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RPPR Final Report
as of 24-Sep-2018

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Major Goals: This project is to develop a new catalyst system that contains nanoparticles (NPs) and nitrogen-doped graphene (NG) with enhanced electrocatalysis for important energy conversion reactions. The single sheet NG is prepared by high temperature (900°C) decomposition of graphene oxide (GO) and melamine. The monodisperse NPs are prepared by high temperature (up to 300°C) organic phase reaction. By mixing the dispersions of both NG and NPs, NPs can self-assemble on the NG surface, giving a monolayer array of NPs on NG. Alternatively, the NPs are assembled on a solid electrode surface via the novel water-air interface assembly method and are then covered with a layer of NG. The strong NP-NG interactions should make the NG-NP composite an ideal catalyst system for controlling charge transfer across the NP-NG interface and for rationalizing electrocatalysis on NP and NG surfaces. The project intends to use noble meal (Pt or Au)-based alloy NPs as model catalysts to study NG-NP interaction and its effect on enhancing NP or NG catalysis for electrochemical reactions. The final goal of the project is to develop Fe- or Co-based NP-NG composites with their catalysis comparable with or surpassing the noble metal catalysts for important electrochemical reduction and oxidation reactions.

The unique part of this project is that NG is made dispersible in a solvent and the dispersible NPs are pre-made with controlled sizes, shapes and compositions. The dispersible NG and NPs facilitate self-assembly of NPs onto NG in a solution phase or water-air interface self-assembly process. Such a control, once achieved, is unprecedented, and should allow us to answer the following questions: 1) how NPs can be assembled on NG surface; 2) if NPs are assembled on one side or both sides of the NG; 3) if NP interaction with NG can be tuned by NP sizes, shapes, and compositions; 4) how the NP-NG catalysts can be optimized for electrochemical reactions or other chemical reactions. Compared to what have been published on the N-doped carbon supports, including graphene (G), this proposed research should help to achieve atomic level control and optimization of NP catalysts for efficient energy conversion.

This project is in line with Army's interest in supporting fundamental electrochemical studies to understand and control electrochemical redox reactions. The work should help Army to achieve its missions in building economical, light-weight and efficient fuel cells, batteries and in electrochemical production of fuels for power and energy applications.

Accomplishments: 1) Stable Cobalt Nanoparticles (NPs) and Their Monolayer Array as an Efficient Electrocatalyst for Oxygen Evolution Reaction (OER): We synthesized monodisperse 10 nm Co NPs and tested their monolayer assembly on a graphite electrode for OER. We successfully developed a water-air interface

assembly approach to assemble 10 nm Co NPs on a flat graphite surface. In this process, a controlled amount of NP dispersion in toluene/hexane was dropped onto the water surface. Evaporation of the solvent left behind a monolayer assembly of Co NPs on the water surface. By lifting a solid substrate from water phase, the NP assembly could be transferred onto the substrate, giving a monolayer assembly of Co NPs, as demonstrated in the representative monolayer array of the Co NPs on a graphitic carbon (GC) plate (0.6 cm × 0.7 cm). The NP packing density was estimated at 4000 NPs/um2. The monolayer Co NP array on the GC plate was pre-annealed at 600C in Ar + 4% H2 to stabilize these Co NPs against fast air oxidation, and was then used as a working electrode for studying their electrocatalysis. The Co NP array showed high activity in catalyzing the OER in 0.1 M KOH. We calculated the catalytic turnover frequency (TOF) by assuming that every Co NP is catalytically active and obtained the TOFs 2.13 s-1 at the overpotential of 0.4 V, which was 15 times of that from the same Co NPs deposited on the conventional carbon support (C-Co). The monolayer catalyst exhibited a dramatic enhancement in mass activity (1949 A/g) compared to the C-Co (126 A/g). This value was much higher than the 500 A/g obtained from the commercial C-Ir catalyst.

2) Controlled Assembly of Cu NPs on Pyridinic-N Rich Graphene (p-NG) for Electrochemical Reduction of CO2: We prepared monodisperse 7 nm Cu NPs by reductive decomposition of copper(I) acetate, CuAc, in trioctylamine, oleylamine and tetradecylphosphonic acid at 250°C. The oleylamine coated NPs could be dispersed in hexane. We synthesized p-NG by high-temperature (900°C) pyrolysis of graphene oxide (GO) and melamine, which could be dispersed in isopropanol. We assembled the Cu NPs onto the p-NG (at a mass ratio of 1:1) by mixing the hexane dispersion of Cu NPs and p-NG in hexane + isopropanol (v:v 2:1) under sonication, obtaining p-NG-Cu. The p-NG-Cu was activated by n-butylamine/ethanol/water washing to remove oleylamine coating, after which the NPs were still dispersed on the p-NG surface without noticeable aggregation. The NP sample was grounded with polyvinylidene fluoride (PVDF) and N-methyl-2-pyrrolidone (NMP) into a paste and then painted the paste directly onto the carbon paper for electrochemical studies. We studied the electrochemical reduction of CO2 in 0.5 M KHCO3 catalyzed by the p-NG-Cu catalyst. We used GC-MS to analyze the gaseous products, and 1H NMR to identify the liquid product, which were collected at a constant reduction potential. We calculated the Faradaic efficiency (FE) of the reduction reaction at each reduction potential. When reducing CO2 on p-NG-Cu at -0.8 V, formate (FE 62%) and C2H4 (FE 1.4%) were initially detected. At more negative potentials, C2H4 was predominately formed and the formate generation was suppressed. The FE for the C2H4 formation reached 19% at -0.9 V, where other hydrocarbons (3.8% formate, 0.9% CH4 and 0.6% C2H6) were also observed but the total FE was less than 5.3%. Among all hydrocarbons produced on the p-NG-Cu at -0.9 V, C2H4 selectivity reached 79%. When normalized against the Cu mass, the p-NG-Cu had a C2H4 formation mass activity of 2.9 A/gCu, This work demonstrated that the p-NG as a support enhanced significantly the Cu NP catalyst selectivity toward C2H4 at -0.9 V or more negative potentials.

