

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/233793348>

# Designing Enhanced One-Dimensional Electrocatalysts for the Oxygen Reduction Reaction: Probing Size- and Composition-Dependent Electrocatalytic Behavior in Noble Metal Nanowires

ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · NOVEMBER 2012

Impact Factor: 7.46 · DOI: 10.1021/jz301457h

---

CITATIONS

35

---

READS

92

## 4 AUTHORS, INCLUDING:



Christopher Koenigsmann

Fordham University

36 PUBLICATIONS 891 CITATIONS

[SEE PROFILE](#)



Megan E. Scofield

Stony Brook University

9 PUBLICATIONS 49 CITATIONS

[SEE PROFILE](#)



Haiqing Liu

Stony Brook University

15 PUBLICATIONS 89 CITATIONS

[SEE PROFILE](#)

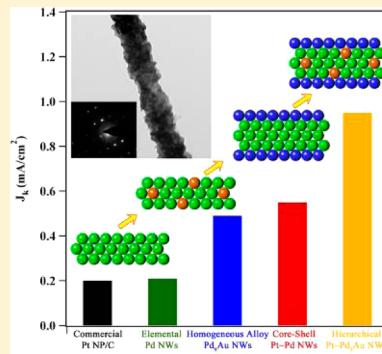
# Designing Enhanced One-Dimensional Electrocatalysts for the Oxygen Reduction Reaction: Probing Size- and Composition-Dependent Electrocatalytic Behavior in Noble Metal Nanowires

Christopher Koenigsmann,<sup>†</sup> Megan E. Scofield,<sup>†</sup> Haiqing Liu,<sup>†</sup> and Stanislaus S. Wong<sup>\*,†,‡</sup>

<sup>†</sup>Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794-3400, United States

<sup>‡</sup>Condensed Matter Physics and Materials Sciences Department, Brookhaven National Laboratory, Building 480, Upton, New York 11973, United States

**ABSTRACT:** Despite increasing interest in the use of one-dimensional (1D) noble metal nanostructures for the oxygen reduction reaction, there has been a surprising lack of effort expended in thoroughly and rationally examining the influence of various physicochemical properties of 1D electrocatalysts with respect to their intrinsic performance. In this Perspective, we address this important issue by investigating and summarizing recent theoretical and experimental progress aimed at precisely deducing the nature of the complex interplay among size, chemical composition, and electrocatalytic performance in high-quality elemental and bimetallic 1D noble metal nanowire systems. In terms of these structural parameters, significant enhancements in both activity and durability of up to an order of magnitude in the case of Pt–Pd<sub>1-x</sub>Au<sub>x</sub> nanowires, for example, can be achieved by rationally tuning both wire size and composition. The fundamental insights acquired are then utilized to discuss future and potentially radically new directions toward the continuous improvement and optimization of 1D catalysts.



Designing effective electrocatalysts for the oxygen reduction reaction (ORR) has been a key scientific objective because there is an increased need for practical, cost-effective polymer electrolyte fuel cells (PEMFCs) as sustainable portable energy sources.<sup>1–3</sup> Recently, one-dimensional (1D) nanostructures, particularly those composed of noble metals, have become the focus of significant attention and effort as potentially effective materials in a broad range of applications.<sup>4–6</sup> Accordingly, the uniquely anisotropic nature of these materials has rendered them as an exciting new structural paradigm for PEMFC electrocatalysts, particularly for ORR.<sup>7</sup> Not surprisingly, the observed intrinsic shape-dependent performance of these 1D catalyst systems enables them to consistently outperform commercially available catalysts in both the cathodic oxygen reduction and alcohol oxidation reactions (AOR).<sup>7–10</sup>

Typical commercially available ORR catalysts consist of metallic platinum nanoparticles physisorbed onto conductive, nanoparticulate carbon supports (Pt NP/C).<sup>11,12</sup> Despite the inherent gains in surface area, the measured ORR activity when normalized to the Pt surface area or so-called “specific activity” of commercial Pt NP/C is considerably lower than that of bulk Pt, and significant overpotentials are often required to achieve suitable kinetics for practical use. Concurrently, an extensive amount of attention has been dedicated to examining and understanding the reasons behind the relatively poor performance of Pt NP/C, in order to develop an effective paradigm for preparing more active and efficient catalysts.<sup>13–15</sup> The origin of the overpotential in Pt NP/C has been largely attributed to the relatively strong adsorption of oxygen species (e.g., O and OH) onto the surface of these catalysts at low overpotentials,

a deficiency that needs to be improved upon in order to initiate effective electrocatalytic oxygen reduction.<sup>16–19</sup> This phenomenon has been attributed to a combined size-dependent electronic effect as well as the high defect density inherent to Pt NPs with diameters of less than 2–3 nm.<sup>20–25</sup> The high defect density associated with small-diameter commercial Pt NP/C has also led to problems with relatively poor durability and stability because defect sites are more susceptible to oxidation and dissolution.<sup>26–28</sup>

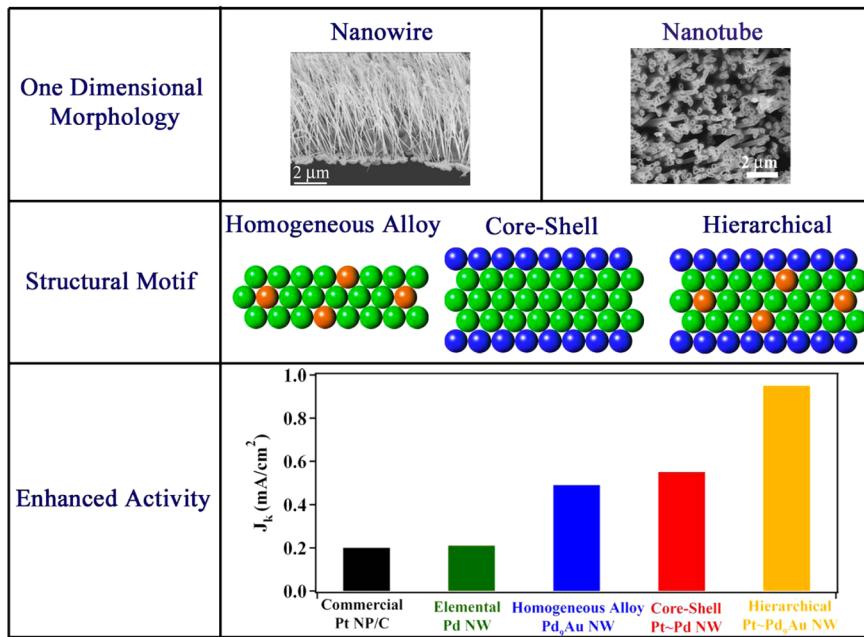
The inherent technological and performance shortfalls associated with elemental Pt NP/C have sparked great interest in designing more efficient electrocatalysts by tuning relevant synthetic and structural parameters.<sup>7–10,29,30</sup> One strategy is to create architectural alternatives to standard, spherical nanoparticles. Specifically, improvements in activity have been achieved by judiciously manipulating the shape of symmetrical nanoparticles in order to produce faceted cubes and octahedra composed of Pt and Pd.<sup>31–34</sup> Highly active catalysts have also been prepared by rationally manipulating the chemical composition so as to include homogeneous alloy-type formulations,<sup>9,13,35–38</sup> hierarchical core–shell structures,<sup>39,40</sup> and platinum monolayers supported on elemental and alloy nanoparticles.<sup>41,42</sup> Although tangible gains have been achieved in the continued development of the nanoparticle motif, generating viable, permanent solutions to many of these inherent performance

Received: September 18, 2012

Accepted: October 25, 2012

Published: November 6, 2012





**Figure 1.** A schematic representation of how the ORR performance of 1D nanostructures such as NWs and NTs (top) can be enhanced by rationally manipulating the composition and structure so as to include core–shell motifs, alloy-type compositions, and hierarchical structures (middle). In the case of Pd-based NWs, the plot of area-normalized ORR activity (bottom) demonstrates that significant enhancements of as much as 5-fold can be achieved by rationally optimizing the structure and composition of as-prepared NWs.

issues continues to remain elusive, particularly in the context of catalyst durability.

By contrast with zero-dimensional (0D) nanoparticulate motifs, 1D motifs represent an exciting and promising structural paradigm, which may solve many of the inherent technological shortfalls associated with Pt NP/C.<sup>7,10,43</sup> Nanostructures possessing 1D morphologies are characterized by their unique anisotropic structure, which possesses several properties that are inherently beneficial to efficient ORR performance.<sup>4,5</sup> For example, the anisotropic structure of 1D noble metal nanostructures leads to the preferential surface exposure of smooth, defect-free, low-energy facets.<sup>44</sup> These intrinsic structural and electronic properties are collectively expected to culminate in a weakened interaction with adsorbed oxygen species and to delay passivation of the nanostructure’s surface to higher potentials, thereby effectively reducing the overpotential necessary for high ORR kinetics.<sup>7</sup> Furthermore, the relatively low defect density associated with 1D structures also represents a promising route toward achieving increased durability because these structures are significantly less susceptible to both dissolution and ripening.<sup>45,46</sup>

Recently, several reports have shown that both elemental Pt and Pd nanowires (NWs) and nanotubes (NTs) consistently maintain improved activity and durability as compared with analogous NP/C motifs.<sup>34,46–55</sup> Not surprisingly, the intrinsic and outstanding performance of 1D NWs and NTs has been additionally enhanced by further tailoring the chemical composition and physical structure of these catalysts. Recently, NWs and NTs have been prepared with a wide range of bimetallic and ternary compositions, wherein metals such as Cu, Au, and Fe are combined with Pt or Pd.<sup>34,46,56–63</sup> In addition, our group has pioneered the development of high-quality core–shell-type NWs prepared by depositing Pt monolayer (Pt<sub>ML</sub>) shells onto elemental Pd<sup>64–66</sup> as well as more sophisticated Pd<sub>1-x</sub>Au<sub>x</sub><sup>56,57</sup> bimetallic NW cores, leading to outstanding Pt mass activities (i.e. of up to 2.54  $\text{A}/\text{mg}_{\text{Pt}}$ ), representing a 10-fold increase over the corresponding values associated with commercial

Pt NP/C analogues (0.10–0.20  $\text{A}/\text{mg}$ ). The evolution of the development of Pd-based nanowires toward advanced hierarchical structures is presented schematically in Figure 1.

Although noble metal nanowires have been widely demonstrated in recent literature to maintain significantly better activity and durability than commercial Pt NP/C, several critical challenges remain in their practical application as feasible commercial catalysts.

Although noble metal nanowires have been widely demonstrated in recent literature to maintain significantly better activity and durability than commercial Pt NP/C, several critical challenges remain in their practical application as feasible commercial catalysts. For example, 1D nanostructures possess inherently lower specific surface areas as compared with 0D spherical particles of the same diameter. Thus, the greatly enhanced specific activities observed in these anisotropic systems may not necessarily lead to corresponding enhancements in terms of mass-specific performance. Although several promising examples in the literature have corroborated the reproducibility of enhanced platinum group metal (PGM)-normalized activities in 1D structures,<sup>56,59,64</sup> the mass activities typically observed in existing NW and NT electrocatalyst systems are actually similar to what has been correspondingly observed for Pt NP/C. Therefore, a key step in designing practical 1D catalysts will be to minimize the necessary precious metal loading while simultaneously continuing to improve the inherent activity of these materials.

