RESORCINARENE CAVITAND THIOL MEDIATED SYNTHESIS OF TAILORABLE NANOWIRE ELECTROCATALYSTS

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Proton exchange membrane fuel cells (PEMFCs), a clean and efficient energy source that has found use in space exploration and commercial applications, require a catalyst for the oxygen reduction reaction (ORR). The most commonly used catalyst for PEMFCs is the platinum carbon (Pt/C) catalyst due to its relatively high catalytic efficiency compared to other metal catalysts. However, these traditional Pt/C catalysts have the significant drawbacks of high cost and poor long-term stability. Platinum based alloys can offer improved cost effectiveness as well as superior catalytic performance. Nanowires can increase long-term stability through their 1D structure while maintaining high surface area to volume ratio. Nanowires have been synthesized through a variety of methods, including template-based, seed-mediated, and one-pot approaches. This work details the synthesis of platinum nanowires using the Brust-Schiffrin approach in the presence of resorcinarene benzyl thiol cavitand surfactant. Further, the influence of reaction conditions on nanowire growth are probed, specifically the choice of halide ion, solvent, and precursor oxidation state. Finally, the approach is applied to a coreduction of metal salts to test the generalizability of the Brust-Schiffrin synthesis in the presence of a resorcinarene surfactant.

Introduction

Fuel cells, specifically proton exchange membrane fuel cells (PEMFCs), are an important power source for space travel, research, and exploration. Fuel cells have also found broader application in areas such as the automotive industry and have the potential for further commercialization.[1] Advantages of fuel cells include their relative light weight, clean waste products, non-reliance on fossil fuels, and potential to be regenerated. PEMFCs generate electrical energy by utilizing the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR), producing water as the by product. The ORR at the cathode is the rate limiting step in the reaction and determines the efficiency of the cell.

In order to increase the energy conversion efficiency of fuel cells, it is necessary to use and develop more efficient catalysts for the ORR. Often, platinum (Pt) based catalysts are used due to their high oxygen reduction activity, ideal binding energy, and preferential use of the 4-electron pathway to avoid H_2O_2 generation.[2] Pt nanoparticles are used due to the high surface area to volume ratio and exposure of active crystal facets; however, commercial Pt catalysts of this nature are expensive and prone to agglomerate, reducing their effectiveness.[3] Thus, efforts have been directed toward synthesizing more stable, efficient, and cost-effective catalysts for oxygen reduction.

Among the methods that can be used to do this, combining the Pt catalyst with other metals to make alloys and varying the morphology of the catalyst are noteworthy.[4] Alloying Pt-based nanoparticles can improve cost-effectiveness as well as improve catalytic efficiency though the availability of active sites, reduced poisoning though alternative pathways, and differential binding of reactants, products, and intermediate species.[5,6] For example, Yan *et al*. synthesized Pt/Cu nanowires by galvanic displacement for the ORR, finding that they offered higher area ORR activities (1.5 mA cm^{-2}) than commercial Pt/C catalysts.[7]

To avoid agglomeration of nanoparticles by Ostwald ripening, one-dimensional nanostructures such as nanowires can be used.[8] These structures offer superior stability due to greater contact with the support structure and can preferentially expose active (111) crystal facets.[1] Morphological control of Pt based nanocatalysts has been shown to be effective using various synthetic approaches, from seed-mediated to one-pot syntheses. Ballav and coworkers showed that a seed-mediated approach allows for bi-metallic Au@Pt core-shell structures to be formed, improving electrocatalytic performance of the ORR.[9] Pt-Co nanowire assemblies have been synthesized by Xia and coworkers through a one-pot, solvothermal synthesis.[10] Despite these successes, there remains room for improvement in the precise morphological control of nanowire synthesis through colloidal approaches. Oriented attachment has been implicated as an effective mechanism for nanowire growth, using nanocrystals as building blocks and resulting in diverse structures that can branch and retain defects.[11] This mechanism has recently been used by Gao *et al.* to form branched Pt and Pt-Ir nanowires with twin defects for application as a peroxidase-like catalyst.[12] The ease of synthesis, control of structure, and potential to alloy make approaches using this mechanism an excellent option for Pt-based catalysts with regard to application in the ORR.