3) NPs/G or NPs/WO2.72 for Catalytic Dehydrogenation of Ammnia Borane (AB) or Formic Acid (HCOOH) to Hydrogen (H2): AB and HCOOH have been explored extensively as a new H2 storage material for easy H2 transportation. H2 is released via AB hydrolysis or HCOOH dehydrogenation in the presence of a catalyst. We found the CuNi alloy NPs deposited on G, CuNi/G, to be an efficient catalyst for AB hydrolysis to H2. We prepared the monodisperse 16 nm CuNi NPs by the co-reduction of nickel(II) acetylacetonate (Ni(acac)2) and copper (II) acetylacetonate (Cu(acac)2) with borane-t-butylamine in oleylamine and oleic acid. We assembled the CuNi NPs on G through the sonication of the ethanol dispersion of G and the hexane dispersion of NPs to produce CuNi/G. We activated CuNi NPs by immersing the NPs in t-butylamine in a N2 atmosphere to remove oleate/oleylamine, and by washing with ethanol. The highest TOF of the CuNi/G was calculated to be 49.1 molH2 molCuNi-1•min-1. The activation energy was evaluated to be Ea = 24.4 kJ/mol. Our CuNi/G is the most efficient catalyst among all Cu- or Ni-catalysts ever reported for AB hydrolysis to H2. We extended our studies to the formation of H2 from HCOOH dehydrogenation by using a new nanoscale support WO2.72. We prepared the WO2.72 nanorods (NRs) by reacting WCl4 with oleic acid and oleylamine in 1-octadecene at 280C. We grew 2 nm AgPd NPs by the co-reduction of silver(I) acetate and Pd(acac)2 at 180C in the presence of WO2.72 NRs, and obtained the strongly coupled AgPd/WO2.72. The catalyst had an initial TOF of 1718 h-1 and an activation energy of Ea = 31 kJ/mol. It was one of the most active heterogeneous catalysts ever reported for HCOOH dehydrogenation to H2. More importantly, the AgPd/WO2.72 was active for one-pot conversion of nitrophenol into benzoxazole, an essential core structure found in some mechanically robust rigid organic polymers for uses as ballistic fiber and flame retardant materials.

4) Pd(CuPd)/WO2.72 for Formic Acid Oxidation Reaction (FAOR): By further exploring the WO2.72 supporting effect, we developed a new strategy to enhance Pd (CuPd) catalytic efficiency for FAOR in 0.1 M HClO4. The WO2.72-coupled 5 nm Pd (CuPd) NPs showed much improved FAOR catalytic activity in 0.1 M HClO4 + 0.1 M HCOOH with the mass activity reaching ~1600 mA/mgPd (for the Pd NPs) and 2086 mA/mgPd (for the CuPd NPs),

and showed no sign of catalyst degradation after the 12 h chronoamperometry test at 0.4 V. The Pd(CuPd)/WO2. 72 was the most active Pd-based FAOR catalysts ever reported.

5) Maximizing Catalytic Activity by NP Assembly on NG: We extended our water-air NP assembly method and prepared a monolayer array of NPs on NG (NPs-NG) onto a Si substrate. This NPs-NG-Si was used as a catalyst probe to turn a catalytic reaction “on” by inserting the probe into the reaction solution and “off” by pulling the probe out of the solution. Using 3 nm NiPd NPs as an example,we demonstrated that the monolayer NiPd-NG-Si showed the maximum catalysis not only for AB hydrolysis, but also for the following transfer hydrogenation and condensation of aromatic amine-compounds and aldehydes, leading to the one-pot, high-yield synthesis of quinazolines in water. The catalyst was even active for the hydrodehalogenation of halogenatedaromatics under mild reaction conditions, offering a powerful, low-cost, and safe green technology for the degradation of polyhalogenated aromatics.

Overall, this ARO support allows us to demonstrate a new and reliable 2D NP platform on NG, which helps to optimize NP catalysis for some important chemical reactions. Most goals proposed initially were accomplished after three years of research. However, the intended fabrication of NG-NP-NG layered structures for studying catalysis on the NG surface was not successful due to the difficulty in using our chemical approach to cover NPs with NG. Giving more time, our new assembly approach to monolayer array of NPs on single sheet NG on water surface should allow us to prepare the NG-NPs-NG sandwich structure. Once this structure is prepared with NPs being Fe- or Co-based, NP-enhanced electrocatalysis, such as ORR, OER, HER, FAOR, or even alcohol oxidation reaction, on NG can be studied in details. Su

Training Opportunities: This ARO project was used to support two graduate students, Liheng Wu and Zheng Xi and two postdoctors (partial support), Qing Li and Chao Yu.

Liheng Wu defended his PhD thesis in 2015 and is now a postdoctoral fellow at Stanford University.
Zheng Xi defended his PhD thesis in 2018 and is now a postdoctoral fellow at Central Florida University.

Qing Li worked initially on this ARO project in 2015 and is now a Professor in Materials Sciences and Enginnering of Huazhong University of Science and Technology.
Chao Yu was partially supported by this ARO project, developing NG-NP catalysis for chemical conversions. He is now working to extend the reactions for rigid organic polymer formation.

RPPR Final Report
as of 24-Sep-2018

Results Dissemination: A. Journal Publications:

1. L. Wu, Q. Li, C. H. Wu, H. Zhu, A. Mendoza-Garcia, B. Shen, J. Guo, S. Sun, “Stable Cobalt Nanoparticles and Their Monolayer Array as an Efficient Electrocatalyst for Oxygen Evolution Reaction”, J. Am. Chem. Soc. 2015, 137, 7071–7074.
2. Q. Li, W. Zhu, J. Fu, H. Zhang, G. Wu, S. Sun, “Controlled Assembly of Cu Nanoparticles on Pyridinic-N Rich Graphene for Electrochemical Reduction of CO2 to Ethylene”, Nano Energy, 2016, 24, 1-9.
3. L. Wu, A. Mendoza-Garcia, Q. Li, S. Sun, “Organic Phase Syntheses of Magnetic Nanoparticles and Their Applications", Chem. Rev. 2016, 116, 10473–10512.
4. Q. Li, S. Sun, “Recent Advances in the Organic Solution Phase Synthesis of Metal Nanoparticles and Their Electrocatalysis for Energy Conversion Reactions”, Nano Energy, 2016, 29, 178–197.
5. C. Yu, J. Fu, M. Muzzio, T. Shen, D. Su, J. Zhu, S. Sun, “CuNi Nanoparticles Assembled on Graphene for Catalytic Methanolysis of Ammonia Borane and Hydrogenation of Nitro/Nitrile Compounds”, Chem. Mater. 2017, 29, 1413–1418.).
6. C. Yu, X. Guo, Z. Xi, M. Muzzio, Z. Yin, B. Shen, J. Li, C. T. Seto, S. Sun, “AgPd Nanoparticles Deposited on WO2.72 Nanorods as an Efficient Catalyst for One-Pot Conversion of Nitrophenol/ Nitroacetophenone into Benzoxazole/Quinazoline”, J. Am. Chem. Soc. 2017, 139, 5712-5715.
7. Z. Xi, D. P. Erdosy, A. Mendoza-Garcia, P. N. Duchesne, J. Li, M. Muzzio, Q. Li, P. Zhang, S. Sun, “Pd Nanoparticles Coupled to WO2.72 Nanorods for Enhanced Electro-chemical Oxidation of Formic Acid”, Nano Lett. 2017, 17, 2727–2731.
8. Z. Xi, A. Mendoza-Garcia, H. Zhu, M. Chi, D. Su, D. P. Erdosy, J. Li, S. Sun, “NixWO2.72 Nanorods as an Efficient Electrocatalyst for Oxygen Evolution Reaction”, Green Energy & Environment, 2017, 2, 119-123.
9. Z. Xi, H. Lv, D. P. Erdosy, D. Su, Q. Li, C. Yu, J. Li, S. Sun, “Atomic Scale Deposition of Pt around Au Nanoparticles to Achieve Much Enhanced Electrocatalysis of Pt”, Nanoscale, 2017, 9, 7745 – 7749.
10. Z. Xi, J. Li, D. Su, M. Muzzio, C. Yu, Q. Li, S. Sun, “Stabilizing CuPd Nanoparticles via CuPd Coupling to WO2. 72 Nanorods in Electrochemical Oxidation of Formic Acid”, J. Am. Chem. Soc. 2017, 139, 15191–15196.
11. C. Yu, X. Guo, M. Shen, B. Shen, M. Muzzio, Z. Yin, Q. Li, Z. Xi, J. Li, C. T. Seto, S. Sun, “Maximizing the Catalytic Activity of Nanoparticles through Monolayer Assembly on Nitrogen-Doped Graphene”, Angew. Chem. Int. Ed. 2018, 57, 451-455.
12. X. Guo, C. Yu, Z. Yin, S. Sun, C. T. Seto, "Hydrodehalogenation of polyhalogenated aromatics catalyzed by NiPd nanoparticles supported on nitrogen-doped graphene", ChemSusChem, 2018, 11, DOI: 10.1002/cssc. 201800289.
13. H. Xie, T. Wang, J. Liang, Q. Li, S. Sun, “Cu-based Nanocatalysts for Electrochemical Reduction of CO2”, NanoToday, 2018, doi.org/10.1016/j.nantod.2018.05.001.

