finished, we changed the power program to a fast heating and quenching profile for lignin decomposition. We could tune the temperature and heating speed at same time in this step for an optimal collection of bio-oil (mostly phenols and can serve as precursors to produce SAFs). Potentially, gas phase product and char generated by the process could be collected for further usage of fuel or soil fertilizer. Furthermore, the obtained bio-oil product will be separated, purified, and undergo hydrogenation (HDO) to jet-range aromatics as shown in Figure 7.2.

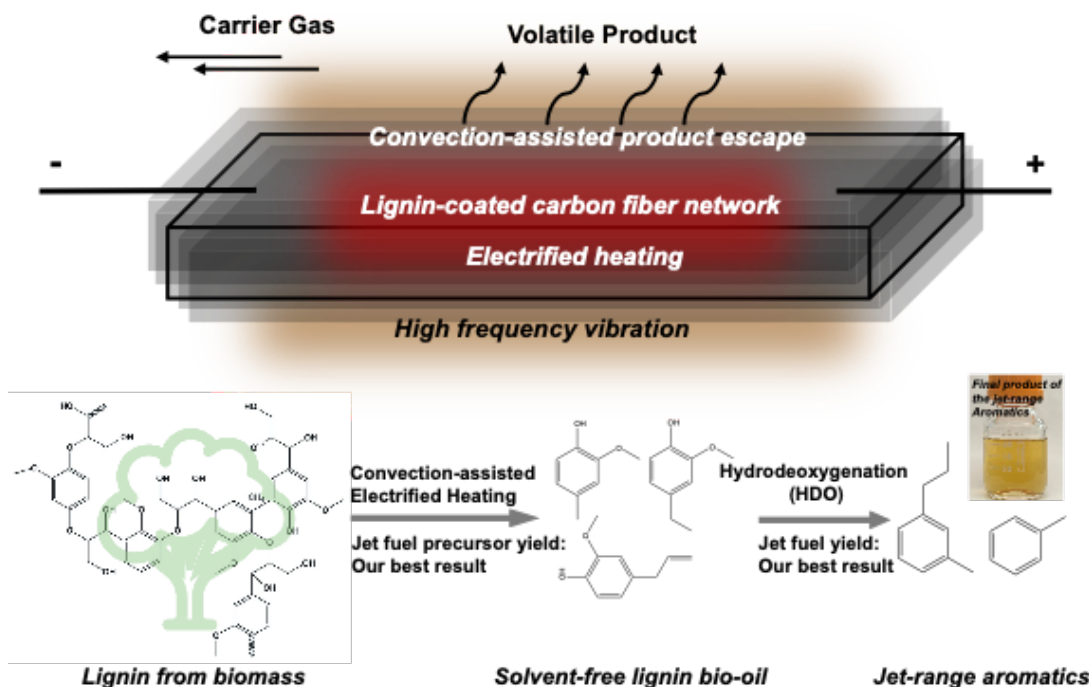


Figure 7.2. Schematics of the convection-assisted electrified heating process (upper) and the a (lower).

In addition to the fast heating and quenching pulse design of the pyrolysis setup, we designed a convection generating device to further promote mass transport within the carbon felt heater. In Figure 7.2 (upper), we demonstrated that with the assistance by the device, carbon felt heater can vibrate under high frequency while undergoing fast heating and quenching pulse to decompose lignin. The vibration of the heater would significantly increase the convection within the porous carbon fiber networks thus promote the releasing of sticky and heavy bio-oil volatile. The detachment of bio-oil of the carbon fiber networks is crucial to the pyrolysis performance for it would reduce the chance of potential repolymerization and secondary cracking, which are two major side reactions of the process. Together with a proper designed heating temperature, the convection-driven pulse process could help maximize the bio-oil yield

of lignin decomposition by suppressing the formation of char and gas. This design also provides a new time scale of the fast heating and quenching pulse process, coupled with tunable frequency and amplitude of the vibration (Figure 7.3A), we could obtain more capability on product selectivity. The device design is shown in Figure 7.8, a vibration source with tunable frequency is connected to two wood rods while the Cu coil connected to the heater is directed twined on the woods on both sides. The vibration generated by the source would transmit through the rods and Cu coil and finally reaches the heater.

