**Ultrathin Metallic Nanowire-Based Architectures as High-Performing Electrocatalysts**

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**ABSTRACT:** Fuel cells (FCs) convert chemical energy into electricity through electrochemical reactions. They maintain desirable functional advantages that render them as attractive candidates for renewable energy alternatives. However, the high cost and general scarcity of conventional FC catalysts largely limit the ubiquitous application of this device configuration. For example, under current consumption requirements, there is an insufficient global reserve of Pt to provide for the needs of an effective FC for every car produced. Therefore, it is absolutely necessary in the future to replace Pt either completely or in part with far more plentiful, abundant, cheaper, and potentially less toxic first row transition metals, because the high cost-to-benefit ratio of conventional catalysts is and will continue to be a major limiting factor preventing mass commercialization. We and other groups have explored a number of nanowire-based catalytic architectures, which are either Pt-free or with reduced Pt content, as an energy efficient solution with improved performance metrics versus conventional, currently commercially available Pt nanoparticles that are already well established in the community. Specifically, in this Perspective, we highlight strategies aimed at the rational modification of not only the physical structure but also the chemical composition as a means of developing superior electrocatalysts for a number of small-molecule-based anodic oxidation and cathodic reduction reactions, which underlie the overall FC behavior. In particular, we focus on efforts to precisely, synergistically, and simultaneously tune not only the size, morphology, architectural motif, surface chemistry, and chemical composition of the as-generated catalysts but also the nature of the underlying support so as to controllably improve performance metrics of the hydrogen oxidation reaction, the methanol oxidation reaction, the ethanol oxidation reaction, and the formic acid oxidation reaction, in addition to the oxygen reduction reaction.

1. **INTRODUCTION**

A number of innovative technologies are currently being considered as potentially efficient, low-cost renewable energy alternatives to conventional, combustion energy-based sources. At the forefront of many of these efforts are fuel cell (FC) configurations, which convert chemical energy, via an oxidation process (at the anode) with a corresponding reduction (at the cathode) of that fuel source, into electrical energy. A variety of FCs exist, including solid-oxide FCs, molten carbonate FCs, and proton exchange membrane fuel cells (PEMFCs), with each configuration possessing specific advantages and disadvantages.1,2

In terms of how these specialized FCs typically work, in a conventional PEMFC membrane electrode assembly, hydrogen gas is supplied to the anode, wherein protons are generated that subsequently migrate to the cathode through the mediation of the proton exchange membrane. Electrons are produced and migrate to the cathode, whereas the analogous protons combine with the incoming O2 molecules to yield H2O, electrical energy, and heat. These processes are summarized in eqs 1 and 2.

\[
\begin{align*}
H_2 & \rightarrow 2H^+ + 2e^- \quad E^\theta = 0 \text{ V} \\
1/2O_2 + 2H^+ + 2e^- & \rightarrow H_2O, \quad E^\theta = 1.23 \text{ V}
\end{align*}
\]

Given the conceptual simplicity of this device, PEMFCs are viewed as a key technology moving forward because of their rapid "start-up" capabilities, "low-temperature" operation, low "weight-to-power production" ratio, and effective responsiveness to changes in demands for power, all of which are highly advantageous attributes for both transportation and portable applications.3 However, PEMFCs also have a number of practical drawbacks in terms of their instability, high cost, decreased proton conductivity at high temperatures, fairly low relative humidity values, and relatively poor constituent component durability.4 Specifically, PEMFCs are prone to air starvation, membrane degradation, and catalyst aggregation, which are detrimental to normal operation.5

Alkaline fuel cells (AFCs) utilize a basic solution as the electrolyte, such as potassium hydroxide. Under similar operating conditions, AFCs produce current densities that are comparable to those of their acidic counterparts, consisting of conventional PEMFCs that run in media such as sulfuric acid or perchloric acid, for instance.6 Moreover, in terms of overall costs, AFCs are competitive with PEMFCs for low-power applications, such as hybrid vehicles.7 An AFC generates...
electricity through the hydrogen oxidation reaction (HOR) and the corresponding oxygen reduction reaction (ORR).

It should be noted that apart from utilizing hydrogen as the fuel source, other liquid reagents such as alcohols have also been utilized as potentially viable energy sources, because liquid fuels tend to maintain a relatively high solubility in an aqueous electrolyte, and moreover, they can be easily stored and transported. Direct alcohol fuel cell (DAFC) technology, therefore, represents a potential FC option for future applications in the automotive, portable power, and electronics industries. In spite of this tremendous promise, today’s DAFCs, such as direct methanol fuel cells (DMFCs) and direct ethanol fuel cells, powered by methanol and ethanol, respectively, suffer from high production costs and relatively low efficiencies. These shortfalls can be traced in large part to the metal-based catalysts that are employed at both the anode and the cathode. In effect, state-of-the-art DAFC electrocatalysts primarily consist of nanostructured precious metals (i.e., Pt) and metal-based alloys supported onto carbon supports; these metals tend to be both scarce and expensive. Moreover, these electrocatalysts possess slow kinetics and preferentially form partially oxidized products, such as formate and formic acid, as opposed to CO2. In addition, typical electrocatalysts lack the stability and durability required for long-term FC applications, because of CO poisoning, metal dissolution, and surface oxidation. To address these deficiencies, high precious metal loadings (i.e., 2 to 4 mg/cm²) are often needed, rendering the DAFCs less cost-effective, because Pt is both expensive (> $1000 per ounce) and scarce.