B. Book Chapter: L. Wu, Z. Xi, S. Sun, “Well-defined Metal Nanoparticles for Electrocatalysis”, in Morphological, Compositional, and Shape Control of Materials for Catalysis of the series “Studies in surface science and catalysis”, ed. M. Cargnello, P. Fornasiero, Elsevier, 2017, Chapter 4.

C. Invention Disclosures:

1. “Graphene-Co/CoO nanoparticle composite, manufacture, and use in an electrochemical cell”, with S. Guo, S. Zhang, and L. Wu, WO2014055485.
2. “Composite AgPd-WO2.72 catalyst for One-Pot Conversion of nitrophenol/nitroacetophenone into benzoxazole/quinazoline” with C. Yu, X. Guo, and C. T. Seto, US Provisional Patent Application.
3. “Hydrodehalogenation of polyhalogenated aromatics catalyzed by NiPd nanoparticles supported on nitroget-doped graphene”, with X. Guo, C. Yu, C. T. Seto, and Z. Yin, U.S. Provisional Patent Application No.: 62/607,821.

D. Scientific Presentations (All Invited):

1. “Synthesis and Assembly of Nanocatalysts for Efficient Electrochemical Reduction Reactions”, the 250th ACS National Meeting, August 15-20, 2015. Boston, MA.
2. “Tuning Nanocatalysts for Efficient Electrochemical Reactions”, MRS Spring Meeting, Nov 30-Dec 3, 2015, Boston, MA.
3. “Rational synthesis and assembly of nanocatalysts for energy applications”, Pacifichem2015, Dec 15 - 20, 2015, Honolulu, Hawaii.
4. “Controlled Assembly of Nanoparticles for Energy Conversions”, 11th China-US Nano-Forum, June 18-20, 2016, Nanjing University, China.

“Controlled Synthesis and Assembly of Nanoparticles for Electrocatalysis”, International Workshop on Nanomaterials and Nanodevices, July 8-10, 2016, Institute of Physics, Beijing, China.

6. Plenary Talk, “Tuning Nanoparticle Catalysis for Efficient Electrochemical Reactions”, 2nd Zing Nanocrystals

Conference, August 2-5, 2016, Dublin, Ireland.
7. XingDa Lecture, “Tuning Nanoparticle Catalysis for Efficient Electrochemical Reactions”, Dec 9, 2016, Peking University.
8. “Tuning Nanoparticle Catalysis to Optimization for Energy Conversion Reactions”, Huazhong Universirty of Science and Technology, China, June 30, 2017.
9. Plenary Speaker, “Formation of Atomic Scale Pt around a Nanoparticle Core to Achieve Much Enhanced Electrocatalysis of Pt”, International Workshop on Nanomaterials and Nanodevices, Institute of Physics, Beijing, China, July 4, 2017.
10. “Wenqui” Lecture on Tuning Nanoparticle Catalysis for Electrochemical Reactions, Lanzhou University, China, July 20, 2017.
11. Honorable Speaker on Tuning Nanoparticle Catalysis for Electrocatalysis, Frontier in Nanoscience Forum, Key Laboratory of Molecular Nanostructure and nanotechnology, Chinese Institute of Chemistry, CAS, July 23, 2017.
12. “Controlling Metal Nanoparticle Interactions with Nanoscale-Supports to Enhance Nanoparticle Catalysis”, the 254th ACS National Meeting, August 20-24, 2017. Washington, DC.
13. “Synthetic Tuning of Nanoparticles to Achieve High Efficiency in Electrocatalysis”, MRS Spring Meeting, April 2-6, 2018, Phoenix, AZ.
14. Inorganic and Organic Seminar on electrocatalysis tuning and optimization, Department of Chemistry, University of Chicago, May 11, 2018.
15. “Synthetic Tuning of Nanoparticles to Achieve High Efficiency in Electrocatalysis”, 13th Sino-US Forum on Nanoscale Science and Technology, June 29 –July 3, 2018, Chengdu, China.
16. “Enhancing Nanoparticle Catalysis for Chemical Transformations”, the 256th ACS National Meeting, August 19-23, 2018, Boston, MA.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Faculty
Participant: Shouheng Sun
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
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International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
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Person Months Worked: 6.00 **Funding Support:**
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International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Chao Yu
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Project Contribution:
International Collaboration:
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National Academy Member: N

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Final Report for W911NF-15-1-0147

New Composite Catalysts Based on Nitrogen-Doped Graphene and Nanoparticles for Advanced Electrocatalysis

Project Period: May 01, 2015 to April 30, 2018

PI: Shouheng Sun
Department of Chemistry, Brown University, Providence, Rhode Island 02912

I. Project Goals

This project is to develop a new catalyst system that contains nanoparticles (NPs) and nitrogen-doped graphene (NG), as highlighted in **Figure 1**, with enhanced electrocatalysis for important energy conversion reactions. The single sheet NG is prepared by high temperature (900°C) decomposition of graphene oxide (GO) and melamine. The monodisperse NPs are prepared by high temperature (up to 300°C) organic phase reaction. By mixing the dispersions of both NG and NPs, NPs can self-assemble on the NG surface, giving a monolayer array of NPs on NG (**Figure 1a**). Alternatively, the NPs are assembled on a solid electrode surface via the novel water-air interface assembly method and are then covered with a layer of NG (**Figure 1b**). The strong NP-NG interactions should make the NG-NP composite an ideal catalyst system for controlling charge transfer across the NP-NG interface and for rationalizing electrocatalysis on NP (**Figure 1a**) and NG (**Figure 1b**) surfaces. The project intends to use noble meal (Pt or Au)-based alloy NPs as model catalysts to study NG-NP interaction and its effect on enhancing NP or NG catalysis for electrochemical reactions. The final goal of the project is to develop Fe- or Co-based NP-NG composites with their catalysis comparable with or surpassing the noble metal catalysts for important electrochemical reduction and oxidation reactions.