The Brust-Shiffrin reaction is a facile method for nanoparticle synthesis that involves a phase transfer of metal salt, stabilization and partial reduction by a thiol, followed by reduction using sodium borohydride.[13] While this technique was originally used for synthesizing 1-3 nm gold nanoparticles it has been extended to other metals as well. However, using platinum with the Brust-Schiffrin method has led to issues with Pt(II) thiolate complex formation, which cannot be reduced.[14] Han and colleagues have investigated the influence of resorcinarene surfactants with different headgroups on monometallic Pt nanoparticles.[15] In this study, a Brust-Schiffrin reaction was used in the presence of resorcinarene benzyl thiol (Figure 1) to synthesize highly branched Pt nanowires. Resorcinarene surfactants are multidentate, macrocyclic compounds consisting of long, alkyl chain tails and a variable, polar head group. For these reasons, they are highly suitable for nanoparticle stabilization. TEM analysis of the formed nanostructures showed the presence Pt (111) and (200) crystal planes. Further, the morphology of the nanowires was influenced by changes in the concentration of resorcinarene surfactant and metal precursor, with higher concentrations of Pt precursor leading to higher branching.

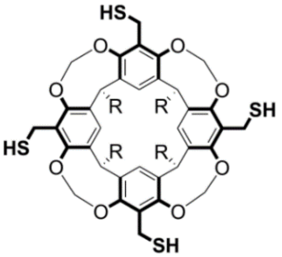

Figure 1: Structure of resorcinarene benzyl thiol

This work probes the formation of Pt nanowires under Brust-Schiffrin conditions in the presence of resorcinarene benzyl thiol and the generalizability of the approach for a metal salt coreduction.

Experimental

General remarks

Hydrogen hexachloroplatinate (IV) hexahydrate (Acros, 99.9%), potassium tetrachloroplatinate (II) (Acros, 46.5-47.0% Pt), copper (II) nitrate (Acros, 98+%), hydrogen tetrachloroaurate (III) hydrate (Alfa Aesar, 99.9%), tetraoctylamonium bromide (Aldrich, 98%), and sodium borohydride (Sigma-Aldrich, ≥ 98.5%) were used as received. All organic solvents used were dried and distilled prior to their use. Barnstead Nanopure water (18.2 MΩ cm) was used for all syntheses. The glassware used in this study was silanized.

Synthesis of resorcinarene benzyl thiol

Resorcinarene benzyl thiol cavitand surfactant was synthesized in four steps according to previously described methods.[15] Briefly, 2-methyl resorcinol and heptanal undergo acid-catalyzed condensation to form tetramethyl resorcinarene. Tetramethyl resorcinarene is combined with bromochloromethane and activated cesium carbonate to form the corresponding cavitand through acetal formation. The product then undergoes radical bromination to form resorcinarene tetrabenzylbromo cavitand. Finally, bromide is substituted using thiourea to form resorcinarene benzyl thiol cavitand surfactant.

Preparation of monometallic Pt nanowires via Brust-Schiffrin synthesis

To a solution of tetraoctylammonium bromide (29.2 mg, 0.053 mmol) dissolved in 10 mL chloroform, 4 mL of water and 1 mL of an aqueous solution of H_2PtCl_6 (18.3 mg, 0.035 mmol) were added and the reaction mixture stirred for 30 minutes at room temperature under argon atmosphere. The organic phase changed color from colorless to yellow, while the aqueous phase changed from yellow to colorless, indicating successful phase transfer of the metal salt. The organic phase was separated and a solution of resorcinarene benzyl thiol cavitand surfactant (10.2 mg, 0.010 mmol) in 10 mL chloroform was added. This reaction mixture was stirred for 30 minutes at room temperature under argon atmosphere. After this, the mixture was cooled to 0 °C and allowed to equilibrate for 15 minutes. A $NaBH_4$ solution was freshly prepared with ice cold water and 14.2 mg in 2 mL was quickly added to the reaction mixture with stirring under argon atmosphere. The mixture exhibited an immediate color change from yellow to brown, increasing to a darker brown over the first minute. The reaction was stirred under argon atmosphere for 2 hours at 0 °C. The organic layer was then collected and washed with water (3 x 20 mL). The nanowires were redispersed in 9 mL of toluene after rotary evaporation of chloroform for prolonging their shelf-life.

Preparation of monometallic Pt nanostructures using a chloride-based phase transfer agent

The above Brust-Schiffrin synthesis was completed replacing tetraoctylammonium bromide with Aliquat 336 (22.7 mg, 0.056 mmol) using the same quantities of other reactants.