Additionally, the goal of achieving enhanced performance in 1D nanostructures is further complicated by the fact that the

origin of electrocatalytic enhancement, as a result of the unique anisotropic structure, remains elusive. This issue is particularly apparent in multimetallic 1D catalysts, wherein both morphology and chemical composition mutually and synergistically contribute to improved performance. Therefore, a key step in terms of producing practical 1D electrocatalysts is to probe ORR performance as a function of both particle size and composition. This endeavor is important not only to gain critical insights into the correlation between structure and activity but also, more practically, to establish a means of reducing Pt content and overall precious metal loading in functional electrocatalysts because, presumably, both catalyst size and composition can be further optimized. For example, decreasing the diameter of a NW catalyst of a fixed length by a factor of 2 can more than double the effective specific surface area expected, thereby leading to plausibly greater improvements in PGM utilization.

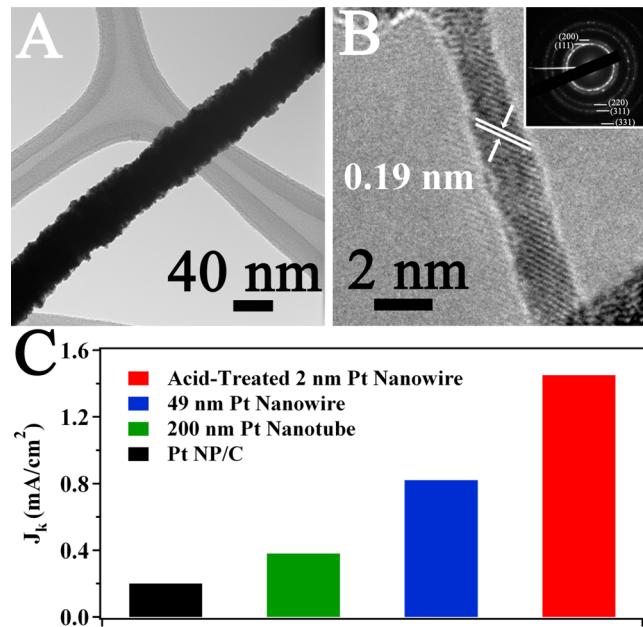
In this Perspective, we examine both the recent and complementary theoretical and experimental progress aimed at precisely deducing the nature of the complex interplay among size, chemical composition, and electrocatalytic performance in high-quality elemental and bimetallic 1D noble metal nanowire systems, with an emphasis on achieving efficient and sustainable methods for catalyst preparation. In terms of catalyst dimensions, an interesting and measurable size-dependent trend emerges in the case of elemental Pt and Pd NWs as well as in more complex hierarchical core–shell Pt–Pd and Pt–Pd<sub>1-x</sub>Au<sub>x</sub> NWs. In fact, outstanding enhancements in catalyst performance are measured when the diameter of 1D nanowire electrocatalysts is purposely decreased into the ultrathin size regime. In a similar context, we have considered the role of composition in 1D electrocatalysts and noted significant composition-dependent enhancements in activity and durability in high-quality, bimetallic Pd<sub>1-x</sub>Au<sub>x</sub> and Pd<sub>1-x</sub>Pt<sub>x</sub> NWs. A key finding that is apparent from these experimental results is that widely seen behavioral trends in the composition- and size-dependent performance for 0D nanoparticle-based catalysts do not hold in the case of 1D architectures because of the patently unique structural and electronic effects associated with their anisotropic structures.

As a culmination of our efforts to take advantage of these intrinsic structure–activity correlations, our group developed a morphology-, size-, and composition-optimized Pt–Pd<sub>2</sub>Au NW electrocatalyst with an ultrathin 2 nm diameter, which possessed outstanding Pt mass and PGM activities of 2.56 A/mg<sub>Pt</sub> and 0.64 A/mg<sub>PGM</sub>, respectively, surpassing the activity of conventional state-of-the-art Pt NP/C by more than 10-fold. This exciting result demonstrably confirmed that the fundamental insights gained into the intimate correlation between size, shape, composition, and catalyst performance can lead to very practical improvements in terms of both catalyst efficiency and cost-effectiveness. In this context, we discuss a plausible vision for pursuing future and potentially radically new directions in the development of 1D catalysts.

**Size-Dependent Electrocatalytic Performance in Elemental Platinum and Palladium Nanowires.** Elemental platinum and palladium represent exciting systems to examine size-dependent phenomena in 1D structures because the electrocatalytic performance of these noble metal systems has been well-characterized in both bulk and 0D catalytic morphologies. Therefore, commercial Pt NP/C and Pd NP/C can serve as a useful reference system with predictable activity and durability. Recently, our group has systematically investigated the size-dependent performance in these elemental systems by tuning the diameter of high-quality 1D nanostructures from the submicrometer range

(1000 >  $d$  > 100 nm) to the ultrathin range ( $d$  < 5 nm) and measuring the corresponding ORR performance.<sup>52,64,65</sup>

To prepare high-quality submicrometer and nanosized Pt and Pd nanostructures with 1D morphologies, we employed a reasonably straightforward and highly efficient template-based technique under ambient, catalyst-free, and surfactantless conditions so as to prepare crystalline NWs and NTs with predictable diameters.<sup>55,57,65</sup> For example, a representative Pt NW with a diameter of 49 nm is shown in Figure 2A. In prior reports,<sup>57,65</sup>



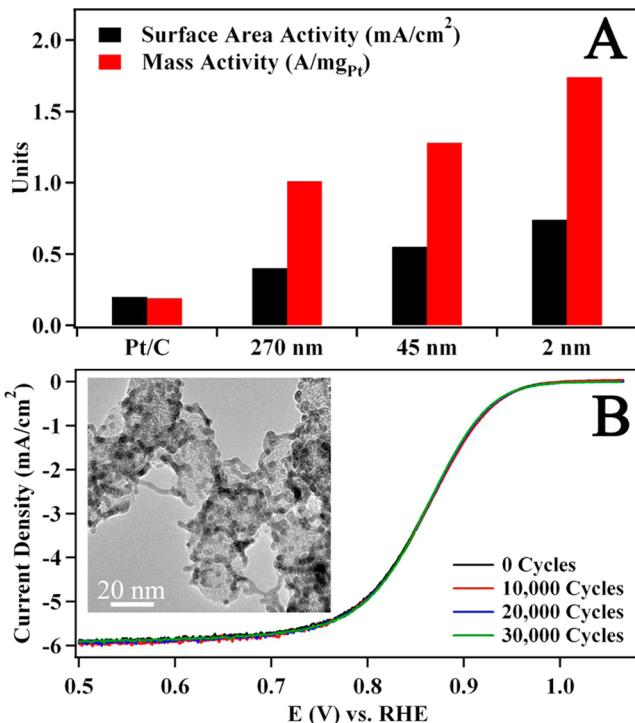
**Figure 2.** Representative TEM images collected from individual isolated Pt NWs possessing diameters of 49 (A) and 2 nm (B). A representative selected area electron diffraction pattern collected from an ensemble of individual 2 nm NWs is shown as an inset. The size-dependent trend in 1D Pt nanostructures of specific ORR activity measured at 0.9 V with commercial Pt NP/C serving as a commercial reference system is illustrated in (C).

we have demonstrated that the growth of these NWs proceeds via a unique growth mechanism within the spatially confined pores of commercially available filter membranes, leading to the formation of highly faceted, single-crystalline NWs, in most cases. The apparent roughened outer surface texture of these nanowires arises from the inherent structural imperfections associated with the internal pore walls of the template itself. However, a detailed HRTEM examination<sup>65</sup> confirms that the NWs are indeed highly faceted and expose catalytically desirable low-energy (111) and (100) facets.

To achieve nanowires with ultrathin diameters, we employed ambient, solution-based techniques<sup>52,64</sup> to prepare high-quality Pt and Pd nanowires with predictable diameters ranging between 1 and 2 nm. In the case of our ultrathin Pt and Pd NWs, we used a variety of surface treatments, including (a) an acid etch<sup>52</sup> in the case of the Pt NWs and (b) a UV-ozone treatment coupled with a selective CO adsorption process<sup>64</sup> in the case of the Pd NWs, to remove residual impurities and defects while also suitably exfoliating as-prepared nanowires. Characterization of these ultrathin Pt NWs shown in Figure 2B, for example, confirms that they are composed of multiple, discrete, interconnected, single-crystalline subunits oriented axially along the NW itself. A representative single-crystalline segment is shown in Figure 2B, which highlights the lattice planes of FCC platinum. The corresponding selected-area electron diffraction

(SAED) pattern (inset to Figure 2B), which has been indexed, is suggestive of the presence of single-crystalline segments composing the whole ensemble of NWs produced.

Much like the as-prepared Pt NWs, extensive structural characterization<sup>64,65</sup> of our Pd NWs (i.e., inset to Figure 3B) has



**Figure 3.** The surface area and Pt mass-normalized ORR activities (A) of core–shell type-Pt–Pd NWs at 0.9 V are shown by comparison with Pt NP/C. Polarization curves obtained from ultrathin Pt–Pd NWs (B) are depicted over the course of 30 000 cycles of an extended durability test. A representative TEM image of the ultrathin Pd NWs before Pt<sub>ML</sub> deposition is shown as an inset to (B).

verified that our as-synthesized elongated NWs are effectively composed of discrete, relatively defect-free single-crystalline modular segments, which constitute the active catalytic components of these materials. Additional detailed discussion of the crystallinity, surface texture, and growth mechanism of our elemental NWs has been presented elsewhere in prior reports.<sup>7,52,55–57,64,65,67</sup> Nevertheless, the key and fundamental point to underline is that our group has succeeded in developing efficient sustainable synthesis methods to produce high-quality NWs, whose size, morphology, and composition can be readily and reproducibly controlled, such that we have high confidence in the validity of the catalytic trends, described in this Perspective.