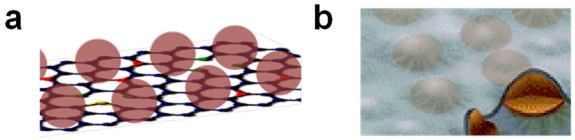

Figure 1. Schematic illustration of NG-NP catalysts for electrochemical reactions: **a**) Monolayer NPs assembled on NG; **b**) monolayer NPs covered with NG.

The unique part of this project is that NG is made dispersible in a solvent and the dispersible NPs are pre-made with controlled sizes, shapes and compositions. The dispersible NG and NPs facilitate self-assembly of NPs onto NG in a solution phase or water-air interface self-assembly process. Such a control, once achieved, is unprecedented, and should allow us to answer the following questions: 1) how NPs can be assembled on NG surface; 2) if NPs are assembled on one side or both sides of the NG; 3) if NP interaction with NG can be tuned by NP sizes, shapes, and compositions; 4) how the NP-NG catalysts can be optimized for electrochemical reactions or other chemical reactions. Compared to what have been published on the N-doped carbon supports, including graphene (G), this proposed research should help to achieve atomic level control and optimization of NP catalysts for efficient energy conversion.

This project is in line with Army's interest in supporting fundamental electrochemical studies to understand and control electrochemical redox reactions. The work should help Army to achieve its missions in building economical, light-weight and efficient fuel cells, batteries and in electrochemical production of fuels for power and energy applications.

II. Project Accomplishments

II.1. Stable Co NPs and their monolayer array as an efficient electrocatalyst for oxygen evolution reaction

Oxygen evolution reaction (OER) is commonly referred to as electrochemical oxidation of "O^{2-}" to O_2. It is an important half-cell reaction in a water-splitting cell or in a rechargeable metal-air battery for efficient hydrogen (H_2) or metal generation. As a thermo-dynamically "up-hill" reaction that involves multi-electron transfer, it requires the input of energy to drive its completion. In order to lower the kinetic barrier, an efficient catalyst is needed to promote the 4-electron oxidation process. For this purpose, nanostructured iridium (Ir) and ruthenium (Ru) have been chosen as the-state-of-the-art OER catalysts. Recently, earth-abundant transition metal oxides/hydroxides are also explored as promising alternative catalysts for the OER. However, these oxides have generally low electronic conductivity, limiting their potential in electrocatalysis.

In our first ARO-supported publication ("Stable Cobalt Nanoparticles and Their Monolayer Array as an Efficient Electrocatalyst for Oxygen Evolution Reaction", *J. Am. Chem. Soc.* **2015**, *137*, 7071.), we reported that metallic Co NPs can be stabilized to serve as a new class of efficient catalyst for OER in 0.1 M KOH and monolayer Co NPs show maximum catalytic activity among all Co-based catalysts ever reported. In this work, we synthesized monodisperse 10 nm Co NPs and tested their monolayer assembly on a graphite electrode. We successfully developed a water-air interface assembly approach to assemble these 10 nm Co NPs on a flat graphite surface, as shown in the TEM (**Figure 2a**) and SEM (**Figure 2b**) images of the assembly. In this process, a controlled amount of NP dispersion in toluene/hexane was dropped onto the water surface. Evaporation of the solvent left behind a monolayer assembly of Co NPs on the water surface. By lifting a solid substrate from the water phase, the NP assembly could be transferred onto the substrate, giving a monolayer assembly of Co NPs on a graphite carbon (GC) plate (0.6 cm × 0.7 cm) with the NP packing density estimated at 4000 NPs/μm^2. The monolayer Co NP array on the GC plate was pre-annealed at 600°C in Ar + 4% H_2 to stabilize these Co NPs against fast air oxidation, and was then used as a working electrode for studying their electrocatalysis. The Co NP array showed high activity in catalyzing the OER in 0.1 M KOH with the catalytic turnover frequency (TOF) reaching 2.13/s at the overpotential of 0.4 V, which was 15 times of that from the same Co NPs deposited on the conventional carbon support (C-Co) (**Figure 2c**). The monolayer NP catalyst had a dramatic increase in mass activity (1949 A/g) compared to the C-Co (126 A/g) (**Figure 2d**). This value was much higher than the 500 A/g obtained from the commercial C-Ir catalyst.

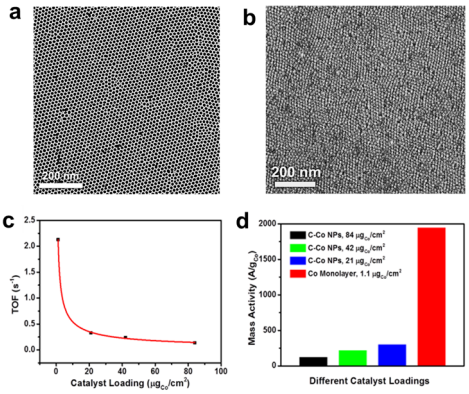

Figure 2. (**a**) TEM image and (**b**) SEM image of the monolayer assembly of the 10 nm Co NPs. (**c**) TOFs and (**d**) mass activity of the Co NP catalysts with different catalyst loadings at an overpotential of 0.4 V.

II.2. Controlled assembly of Cu NPs on NG for electrochemical reduction of CO_2

Electrochemical reduction of CO_2 is a promising green chemistry approach to convert CO_2 into a reusable form of carbons. Unlike conventional thermal catalysis approach where high pressure and high temperature are needed to initiate the reaction, electrochemical reduction can proceed under ambient environments and the reaction can in principle achieve much higher

selectivity. In reality, however, multi-electron reduction of CO_2, combined with hydrogenation and carbon-carbon (C-C) coupling reactions required for hydrocarbon formation, makes it extremely difficult to control a specific reaction pathway toward a targeted hydrocarbon product. To convert CO_2 to hydrocarbons, especially to C-C hydrocarbons, a specific form of Cu metal has to be used as the catalyst. Despite the extensive efforts devoted to both experimental and theoretical studies, a practical approach to increase Cu catalytic selectivity to a hydrocarbon molecule had not yet been demonstrated.