Preparation of monometallic Pt nanostructures with toluene as solvent

The original Brust-Schiffrin synthesis was completed using an equal volume of toluene to replace chloroform. All other quantities of reactants remained the same.

Brust-Schiffrin synthesis using a Pt(II) precursor

The original Brust-Schiffrin synthesis was completed using K_2PtCl_4

(14.7 mg, 0.035 mmol) to replace H_2PtCl_6. All other quantities and conditions remained the same. No color change was seen after addition of $NaBH_4$, indicating a lack of reduction.

Preparation of bimetallic Pt-based nanostructures via Brust-Schiffrin synthesis

Bimetallic syntheses were performed using the same method as above, with equal amounts of metal ion. For the Pt-Cu synthesis, H_2PtCl_6 (9.32 mg, 0.018 mmol) and $Cu(NO_3)_2$ (4.19 mg, 0.018 mmol) in a total of 5 mL water were added to a solution of tetraoctylammonium bromide (30.8 mg, 0.056 mmol) in 10 mL chloroform. After stirring for 30 minutes at room temperature under argon atmosphere, the organic layer containing the metal ions was separated and resorcinarene benzyl thiol cavitand surfactant (9.9 mg, 0.009 mmol) in 10 mL chloroform was added and stirred for another 30 minutes at room temperature under argon atmosphere. After equilibrating to 0 °C, freshly prepared $NaBH_4$ (13.9 mg, 0.367 mmol) in 2 mL ice cold water was added to the mixture under argon atmosphere and stirred for 2 hours. After washing the organic layer with water (3 x 20 mL), the nanoparticles were redispersed in 9 mL of toluene.

For the Pt-Au synthesis, H_2PtCl_6 (9.32 mg, 0.018 mmol) and $HAuCl_4$ (7.09 mg, 0.018 mmol) were used and the above process replicated. After addition of $NaBH_4$, the reaction mixture changed color from yellow to dark brown within 10 seconds.

For the Pt-Pd synthesis, H_2PtCl_6 (9.32 mg, 0.018 mmol) and Na_2PdCl_4 (5.30 mg, 0.018 mmol) were used and the same Brust-Schiffrin synthesis repeated. After addition of $NaBH_4$, the reaction mixture changed color from yellow to brown within 5 minutes, reaching its final dark brown color after an hour.

Characterization

TEM and EDS analysis were carried out using a JEOL JEM-2100F field emission microscope operating at 200 kV equipped with an Oxford INCAx-sight EDSdetector and a Gatan SC1000 ORIUS CCD camera (11 megapixel). Unless otherwise mentioned, all EDS analysis reported here were carried out in TEM mode. TEM samples were prepared by dropcasting toluene dispersions of nanoparticles on holey carbon film coated copper grids. Nanostructure dimensions and *d* spacings were measured using ImageJ software.

Results and Discussion

TEM/HRTEM analysis confirmed the synthesis of monometallic Pt nanowires (Figure 2). The typical diameter of these nanowires was 2 to 3 nm and several nanometers in length. HRTEM analysis revealed that they are polycrystalline with a spacing of 0.228 nm corresponding to the (111) plane. The nanowires can be seen to wrap around each other in rope-like fashion, creating the appearance of thicker wires (Figure 2 b-c). The wires as a whole are well separated, which may serve to increase the available catalytic surface area. Spherical particles were obtained as well using this method, typically 3 nm in diameter.