Hence, approaches toward creating a novel, highly stable, and well-performing catalyst have relied on either maximizing Pt loading or minimizing overall Pt content. Nonetheless, achieving ground-breaking, paradigm-changing progress in practical FCs requires more than just moving forward with small, incremental improvements on past electrocatalyst designs. As such, a compelling strategy we have closely followed has been to probe the individual components of the entire ‘catalyst-support’ system not only independently but also holistically, wherein the physical size, morphology, structure, surface chemistry, and chemical composition of the catalyst coupled with the nature of the underlying support can be precisely, synergistically, and simultaneously tuned.

Therefore, the key question that we and many others have tried to address can be formulated, as follows. What structural and chemical parameters make a difference and why? On the basis of a large body of relevant literature, we believe that precise control over variables, such as (a) size (i.e., nanoscale), (b) morphology (i.e., anisotropic motifs), (c) chemical composition (i.e., alloys), (d) the presence of a core–shell architecture, and (e) the nature of the underlying support, is relevant and important. Hence, in a number of complementary and intertwined studies, we explore the nature and significance of every single one of these key reaction parameters acting not only separately but also in close, intimate coordination with each other. In particular, we analyze their importance in the context of (i) a representative cathodic reaction such as ORR and (ii) model anodic reactions such as the methanol oxidation reaction (MOR), the ethanol oxidation reaction (EOR), the formic acid oxidation reaction (FAOR), and HOR.

2. IMPORTANCE OF SIZE AND MORPHOLOGY

2.1. Why an Ultrathin One-dimensional (1D) Morphology? Conventional Pt nanoparticles (NPs) tend to (i) decompose by oxidation, (ii) dissolve and undergo subsequent Ostwald ripening, (iii) passivate by the formation of either a surface oxide layer or partially oxidized carbon species including CO as an example, and (iv) experience slow kinetics, thereby resulting in an undesirable overpotential. To account for their electrochemical behavior in terms of their relatively poor durability and low activity, Pt NPs (a) may possess additional potentially deleterious lattice boundaries, (b) are often characterized by a higher amount of defects, and (c) are furthermore prone to aggregation.

By contrast, crystalline 1D nanostructures evince both enhanced activity and stability. In terms of activity, they (i) preferentially display long segments of highly active, smooth, low-energy crystal planes, (ii) maintain improved electronic transport characteristics, minimizing the need for conductive carbon additives, and (iii) possess advantageous surface properties when their diameters are decreased to ultrathin sizes. In terms of stability, they often (i) possess fewer atoms in defect sites, delaying oxidation of the active surface area to higher potentials, (ii) suppress dissolution and ripening, leading to improved stability under operating conditions, and (iii) minimize lattice boundaries and defect sites, thereby lowering susceptibility to permanent oxidation and catalyst degradation. All of these are desirable attributes for FC catalysts. Moreover, ultrathin nanowires (NWs) are expected to maintain slightly contracted surfaces, which can weaken the interaction with O2 and prevent passivation of the catalyst by O2. In addition, ultrathin NWs may also be more chemically homogeneous and structurally monodisperse, and maintain fewer defect sites. In particular, ultrathin Pt NWs maximize the surface area-to-volume ratio, minimize noble metal catalyst loading, and decrease the amount of catalytically inaccessible material within the interior of the wire, all of which in turn can generate superior activity as compared with both Pt nanotubes (NTs) and NPs.

In our group, we have employed and adapted a facile synthesis protocol to fabricate monometallic (in addition to more complex alloys) Pt NWs with ultrathin diameters (1−2 nm). In effect, we have previously shown that we are able to routinely achieve pure, crystalline, and dispersed ultrathin NWs of arbitrary chemical composition with average diameters of ~2.02 ± 0.2S nm using modified “surfactant-mediated” protocols. As typical surfactants, our group and others have successfully utilized various long-chain organic fatty acid molecules, such as cetyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium bromide (DTAB), under ambient, solution-based conditions to create noble metal-based NWs possessing tunable chemical compositions, dictated by the concentrations of metal precursors used.

In a typical CTAB-based method, a “soft” template consisting of wormlike micellar networks is generated in the presence of CTAB within a two-phase water-chloroform system, as an example. The relevant metal precursor ions are subsequently trapped within the “micellar pores.” Hence, porous, high surface area networks of interconnected, “wormlike,” and homogeneous metallic NWs, possessing average diameters as small as 1.9 nm, can be formed upon reduction of these metal precursors with a conventional reducing agent, such as sodium borohydride. In a representative DTAB-based protocol, the
relevant inorganic metal precursors are initially transferred under an inert gas (such as Ar) into a mixture of octadecylamine and toluene using DTAB as a phase-transfer agent. The metal-based precursors are then reduced in the presence of an excess of reducing agent, such as NaBH₄, to form elongated primary nanostructures (PNs). Secondary growth and elongation of these PNs take place in preferred directions (along the [111] axis, for instance), leading to the formation of threadlike, wispy NWs of a tailororable chemical composition, dictated by the relative molar ratios of metal precursor concentrations used. We should note that variations on this theme of modulating growth through surfactant self-assembly, using molecules such as dioctadecyldimethylammonium chloride, also exist.