To examine the ORR performance of our as-prepared Pt NW catalysts, polarization curves were obtained in oxygen-saturated 0.1 M HClO<sub>4</sub> electrolyte of the submicrometer ( $200 \pm 20$  nm) NTs, nanosized ( $49 \pm 8$  nm) NWs, and ultrathin ( $1.3 \pm 0.4$  nm) NWs. The kinetic current measured at 0.9 V (all potentials reported in this manuscript are measured with respect to the reversible hydrogen electrode) was normalized to the electrochemically accessible surface area (ESA) in order to calculate the area-normalized kinetic current density or so-called specific activity. Interestingly, the measured specific activities of our NW systems, shown in Figure 2C, denoted a remarkable size-dependent enhancement in electrocatalytic ORR performance. Specifically, the unsupported ultrathin Pt NWs possessed an

exceptional specific activity of  $1.45$  mA/cm<sup>2</sup>, representing nearly a 2-fold and 4-fold enhancement over the nanosized ( $0.82$  mA/cm<sup>2</sup>) and submicrometer ( $0.38$  mA/cm<sup>2</sup>) NWs, respectively. To verify the outstanding performance of our as-treated ultrathin Pt NWs, the electron exchange parameter (*B* factor) was experimentally determined to be  $0.096$  mA·s<sup>-1/2</sup> from a series of Koutecky–Levich curves, a result that is in excellent agreement with the calculated value for an ideal  $4e^-$  process ( $0.092$  mA·s<sup>-1/2</sup>). These data suggested that the mechanism of oxygen reduction closely matched that of the ideal  $4e^-$  process and that the process retained first-order kinetics, both of which are desirable for ORR catalysis.<sup>68</sup>

Given the quantifiable and significant size-dependent enhancement in elemental Pt NWs, similar experiments were conducted on analogous submicrometer ( $270 \pm 45$  nm), nanosized ( $45 \pm 9$  nm), and ultrathin ( $2.2 \pm 0.8$  nm) Pd NWs. Our ultrathin Pd NWs were purposefully supported onto Vulcan XC-72R carbon, shown as an inset to Figure 3B, so as to improve the dispersion of the NWs and to optimize precious metal utilization. Not surprisingly, the specific activity measured at 0.8 V again drew attention to an increase in ORR kinetics from  $1.84$  to  $3.62$  mA/cm<sup>2</sup> as the diameter was systematically decreased from  $270$  to  $2$  nm. Additionally, it is important to note that as-prepared ultrathin Pd NWs also consistently outperformed commercial Pd NP/C ( $1.80$  mA/cm<sup>2</sup>), once more demonstrating the excellent intrinsic performance in catalysts, possessing 1D morphologies. The unambiguous size-dependent enhancement in performance observed in the Pt and Pd NW systems suggests that this phenomenon is quite generalized in noble metal NW systems.

The issue of a size-dependent enhancement raises an interesting question in terms of ORR electrocatalysis because the experimental trend in 1D systems contrasts starkly with that observed in analogous 0D nanoparticulate systems.

The issue of a size-dependent enhancement raises an interesting question in terms of ORR electrocatalysis because the experimental trend in 1D systems contrasts starkly with that observed in analogous 0D nanoparticulate systems. In the case of Pt and Pd NP/C, decreases in particle size tend to result in lower activity as a result of size-dependent variations in the electronic properties of the particle as well as an increased density of defect sites and low coordination atoms (LCAs).<sup>24</sup> By contrast with nanoparticles, our collective experimental results including CV and HRTEM data confirm that the ultrathin NWs maintain well-ordered (111) and (100) facets, possessing very few defect sites as compared with their nanoparticulate analogues.<sup>52,64,65,67</sup> Accomplishing this feat necessitated the use of basic amine-terminated surfactants such as octadecylamine (ODA) and triethylamine (TEA) to selectively promote the exposure of the (100) facet and lead to the desirable ⟨111⟩ growth direction (cf. Figure 2B) in our Pd and Pt NWs, respectively. Moreover, cathodic and anodic features typically associated with (110)-type defect sites, which are clearly observed in Pt NPs, are almost indiscernible in the corresponding data associated with our acid-treated ultrathin Pt nanowires.<sup>52,67</sup> Additional electrochemical

characterization of the Pd NWs by means of CV and carbon monoxide (CO) stripping experiments also supports the notion that these wires are relatively defect-free.<sup>64,65</sup> The key point to emphasize is that our 1D motifs do not necessarily suffer from higher defect densities and LCAs as the diameter is decreased into the ultrathin size regime, and this observation may explain the general enhancement in activity, characteristic of the 1D morphology.

Nevertheless, the size-dependent performance is neither completely nor solely explained by the relatively defect-free nature of 1D catalysts. More recently, the unique structural and electronic properties inherent to NWs have been postulated to be a key element in the origin of their size-dependent performance. That is, in terms of size-dependent electronic and structural effects, several theoretical<sup>69–71</sup> and experimental<sup>72–74</sup> studies have asserted that noble metal nanowires (e.g., Pt, Pd, Ir, Au etc.) undergo a characteristic contraction of the surface atoms as the nanowire is decreased into the ultrathin regime, particularly when the NW diameter is below 2 nm. Contractions of the surface atoms are predicted to cause a down shift of the d-band center to lower energies and thereby result in significantly weakened interactions with adsorbates, such as CO and oxygen species.<sup>14,41,75</sup> In fact, recent theoretical work performed by Matanović et al. has provided for excellent DFT evidence in favor of a size-dependent enhancement in ORR activity as the diameter of 1D platinum nanostructures is decreased below 2 nm.<sup>76</sup> Recently, X-ray photoelectron spectra (XPS) data collected from ultrathin 2 nm Pt NWs by Guo and co-workers have yielded the first spectroscopic evidence of a d-band shift in ultrathin NWs prepared analogously, as indicated by the noteworthy lower binding energies for the Pt 4f<sub>7/2</sub> signal in the NWs as compared with commercial Pt NPs.<sup>74</sup>

The CV data obtained from our submicrometer and ultrathin Pt NWs reveal that the oxide reduction peak is shifted to higher potentials by ~10 mV as the size of the NWs is decreased into the ultrathin regime. Not only is this observation in agreement with the XPS results, but also it provides strong evidence of a systematic decrease and weakening in the interaction with adsorbates as the NW diameter is decreased into the ultrathin regime. In the case of our Pd NW systems, we used CO stripping voltammetry to probe the relative interactions with adsorbates. As expected, the measured CO stripping peak was observed to shift negatively from 0.925 to 0.906 V as the size of the NWs was decreased from 270 to 2 nm. Thus, the CO stripping results obtained for ultrathin Pd NWs, the oxide reduction results gathered for Pt NWs, and the XPS results collected for ultrathin Pt NWs and NPs collectively provide for a strong argument for a surface reconstruction process and a corresponding down shift in the d-band center, thereby resulting in an enhanced ORR performance. Furthermore, the excellent CO stripping kinetics observed may also render these ultrathin catalysts as potentially effective alcohol oxidation catalysts.<sup>67,74</sup> Recently, Brankovic and co-workers have deduced interesting trends in hydrogen oxidation activity in the case of Pt submonolayers (Pt<sub>SML</sub>) supported on Au(111) single-crystalline surfaces as the sizes of the Pt<sub>SML</sub> clusters are varied, thereby highlighting the unique electrocatalytic behavior associated with these core–shell-type electrocatalysts.<sup>77</sup>

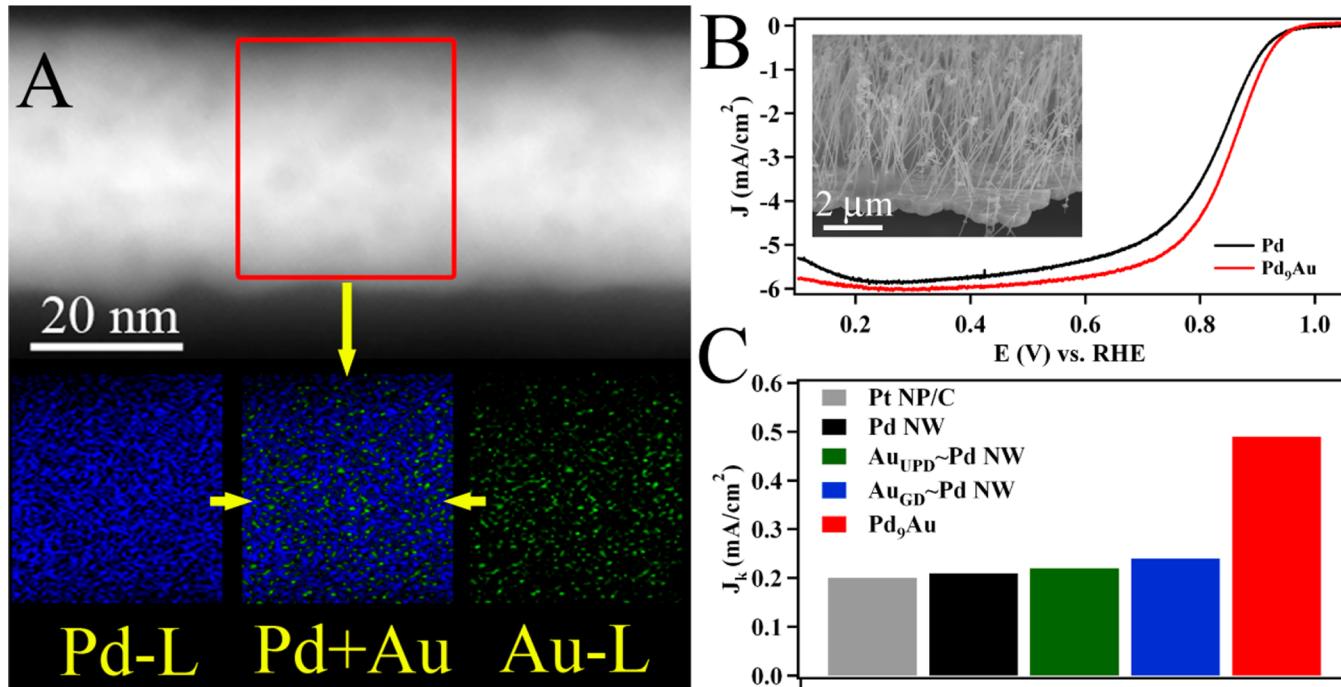
**Size-Dependent Performance in Pt Monolayer Shell–Pd NW Core Nanostructures.** Recently, the use of core–shell architectures incorporating Pt monolayers or skins has contributed to significant reductions in platinum loading and utilization because expensive precious metals can be replaced by more abundant and less expensive metals in the catalytically inactive core of the material.<sup>39,41</sup> Although extensive work has been dedicated to manipulating the chemical composition of nanoparticulate cores,

the outstanding performance and unique size-dependent phenomena observed in elemental NW systems suggest that these metallic motifs may represent a relatively novel and significantly improved core material architecture. In this context, our group has rationally developed 1D core–shell catalysts, utilizing Pd NWs as high-performance supports for the subsequent deposition of coaxial, homogeneously uniform Pt<sub>ML</sub> shells and correlated the size dependence of the Pd NW core with the corresponding ORR activity of the resulting composite core–shell structure.<sup>64,65</sup>

Experimentally, the Pt<sub>ML</sub> shells were deposited by first electrodepositing a conformal Cu monolayer utilizing underpotential deposition (UPD) and subsequently displacing the Cu adatoms with Pt via simple galvanic displacement.<sup>42</sup> The specific and platinum mass activities (Figure 3A) were found to increase significantly from 0.40 mA/cm<sup>2</sup> and 1.01 A/mg<sub>Pt</sub> to 0.74 mA/cm<sup>2</sup> and 1.74 A/mg<sub>Pt</sub> as the diameters of the nanowires were decreased from 270 to 2 nm, respectively. Interestingly, the CVs obtained from the various NW catalysts also displayed a complementary shift in the oxide reduction feature to higher potentials (788–803 mV). This finding suggested that the smaller NW cores promote weaker interactions with the oxygen adsorbate and the Pt<sub>ML</sub> shell, thereby leading to more facile interfacial ORR kinetics.