The convection generating device is detachable and portable, which mean it could be repurposed to other thermal pulse device when good mass transport is preferred. As a proof-of-concept, we demonstrated the convection-driven thermal pulse method with Kraft lignin. Kraft lignin is a major waste in the pulp industry with a cheap price and very limited utilization. We used a pulse peak temperature of ~ 400 °C, a power on (heating) duration of 55 ms, and a power off (cooling) duration of 1045 ms. We obtained a bio-oil yield up to 52%, which is among the highest in the literature on catalyst-free lignin pyrolysis. After the process, the morphology of the carbon felt was characterized again by the SEM and showed a close-to-pristine surface (Figure 7.3C), which means minimum formation of coke residue.

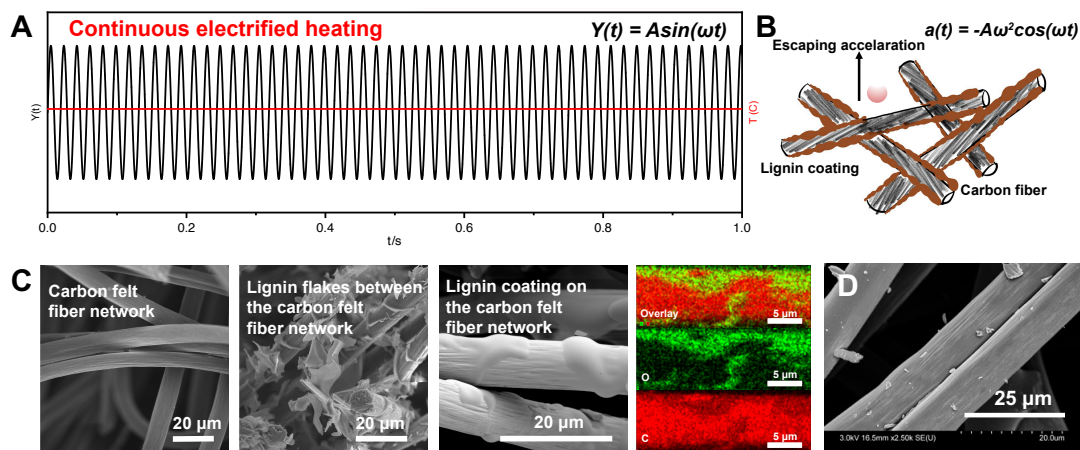


Figure 7.3. **A** Two tunable time scales in the process, including temperature profile and vibration waveform. **B** Two tunable time scales in the process, including temperature profile and vibration waveform. **C** SEM images of the pristine, lignin-loaded, coating formed heater, and C/O EDX maps (from left to right). **D** SEM images of the post-reaction heater.

Our approach is broadly applicable to different types of lignin, including soda lignin, Kraft lignin, hydrolyzed lignin, organosolv lignin, liginosulfonates, or other special engineered lignin and derivatives, with an optimized bio-oil yield over 50% expected depending on the structures and density of C-O bonds.

Our approach is also applicable to different natural macromolecules with a coating formation ability, such as cellulose, lipids, carbohydrates, proteins, and their natural form of biomass, including algae, saw dust, or grass. Bio-oil, gas and biochar can be produced at the same time by designed distribution due to the tunable pulse profile and convection density. High selectivity of platform chemical is possible with pre-processing and controlled pulse design.