2.2. MOR and ORR Examples. In the case of methanol oxidation, our group and several others have extensively studied the morphology-dependent performance in the context of Pt-based catalysts for MOR. In nearly all cases, 1D structures...
maintained increased MOR kinetics by comparison with commercial nanoparticulate analogues, owing to their beneficial anisotropic structure. In Figure 1C, for example, we provide a direct comparison of the MOR kinetics associated with our Pt NWs (diameter = 50 nm) with commercial Pt NP/C. These Pt NWs maintain a nearly 3-fold higher current density after onset (Figure 1C inset) as compared with Pt NP/C. This can readily be attributed to their improved CO stripping performance (Figure 1A), as compared with Pt NP/C (Figure 1B), an assertion, which is demonstrated by the significant shift of the primary CO stripping peak to lower potentials by 80 mV. In addition, we have seen essentially identical results in the case of ultrathin 2 nm Pt NWs with respect to commercial Pt NP/C. In both cases, the enhanced CO stripping performance and MOR kinetics can be readily ascribed to the beneficial structural and electronic effects associated with anisotropic nanostructures. The net consequence of these structure-induced "advantages" in terms of MOR activity is that, with respect to Pt NPs alone, for example, ultrathin FePtPd NWs with diameters of 2.5 nm and lengths <100 nm evinced a much higher mass current density of 489 mA/mg, and a favorably lower oxidation peak potential of 0.614 V. PtRh and PtRu NWs show better stability and 30% higher mass activity (MA) than the corresponding highly dispersed NPs on carbon. Moreover, three-dimensional (3D) screw thread-like PtCu alloy NWs yielded greater stability and larger mass current densities for both MOR (i.e., 1.56 A/mg) and EOR (i.e., 1.02 A/mg) versus Pt NPs alone.

In addition to enhanced MOR kinetics, anisotropic nanostructures have also been widely demonstrated to be more stable toward degradation under realistic FC conditions. For instance, the rate of undesirable dissolution and ripening processes has been demonstrated to be measurably and significantly slower in the case of 1D nanostructures by comparison with that noted for commercial Pt NP/C. In fact, we have shown that the ultrathin Pt monolayer (ML) shell—Pd NW core (diameter = 2 nm) motif undergoes essentially no loss in MA over the course of an extended durability protocol of up to 30 000 electrochemical cycles (0.6–1.0 V) when employed as ORR electrocatalysts. However, the corresponding activity of analogous Pt NP/C declines by as much as 40–50% over the same durability test. Similar improvements in durability have also recently been observed by our group in the context of Pt-modified Ru NWs, when compared with analogous Pt-modified Ru NPs. These results confirm that 1D motifs are promising structural paradigms as high-performance electrocatalytic platforms.

2.3. EOR and FAOR Examples. In terms of morphology-dependent EOR electrochemical performance, a comparison of the relevant activity and durability of the as-synthesized ultrathin Pt NWs and commercial Pt NP/C counterparts highlights a clear effect. Figures 2A and 2B present some preliminary cyclic voltammetry (CV) scans related to the initial CO ML stripping of the as-prepared Pt NWs and NPs. A significant negative onset potential shift was observed for Pt NWs with respect to Pt NPs, indicative of a more effective elimination of surface CO species. Because the removal of absorbed surface intermediates had been reported to be the rate-limiting step at low potentials for EOR on polycrystalline Pt surfaces, the efficient oxidation of surface CO adsorbates at these relatively low potentials presumably benefited Pt NW EOR performance.

To determine the corresponding EOR activity and durability, CV curves and stability-relevant chronoamperometric (CA) data were collected in ethanol within an acidic electrolyte and are plotted in Figure 2C,D, and E. With respect to their CV curves, Pt NWs displayed a much lower onset potential and a significantly higher activity at the peak potential as compared with Pt NPs alone. Regarding the CA curves, the Pt NWs yielded a 2-fold higher activity as compared with Pt NPs after 3600 s of reaction time. The performance enhancement of 1D Pt NWs with respect to Pt NPs may be indicative of not only the preferential exposure of active terrace-step sites for ethanol adsorption but also the helpful surface removal of potentially poisoning CO species.

High-quality ultrathin Pd NWs have been synthesized by a number of methods, including hydrothermal-based and polyol-centric syntheses. The as-obtained NWs evinced not only a decrease in the onset potential but also a 1.5 times higher peak current in addition to a 2.5-fold improvement in the current density as compared with conventional Pd/C toward FAOR.

3. IMPORTANCE OF CHEMICAL COMPOSITION

3.1. Rationale. By analogy with DMFC cathodes, the MOR electrocatalysts are based upon carbon-supported Pt metal and alloy NPs. However, the state-of-the-art Pt-based DMFC anode electrocatalysts suffer from poor reaction kinetics, and are easily contaminated by oxygen-containing carbon species, such as CO.