To further generalize the excellent performance of our as-prepared materials, we note that the activity of the ultrathin Pt<sub>ML</sub>–Pd NW core–shell catalyst clearly surpassed that of the state-of-the-art Pt<sub>ML</sub>–Pd NP catalyst (0.5 mA/cm<sup>2</sup>, 0.9 A/mg),<sup>78</sup> thereby confirming the enhanced performance of 1D core supports for Pt<sub>ML</sub> catalysts. In more recent work, similar results have been independently observed by Bliznakov et al.<sup>66</sup> in the case of Pt<sub>ML</sub>–Pd nanorods. Promising results have also been noted in Pt@Pd NW systems, prepared by a chemical deposition process. Nonetheless, additional optimization of the Pt coating will likely be necessary in order to improve PGM mass performance.<sup>79</sup>

The observed activity trend in our as-prepared Pt<sub>ML</sub>–Pd NW core–shell catalysts is a noteworthy result and demonstrates that the size-dependent ORR enhancement in 1D systems can be further generalized from specific 1D elemental systems (e.g., Pt and Pd) to broader classes of more active, state-of-the-art 1D core–shell catalysts. Interestingly, the activity data in the case of Pt<sub>ML</sub>–Pd NW catalysts are in direct contrast with similar results, obtained for analogous 0D Pt<sub>ML</sub>–Pd NP catalysts, measured by Adzic and co-workers.<sup>78</sup> In the existing literature, the enhanced performance in Pt<sub>ML</sub> catalysts has been widely attributed to the strain induced in the Pt<sub>ML</sub> by the Pd substrate and a so-called “ligand” effect, which mutually contribute to more facile ORR kinetics.<sup>80</sup> On the basis of our results with elemental NWs, the size-induced structural and electronic properties observed in the ultrathin NWs are expected to increase the synergistically beneficial interactions between the Pd core and the Pt<sub>ML</sub> shell, thereby leading to correspondingly favorable improvements in ORR activity and durability. From a practical, device-oriented perspective, the generalized size-dependent enhancement in NW catalysts is extremely useful because significantly enhanced activities can be nominally achieved with 100-fold smaller catalyst diameters. Hence, the coupled effect of the increased activity and the high surface-area-to-volume ratio in ultrathin catalysts gives rise to an outstanding PGM activity, measured to be 0.55 A/mg<sub>PGM</sub> in the ultrathin 2 nm Pt<sub>ML</sub>–Pd NWs, which represents a definitive and reproducible improvement with respect to even state-of-the-art Pt<sub>ML</sub>–Pd NP/C (0.25 A/mg<sub>PGM</sub>) systems.



**Figure 4.** Structural characterization of the composition and homogeneity of single-crystalline Pd<sub>9</sub>Au NWs is shown, including a HAADF image of a representative NW (A, top). Immediately below the HAADF image is a spatially resolved EDAX map (A, bottom), obtained from the area denoted by the red square. Polarization curves associated with the Pd<sub>9</sub>Au and Pd NWs are also shown (B) with a SEM image of a free-standing Pd<sub>3</sub>Pt<sub>7</sub> NW array (inset), highlighting the uniformity of the NWs. Experimentally determined ORR kinetic currents normalized to the catalyst surface area are displayed (C) for the Pd<sub>9</sub>Au NWs by comparison with commercial Pt NP/C, as-prepared Pd NWs, and Pd NWs modified by two distinctive galvanic displacement protocols.

In the context of developing practical commercial catalysts, the high initial activity of these catalysts must be accompanied by reasonable stability and durability over the lifetime of the catalyst within a working fuel cell device. Accordingly, we performed an accelerated durability test, as defined by the U.S. Department of Energy, on our as-prepared ultrathin Pt<sub>ML</sub>–Pd NWs. This trial consisted of subjecting these materials to the “wear-and-tear” rigors associated with 30 000 electrochemical cycles from 0.6 to 1.0 V in a 0.1 M HClO<sub>4</sub> solution medium, maintained under ambient conditions. Polarization curves obtained over the course of this test are highlighted in Figure 3B and confirmed the excellent durability of these hierarchical catalysts with essentially no decline in either the half-wave potential ( $\sim 3$  mV) or the diffusion-limited current of the polarization curve after 30 000 cycles.

TEM images of the Pt<sub>ML</sub>–Pd NW catalysts after the full 30 000 cycles of the test revealed that the long nanowires are largely converted into wire fragments with lengths that are commensurate with the single-crystalline subunits observed in as-prepared Pd NWs.<sup>64</sup> From these results, it is evident that these anisotropic single-crystalline NW fragments represent the active subunits of the overall catalyst and are preserved as a consequence of the uniquely advantageous properties of 1D structures, such as the presence of fewer surface defect sites.<sup>7</sup> High-performance 0D Pt NP/C were also subjected to the same durability test protocol, and the data<sup>64</sup> substantiate a significant loss in both the half-wave potential and the diffusion-limited current, thereby suggesting significant particle dissolution and ripening and confirming that the presence of both a 1D morphology and core–shell structure synergistically lead to better activity and durability.

**Composition-Dependent Performance in Pd<sub>1-x</sub>Au<sub>x</sub> NWs.** A key objective in advancing the performance of elemental platinum

group metals as ORR electrocatalysts has been to rationally control their chemical composition so as to manipulate their corresponding electronic and structural properties for enhanced activity. As discussed in the previous section, core–shell-type structures combine two or more elements into hierarchical configurations, thereby resulting in enhanced performance. In addition, sizable electrocatalytic improvements have also been achieved in bimetallic and ternary alloy systems, wherein the elemental composition is uniform throughout the entire catalyst.<sup>1,2</sup>

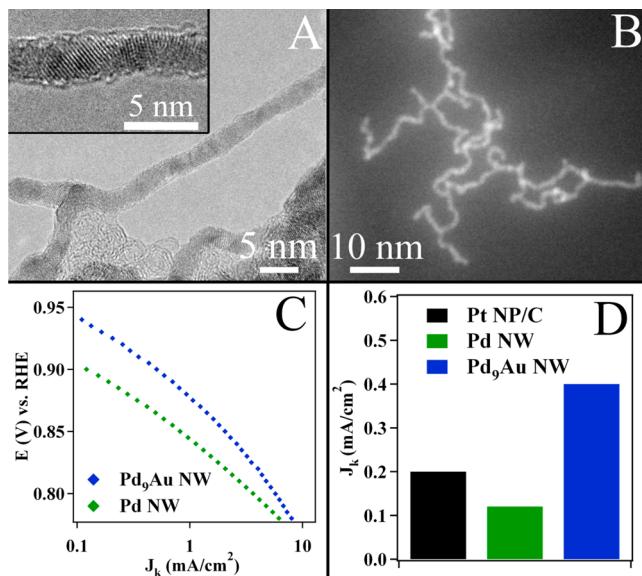
Not surprisingly, this principle has been applied toward the preparation of 1D electrocatalysts with chemical compositions including but not limited to PdPt,<sup>34,46,57</sup> PdCu,<sup>58</sup> PdAu,<sup>56,57</sup> PtFe,<sup>59,60</sup> and PtAu,<sup>63</sup> thereby leading to detectable enhancements in performance in every case. For example, Li and co-workers have prepared Pt<sub>1-x</sub>Fe<sub>x</sub> NWs with ultrathin diameters of  $\sim 3$  nm, which possess noticeable enhancements in mass activity as compared with commercial Pt NP/C, even after a mild durability test.<sup>59</sup> However, a lingering challenge that remains in the further development of these multimetallic 1D catalysts has been to systematically examine the role of chemical composition in the context of complementing and strengthening the already distinctive properties of 1D architectures. This issue is important because despite their improved specific activity, many of these bimetallic 1D systems continue to maintain mass activities that fall within the range, typically measured for commercial 0D Pt NP/C (0.1–0.2 A/mg).

To address this deficiency, our group has rationally examined the role of chemical composition in high-quality 1D nanowire systems consisting of homogeneous Pd<sub>1-x</sub>Au<sub>x</sub> alloys. This particular bimetallic system is of broad interest because this chemical composition is highly active toward ORR without any Pt loading whatsoever. High-quality, alloyed Pd<sub>1-x</sub>Au<sub>x</sub> NWs with nanoscale diameters of  $50 \pm 9$  nm were synthesized

as either individual NWs or as free-standing NW arrays (inset to Figure 4B), utilizing a modification of the template-based technique employed in the synthesis of our single-crystalline Pd NWs.<sup>56,57</sup>

This synthetic approach is uniquely valuable because the chemical composition of the alloyed NW can be controlled over the entire regime probed (e.g.  $x = 0\text{--}1$ ). In this case, our as-prepared  $\text{Pd}_x\text{Au}$  NWs are largely single-crystalline by analogy with their elemental (i.e., Pd NW) counterparts because a similar growth mechanism predominates in the formation of these NWs.<sup>57</sup> Moreover, a suite of structural characterization techniques, including high-angle annular dark field (HAADF) imaging and spatially resolved energy dispersive X-ray spectroscopy (EDAX) mapping on representative NWs, shown in Figure 4A, reveals that the gold additive is incorporated homogeneously throughout the  $\text{Pd}_{1-x}\text{Au}_x$  alloy NWs. Surprisingly, polarization curves (Figure 4B) obtained from the bimetallic  $\text{Pd}_x\text{Au}$  NWs highlighted significantly increased ORR kinetics by comparison with analogous elemental Pd NWs. In effect, the measured activity of the bimetallic  $\text{Pd}_x\text{Au}$  NWs ( $0.49 \text{ mA/cm}^2$ ) was significantly enhanced as compared with Pd NWs ( $0.21 \text{ mA/cm}^2$ ), which served as a reference system for elemental NWs. Notably, the activity of the  $\text{Pd}_x\text{Au}$  NWs not only surpassed that of analogous elemental Pd NWs but also significantly outperformed Pt NP/C ( $0.20 \text{ mA/cm}^2$ ), without any discernible Pt loading present.

Recently, we have also confirmed a similar composition-dependent enhancement in the case of ultrathin  $\text{Pd}_{1-x}\text{Au}_x$  NWs. Specifically, carbon-supported  $\text{Pd}_{1-x}\text{Au}_x$  NWs possessing homogeneous alloy-type compositions and ultrathin diameters ( $2.0 \pm 0.5 \text{ nm}$ ) were prepared by employing our ambient solution-based technique.<sup>56</sup> Representative HR-TEM and HAADF images of collections of these as-prepared composites are shown in Figure 5A



**Figure 5.** High-resolution TEM images (A) of an individual  $\text{Pd}_9\text{Au}$  NW/C and a HAADF image (B) from a representative collection of unsupported NWs. Also shown are the potential versus specific activity ( $E$  versus  $J_k$ ) plot (C) and the measured area-normalized ORR kinetic current densities (D), which highlight the enhanced performance of the alloyed  $\text{Pd}_9\text{Au}$  NWs by comparison with Pd NWs and Pt NP/C.

and B, respectively. On the basis of these images, the  $\text{Pd}_{1-x}\text{Au}_x$  NWs are similar in structure to elemental Pd NWs and are composed of discrete, interconnected single-crystalline segments.