8.3 Supporting Information

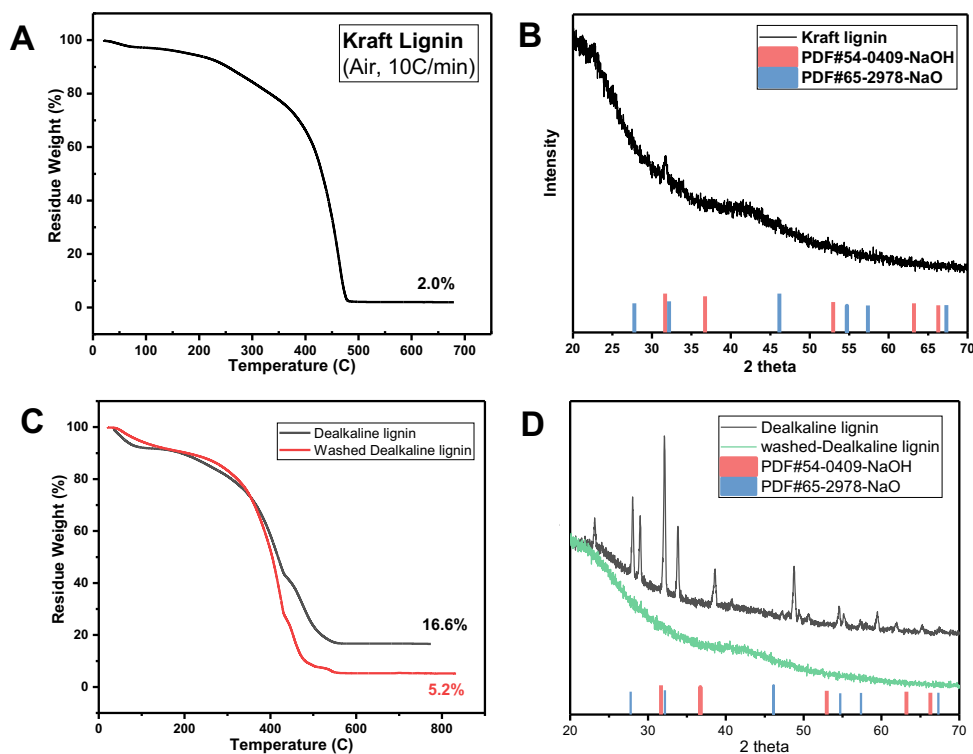


Figure 7.4. **A** TGA curve of the kraft lignin thermal weight loss in air. **B** XRD characterization of the kraft lignin, showing minimum crystalline residue. **C** TGA curve of the dealkaline lignin (black: before wash; red: after wash) thermal weight loss in air. **D** XRD characterization of the dealkaline lignin (black: before wash; red: after wash).