We and others have found that 1D alloys are a much better option. For example, bimetallic PtIrNPs are considered to be superior to both Pt black and Pt/C on the basis of their low onset potential, high catalytic activity, and tolerance to CO poisoning. Similarly, due in part to their enhanced CO removal ability and high density of active surface sites, Pt–Cu3, wavy NWs, Pt–Ni bimetallic nanoassemblies, 3D porous Pt–Rh nanoassemblies, and Pt–Co alloy NW assemblies are often more durable and more highly active than Pt NPs alone for alcohol electro-oxidations, such as MOR and EOR.

Moreover, the selectivity with respect to the complete oxidation of ethanol to CO2 improved by as much as a factor of 3, when using ultrathin Rh/Pt bimetallic NWs as compared with commercial Pt black. As additional illustrative examples, ultrathin Pt,Pb “nervelike” NWs with diameters of ~3.6 nm exhibited very high specific activity (SA) values of 2.78 mA/cm2 in acidic media and 6.51 mA/cm2 in alkaline media toward MOR, denoting performance enhancements of ~5.24 and 4.12 times over those of commercial Pt/C catalysts, whereas ultrathin veinlike Ir3Sn3 NWs displayed a very high MA of 95.6 mA/mg, for EOR at a low potential of 0.4 V, representing improvements of ~4.1- and 20-fold over those of Ir/C and commercial Pt/C, respectively.

By analogy, ultrathin Pt–Fe alloy NWs, ultrathin Pt–Ir NWs, and Pt–Al/Pt–Y-based NW networks are clearly superior ORR catalysts as compared with Pt NPs alone in both activity and stability, because of a smaller accessible reactive area and the deliberate introduction of the extra metal.

Furthermore, Pt8Pb16 bimetallic alloy nanoflowers yielded FAOR MAs that were ~17 times higher than that of commercial Pt black; nanoporous Pd–M catalysts (wherein “M” = Cd, Pb, Ir, and Pt) with an atomic elemental ratio of 90:10 showed improved stability coupled with equal if not improved FAOR activity.
To fully explore the benefits of a tailored chemical composition, we can consider MOR in the context of a Pt−Ru system in greater detail. Specifically, significant efforts have focused on the synthesis of nanostructured alloys of Pt with Ru, so as to improve their CO tolerance. It has been theoretically postulated that the MOR enhancement of PtRu alloys is due to not only the enablement of the direct conversion of methanol to CO2 (without any intermediate CO, i.e., non-CO pathway) but also the promotion of CH3OH adsorption and formation of active OH species from H2O, which oxidizes intermediate (and poisoning) CO bound to Pt sites. Moreover, the strain effect resulting from the lattice mismatch between Pt and Ru decreases the binding energy of reaction intermediates, thereby favoring high CO tolerance.

Both theory and experiment imply that a judicious variation of the Pt to Ru ratio within Pt−Ru alloys can yield MOR catalysts that outperform commercial Pt NPs in terms of activity, selectivity, and stability. As such, optimization of these alloys has shown that maximum efficiency can be obtained when Ru concentrations are in the range of "x" = 0.07−0.33 within Pt1−xRu x systems. Specifically, when alloyed at low-to-moderate Ru concentrations (xRu = 0−0.6), the PtRu alloy forms a solid solution, with Ru atoms occupying sites within the face-centered cubic lattice of Pt. As implied, surface Ru sites can catalyze the oxidation of CO and other C-containing intermediates to CO2 at lower potentials, thereby decreasing the amount of irreversible binding of CO to active Pt sites and consequentially promoting stability.

Figure 3. (A,C,E,G,I) HAADF images and (B,D,F,H,J) the corresponding EELS line-scan profiles of the NW catalysts: (A,B) Pt7Ru3 NWs, (C,D) Pt7Fe3 NWs, (E,F) Pt7Co3 NWs, (G,H) Pt7Cu3 NWs, and (I,J) Pt7Au3 NWs. HOR CVs for (K) Pt7Ru3 NWs, Pt7Fe3 NWs, and Pt7Co3 NWs as well as for (L) Pt7Cu3 NWs and Pt7Au3 NWs. (M) Bar graph summarizing the measured activity values as a function of the binary NW composition for the HOR in alkaline media. Reproduced from ref 85.
Indeed, a promising solution to addressing the challenge associated with CO oxidation has come from purposefully incorporating 3d transition metals into existing Pt alloys. For example, the role of Pd within PtRu-Pd, is thought to promote favorable C–O and C–H bond scission. In general, the introduction of 3d transition metals into bimetallic PtRu alloys to create ternary PtRuM alloys can improve upon the activity of Pt by increasing the amount of oxygenated species at lower potentials to enable more facile CO oxidation, while also rendering the catalysts more cost efficient and less susceptible to poisoning.