However, by contrast with their elemental Pd analogues, the bimetallic  $\text{Pd}_{1-x}\text{Au}_x$  NWs required a less rigorous purification treatment, thereby underscoring an apparent advantage of this system in terms of scalability and processability.<sup>56,64</sup> Notwithstanding, the comparatively similar crystallinity and surface texture of our bimetallic and elemental ultrathin NWs highlights the crucial role of composition in determining the observed electrocatalytic performance.

The specific ORR activities measured from the bimetallic  $\text{Pd}_9\text{Au}$  and elemental Pd NWs as well as commercial Pt NP/C catalysts are summarized in Figure 5D, which essentially confirmed that these nanowires retained a high specific activity of  $0.40 \text{ mA/cm}^2$ . The improved performance was readily apparent in a plot of the potential versus the kinetic current density, or the so-called  $E$  versus  $J_k$  plot (Figure 5C), which showed that the enhanced specific activity is effectively preserved over a broad range of potentials as compared with elemental Pd NW/C. Thus, the ultrathin  $\text{Pd}_9\text{Au}$  NWs not only yielded better performance than Pt NP/C ( $0.20 \text{ mA/cm}^2$ ), but also, more importantly, these results proved that the intrinsic composition-dependent enhancements associated with 1D  $\text{Pd}_{1-x}\text{Au}_x$  are relatively generalized over a broad range of catalyst dimensions.

From a fundamental catalyst design perspective, a key question that emerges is the following. What is the origin of the observed performance enhancement in alloyed Pd–Au electrocatalysts with anisotropic 1D morphologies? In prior literature, the composition-dependent enhancement performance toward ORR and AOR in Pd–Au electrocatalysts has been reasonably ascribed to the presence of bimetallic Pd–Au pair sites at the catalytic interface in some cases<sup>81</sup> and, in other studies, to the unique electronic and structural properties<sup>82,83</sup> of homogeneous  $\text{Pd}_{1-x}\text{Au}_x$  alloys. To resolve this interesting question in 1D ORR electrocatalysts, our group purposefully modified our 50 nm Pd NWs by two different galvanic displacement (GD) protocols in order to create Au@Pd NWs with bimetallic Pd–Au sites localized at the catalytic interface. Interestingly, the measured activities (Figure 4C) of the  $\text{Au}_{\text{UPD}}\text{-Pd}$  NWs, possessing clusters of Au at the interface ( $0.22 \text{ mA/cm}^2$ ), and  $\text{Au}_{\text{GD}}\text{-Pd}$  NWs, associated with a mixture of Au clusters and porous PdAu ( $0.24 \text{ mA/cm}^2$ ), were essentially identical to that of elemental Pd NWs ( $0.21 \text{ mA/cm}^2$ ). Collectively, it is clear that the enhanced performance in the bimetallic  $\text{Pd}_{1-x}\text{Au}_x$  NWs is only observed when the Pd and Au atoms exist as a chemically homogeneous alloy, whereas the coincidental presence and spatial proximity of Pd–Au pair sites at the catalytic interface do not necessarily lead to a noticeable activity enhancement.

The measured activity enhancement can be readily explained by the effect of Au in the  $\text{Pd}_{1-x}\text{Au}_x$  alloy NW, which has been shown to impart an increased electron density onto the Pd active sites, thereby rendering them as essentially “more noble”.<sup>61,83</sup> On this basis, the weakened interactions of the more noble Pd active sites with adsorbed oxygen species contribute to a more facile ORR kinetics and a better stability of the Pd NW toward structural dissolution. Not surprisingly, the weakened interaction of  $\text{Pd}_{1-x}\text{Au}_x$  NWs with respect to oxygen adsorbates is apparent in our CV results, which indicate that the surface oxide feature shifts positively by more than 40 mV as the gold content is increased to 30% in ultrathin  $\text{Pd}_{1-x}\text{Au}_x$  NWs. Moreover, the hydrogen adsorption and desorption ( $H_{\text{ads}}$ ) features observed in the ultrathin and nanosized  $\text{Pd}_9\text{Au}$  NWs are smoother and flatter, as compared with that of analogous Pd NWs, denoting data that may be indicative of a more active surface.

*Composition-Dependent Performance in  $\text{Pd}_{1-x}\text{Pt}_x$  NWs.* In addition to  $\text{Pd}_{1-x}\text{Au}_x$  alloys, homogeneous  $\text{Pd}_{1-x}\text{Pt}_x$  alloys have

also garnered significant interest as ORR electrocatalysts, because the substitution of Pt by more abundant and less expensive Pd results in discernible enhancements in both performance and durability. Recently, Yan and co-workers prepared bimetallic PtPd NTs and observed a specific activity that was 1.5-fold higher than that found for Pt NT analogues.<sup>46</sup> The importance of controlling chemical composition becomes more apparent in this instance because measurable enhancements in Pt mass activity are only achievable in the specific example of a bimetallic structure whose performance is discernibly superior as compared with that of commercial Pt NP/C. Although improved ORR kinetics have been observed, the precise origins of this phenomenon in unique bimetallic structures have remained particularly elusive because little work has been done to systematically correlate the nature of the relevant electrocatalytic performance with a broad range of chemical compositions in these 1D  $Pd_{1-x}Pt_x$  NW systems.

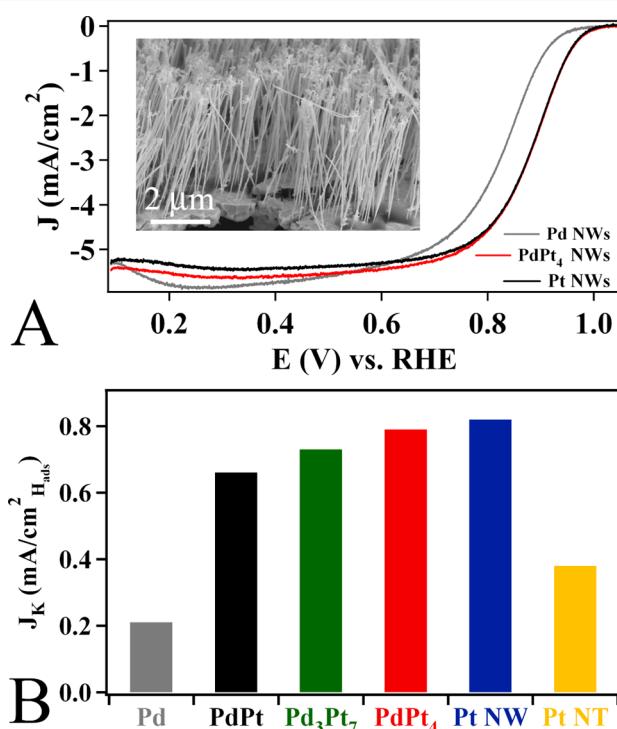
Therefore, to address this issue coherently, our group has prepared high-quality, alloy-type  $Pd_{1-x}Pt_x$  NWs with a span of compositions, including  $x = 0.5, 0.7$ , and  $0.8$ , utilizing the same ambient, aqueous-based, template-directed synthetic technique employed in the analogous synthesis of  $Pd_{1-x}Au_x$  NWs. A representative scanning electron microscopy (SEM) image of a free-standing array of  $Pd_3Pt_7$  NWs is shown as an inset to Figure 6A. CVs collected from as-prepared  $Pd_{1-x}Pt_x$  NWs

content was correspondingly varied, thereby highlighting a conspicuous composition-dependent trend in ORR activity.

Surprisingly, the high specific activity measured in the PtPd NWs is significantly enhanced with respect to commercial Pt NP/C ( $0.21\text{ mA/cm}^2$ ) and, more importantly, exceeds the value obtained with 200 nm Pt NTs, analogously prepared. Thus, it is evident that appreciably increased kinetics can be achieved in these alloyed bimetallic NWs while maintaining only 50% of the total Pt content of elemental catalysts. Although enhanced performance was observed in our as-prepared NWs, the polarization curves (Figure 6A) suggested that the measured activity of the  $PdPt_4$  NWs ( $0.79\text{ mA/cm}^2$ ) was essentially equivalent to that determined from the corresponding elemental Pt NWs ( $0.82\text{ mA/cm}^2$ ). This interesting finding contradicts the results typically obtained with PtPd NPs, which have tended to display an enhanced activity beyond that of elemental Pt NPs when the Pd content was between 10 and 30%.

In the case of 0D nanoparticulate systems, the enhanced performance of PtPd alloys has been largely attributed to the strain-induced contraction of the Pt atoms by the Pd dopant, which contributes to measurably smaller lattice parameters.<sup>84</sup> By contrast, the performance in nanoscale 1D Pt and Pd nanostructures has been found to be strongly dependent on the unique electronic and structural properties that arise from an observed size-induced contraction of the NW surface as the diameter is decreased to the nanoscale regime.<sup>52,65</sup> From the measured specific activity results, it is clear that the chemical composition not only influences the catalytic performance of Pt but also may affect the nature of the size-induced structural transformation in the alloy-type nanowire. In fact, prior DFT calculations performed on elemental Pt and Pd noble metal nanowires have shown that elemental Pt NWs are expected to undergo a more sizable strain-induced contraction as compared with Pd NWs.<sup>70</sup>

Thus, we believe that the incorporation of Pd may suppress, to some extent, the favorable size-induced contraction, thereby leading to a lower observed performance in the  $PdPt_4$  NW alloys as compared with that of the elemental Pt NWs. Interestingly, this same phenomenon may also explain the absence of any noticeable size-dependent electrochemical activity in Pt– $Pd_3Au$  NWs, discussed in more detail in the next section. Although further theoretical and experimental investigation of the influence of composition on the size-dependent structural properties of alloyed  $Pd_{1-x}Pt_x$  NWs is necessary, it is evident that trends established for the composition-dependent electrochemical performance of 0D NP systems are neither fully applicable nor transferable in accurately depicting the behavior of analogous 1D systems, which are governed to a greater extent by their patently unique anisotropic structure.