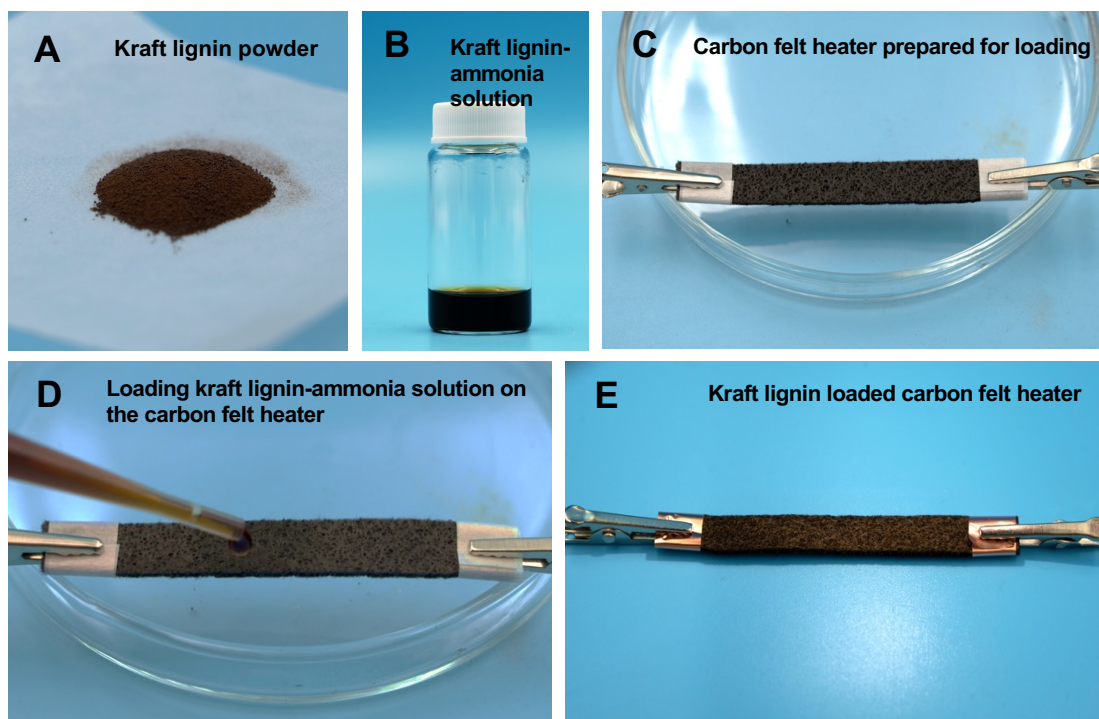


Figure 7.5. Photos of the **A** Kraft lignin powder, **B** Kraft lignin-ammonia solution, **C** carbon felt heater prepared for loading, **D** Loading kraft lignin-ammonia solution on the carbon felt heater, and **E** Kraft lignin loaded carbon felt heater.

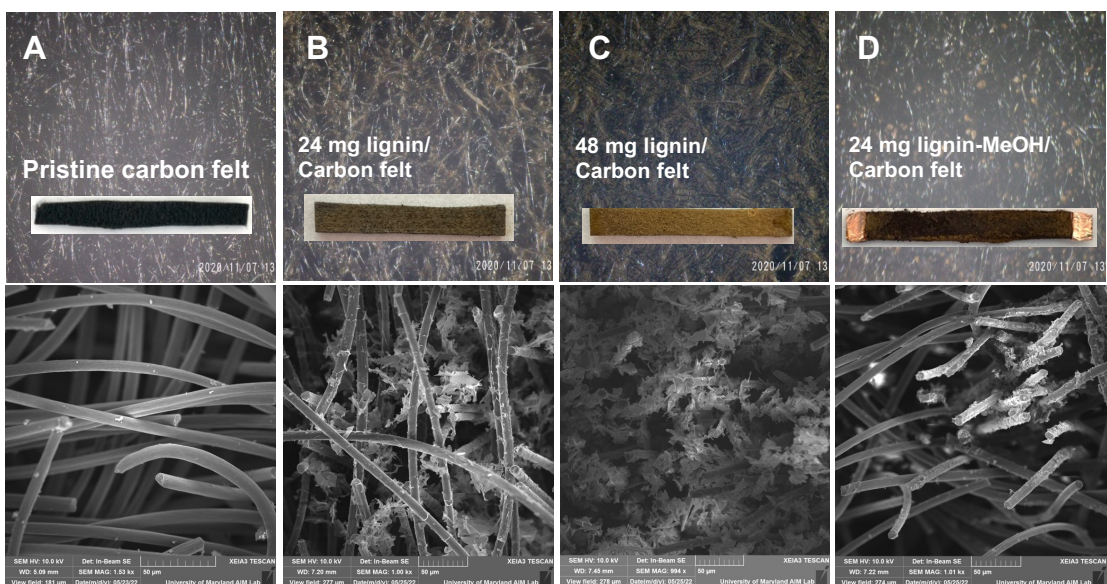


Figure 7.6. Lignin loading effect on the coating morphology **A** Optical (upper) and SEM (lower) images of the pristine carbon felt. **B** Optical (upper) and SEM (lower) images of the 24 mg-carbon felt. **C** Optical (upper) and SEM (lower) images of the 48 mg-carbon felt. **D** Optical (upper) and SEM (lower) images of the 24 mg (MeOH)-carbon felt.