Furthermore, ternary PtRuM alloys (with “M” = Co, Ni, and W) generated by chemical vapor deposition yielded area-specific current densities of 0.016 mA/cm², which were ~8 times higher than that of PtRu alloys and more than 14 times greater than that of Pt alloys. Moreover, in PtRuNi systems, electron transfer from Ni to Pt can enhance the oxidation of CO species on Pt. Specifically, Pt–RuNi pair sites were found to be the most active, because they possessed the lowest overpotential to dissociate water, the highest MOR activity, and the strongest CO tolerance within the potential window of operation.

A review of the experimental work on Co and Ni alloyed with Pt concluded that the addition of non-noble metals at moderate concentrations (i.e., Pt−xRuMx where 0 < x < 0.33 M for Co/Ni) results in both enhanced MOR activity and improved CH₃OH tolerance as compared with pure Pt alone. Analogous studies have found up to 200 mV lower onset potentials for MOR, upon addition of Fe and Sn within ternary nanostructured alloys of PtRuM with “M” = Fe or Sn. Moreover, Pt−Ru−Co−W quaternary anode catalysts yielded MOR activities that are 40 to 70% higher as compared with commercial binary Pt−Ru binary species.

3.2. Pt−M Ultrathin NW Alloys. In our 2016 ACS Catalysis publication, we examined different Pt−M ultrathin NW alloys for use in HOR in an alkaline medium. The shift from standard acidic electrolytes to alkaline environments is highly beneficial and desirable, because acidic solutions are corrosive, a fact which limits the extent to which less robust metal can be realistically used. Therefore, switching to alkaline environments broadens the number of elements that can be potentially incorporated and alloyed with Pt within novel catalyst materials. Hence, the project sought to address the theoretical premise that in alkaline media, the hydrogen bonding energy (HBE) plays a major role during the HOR process. The idea was that significant improvements in electrochemical activity and reaction kinetics could be achieved by alloying Pt with transition metals, thereby resulting in weaker HBE values; in particular, a weaker HBE should effectively lower the barrier to desorption from the catalyst surface following product formation, which often has a significant impact on activity.

Experimentally, we prepared families of PtM, (M = Cu, Au, Co, and Ru) binary ultrathin NWs with consistent composition, morphology, and dimensions. Specifically, representative high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images and electron energy loss spectroscopy (EELS) measurements corroborated the expected anisotropic 1D morphology as well as the chemical homogeneity of all binary samples. Specifically, we found each NW to be composed of multiple crystalline segments associated with single-crystalline planes. It is noteworthy that although d-spacing data for our Pt-based binary alloys were within experimental error of the reported d-spacing for the Pt (111) plane (i.e., 2.26 Å), all of the binary NWs generated, with the exception of PtAu, exhibited a minor decrease in their measured d-spacing values relative to that of pure mononmetallic Pt NW controls.

The HOR kinetics (Figure 3KL) data were collected in a H₂-saturated solution within 0.1 M KOH electrolyte. The observed current of each sample was normalized to the geometric surface area of the electrode. As Figure 3M demonstrates, our electrochemical measurements correlated well with the theoretical HBE calculations, with the exception of the Cu alloy, a finding which was attributed to Cu dissolution at higher positive potentials. In fact, we found that the Pt−Ru NW catalyst exhibited the highest HOR activity and notably a favorable exchange current density of 0.493 mA/cm², a value even better than that of pure Pt NWs alone. In terms of the performance of the other metal alloys, we found that Pt−Fe₃ NW (0.459 mA/cm²) > Pt−Co₃ NW (0.394 mA/cm²) > Pt NW (0.229 mA/cm²) > Pt−Cu₉ NW (0.191 mA/cm²) > Pt−Au NW (0.162 mA/cm²). The order of experimental activities for the binary alloys does not necessarily correspond entirely with the theoretical, calculated HBE values. We believe that the different HOR catalytic activities observed for our PtM binary NWs can be rationalized according to two key factors: (1) First, the addition of a second metal to Pt modifies the d-band structure and electron density of Pt, a phenomenon which is known as the “ligand effect.” (2) The Pt−Pt bond distances as well as the intrinsic electronic properties of the underlying Pt lattice are altered to some degree by the presence of the second metal, manifesting themselves as a “ligand strain effect.” Hence, our data demonstrated the composition-dependent behavior of PtM binary NWs toward HOR, because we confirmed the presence of desirable electronic interactions (and enhanced activity) with the introduction of the second metal with Pt.

These critically relevant ligand and lattice strain effects manifested themselves in not only perceptible shifts in the Pt 4f region associated with chemically specific X-ray photoelectron spectroscopy spectra for each binary catalyst tested but also corresponding shifts in both the hydrogen adsorption and oxide regions with respect to Pt. In the case of PtRu, PtFe, PtCo, and PtCu NW alloyed systems, these phenomena collectively explained the expected decrease in HBE values (vs Pt) because of the lowering and transitioning of the d-band center away from the Pt Fermi level through electron withdrawal induced by alloying of Pt with other metals. The net result was a weakening of the metal–adsorbed hydrogen (i.e., M−H₃) interaction and an improvement in the desorption kinetics.