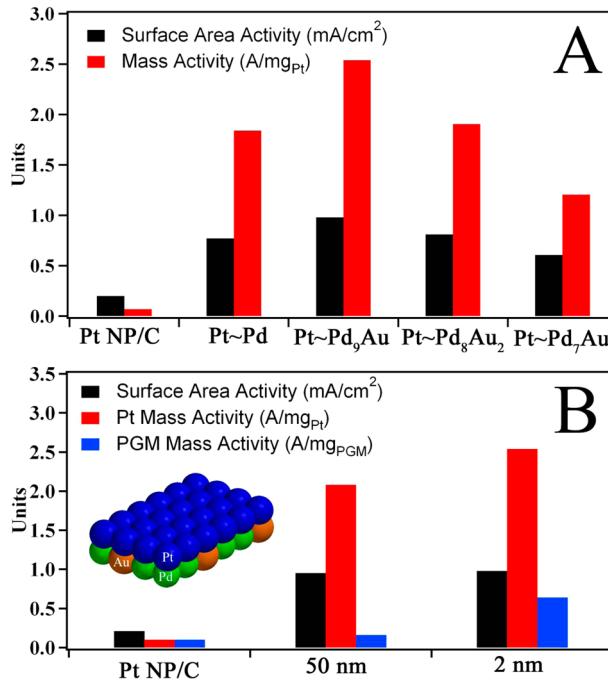


**Figure 6.** The composition-dependent performance of  $Pd_{1-x}Pt_x$  NWs by comparison with elemental Pt and Pd NWs, prepared analogously, is indicated. Polarization curves of the  $PdPt_4$  NWs are noted (A) by comparison with Pd and Pt NWs. A SEM image of a free-standing array of  $Pd_3Pt_7$  NWs is presented as an inset. The measured specific ORR activities (B) of the  $Pd_{1-x}Pt_x$  NWs (with  $x = 0, 0.5, 0.7, 0.8$ , and  $1$ ) are also displayed by comparison with previously reported Pt NTs.

suggested a well-defined transition in the structure of the  $H_{ads}$  and oxide regions that resembled those of the Pt NWs as the Pt content was increased from 50 to 80%. Moreover, the specific activity of these as-prepared  $Pd_{1-x}Pt_x$  nanowires (Figure 6B) demonstrably increased from  $0.64$  to  $0.79\text{ mA/cm}^2$  as the Pd

It is evident that trends established for the composition-dependent electrochemical performance of 0D NP systems are neither fully applicable nor transferable in accurately depicting the behavior of analogous 1D systems, which are governed to a greater extent by their patently unique anisotropic structure.

**Composition-Dependent Performance in Hierarchical Pt– $Pd_{1-x}Au_x$  NWs.** Given the high performance of the  $Pd_{1-x}Au_x$  NW system, we separately probed the effects of size and chemical composition of high-quality  $Pd_{1-x}Au_x$  NW cores on the performance of a conformal  $Pt_{ML}$  coating deposited at the NW surface.<sup>56,57</sup> To examine the role of composition, we used our ultrathin  $Pd_{1-x}Au_x$  NWs with a variety of chemical compositions (e.g.,  $x = 0, 0.1, 0.2$ , and  $0.3$ ) as high-quality substrates for subsequent  $Pt_{ML}$  deposition.<sup>56</sup> The specific activities of the  $Pt-Pd_{1-x}Au_x$  composites measured at  $0.9\text{ V}$  (Figure 7A) revealed that there is a distinctive “volcano-type”



**Figure 7.** The specific and mass-normalized ORR activities (A) obtained from core–shell  $Pt-Pd_{1-x}Au_x$  NWs are presented and illustrate a volcano-type trend in performance as the gold content of the alloy is increased to 30%. Also shown is the size dependence of ORR activity (B) in  $Pt-Pd_9Au$  NWs possessing core diameters of 50 and 2 nm. A schematic representation of a hierarchical alloy-type core– $Pt_{ML}$  shell structure is shown as an inset.

dependence of the measured ORR activity with respect to the chemical composition of the nanowires. Maximum kinetics were achieved in the  $Pt-Pd_9Au$  NW/C sample, which possesses an outstanding specific ( $0.98\text{ mA/cm}^2$ ) and platinum mass activity ( $2.54\text{ A/mg}_{Pt}$ ), far exceeding the corresponding measured activity values of commercial Pt NP/C (i.e.,  $0.20\text{ mA/cm}^2$  and  $0.10\text{ A/mg}_{Pt}$ ). In addition, the activity of the core–shell nanowires surpasses that of analogous  $Pt-Pd_{1-x}Au_x$  0D NP/C<sup>82,83</sup> ( $0.5\text{ mA/cm}^2$ ) by 2-fold, which again emphasizes the characteristic advantages of 1D architectures.

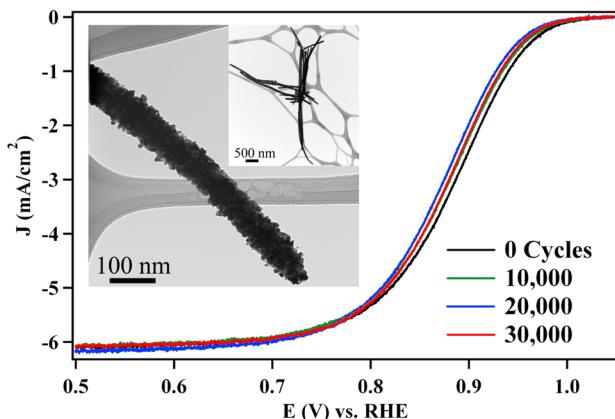
In terms of catalyst morphology, the volcano-type dependence of the measured ORR activity was also observed by Adzic and co-workers<sup>83</sup> in analogous  $Pt-Pd_{1-x}Au_x$  NP/C materials, with  $Pt-Pd_9Au$  representing the optimal composition for ORR kinetics. Although the NWs possess generally higher activities, the presence of a similar correlation between chemical composition and ORR activity of both NWs and NPs is evidence that the performance of the  $Pt_{ML}$  shell overlayer is largely governed by the chemical composition of the underlying

bimetallic substrate. Hence, the origin of the measured volcano-type dependence as a function of chemical composition in both NW and NP systems is an interesting point of contention because it is intrinsically related to the nature of the bimetallic heterostructured electrocatalysts.

As previously mentioned, the improved electrocatalytic performance of  $Pt_{ML}$  catalysts can be attributed to a combined structural and electronic interaction between the core and shell.<sup>14,41</sup> On the basis of the activity trend and CV data, the volcano-type dependence arises from the homogeneous distribution of the gold additive, which can significantly influence the interactions between the bimetallic core and the  $Pt_{ML}$  shell itself. On one hand, the addition of gold is expected to suppress the lattice mismatch between the alloy core and  $Pt_{ML}$  shell, thereby suppressing the gains in activity garnered by the structural effect. By contrast, the addition of gold within the context of a  $Pd_{1-x}Au_x$  FCC alloy structure can lead to a perceptible increase of electron density localized on the Pd and Pt atoms. This factor may therefore contribute to significantly weakened interactions with oxide adsorbates on the  $Pt-Pd_{1-x}Au_x$  NW surface as the gold content is increased from 10 to 30%. This postulate is supported by an observed shift in the oxide reduction feature of more than  $10\text{ mV}$  to higher potentials. Overall, it is clear that an increased gold content in the  $Pd_{1-x}Au_x$  alloy system is expected to yield favorable electronic effects while suppressing the beneficial strain-induced effect. Hence, the volcano-type dependence that we observe is believed to arise from a competition between these two composition-dependent parameters, which favor essentially diametrically opposite behaviors, with the composition of  $Pt-Pd_9Au$ , representing an optimum point wherein a favorable synergistic effect can be achieved.

From a fundamental perspective, the origin of the enhancement in these unique bimetallic, heterostructured electrocatalysts is of critical importance in moving toward more effective 1D electrocatalysts. For example, the volcano-type dependence observed in  $Pt-Pd_{1-x}Au_x$  highlights the critical importance of rationally examining the effect of chemical composition over a broad regime, so as to identify an optimal composition. From a practical standpoint, a careful study of the composition-dependent trends can lead to outstanding enhancements in Pt and PGM normalized activities while only requiring small quantities of non-Pt additives into the host structure. As an example, our optimized ultrathin  $Pt-Pd_9Au$  NWs maintained a PGM normalized activity of  $0.64\text{ A/mg}$ , representing a more than 6-fold improvement over analogous commercial Pt NP/C systems. In addition, the use of the bimetallic NW core contributed to appreciably enhanced durability in  $Pt-Pd_9Au$  NWs.

Indeed, after 30 000 cycles of an extended durability test conducted on the 50 nm  $Pt-Pd_9Au$  NWs, the measured half-wave potential of the polarization curve (Figure 8) decreased by only  $6\text{ mV}$ , and no perceptible change was apparent in either the structural integrity or the texture of the isolated NWs, shown in the inset. By contrast, Pt–Pd NWs prepared analogously underwent significant dissolution and considerable activity loss when subjected to the same durability protocol, thereby further highlighting the benefits and importance of the gold additive.<sup>57</sup> Comparison of the durability results in the  $Pt-Pd_9Au$  NWs with those obtained from state-of-the-art Pt NP/C catalysts<sup>64</sup> substantiates our assertion that  $Pt-Pd_9Au$  NWs possess superior durability performance. Interestingly, a recent report has shown that the constituent units of extended thin films composed of polycrystalline 1D nanostructures were found to lose their unique 1D morphology in favor of forming a



**Figure 8.** Polarization curves of Pt–Pd<sub>9</sub>Au NWs are shown over the course of an extended 30 000 cycle durability test. TEM images of the NWs collected from the electrode after 30 000 cycles (inset) confirm that there is essentially no loss of the desirable 1D morphology to either dissolution or ripening.

smooth flat film.<sup>85</sup> By contrast, the TEM results presented in Figure 8 and in our prior reports suggest that the unique 1D morphology of single-crystalline nanostructures presented herein is essentially preserved. Hence, the addition of 10% gold, forming a stabilized uniform alloy, resulted in substantial and quantifiable enhancements with respect to both ORR activity and durability.

**Size-Dependent Performance in Pt–Pd<sub>9</sub>Au NWs.** The size-dependent performance of Pt–Pd<sub>9</sub>Au NWs was also evaluated by comparing the cathodic ORR kinetics of ultrathin 2 nm Pt–Pd<sub>9</sub>NW/C composites with that of larger 50 nm single-crystalline NW analogues.<sup>56</sup> The specific and mass-normalized activities are summarized in Figure 7B. Interestingly, the measured specific activities obtained from the 2 nm (0.98  $\text{mA}/\text{cm}^2$ ) and 50 nm (0.95  $\text{mA}/\text{cm}^2$ ) NWs did not display a significant size-dependent trend in performance. These results were clearly different from and contrasted sharply with the corresponding data associated with elemental NW systems (e.g., Pt, Pd, and Pt–Pd NWs).<sup>52,64,65</sup> The absence of an unambiguous size dependence in the specific activity measured is therefore of significant interest and can be attributed to the unique electronic and structural effects associated with the bimetallic PdAu alloy core. In this context, the size-dependent contraction observed for elemental Pt and Pd NWs is likely mitigated by the presence of the Au dopant, which not only expands the Pd lattice but also may serve to stabilize the surface toward reconfiguration and reconstruction in the ultrathin size regime. However, a thorough investigation of the size-dependent surface structure and electronic properties utilizing theoretical methods may lead to further insights into the apparent lack of enhancement in the observed specific activity of ultrathin Pt–Pd<sub>9</sub>Au NWs.