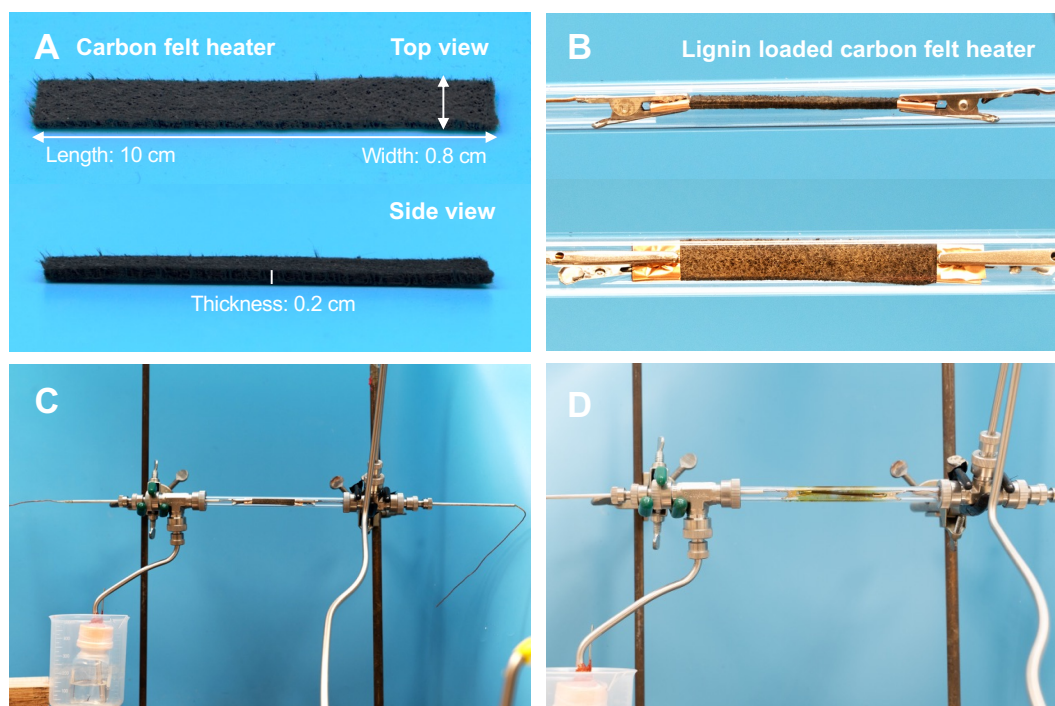


Figure 7.7. Schematics of the convection-driven pulse device design. **A** Rationale of the convection -driven pulse to increase bio-oil yield. **B** Two tunable time scales in the process, including temperature profile and vibration waveform. **C** Device design of the convection-driven pulse setup.

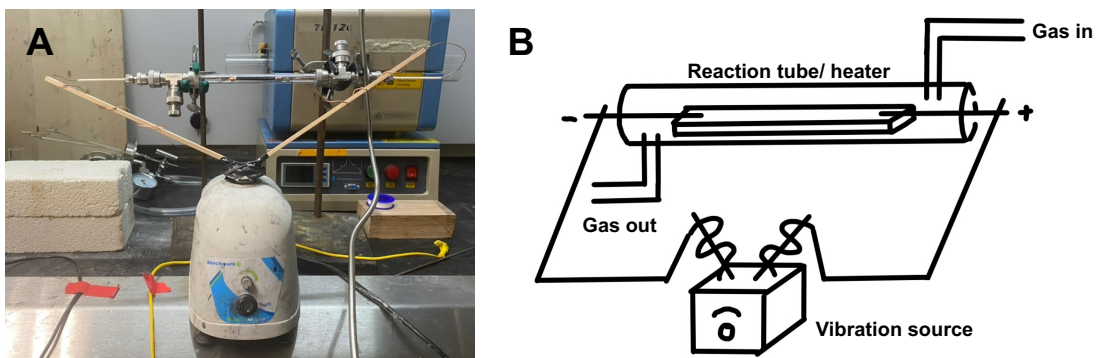


Figure 7.8. Schematics of the convection-driven pulse device design. **A** Photos of the convection-driven pulse device connected to the electrified heating setup. **B** Device design of the convection-driven pulse setup.