3.3. PtRuFe NWs. We also synthesized ultrathin, ternary PtRuFe NWs, possessing different chemical compositions, to probe their CO tolerance as well as electrochemical activity as a function of composition for both (i) MOR and (ii) FAOR. The as-prepared “multifunctional” ternary NW catalysts exhibited both higher MOR and FAOR activities as compared with binary Pt−Ru NW controls, monometallic Pt NWs, and commercial catalyst samples. In terms of synthetic novelty, we utilized a sustainably mild, ambient, wet-synthesis method, never previously applied to the fabrication of crystalline, pure ternary systems, to generate ultrathin, homogeneous alloy PtRuFe NWs with a range of controlled compositions. These NWs were subsequently characterized using a suite of techniques including X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area diffraction pattern (SAED), and energy-dispersive X-ray spectroscopy to verify not only the incorporation of Ru and Fe into the Pt lattice but also their chemical homogeneity in addition to their physical
structure, morphology, and integrity. Representative images (Figure 4A−D) indicate that the ternary motifs with various metal compositions possessed an average diameter ranging from 1.9 to 2.2 nm.

Last, these NWs were electrochemically tested for their MOR (Figure 4E,F) and FAOR (Figure 4G,H) activities. Relevant MOR data were measured in a deoxygenated 0.5 M methanol solution supported in an acidic electrolyte, whereas analogous FAOR kinetic results were collected in the same acidic electrolyte but in the presence of 0.5 M formic acid. Specifically, at a potential of 0.8 V (vs reversible hydrogen electrode (RHE)), PtRuFe ternary NWs and binary NW controls evinced an MOR activity trend of Pt7Ru2Fe1 NWs (2.27 mA/cm²)>Pt7Ru1.5Fe1.5 NWs (1.86 mA/cm²)>Pt7RuFe2 NWs (1.46 mA/cm²)>Pt7Ru0.5Fe2.5 NWs (1.22 mA/cm²)>Pt7Fe3 NWs (0.67 mA/cm²). A similar pattern of behavior was noted at a lower potential of 0.65 V (vs RHE). Analogous FAOR activities measured at 0.65 V (vs RHE) also reinforced the importance of tailoring the chemical composition to yield a desired electrochemical performance. In effect, the analogous trend was deemed to be Pt7Ru1.5Fe1.5 NWs (2.15 mA/cm²)>Pt7Ru2Fe1 NWs (1.90 mA/cm²)>Pt7RuFe2 NWs (1.83 mA/cm²)>Pt7RuFe3 NWs (1.50 mA/cm²)>Pt7Ru0.5Fe2.5 NWs (1.22 mA/cm²)>Pt7Fe3 NWs (0.55 mA/cm²).

It turned out that the optimal chemical composition for FAOR was Pt7Ru1.5Fe1.5, which is different from that for MOR (i.e., Pt7Ru2Fe1). Specifically, MOR appeared to be mainly influenced by the Ru content, whereas FAOR was primarily impacted by the corresponding Fe content within the ternary metal alloy catalyst itself. To explain our MOR observations, it is known that in the case of Pt1−xRux alloys, the presence of Pt−Ru pair sites increases the MOR catalytic performance by facilitating the oxidation of adsorbed CO species at potentials lower than those observed on elemental Pt as a result of a process referred to as "carbonyl-spillover";86,87 in particular, in the presence of Ru, adsorbed CO species generated by the rapid dehydrogenation of methanol at Pt active sites can functionally "spill over" and react with RuOH species, thereby forming CO2. Thus, the CV results suggested that the Fe-doped PtRu NWs may actually benefit from the complementary beneficial effects of (i) the bifunctional mechanism, wherein the
OH species dissociated from water and adsorbed onto the Ru surface catalyzes the removal of CO adsorbed onto Pt active sites at lower potentials, thereby increasing the overall activity of Pt1−xRu x-based alloys, as well as (ii) the favorable electronic effects associated with PtFe alloys, in which the presence of the Fe “ligand” lowers the d-band center of Pt, thereby resulting in more d-band vacancies and an overall lower susceptibility to poisoning of active sites by CO species formed as intermediates in the indirect oxidation of methanol. Additional CA tests were performed on both the optimized ternary sample (i.e., Pt7Ru2Fe1 NWs) and the commercial PtRu/C NP in the presence of methanol. Not surprisingly, our ternary NWs outperformed the PtRu/C standard sample in terms of MOR stability.

3.4. PdCu. PdCu alloys with various morphologies have previously been reported as promising catalysts toward FAOR. Specifically, nanoporous PdCu alloys were found to exhibit enhanced activity and excellent durability toward FAOR, whereas 3D PdCu motifs gave rise to a 30% enhancement in the MA value with respect to commercial Pd NPs. High-resolution TEM (HRTEM) images in Figure SA–D confirm the 1D morphology of our as-generated PdCu1−x NWs, all of which possessed diameters less than 3 nm. The SAED pattern implied not only the overall polycrystalline nature but also a crystallographically well-defined face-centered cubic structure for all Pd-based binary NWs. To examine the electrocatalytic performance of our as-prepared, ultrathin PdCu NWs toward FAOR, CV and CA curves were collected in the presence of formic acid, supported in an acidic electrolyte. The as-collected FAOR results of a series of PdCu1−x binary systems are presented in Figure SE–G. On the basis of these data, we observed a volcano-type trend for FAOR activities as a function of the metal alloy composition. Our best sample, Pd9Cu NWs, gave rise to an activity of 9.52 mA/cm², a value which was approximately twice greater than that of analogous ultrathin Pd NWs (5.55 mA/cm²) and 3 times larger than that of commercial Pd NPs (3.44 mA/cm²). It was postulated that because the activity of