In our 2016 publication in *Nano Energy* ("Controlled Assembly of Cu Nanoparticles on Pyridinic-N Rich Graphene for Electrochemical Reduction of CO_2 to Ethylene", *Nano Energy*, **2016**, *24*, 1.), we prepared monodisperse Cu NPs and studied their catalysis for electrochemical reduction of CO_2 in 0.5 M $KHCO_3$. The Cu NPs deposited on conventional carbon support or graphene oxide (GO) showed poor activity to hydrocarbons. But when they were assembled on NG, they exhibited both N-doping and Cu NP-dependent reduction activity and selectivity.

We prepared monodisperse 7 nm Cu NPs by reductive decomposition of copper(I) acetate, CuAc, in trioctylamine, oleylamine and tetradecylphosphonic acid at 250°C. The oleylamine coated NPs could be dispersed in hexane. We synthesized pyridine-rich NG (p-NG) by high-temperature (900°C) pyrolysis of GO and melamine, which could be dispersed in isopropanol. We assembled the Cu NPs onto the p-NG by mixing the hexane dispersion of Cu NPs and p-NG in hexane + isopropanol under sonication, obtaining p-NG-Cu (**Figure 3a**). The p-NG-Cu was activated by n-butylamine/ethanol/water washing to remove oleylamine coating, after which the NPs were still dispersed on the p-NG surface without noticeable aggregation. The NP sample was grounded with polyvinylidene fluoride (PVDF) and N-methyl-2-pyrrolidone (NMP) into a paste and then painted the paste directly onto the carbon paper for electrochemical studies. We studied the electrochemical reduction of CO_2 in 0.5 M $KHCO_3$ catalyzed by the p-NG-Cu catalyst. We used GC-MS to analyze the gaseous products, and ^1H NMR to identify the liquid product, which were collected at a constant reduction potential. We calculated the Faradaic efficiency (FE) of the reduction reaction at each reduction potential. When reducing CO_2 on p-NG-Cu at -0.8 V, formate (FE 62%) and C_2H_4 (FE 1.4%) were initially detected. At more negative potentials, C_2H_4 was predominately formed and the formate generation was suppressed. The FE for the C_2H_4 formation reached 19% at -0.9 V, where other hydrocarbons (3.8% formate, 0.9% CH4 and 0.6% C_2H_6) were also observed but the total FE was less than 5.3% (**Figure 3b**). Among all hydrocarbons produced on the p-NG-Cu at -0.9 V, C_2H_4 selectivity reached 79%. When normalized against the Cu mass, the p-NG-Cu had a C_2H_4 formation mass activity of 2.9 A/gCu. This work demonstrated that p-NG as a support enhanced significantly the Cu NP selectivity toward C_2H_4 at -0.9 V or more negative potentials. Our work demonstrates a promising approach to improve Cu NP catalysis by NG for selective electrochemical reduction of CO_2 to C_2H_4.

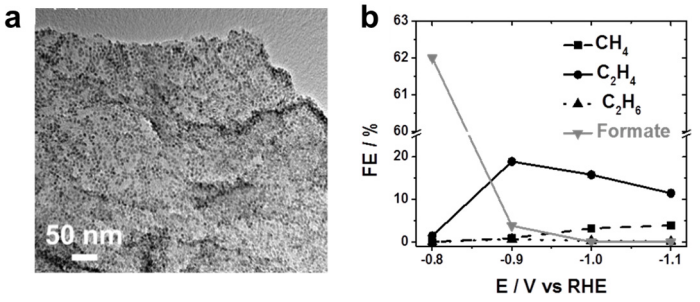

Figure 3. (**a**) TEM image of the p-NG-Cu catalyst after Cu NP assembly on the p-NG. (**b**) Reduction potential dependent FE's of the p-NG-Cu catalyzed electrochemical reduction of CO_2 to various hydrocarbons.

II.3. NPs/G or NPs/$WO_{2.72}$ for catalytic dehydrogenation of ammonia borane or formic acid to hydrogen

Ammonia borane (AB, $H_3N{\bullet}BH_3$) and formic acid (HCOOH) have been explored extensively as a new H_2 storage material for easy H_2 transportation. H_2 is released via AB hydrolysis or HCOOH dehydrogenation in the presence of a catalyst.

In our 2017 publication ("CuNi Nanoparticles Assembled on Graphene for Catalytic Methanolysis of Ammonia Borane and Hydrogenation of Nitro/Nitrile Compounds", *Chem. Mater*. **2017**, *29*, 1413.), we tested CuNi NPs supported on G for enhanced AB hydrolysis into H_2. We prepared the monodisperse 16 nm CuNi NPs by the co-reduction of nickel(II) acetylacetonate ($Ni(acac)_2$) and copper (II) acetylacetonate ($Cu(acac)_2$) with borane-*t*-butylamine in oleylamine and oleic acid. We then assembled the CuNi NPs on G through the sonication of the ethanol dispersion of G and the hexane dispersion of NPs to produce CuNi/G. We activated CuNi NPs by immersing the NPs in *t*-butylamine under a N_2 atmosphere to remove oleate/oleylamine, and by washing with ethanol, giving catalytically active $Cu_{36}Ni_{64}$/G (**Figure 4a**). We studied CuNi composition-dependent AB hydrolysis in methanol at room temperature and found $Cu_{36}Ni_{64}$/G to be the most active catalyst (**Figure 4b**). The hydrolysis TOF on the $Cu_{36}Ni_{64}$/G surface was calculated to be 49.1 $mol_{H2}/(mol_{CuNi}{\bullet}min)$. The activation energy was evaluated to be E_a = 24.4 kJ/mol. Our CuNi/G was the most efficient catalyst among all Cu- or Ni-catalysts ever reported.

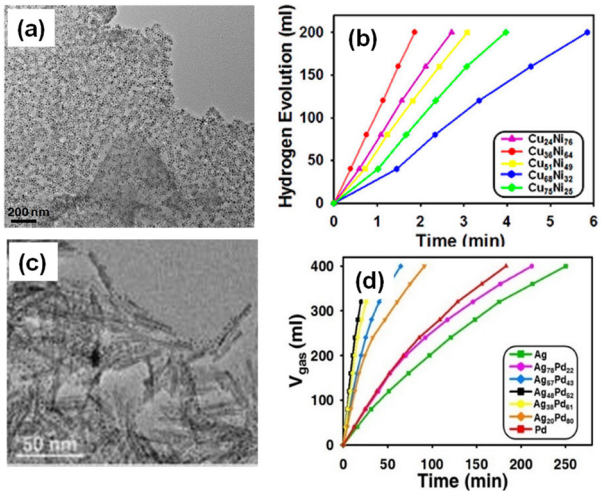

Figure 4. (**a**) TEM image of the $Cu_{36}Ni_{64}$ NPs assembled on G. (**b**) Plot of time vs volume of H_2 generated from AB hydrolysis catalyzed by CuNi/G with different CuNi compositions (CuNi NPs = 9.8 mM, [AB] = 300 mM, T = 298 K). (**c**) TEM image of $Ag_{48}Pd_{52}/WO_{2.72}$. (**d**) Plot of time vs volume of H_2 generated from HCOOH dehydrogenation catalyzed by $AgPd/WO_{2.72}$ with different AgPd composition ([catalyst] = 3.1 mM, [FA] = 900 mM, T = 323 K).