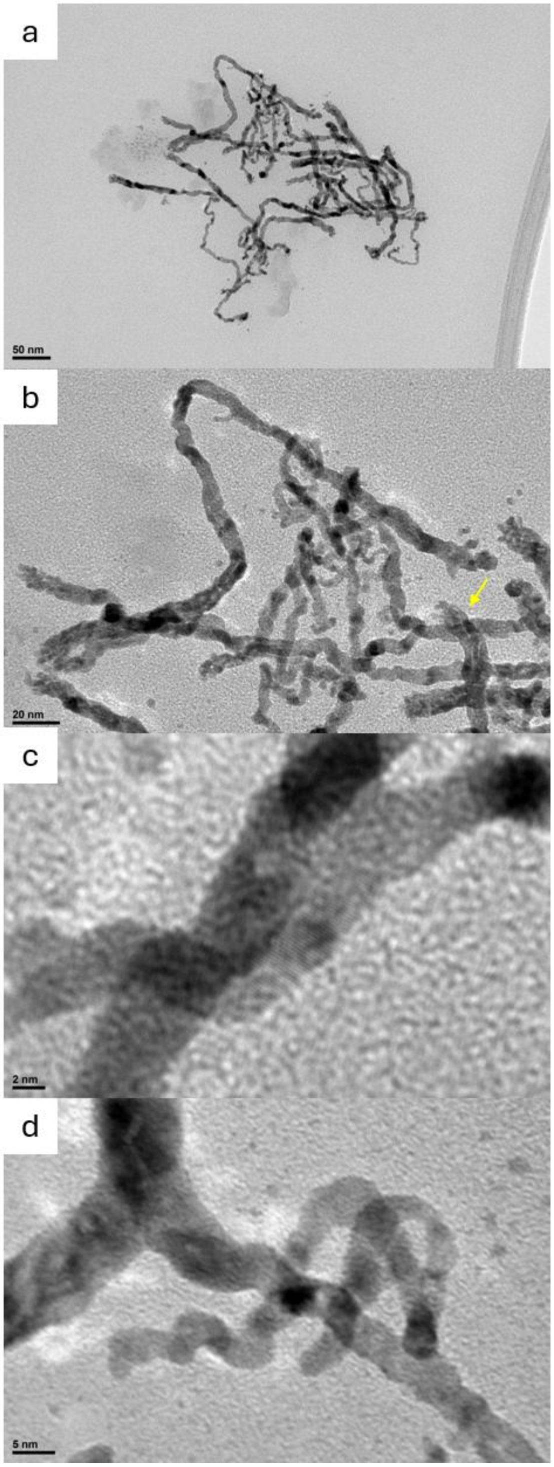

Figure 2: Pt nanowires at (a) 50 nm scale (b) 20 nm scale (note intertwined nanowires at arrow) (c) 2 nm scale (d) 5 nm scale

Several reaction conditions were altered to probe their effect on nanowire formation. First, the phase transfer agent tetraoctylammonium bromide was replaced with Aliquat 336, a quaternary ammonium salt with a chloride counterion, to investigate the importance of the halide ion. This synthesis led to the ultrasmall 1.1 nm nanoparticles seen in Figure 3a. This highlights the importance of bromide in the growth of nanowires. Replacing chloroform with toluene as the solvent led to poorly defined, smaller nanoparticles (Figure 3b), emphasizing the importance of solvent in nanowire growth. Finally, when altering the oxidation state of platinum by replacing H_2PtCl_6 with K_2PtCl_4, no color change was observed after addition of $NaBH_4$, indicating that the metal salt was not reduced under these conditions.

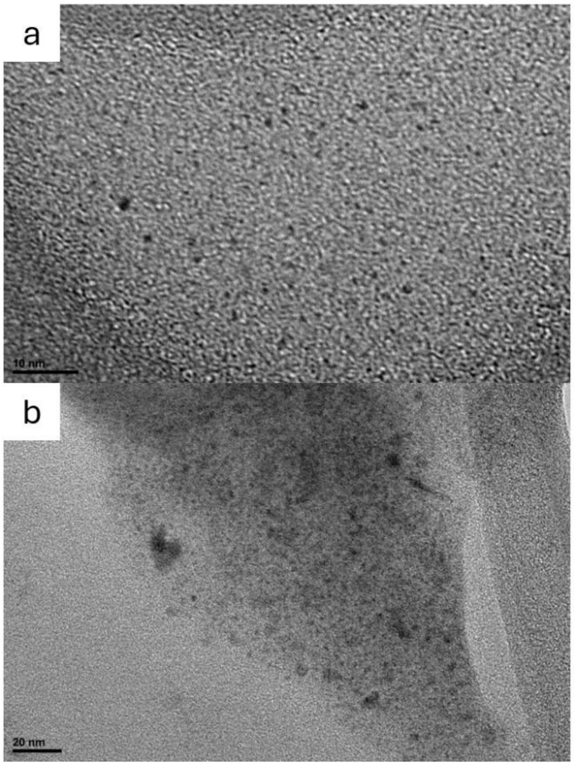

Figure 3: Nanoparticles formed under (a) altered transfer agent (Aliquat 336) conditions (b) altered solvent (toluene) conditions

Bimetallic coreduction with H_2PtCl_6 and $Cu(NO_3)_2$ led to both anisotropic, elongated nanowire-like structures with a typical width of 2 nm, as well as smaller spherical nanoparticles (Figure 4). Notably, longer nanowires were not observed under these conditions. EDS analysis revealed the presence of both Pt and Cu in the sample. Further analysis is required to unambiguously determine the composition of these anisotropic nanostructures.