Figure 5. Representative higher magnification HRTEM images for (A) Pd NWs, (B) Pd9Cu NWs, (C) Pd8Cu2 NWs, and (D) Pd7Cu3 NWs. (E) Cyclic voltammograms for the FAOR with the current normalized to the electrochemically active surface area (ECSA). (F) Bar graph highlighting the FAOR activity at the respective peak potential values for commercial Pt NPs, commercial Pd NPs, Pd NWs, PdCu NWs, Pd8Cu2 NWs, and Pd7Cu3 NWs. (G) CA measurements collected in an argon-saturated 0.1 M HClO4 + 0.5 M HCOOH solution, obtained at a potential of 0.4 V vs RHE for a period of 60 min. Reproduced from ref 93.
commercial Pt NPs toward FAOR was considerably lower than that of our PdCu alloys, it was plausible that Pd-based alloys may in fact have been governed by a completely different FAOR mechanistic pathway. Additionally, our optimized composition (i.e., Pd 9Cu) not only exhibited the highest activity measured but also the best long-term stability within the overall series of ultrathin Pd\textsubscript{x}Cu\textsubscript{1−x}NWs analyzed.

3.5. PdNi. With respect to ORR, our group has developed a number of binary Pd-based NW systems focused on PdAu\textsuperscript{30} and PdPt\textsuperscript{94} as examples highlighting the significance of carefully tailoring the chemical composition as a means of enhanced observed performance. Because Pt and Au are relatively expensive and scarce metals, we sought to create practical alloy-based alternatives, incorporating cheaper, more plentiful, and relatively nontoxic elements such as Ni, Cu, and Fe, as implied by the case studies featured within this Perspective.

Within any Pd-based alloy, the presence of an additional element can result in "ligand" and "strain" effects, meaning that Pd is not only electronically modified but also structurally altered by the lattice mismatch created by the "dopant" atoms. Not surprisingly, within a PdNi alloy,\textsuperscript{95} theory has suggested that a perceptible 1.00 eV downshift in the Pd d-band to lower energies\textsuperscript{30} can be achieved by incorporating Ni within the lattice, which manifests itself in terms of weakened d-\(\pi^*\) interactions between the surface-adsorbed oxygen species and the underlying Pd.\textsuperscript{96} What we found experimentally was that the positions of the oxide reduction peak, which are correlated with the material’s oxygen-binding abilities, could be deliberately altered by controlling the amount of Ni dopant within a series of ultrathin, segmented NW structures (i.e., Pd\textsubscript{x}Ni\textsubscript{1−x} with “x” = 0.9, 0.8, and 0.7), possessing a homogeneous distribution of elements, as verified by a combination of TEM (Figure 6A−D) and energy-dispersive spectroscopy (EDS) data.

In effect, Pd\textsubscript{0.90}Ni\textsubscript{0.10} NW samples possessed the highest potential for the oxide reduction peak, corresponding to the highest ORR activity (i.e., 1.96 mA/cm\textsuperscript{2} at 0.8 V) observed among the series of NWs tested with improved performance as compared with both commercial Pd NPs and analogous ultrathin Pd NWs. These data presented in Figure 6E confirm our theme of a clear and tunable (i.e., "volcano"-type in this case) dependence between the chemical composition and the corresponding ORR performance. Moreover, our purified Pd\textsubscript{0.90}Ni\textsubscript{0.10} NWs maintained 85% of their initial activity in the presence of a potential passivating species under realistic...
operating conditions, such as 4 mM methanol. Our data (Figure 6F,G) designated a tangible improvement as compared with both commercial elemental zero-dimensional Pt NP/C (79%) and 1D Pt NWs (43%). Furthermore, even under a set of more challenging conditions, the main defining features of Pd$_{0.90}$Ni$_{0.10}$ CVs were still preserved, even after the addition of 100 mM methanol, indicative not only of the absence of a CO-poisoning effect but also of the intrinsically high tolerance of our NW systems to deleterious catalytic poisoning and deactivation.

4. CORE−SHELL MOTIF OF THE CATALYST

4.1. Rationale. Within a core−shell configuration, studies have suggested that excellent electrochemical activity and durability can be achieved through favorable synergistic interactions between the core and the shell, including taking advantage of a combination of ligand and strain effects. As such, core−shell motifs have been reported in the form of more unusual morphologies such as dendrites, cubes, raspberries, porous hierarchical motifs, and flowers. In particular, an "M" (where "M" = transition metal) core−Pt-based shell motif has four primary benefits toward enhancing the intrinsic activity of electrocatalysts. First, it maximizes the use of Pt so that such a structure will not only minimize Pt loading but also allow for every Pt atom to be catalytically accessible. Second, the addition of the transition metal "M" lowers the energy of the Pt d-band and creates d-band vacancies. Third, it increases the stability of Pt toward CO poisoning by lowering the affinity of Pt for irreversibly binding CO.