Although the specific activity provides important insights into the activity of NWs as a function of size, chemical composition, and structure, mass-normalized activity data actually yield far more useful insights into the practicality and cost-effectiveness of precious metal catalysts. In the context of mass-normalized performance, the Pt mass and PGM activities of the ultrathin NWs (namely, 2.54  $\text{A}/\text{mg}_{\text{Pt}}$  and 0.64  $\text{A}/\text{mg}_{\text{PGM}}$ , respectively) highlight a distinctive size-dependent enhancement as the NWs diameter are decreased from 50 nm (namely, 2.08  $\text{A}/\text{mg}_{\text{Pt}}$  and 0.16  $\text{A}/\text{mg}_{\text{PGM}}$ , respectively) to the ultrathin

regime. In this case, the lack of an enhancement in specific activity confirms that the size-dependent enhancement in mass activity occurs as a consequence of the smaller catalyst diameter, increased specific surface area, and improved dispersion of the NWs on the carbon surface, which collectively contribute to improved catalyst utilization. Hence, these results further reveal the critical significance of a holistic approach toward optimizing particle dimensions in 1D electrocatalysts because size- and composition-dependent trends in specific activity do not always correlate with the corresponding trends in the mass-specific performance.

**Summary and Outlook.** One-dimensional nanostructures represent an exciting structural paradigm in the continuing search for high-performance ORR electrocatalysts, particularly because of their inherent structural anisotropy. Despite the growing interest in preparing, synthesizing, and using robust 1D catalysts in practical applications, there has been a surprising lack of effort placed on cogently scrutinizing and correlating the influence of various physicochemical properties of 1D electrocatalysts (e.g., chemical composition, particle dimensions, and structural geometry, all of which can be controlled experimentally) with their intrinsic electrochemical performance and durability. Hence, the lack of fundamental insights into the unique structural properties of these catalysts may provide, in part, an explanation for the continuing challenge of consistently achieving enhanced mass activities in 1D architectures in excess of those measured with their 0D NP analogues.

Therefore, in this Perspective, we have sought to focus on understanding the key structure–activity correlations, such as the role of particle size and chemical composition, in dictating the electrocatalytic properties of 1D materials so as to provide a useful foundation for generating highly effective and practical catalysts. In terms of catalyst dimensions, an interesting size-dependent enhancement is observed when the diameter of 1D nanowire electrocatalysts is decreased into the ultrathin size regime. In a similar context, a reasonable examination of composition-dependent trends in high-quality bimetallic Pd<sub>1-x</sub>Au<sub>x</sub> and Pd<sub>1-x</sub>Pt<sub>x</sub> NWs has confirmed that significant enhancements in performance can be achieved by tuning the composition of NWs, so as to maximize the unique size-dependent structural and electronic properties observed in these anisotropic systems.

Practically, these results are highly promising because the surface-area-to-volume ratio of 1D catalysts can be maximized and the Pt content minimized without sacrificing performance, attributes which have been commonly observed with analogous 0D NP motifs. Building on these past trends, our group has prepared size- and composition-optimized Pt–Pd<sub>9</sub>Au NWs with ultrathin diameters that are notable for their outstanding Pt mass and PGM activity values of 2.54  $\text{A}/\text{mg}_{\text{Pt}}$  and 0.64  $\text{A}/\text{mg}_{\text{PGM}}$ , representing a 10-fold enhancement over analogous data for commercial Pt NP/C. The key principle is that we are able to achieve similar or even better performance as compared with conventional catalysts but with the use of reduced precious metal content due to the size and morphological advantages of our 1D systems.

Nonetheless, several key issues remain in the practical progression and incorporation of 1D catalysts in true fuel cell applications. First, a crucial prerequisite for effectively examining structure–activity trends in 1D systems necessitates that these catalysts possess similar crystallinity, purity, surface texture, and homogeneity, so as to isolate either the particle composition or dimension as the major parameter responsible for defining performance. From a rational design perspective, such a synthetic

need requires the continued development of synthetic protocols that are both reasonably flexible and robust in terms of tailoring the size and composition of as-prepared catalysts, while also maintaining a high degree of consistency. This goal is further complicated by the need for these processes to adhere to relatively high standards of sustainability, efficiency, and scalability in terms of reagent use, energy consumption, and life cycle considerations in order to gain any measure of commercial relevance and acceptance, moving forward.

The point is that pure, relatively benign catalytic nanomaterials need to be produced relatively easily and cheaply in high yield and large quantities with minimal amounts of byproducts. Thus, continued research into so-called “green techniques” is essential for the reliable and scalable production of 1D nano-scale electrocatalysts.<sup>6</sup> For example, our group has been deeply involved over the years with developing and optimizing the use of ambient, template-based approaches, which can tailor both NW diameter and chemical composition predictably, without sacrificing either purity or homogeneity. However, these template-based approaches are necessarily limited in the production of highly active ultrathin NWs because commercially available membranous templates tend not to possess pore channel diameters below 10 nm. In moving forward, it is clear that the future of ultrathin NW-based electrocatalysts will require the concurrent development of surfactantless, catalyst-free, ambient, solution-based techniques that retain the same flexibility as template-based methods without necessarily being restricted in their ability to yield products possessing ultrasmall diameters on a large scale.

Second, the emerging literature on 1D electrocatalysts has established that significant enhancements can be garnered by moving toward complex structural motifs (e.g., including but not limited to core–shell, axial segmented, and 3D hierarchical architectures). Not surprisingly, this growing degree of structural complexity and sophistication inevitably requires a concurrent and parallel push for a broad range of effective characterization techniques in order to effectively probe the structure of the material and the accompanying catalytic interface within. Currently, traditional *ex situ* methods such as electron microscopy, spatially resolved elemental analysis, and electrochemical techniques have become essential in accurately probing the structures and properties of these interesting systems and their corresponding active sites. However, effective *in situ* characterization of materials under realistic operating conditions will necessitate the development and general use of a broader spectrum of arguably more advanced characterization techniques. For instance, synchrotron X-ray absorption spectroscopy (XAS)-based techniques represent an exciting platform with which to examine the nature of the electronic properties and bonding of 1D catalysts under standard operating electrochemical conditions. It is likely that the fundamental insights gained in the performance of 1D electrocatalysts using these tools will likely guide future research in terms of defining new directions for substantially improving durability and stability, for example.

Third, theoretical and first-principles methods such as DFT have already been invaluable in terms of correlating the physicochemical properties of 1D architectures with their corresponding performance. For example, first-principles calculations have played a key role in elucidating the origin of enhanced performance in ultrathin Pt, Pd, and Pt–Pd NWs. However, the recent development of bimetallic 1D electrocatalysts poses a particularly interesting problem because the activity in these systems appears to be related not only to size and structure but

also to chemical composition in unforeseen ways. This situation is further complicated by the uniqueness of 1D nanostructures in terms of their inimitable structural and electronic effects arising from their anisotropy. Therefore, a key step in constructing a plausible rationale for understanding the structure–activity correlations in these complex systems will be to deploy the predictive power of DFT to systematically probe and correlate the role of composition with catalytic activity in these 1D architectures. Without doubt, the successful marriage of viable synthetic methodologies with effective first-principles approaches should provide an excellent framework for routinely preparing high-quality catalysts, essentially from scratch, and subsequently targeting their optimal chemical composition and morphology for enhanced performance with minimum PGM content.

**The successful marriage of viable synthetic methodologies with effective first-principles approaches should provide an excellent framework for routinely preparing high-quality catalysts, essentially from scratch, and subsequently targeting their optimal chemical composition and morphology for enhanced performance with minimum PGM content.**

Collectively, the future development of 1D electrocatalysts requires a rigorous effort towards understanding their inherent structural individuality, which differentiates their behavior from that of their conventional, broadly commercialized nanoparticulate brethren. Hence, as the development of these 1D catalysts continues to advance, it is clear that a coherent optimization of size, composition, and structure will allow for significant improvements in terms of their cost-effectiveness and practicality as potential replacements for existing 0D catalysts. In so doing, a bright and promising future exists for the broader inclusion and use of 1D catalysts as key components of future commercial PEMFCs.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: stanislaus.wong@stonybrook.edu; sswong@bnl.gov.

### Notes

The authors declare no competing financial interest.

### Biographies

**Christopher Koenigsmann** received his B.S. in Chemistry from Fairfield University in 2008. He is also a certified secondary school educator in the field of Chemistry in the state of Connecticut. Currently, he is pursuing a Ph.D. in Chemistry under the mentorship of Dr. Stanislaus S. Wong at the State University of New York at Stony Brook. His research interests include the synthesis, characterization, and electrochemical properties of metallic nanostructures, particularly for electrocatalysis.

**Megan E. Scofield** received her B.A. in Chemistry in 2011 from Binghamton University. She is currently studying for her Ph.D. in the Department of Chemistry at the State University of New York at

Stony Brook under the guidance of Prof. Stanislaus S. Wong. Her research interests include the development of nanomaterials for applications in Li ion batteries and fuel cells.

**Haiqing Liu** earned his B.S. in Chemistry in 2010 from the Beijing University of Chemical Technology. He came to United States in 2011 in pursuit of his Master's degree and is currently studying for his Ph.D. in Chemistry at the State University of New York at Stony Brook, under the direction of Prof. Stanislaus S. Wong. His research interests include the synthesis and characterization of nanomaterials for solar energy and fuel cell applications.

**Stanislaus S. Wong** completed a Ph.D. from Harvard University under the mentorship of Charles M. Lieber and finished postdoctoral studies at Columbia University with Professor Louis E. Brus. Currently, he is Professor of Chemistry at SUNY Stony Brook with a joint appointment at Brookhaven National Laboratory. He and his group maintain a broad range of interests, most notably in carbon nanotube chemistry and in the sustainable synthesis of noncarbonaceous nanostructures, with the fundamental goal of employing novel nanomaterials for applications in energy and nanomedicine.

## ACKNOWLEDGMENTS

Research (including support for S.S.W. and electrochemical experiments) was supported by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division. We especially thank Dr. Radoslav R. Adzic and Dr. Eli Sutter for their assistance and support with the electrochemical measurements and electron microscopy data, respectively, throughout the prior work presented in this manuscript. We also acknowledge M. Cich for assistance with preparing schematic representations of the hierarchical NW surface. Experiments in this Perspective, described in the figures, were performed in part at the Center for Functional Nanomaterials, located at Brookhaven National Laboratory, which is supported by the U.S. Department of Energy under Contract No. DE-AC02-98CH10886.