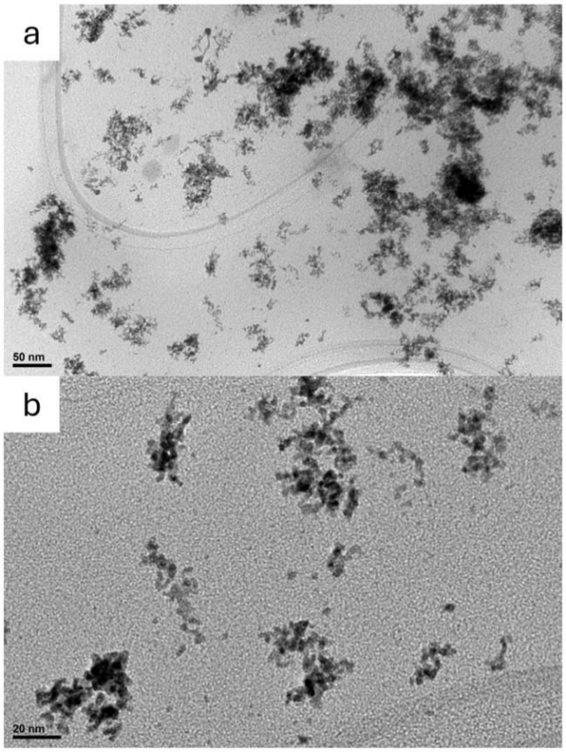

Figure 4: Nanostructures formed from bimetallic coreduction with H_2PtCl_6 and $Cu(NO_3)_2$ at (a) 50 nm scale (b) 20 nm scale

Coreduction with H_2PtCl_6 and $HAuCl_4$ led to nanoparticles of varying morphologies and dimensions (Figure 5a). Given the miscibility challenges reported in the literature, these results were not entirely surprising.[16] The larger nanocrystals (40 – 50 nm) were composed of Au and displayed three distinct morphologies: spherical, triangular, and bipyramidal. A representative bipyramidal structure can be seen in Figure 5b, with smaller, spherical nanoparticles behind. EDS analysis of these smaller (2.5 - 4 nm) nanoparticles confirmed the presence of both Pt and Au. However, no nanowire growth was observed using these conditions.

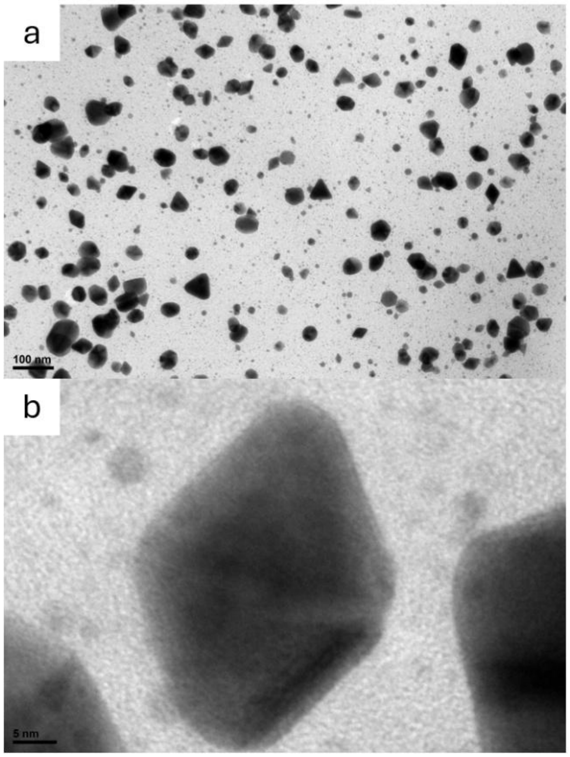

Figure 5: (a) Au and Pt-Au nanostructures (b) Bipyramidal Au nanostructure along with smaller Pt-Au nanoparticles