While studying G effect on NP catalysis, we also found oxygen deficient $WO_{2.72}$ to be especially interesting as a support to enhance NP catalysis ("AgPd Nanoparticles Deposited on $WO_{2.72}$ Nanorods as an Efficient Catalyst for One-Pot Conversion of Nitrophenol/ Nitroacetophenone into Benzoxazole/Quinazoline", *J. Am. Chem. Soc*. **2017**, 139, 5712.). We prepared 40 x 4 nm $WO_{2.72}$ nanorods (NRs) by reacting WCl_4 with oleic acid and oleylamine in 1-octadecene at 280 °C. We also synthesized AgPd NPs by co-reduction of silver(I) acetate and $Pd(acac)_2$ at 180°C. We prepared $AgPd/WO_{2.72}$ by seed-mediated growth of AgPd NPs in the presence of $WO_{2.72}$ NRs. The in-situ nucleation and growth of AgPd NPs along the $WO_{2.72}$ NRs led to the formation of $AgPd/WO_{2.72}$. By controlling the molar ratios of metal precursors, we obtained $AgPd/WO_{2.72}$. **Figure 4c** shows the representative TEM image of the $Ag_{48}Pd_{52}/WO_{2.72}$ with 2.3 nm $Ag_{48}Pd_{52}$ NPs attached to $WO_{2.72}$ NRs. We studied catalytic properties of the $AgPd/WO_{2.72}$ for HCOOH dehydrogenation into H_2 and CO_2 (**Figure 4d**) and found $Ag_{48}Pd_{52}/WO_{2.72}$ to be the most active catalyst with an initial TOF of 1718/h and an activation energy of E_a = 31 kJ/mol. It is one of the most active heterogeneous catalysts ever reported for the HCOOH dehydrogenation reaction. More importantly, the $AgPd/WO_{2.72}$ was active for one-pot conversion of nitrophenol and aldehydes into benzoxazoles, an essential core structure found in

some mechanically robust rigid organic polymers for uses as ballistic fiber and flame retardant materials.

II.4. Pd(CuPd)/$WO_{2.72}$ for formic acid oxidation reaction

Having robust catalysts for electrochemical oxidation and reduction reactions is key to producing commercially viable electrochemical devices for renewable energy applications. Various forms of nanostructured Pt have been studied extensively as the choices of the catalysts for the oxidation and reduction reactions. However, the concerns over high costs associated with Pt-containing devices also motivate the searches for new classes of catalysts with minimum or non-Pt contents. Among different non-Pt catalysts investigated, Pd-based NPs evolve as an interesting class of candidates for the same electrochemical reactions, especially for the formic acid oxidation reaction (FAOR). But these Pd catalysts are generally not as stable as the Pt ones in the acidic electrochemical reaction conditions and therefore have little value of practical uses in electrochemical devices.

Studying Pd NP interaction with $WO_{2.72}$, we found that Pd catalytic efficiency for FAOR (in 0.1 M $HClO_4$) was dramatically improved by its coupling with $WO_{2.72}$ NRs ("Pd Nanoparticles Coupled to $WO_{2.72}$ Nanorods for Enhanced Electrochemical Oxidation of Formic Acid", *Nano Lett*. **2017**, 17, 2727.). The Pd/$WO_{2.72}$ was made by seed-mediated growth of $WO_{2.72}$ NRs in the presence of 5 nm Pd NPs. **Figure 5a** shows the TEM image of the Pd/$WO_{2.72}$. Compared with the single component Pd NPs, the $WO_{2.72}$-coupled Pd NPs show much improved FAOR catalytic activity in 0.1 M $HClO_4$ + 0.1 M HCOOH with the mass activity reaching ~1600 mA/mg_{Pd} (**Figure 5b**). In the Pd/$WO_{2.72}$-catalyzed FAOR, the presence of the oxidation "plateau" infers that once the oxidation reaction is initiated, the current quickly reaches to its maximum level at ~0.4 V and stays at this level (with a slow current increase) until the Pd surface is oxidized to Pd (II). Another noticeable feature of the Pd/$WO_{2.72}$ catalyst is that it has much enhanced stability in the FAOR condition and shows no sign of catalyst degradation after the 12 h chronoamperometry test at 0.4 V (**Figure 5b**). As a comparison, after the same stability test, the single component Pd NP catalyst shows the drop of its mass activity from 537.1 mA/mg_{Pd} to 437.0 mA/mg_{Pd} (**Figure 5b**).

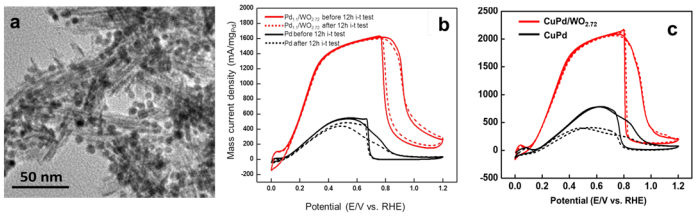

Figure 5. (a) TEM image of Pd/$WO_{2.72}$, (**b**) FAOR CVs of the Pd/$WO_{2.72}$ and Pd before and after 12 h chronoamperometry i-t test at 0.4 V. (**c**) FAOR CVs for the C-CuPd and C-CuPd/$WO_{2.72}$ before (solid line) and after (dashed line) 12 h chronoamperometry test at 0.40 V. The CVs were obtained in the N_2-saturated 0.1 M $HClO_4$ and the FAOR CVs were from the solution of 0.1 M $HClO_4$ + 0.1 M HCOOH with a scan rate of 50 mV/s.