Chapter 8: Discussion and Conclusion

11.1 Summary

High-temperature processes hold significant promise for material and chemical manufacturing. On one hand, elevated temperatures can surmount energy barriers, facilitating the efficient conversion of precursors into desired products. On the other hand, increased temperatures can accelerate reaction rates, enhancing synthesis efficiency. The recent advancement of electrified high-temperature technologies by our research group has unveiled the pivotal role of non-equilibrium conditions in nanomaterial and chemical syntheses. For instance, Joule heating of carbon-based materials via a programmable electrical signal enables the creation of spatial and temporal temperature profiles, allowing manipulation of chemical reaction pathways. Another example involves the use of tunable heating durations and quenching rates to achieve diverse compositions and structures of nanoparticles. This dissertation explores two specific applications of electrified high-temperature technology: (1) Thermal shock synthesis of multi-elemental nanoparticles as selective and stable catalysts; and (2) Efficient waste recycling or biomass upgrading via pulsed electrical heating.

Supported nanoparticle (NP) catalysts find widespread use in various reactions. However, synthesizing high-quality NPs with precise morphological and structural control remains challenging. In this research segment, NP catalysts with specific morphological or structural designs were prepared using high-temperature thermal shock methods. Ultra-small and high-loading carbon-supported Pt₃Ni NPs were achieved through the introduction of a strong electrostatic effect between metal salts and carbon particles. This approach significantly improved the anchoring and

dispersion of precursors, resulting in high NP loading (40 wt%), small NP size, and good distribution (1.66 ± 0.56 nm). Not limited to bimetallic NP synthesis or NPs on carbon black, this method can be extended to various NP compositions on different substrate materials. Thus, providing a general strategy for developing ultrafine and high-loading NPs as electrocatalysts for diverse reactions.

Sustainable aviation fuels (SAFs) are crucial for meeting future air travel demands while reducing the carbon footprint. Among potential feedstocks for SAF production, lignin stands out as an abundant and renewable aromatic biopolymer often treated as waste in the paper industry. However, converting lignin to SAFs through conventional thermochemical processes has been challenging due to poor control over the reaction pathway, leading to undesired product distribution. In this project, a programmed electrified heating method was designed to break down large lignin molecules into small aromatic molecules with a targeted product distribution. A controlled heating step provides sufficient energy input to break down lignin molecules into smaller fragments, and prevents excessive secondary reactions leading to undesired species, such as coke. The thermal decomposition products of lignin were evaluated as potential precursors for SAF generation. This process can be further extended to process other biomass materials, such as algae and sawdust, into value-added chemicals.

11.2 Future Directions

The above results have successfully demonstrated that new structures and properties control on NPs synthesis can be achieved by high temperature engineering protocols, either ultrafast thermal shock, or interface engineering of carbon-based

substrate for well-dispersed nanoparticles. The current thesis serves as the preliminary explorations of using high temperature engineering protocols on nanomaterials.

In the following research, the following topics are of interests: (1) expand high-temperature engineering methods to more nanomaterials, such as semiconductors, composites, and so on; (2) expand the interface engineering and particle design protocols to more different materials compositions; and (3) explore the applications of HEA NPs in a broader range of catalysis applications.

For the next step of the electrified chemical engineering study, I will continue to study the lignin upgrading by convection-assisted electrical heating method. Specifically, I will optimize the experimental methodology such as lignin loading method and pulse program design to achieve optimized selectivity and monomer yield. I would also seek collaboration on further hydrodeoxygenation processing on the obtained phenol products. With this treatment, phenols would be further converted to jet-range aromatic hydrocarbons. Aside from lignin, I will also explore the possibilities to upgrade other abundant natural biomass such as algae or cellulose to valuable platform chemicals.

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