Coreduction of H_2PtCl_6 and Na_2PdCl_4 led to mainly spherical nanoparticle growth, with some instances of anisotropic growth (Figure 6). EDS analysis indicated that these nanoparticles were mainly composed of platinum. This supports prior findings of Pt rich nanostructures synthesized through the Brust-Schiffrin method using a macrocyclic resorcinarene surfactant.[15]

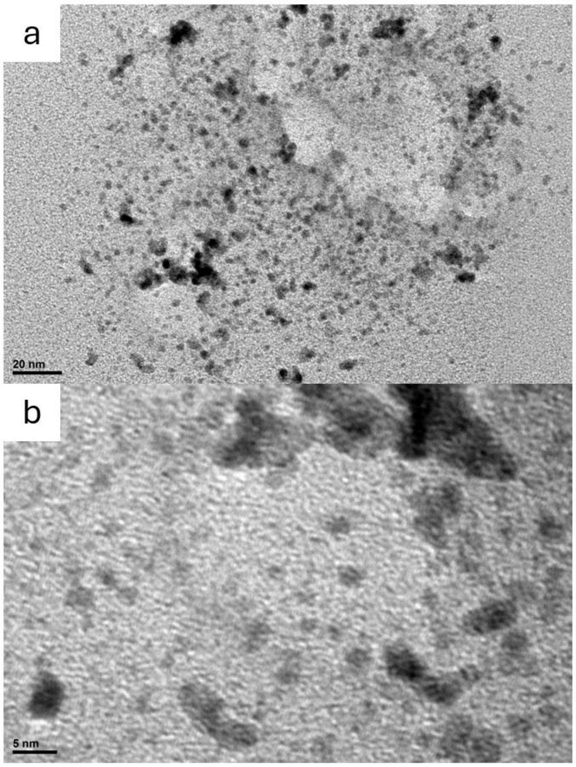

Figure 6: Nanostructures formed from H_2PtCl_6 and Na_2PdCl_4 coreduction

Conclusion

Platinum nanowires were successfully formed using a Brust-Schiffrin approach in the presence of resorcinarene benzyl thiol cavitand surfactant. The choice of the phase transfer agent, solvent, and precursor oxidation state all proved to be critical in the formation of nanowires. These findings advance understanding of the formation of Pt and Pt-based nanowires, which is essential for constructing more efficient catalysts for the ORR. The bimetallic Brust-Schiffrin synthesis led to elongated, anisotropic nanostructures with the Pt-Cu and Pt-Pd combinations, but no anisotropic growth with the Pt-Au combination. However, distinct non-spherical Au morphologies were formed along with smaller Pt-Au nanoparticles. The evaluation of these catalysts in mediating the ORR is currently underway in our laboratory.

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References

(1) Hu, X.; Yang, B.; Ke, S.; Liu, Y.; Fang, M.; Huang, Z.; Min, X. Review and Perspectives of Carbon-Supported Platinum-Based Catalysts for Proton Exchange Membrane Fuel Cells. *Energy Fuels* **2023**, *37* (16), 11532–11566. https://doi.org/10.1021/acs.energyfuels.3c01265.

(2) Zhang, D.; Ding, R.; Shi, S.; He, Y. Efficient Four-Electron Transfer Platinum-Based Oxygen Reduction Catalysts: A Mini Review. *International Journal of Hydrogen Energy* **2023**, *48* (78), 30391–30406. https://doi.org/10.1016/j.ijhydene.2023.04.161.

(3) Karimi, V.; Morgen, P.; Gyergyek, S.; Sharma, R.; Andersen, S. M. An Effective Route to Enhance Pt/C Electrocatalyst Durability through Addition of Ceramic Nanoparticles to Facilitate Pt Redeposition. *ACS Appl. Mater. Interfaces* **2024**, *16* (48), 65993–66007. https://doi.org/10.1021/acsami.4c10430.

(4) Kim, J.-H.; Lee, S. Y.; Lee, H. J.; In Lee, H.; Lim, D.-H.; Lee, Y. S.; Kim, H. S.; Woo, S. H. Strategies for the Design and Synthesis of Pt-Based Nanostructured Electrocatalysts in Proton Exchange Membrane Fuel Cells (PEMFCs). *ACS Eng. Au* **2025**, *5* (1), 1–9. https://doi.org/10.1021/acsengineeringau.4c00032.