The strategy developed here on using $WO_{2.72}$ to enhance Pd catalysis can be further extended to CuPd NPs ("Stabilizing CuPd Nanoparticles via CuPd Coupling to $WO_{2.72}$ Nanorods in Electrochemical Oxidation of Formic Acid", *J. Am. Chem. Soc*. **2017**, 139, 15191.). In this work, 5 nm CuPd NPs were prepared by controlled diffusion of Cu into Pd NPs and $WO_{2.72}$ NRs were grown in the presence of CuPd NPs, forming the CuPd/$WO_{2.72}$ composites. Due to the strong CuPd-$WO_{2.72}$ coupling, Cu is enriched at the CuPd-$WO_{2.72}$ interface and more efficiently stabilized in 0.1 M $HClO_4$. The CuPd/$WO_{2.72}$ was very active and stable in catalyzing the FAOR in 0.1 M $HClO_4$ + 0.1 M HCOOH with its mass activity reaching 2086 mA/mg_{Pd} in a broad potential range of 0.40 to 0.80 V (vs. RHE) without activity drop in the 12 h chronoamperometry test at 0.40 V (**Figure 5c**). The

$CuPd/WO_{2.72}$ is among the most active Pd-based NP catalyst ever reported for the FAOR and has the potential to replace Pt to catalyze the FAOR.

II.5. Maximizing NP catalytic activity by their monolayer assembly on NG

We extended our water-air NP assembly method and prepared a monolayer array of NPs on NG (NPs-NG) onto a Si substrate (Maximizing the Catalytic Activity of Nanoparticles through Monolayer Assembly on Nitrogen-Doped Graphene", Angew. Chem. Int. Ed. 2018, 57, 451.). In this study, 3 nm NiPd NPs were prepared via the co-reduction of nickel(II) acetate and palladium(II) acetylacetonate by borane tert-butylamine in oleylamine and 1-octadecene at 100 °C, and finally dispersed in pentane. The assembly process was performed on the water-pentane interface by first obtaining a 2D NG film on water surface, then a 2D array of NiPd NPs on the NG film before the NPs-NG was transferred onto a Si substrate, giving NPs-NG-Si, which was used as a catalyst probe to turn a catalytic reaction "on" by inserting the probe into the reaction solution and "off" by pulling the probe out of the solution (**Figure 6a**). Using 3 nm NiPd NPs as an example, we demonstrated that the monolayer NiPd-NG-Si showed the maximum catalysis not only for AB hydrolysis, but also for the transfer hydrogenation and condensation of aromatic amine-compounds and aldehydes, leading to the one-pot, high-yield synthesis of quinazolines in water (**Figure 6a**). The catalyst was even active for the hydrodehalogenation of halogenatedaromatics under mild reaction conditions, offering a powerful, low-cost, and safe green technology for the degradation of polyhalogenated aromatics (**Figure 6b**) ("Hydrodehalogenation of polyhalogenated aromatics catalyzed by NiPd nanoparticles supported on nitrogen-doped graphene", *ChemSusChem*, **2018**, 11, 1617.).

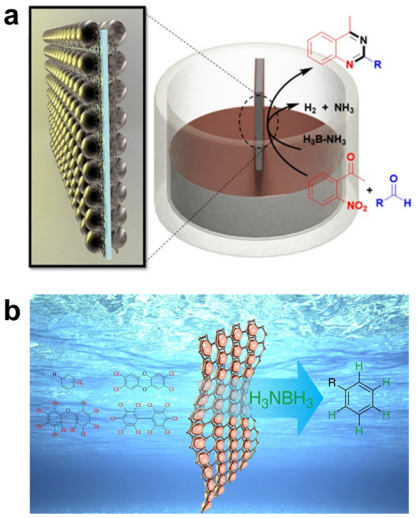

Figure 6. **a**) Assembled NPs-NG on both sides of S as a probe to catalyze a solution phase reaction: inserting the probe into the solution can trigger the catalytic reaction, and pulling the probe from the solution can stop the reaction. **b**) Illustration of NiPd-NG catalyzed hydrodehalogenation of polyhagogenated aromatics.

III. Project Summary

Overall, this ARO support allows us to demonstrate a new and reliable 2D NP platform on NG, which helps to optimize NP catalysis for some important chemical reactions. Most goals proposed initially were accomplished after three years of research. However, the intended fabrication of NG-NP-NG layered structures (**Figure 1b**) for studying catalysis on the NG surface was not successful due to the difficulty in using our chemical approach to cover NPs with NG. Giving more time, our new assembly approach to monolayer array of NPs on single sheet NG on water surface should allow us to prepare the NG-NPs-NG sandwich structure. Once this structure is prepared with NPs being Fe- or Co-based, NP-enhanced electrocatalysis, such as ORR, OER, HER, FAOR, or even alcohol oxidation reaction, on NG can be studied in details. Such studies may lead to the development of non-Pt catalysts for important energy conversion reactions that are key to Army's mission to build economical, light-weight and efficient energy devices for power applications

IV. Training Opportunities

This ARO project allowed us to support two graduate students, Liheng Wu and Zheng Xi, and two postdoctors (partial support), Qing Li and Chao Yu, to perform what are proposed in the project. Liheng Wu defended his PhD thesis in 2015 and is now a postdoctoral fellow at Stanford University. Zheng Xi defended his PhD thesis in 2018 and is now a postdoctoral fellow at Central Florida University. Dr. Qing Li worked initially on this ARO project in 2015 and is now a Professor in Materials Sciences and Engineering of Huazhong University of Science and Technology. Dr. Chao Yu was partially supported by this ARO project, developing NG-NP catalysis for chemical conversions. He is now working to extend the reactions for rigid organic polymer formation.

V. Results Dissemination

V.1. Journal Publications

1. L. Wu, Q. Li, C. H. Wu, H. Zhu, A. Mendoza-Garcia, B. Shen, J. Guo, S. Sun, "Stable Cobalt Nanoparticles and Their Monolayer Array as an Efficient Electrocatalyst for Oxygen Evolution Reaction", *J. Am. Chem. Soc*. **2015**, 137, 7071–7074.

2. Q. Li, W. Zhu, J. Fu, H. Zhang, G. Wu, S. Sun, "Controlled Assembly of Cu Nanoparticles on Pyridinic-N Rich Graphene for Electrochemical Reduction of CO_2 to Ethylene", *Nano Energy* **2016**, 24, 1-9.

3. L. Wu, A. Mendoza-Garcia, Q. Li, S. Sun, "Organic Phase Syntheses of Magnetic Nanoparticles and Their Applications", *Chem. Rev*. **2016**, 116, 10473–10512.

4. Q. Li, S. Sun, "Recent Advances in the Organic Solution Phase Synthesis of Metal Nanoparticles and Their Electrocatalysis for Energy Conversion Reactions", *Nano Energy*, **2016**, 29, 178–197.

5. C. Yu, J. Fu, M. Muzzio, T. Shen, D. Su, J. Zhu, S. Sun, "CuNi Nanoparticles Assembled on Graphene for Catalytic Methanolysis of Ammonia Borane and Hydrogenation of Nitro/Nitrile Compounds", *Chem. Mater*. **2017**, 29, 1413–1418.