## REFERENCES

- (1) Watanabe, M.; Tryk, D. A.; Wakisaka, M.; Yano, H.; Uchida, H. Overview of Recent Developments in Oxygen Reduction Electrocatalysis. *Electrochim. Acta* **2012**, DOI: 10.1016/j.electacta.2012.04.035.
- (2) Rabis, A.; Rodriguez, P.; Schmidt, T. J. Electrocatalysis for Polymer Electrolyte Fuel Cells: Recent Achievements and Future Challenges. *ACS Catal.* **2012**, *2*, 864–890.
- (3) Gewirth, A. A.; Thorum, M. S. Electrocatalysis of Dioxygen for Fuel-Cell Applications: Materials and Challenges. *Inorg. Chem.* **2010**, *49*, 3557–3566.
- (4) Tiano, A. L.; Koenigsmann, C.; Santulli, A. C.; Wong, S. S. Solution-Based Synthetic Strategies for One-Dimensional Metal-Containing Nanostructures. *Chem. Commun.* **2010**, *46*, 8093–8130.
- (5) Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, G.; Yin, Y.; Kim, F.; Yan, H. One-Dimensional Nanostructures: Synthesis, Characterization, and Applications. *Adv. Mater.* **2003**, *15*, 353–389.
- (6) Patete, J. M.; Peng, X.; Koenigsmann, C.; Xu, Y.; Karn, B.; Wong, S. S. Viable Methodologies for the Synthesis of High-Quality Nanostructures. *Green Chem.* **2011**, *13*, 482–519.
- (7) Koenigsmann, C.; Wong, S. S. One-Dimensional Noble Metal Electrocatalysts: A Promising Structural Paradigm for Direct Methanol Fuel Cells. *Energy Environ. Sci.* **2011**, *4*, 1161–1176.
- (8) Morozan, A.; Jousselme, B.; Palacin, S. Low-Platinum and Platinum-Free Catalysts for the Oxygen Reduction Reaction at Fuel Cell Cathodes. *Energy Environ. Sci.* **2011**, *4*, 1238–1254.
- (9) Zhao, X.; Yin, M.; Ma, L.; Liang, L.; Liu, C.; Liao, J.; Lu, T.; Xing, W. Recent Advances in Catalysts for Direct Methanol Fuel Cells. *Energy Environ. Sci.* **2011**, *4*, 2736–2753.
- (10) Antolini, E.; Perez, J. The Renaissance of Unsupported Nanostructured Catalysts for Low-Temperature Fuel Cells: From the Size to the Shape of Metal Nanostructures. *J. Mater. Sci.* **2011**, *46*, 1–23.
- (11) He, C.; Desai, S.; Brown, G.; Bollepalli, S. PEM Fuel Cell Catalysts: Cost, Performance, and Durability. *Electrochim. Soc. Interface* **2005**, *14*, 41–44.
- (12) *Fuel Cell Catalysts*; Koper, M. T. M., Ed.; Wiley Interscience: Hoboken, NJ, 2009.
- (13) Mazumder, V.; Lee, Y.; Sun, S. Recent Development of Active Nanoparticle Catalysts for Fuel Cell Reactions. *Adv. Funct. Mater.* **2010**, *20*, 1224–1231.
- (14) Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jonsson, H. Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. *J. Phys. Chem. B* **2004**, *108*, 17886–17892.
- (15) Nørskov, J. K.; Bligaard, T.; Rossmeisl, J.; Christensen, C. H. Towards the Computational Design of Solid Catalysts. *Nat. Chem.* **2009**, *1*, 37–46.
- (16) Adzic, R. R.; Wang, J. X. Configuration and Site of O<sub>2</sub> Adsorption on the Pt(111) Electrode Surface. *J. Phys. Chem. B* **1998**, *102*, 8988–8993.
- (17) Adzic, R. R.; Wang, J. X. Structure of Active Phases during the Course of Electrocatalytic Reactions. *J. Phys. Chem. B* **2000**, *104*, 869–872.
- (18) Feibelman, P. J.; Hammer, B.; Nørskov, J. K.; Wagner, F.; Scheffler, M.; Stumpf, R.; Watwe, R.; Dumesic, J. The CO/Pt(111) Puzzle. *J. Phys. Chem. B* **2000**, *105*, 4018–4025.
- (19) Markovic, N. M.; Ross, P. N. In *Interfacial Electrochemistry: Theory, Experiment and Applications*; Wieckowski, A., Ed.; Marcel Dekker, Inc: New York, 1999; Vol. 1, pp 821–841.
- (20) Mavrikakis, M.; Hammer, B.; Nørskov, J. K. Effect of Strain on the Reactivity of Metal Surfaces. *Phys. Rev. Lett.* **1998**, *81*, 2819–2822.
- (21) Mayrhofer, K. J. J.; Blizanac, B. B.; Arenz, M.; Stamenkovic, V. R.; Ross, P. N.; Markovic, N. M. The Impact of Geometric and Surface Electronic Properties of Pt-Catalysts on the Particle Size Effect in Electrocatalysis. *J. Phys. Chem. B* **2005**, *109*, 14433–14440.
- (22) Mukerjee, S.; McBreen, J. Effect of Particle Size on the Electrocatalysis by Carbon-Supported Pt Electrocatalysts: An in Situ XAS Investigation. *J. Electroanal. Chem.* **1998**, *448*, 163–171.
- (23) Shao, M.; Peles, A.; Shoemaker, K. Electrocatalysis on Platinum Nanoparticles: Particle Size Effect on Oxygen Reduction Reaction Activity. *Nano Lett.* **2011**, *11*, 3714–3719.
- (24) Tritsaris, G.; Greeley, J.; Rossmeisl, J.; Nørskov, J. Atomic-Scale Modeling of Particle Size Effects for the Oxygen Reduction Reaction on Pt. *Catal. Lett.* **2011**, *141*, 909–913.
- (25) Tsou, Y. M.; Cao, L.; Castro, E. D. Crucial Role of Low Coordination Sites in Oxygen Reduction, CO Stripping, And Size Effect for Nano-Sized Pt Particles. *ECS Trans.* **2008**, *13*, 67–84.
- (26) Shao, Y.; Yin, G.; Gao, Y. Understanding and Approaches for the Durability Issues of Pt-Based Catalysts for PEM Fuel Cell. *J. Power Sources* **2007**, *171*, 558–566.
- (27) Yu, X.; Ye, S. Recent Advances in Activity and Durability Enhancement of Pt/C Catalytic Cathode in PEMFC: Part II: Degradation Mechanism and Durability Enhancement of Carbon Supported Platinum Catalyst. *J. Power Sources* **2007**, *172*, 145–154.
- (28) Shao-Horn, Y.; Sheng, W.; Chen, S.; Ferreira, P.; Holby, E.; Morgan, D. Instability of Supported Platinum Nanoparticles in Low-Temperature Fuel Cells. *Top. Catal.* **2007**, *46*, 285–305.
- (29) Zhong, C. J.; Luo, J.; Njoki, P. N.; Mott, D.; Wanjala, B.; Loukrakpam, R.; Lim, S.; Wang, L.; Fang, B.; Xu, Z. C. Fuel Cell Technology: Nano-Engineered Multimetallic Catalysts. *Energy Environ. Sci.* **2008**, *1*, 454–466.
- (30) Chuan-Jian, Z.; Jin, L.; Bin, F.; Bridgid, N. W.; Peter, N. N.; Rameshwori, L.; Jun, Y. Nanostructured Catalysts in Fuel Cells. *Nanotechnology* **2010**, *21*, 062001/1–062001/20.



- (72) Kondo, Y.; Takayanagi, K. Gold Nanobridge Stabilized by Surface Structure. *Phys. Rev. Lett.* **1997**, *79*, 3455–3458.
- (73) Kondo, Y.; Takayanagi, K. Synthesis and Characterization of Helical Multi-Shell Gold Nanowires. *Science* **2000**, *289*, 606–608.
- (74) Wang, S.; Jiang, S. P.; Wang, X.; Guo, J. Enhanced Electrochemical Activity of Pt Nanowire Network Electrocatalysts for Methanol Oxidation Reaction of Fuel Cells. *Electrochim. Acta* **2011**, *56*, 1563–1569.
- (75) Rossmeisl, J.; Nørskov, J. K. Electrochemistry on the Computer: Understanding How to Tailor the Metal Overlayers for the Oxygen Reduction Reaction. *Surf. Sci.* **2008**, *602*, 2337–2338.
- (76) Matanović, I.; Kent, P. R. C.; Garzon, F. H.; Henson, N. J. Density Functional Theory Study of Oxygen Reduction Activity on Ultrathin Platinum Nanotubes. *J. Phys. Chem. C* **2012**, *116*, 16499–16510.
- (77) Bae, S.-E.; Gokcen, D.; Liu, P.; Mohammadi, P.; Brankovic, S. Size Effects in Monolayer Catalysis—Model Study: Pt Submonolayers on Au(111). *Electrocatalysis* **2012**, *1*–8.
- (78) Wang, J. X.; Inada, H.; Wu, L.; Zhu, Y.; Choi, Y.; Liu, P.; Zhou, W.-P.; Adzic, R. R. Oxygen Reduction on Well-Defined Core–Shell Nanocatalysts: Particle Size, Facet, and Pt Shell Thickness Effects. *J. Am. Chem. Soc.* **2009**, *131*, 17298–17302.
- (79) Alia, S. M.; Jensen, K. O.; Pivovar, B. S.; Yan, Y. Platinum-Coated Palladium Nanotubes as Oxygen Reduction Reaction Electrocatalysts. *ACS Catal.* **2012**, *2*, 858–863.
- (80) Greeley, J.; Nørskov, J. K. Combinatorial Density Functional Theory-Based Screening of Surface Alloys for the Oxygen Reduction Reaction. *J. Phys. Chem. C* **2009**, *113*, 4932–4939.
- (81) Cui, C.-H.; Yu, J.-W.; Li, H.-H.; Gao, M.-R.; Liang, H.-W.; Yu, S.-H. Remarkable Enhancement of Electrocatalytic Activity by Tuning the Interface of Pd–Au Bimetallic Nanoparticle Tubes. *ACS Nano* **2011**, *5*, 4211–4218.
- (82) Sasaki, K.; Naohara, H.; Cai, Y.; Choi, Y. M.; Liu, P.; Vukmirovic, M. B.; Wang, J. X.; Adzic, R. R. Core-Protected Platinum Monolayer Shell High-Stability Electrocatalysts for Fuel-Cell Cathodes. *Angew. Chem., Int. Ed.* **2010**, *49*, 8602–8607.
- (83) Xing, Y.; Cai, Y.; Vukmirovic, M. B.; Zhou, W.-P.; Karan, H.; Wang, J. X.; Adzic, R. R. Enhancing Oxygen Reduction Reaction Activity via Pd–Au Alloy Sublayer Mediation of Pt Monolayer Electrocatalysts. *J. Phys. Chem. Lett.* **2010**, *1*, 3238–3242.
- (84) Li, H.; Sun, G.; Li, N.; Sun, S.; Su, D.; Xin, Q. Design and Preparation of Highly Active Pt–Pd/C Catalyst for the Oxygen Reduction Reaction. *J. Phys. Chem. C* **2007**, *111*, 5605–5617.
- (85) Kongkanand, A.; Liu, Z.; Dutta, I.; Wagner, F. T. Electrochemical and Microstructural Evaluation of Aged Nanostructured Thin Film Fuel Cell Electrocatalyst. *J. Electrochem. Soc.* **2011**, *158*, B1286–B1291.