(5) Smina, N.; Rosen, A.; Sztaberek, L.; Beatrez, W.; Kingsbury, K.; Troia, R.; Wang, Y.; Zhao, J.; Schrier, J.; Koenigsmann, C. Enhanced Electrocatalytic Oxidation of Small Organic Molecules on Platinum-Gold Nanowires: Influence of the Surface Structure and Pt-Pt/Pt-Au Pair Site Density. *ACS Appl. Mater. Interfaces* **2021**, *13* (50), 59892–59903. https://doi.org/10.1021/acsami.1c17244.

(6) Wang, C.; Markovic, N. M.; Stamenkovic, V. R. Advanced Platinum Alloy Electrocatalysts for the Oxygen Reduction Reaction. *ACS Catal.* **2012**, *2* (5), 891–898. https://doi.org/10.1021/cs3000792.

(7) Alia, S. M.; Jensen, K.; Contreras, C.; Garzon, F.; Pivovar, B.; Yan, Y. Platinum Coated Copper Nanowires and Platinum Nanotubes as Oxygen Reduction Electrocatalysts. *ACS Catal.* **2013**, *3* (3), 358–362. https://doi.org/10.1021/cs300664g.

(8) Huo, D.; Kim, M. J.; Lyu, Z.; Shi, Y.; Wiley, B. J.; Xia, Y. One-Dimensional Metal Nanostructures: From Colloidal Syntheses to Applications. *Chem. Rev.* **2019**, *119* (15), 8972–9073. https://doi.org/10.1021/acs.chemrev.8b00745.

(9) Roy, D.; Rajendra, R.; Gangadharan, P. K.; Pandikassala, A.; Kurungot, S.; Ballav, N. Seed-Mediated Growth of Pt on High-Index Faceted Au Nanocrystals: The Ag Lining and Implications for Electrocatalysis. *ACS Appl. Nano Mater.* **2021**, *4* (9), 9155–9166. https://doi.org/10.1021/acsanm.1c01714.

(10) Xia, B. Y.; Wu, H. B.; Li, N.; Yan, Y.; Lou, X. W. (David); Wang, X. One-Pot Synthesis of Pt–Co Alloy Nanowire Assemblies with Tunable Composition and Enhanced Electrocatalytic Properties. *Angewandte Chemie International Edition* **2015**, *54* (12), 3797–3801. https://doi.org/10.1002/anie.201411544.

(11) Chen, R.; Nguyen, Q. N.; Xia, Y. Oriented Attachment: A Unique Mechanism for the Colloidal Synthesis of Metal Nanostructures. *ChemNanoMat* **2021**, *8* (3). https://doi.org/10.1002/cnma.202100474.

(12) Gao, W.; Zhu, X.; Kim, M. J.; Xia, X. Ir- and Pt-Based Nanowires as Peroxidase Mimics for Detection of Carcinoembryonic Antigen. *ACS Appl. Nano Mater.* **2023**, *6* (14), 13208–13215. https://doi.org/10.1021/acsanm.3c01951.

(13) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. Synthesis of Thiol-Derivatised Gold Nanoparticles in a Two-Phase Liquid–Liquid System. *J. Chem. Soc., Chem. Commun.* **1994**, No. 7, 801–802. https://doi.org/10.1039/C39940000801.
(14) Castro, E. G.; Salvatierra, R. V.; Schreiner, W. H.; Oliveira, M. M.; Zarbin, A. J. G. Dodecanethiol-Stabilized Platinum Nanoparticles Obtained by a Two-Phase Method: Synthesis, Characterization, Mechanism of Formation, and Electrocatalytic Properties. *Chem. Mater.* **2010**, *22* (2), 360–370. https://doi.org/10.1021/cm902748k.
(15) Han, S. Synthesis, Morphological Control, Dispersion Stabilization and In Situ Self-Assembly of Noble Metal Nanostructures Using Multidentate Resorcinarene Surfactants, Old Dominion University Libraries, 2016. https://doi.org/10.25777/6TH7-JS72.
(16) Wanjala, B. N.; Luo, J.; Fang, B.; Mott, D.; Zhong, C.-J. Gold-Platinum Nanoparticles: Alloying and Phase Segregation. *J. Mater. Chem.* **2011**, *21* (12), 4012–4020. https://doi.org/10.1039/C0JM02682D.