6. C. Yu, X. Guo, Z. Xi, M. Muzzio, Z. Yin, B. Shen, J. Li, C. T. Seto, S. Sun, "AgPd Nanoparticles Deposited on $WO_{2.72}$ Nanorods as an Efficient Catalyst for One-Pot Conversion of Nitrophenol/ Nitroacetophenone into Benzoxazole/Quinazoline", *J. Am. Chem. Soc*. **2017**, 139, 5712-5715.

7. Z. Xi, D. P. Erdosy, A. Mendoza-Garcia, P. N. Duchesne, J. Li, M. Muzzio, Q. Li, P. Zhang, S. Sun, "Pd Nanoparticles Coupled to $WO_{2.72}$ Nanorods for Enhanced Electro-chemical Oxidation of Formic Acid", *Nano Lett*. **2017**, 17, 2727–2731.

8. Z. Xi, A. Mendoza-Garcia, H. Zhu, M. Chi, D. Su, D. P. Erdosy, J. Li, S. Sun, "$Ni_xWO_{2.72}$ Nanorods as an Efficient Electrocatalyst for Oxygen Evolution Reaction", *Green Energy & Environment* **2017**, 2, 119-123.

9. Z. Xi, H. Lv, D. P. Erdosy, D. Su, Q. Li, C. Yu, J. Li, S. Sun, "Atomic Scale Deposition of Pt around Au Nanoparticles to Achieve Much Enhanced Electrocatalysis of Pt", *Nanoscale* **2017**, 9, 7745 – 7749.

10. Z. Xi, J. Li, D. Su, M. Muzzio, C. Yu, Q. Li, S. Sun, "Stabilizing CuPd Nanoparticles via CuPd Coupling to $WO_{2.72}$ Nanorods in Electrochemical Oxidation of Formic Acid", *J. Am. Chem. Soc*. **2017**, 139, 15191–15196.

11. C. Yu, X. Guo, M. Shen, B. Shen, M. Muzzio, Z. Yin, Q. Li, Z. Xi, J. Li, C. T. Seto, S. Sun, "Maximizing the Catalytic Activity of Nanoparticles through Monolayer Assembly on Nitrogen-Doped Graphene", *Angew. Chem. Int. Ed*. **2018**, 57, 451-455.

12. X. Guo, C. Yu, Z. Yin, S. Sun, C. T. Seto, "Hydrodehalogenation of polyhalogenated aromatics catalyzed by NiPd nanoparticles supported on nitrogen-doped graphene", *ChemSusChem* **2018**, 11, 1617-1620.

13. H. Xie, T. Wang, J. Liang, Q. Li, S. Sun, "Cu-based Nanocatalysts for Electrochemical Reduction of CO_2", *NanoToday* **2018**, 21, 41-54.

V.2. Book Chapter

L. Wu, Z. Xi, S. Sun, "Well-defined Metal Nanoparticles for Electrocatalysis", in Morphological, Compositional, and Shape Control of Materials for Catalysis of the series "Studies in surface science and catalysis", ed. M. Cargnello, P. Fornasiero, Elsevier, **2017**, Chapter 4.

V.3. Invention Disclosures

1. "Graphene-Co/CoO nanoparticle composite, manufacture, and use in an electrochemical cell", with S. Guo, S. Zhang, and L. Wu, WO2014055485.

2. "Composite AgPd-$WO_{2.72}$ catalyst for One-Pot Conversion of nitrophenol/nitroacetophenone into benzoxazole/quinazoline" with C. Yu, X. Guo, and C. T. Seto, US Provisional Patent Application.

3. "Hydrodehalogenation of polyhalogenated aromatics catalyzed by NiPd nanoparticles supported on nitroget-doped graphene", with X. Guo, C. Yu, C. T. Seto, and Z. Yin, U.S. Provisional Patent Application No.: 62/607,821.

V.4. Scientific Presentations (All Invited)

1. "Synthesis and Assembly of Nanocatalysts for Efficient Electrochemical Reduction Reactions", **250th ACS National Meeting**, August 15-20, 2015, Boston, MA.

2. "Tuning Nanocatalysts for Efficient Electrochemical Reactions", **MRS Spring Meeting**, Nov 30-Dec 3, 2015, Boston, MA.

3. "Rational Synthesis and Assembly of Nanocatalysts for Energy Applications", **Pacifichem2015**, Dec 15 - 20, 2015, Honolulu, Hawaii.

4. "Controlled Assembly of Nanoparticles for Energy Conversions", **11th China-US Nano-Forum**, June 18-20, 2016, Nanjing University, China.

5. "Controlled Synthesis and Assembly of Nanoparticles for Electrocatalysis", **International Workshop on Nanomaterials and Nanodevices**, July 8-10, 2016, Institute of Physics, Beijing, China.

6. Plenary Talk, "Tuning Nanoparticle Catalysis for Efficient Electrochemical Reactions", **2nd Zing Nanocrystals Conference**, August 2-5, 2016, Dublin, Ireland.

7. **XingDa Lecture**, "Tuning Nanoparticle Catalysis for Efficient Electrochemical Reactions", Dec 9, 2016, Peking University.

8. "Tuning Nanoparticle Catalysis to Optimization for Energy Conversion Reactions", Huazhong University of Science and Technology, China, June 30, 2017.

9. **Plenary Speaker**, "Formation of Atomic Scale Pt around a Nanoparticle Core to Achieve Much Enhanced Electrocatalysis of Pt", **International Workshop on Nanomaterials and Nanodevices**, Institute of Physics, Beijing, China, July 4, 2017.

10. **"Wenqui" Lecture**, "Tuning Nanoparticle Catalysis for Electrochemical Reactions", Lanzhou University, China, July 20, 2017.

11. **Honorable Speaker**, "Tuning Nanoparticle Catalysis for Electrocatalysis", **Frontier in Nanoscience Forum**, Key Laboratory of Molecular Nanostructure and nanotechnology, Chinese Institute of Chemistry, CAS, July 23, 2017.

12. "Controlling Metal Nanoparticle Interactions with Nanoscale-Supports to Enhance Nanoparticle Catalysis", **254th ACS National Meeting**, August 20-24, 2017, Washington, DC.

13. "Synthetic Tuning of Nanoparticles to Achieve High Efficiency in Electrocatalysis", **MRS Spring Meeting**, April 2-6, 2018, Phoenix, AZ.

14. Inorganic and Organic Seminar on electrocatalysis tuning and optimization, Department of Chemistry, University of Chicago, May 11, 2018.

15. "Synthetic Tuning of Nanoparticles to Achieve High Efficiency in Electrocatalysis", **13th Sino-US Forum on Nanoscale Science and Technology**, June 29 –July 3, 2018, Chengdu, China.

16. "Enhancing Nanoparticle Catalysis for Chemical Transformations", **256th ACS National Meeting**, August 19-23, 2018, Boston, MA.