As a promising case study (i.e., Pt < 30%), it was found that the current density and the output power density of DMFCs were doubled by using a NiO−Pt core−shell system as compared with a conventional PtRu alloy at the anode. Moreover, substrate-induced lateral strain in a Pt ML yielded a nearly 7-fold increase in MOR activity on a Pt/Au(111) single-crystal surface relative to Pt(111) itself. Another relevant example consists of ultrathin Pd−Pt core−shell Pd NWs with controllable shell thickness, which not only could be produced on a relatively large scale but also yielded dramatically enhanced activity and stability toward ORR as compared with a Pt control sample; in addition, Pt-coated Ni NWs provided 3 times greater ORR MA than Pt NPs. Pt-coated Cu NWs exceeded the area and mass exchange current densities of carbon-supported Pt by 3.5 and 1.9 times, respectively, for HOR in base.

Within our group, we have produced core−shell Pt@metal NWs by depositing ML quantities of Pt on our core NW surfaces by utilizing an under-potential deposition (UPD)/galvanostatic deposition (GD) protocol, developed by our close collaborators (i.e., the team of Radoslav R. Adzic at Brookhaven National Laboratory). Experimentally, the Pt "shells" are formed by first electrodепoising a conformal Cu ML utilizing an initial UPD process and subsequently displacing the Cu ad-atoms with Pt via simple galvanic displacement. The initial Pt ML coverage can be systematically increased and appropriately varied by repeating, as needed, the UPD/GD step so as to provide for a thicker, more uniform, and homogeneous protective "Pt coat."

4.2. Pt@Ru Core−Shell NWs. We examined the morphology-dependent performance of the Ru NWs by depositing ML quantities of Pt on our core NW surfaces by utilizing an under-potential deposition (UPD)/galvanostatic deposition (GD) protocol, developed by our close collaborators (i.e., the team of Radoslav R. Adzic at Brookhaven National Laboratory). Experimentally, the Pt "shells" are formed by first electrodепoising a conformal Cu ML utilizing an initial UPD process and subsequently displacing the Cu ad-atoms with Pt via simple galvanic displacement. The initial Pt ML coverage can be systematically increased and appropriately varied by repeating, as needed, the UPD/GD step so as to provide for a thicker, more uniform, and homogeneous protective "Pt coat."

Figure 7. (A) Mass-normalized LSVs obtained in 0.5 M methanol in 0.1 M HClO$_4$ at 20 mV/s with the onset region for MOR highlighted in (B). (C) MAs measured at 0.65 V are shown for the commercial Pt NP/C and PtRu NP/C and for our corresponding as-prepared core−shell Pt−Ru NP/C (i.e., one UPD/GD cycle) and Pt−Ru NW (i.e., six UPD/GD cycles) electrocatalysts. (D) Analogous plots of the mass-normalized current density, measured at 0.64 V as a function of the cycle number in a durability test, are also shown. Reprinted with permission from ACS Appl. Mater. Interfaces, 2013, 5, 5518−5530. Copyright (2013) American Chemical Society.

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type architectures can be further enhanced by employing a Pt ML shell–Ru NW core (Pt@Ru NW/C) structural motif. Therefore, this unique architecture localizes the Pt content at the catalytic interface while preserving the beneficial Pt–Ru pair sites required for the so-called “bifunctional mechanism,” wherein the oxidation of CO is facilitated by more oxophilic Ru surface sites.

The localization of the Pt atoms at the interface contributes to an enhancement in the mass-normalized MOR activity of the Pt@Ru core–shell NWs (0.36 A/mg of Pt) as compared with the corresponding performance of PtRu alloy-type NPs (PtRu NP/C, 0.24 A/mg of Pt) as well as of supported elemental Pt (Pt NP/C, 0.09 A/mg of Pt) serving as commercial standards. In essence, MOR linear sweep voltammetries (LSVs) (Figure 7A,B) revealed that the Pt@Ru NWs possessed more than double the peak current density and yielded an MOR onset potential that was 100 mV lower than that of commercial Pt NP/C, thereby confirming the excellent performance of these hierarchical NWs. The corresponding MAs of Pt@Ru NWs and control samples, measured at 0.65 V, are summarized in a representative bar graph (Figure 7C). Catalytic durability (Figure 7D) was seen in that even after 2000 cycles of a rigorous testing protocol, the activity of our Pt@Ru core–shell NWs still outperformed Pt NP/C.

Indeed, the main benefit of the Pt–Ru core shell motif we have generated is that the structural and electronic interactions between the Pt shell and the Ru core promotes more facile MOR kinetics, as predicted by Nørskov and co-workers. Specifically, in this core–shell motif, the Pt atoms of the shell lie atop the Ru core, occupying the three- and four-fold interstitial sites of the Ru. The inherent lattice mismatch between the Pt shell and the Ru core forces a compression strain upon the Pt lattice, because of the shorter interatomic distance of the surface Ru sites as compared with Pt. In particular, the d-orbital overlap is increased, thereby resulting in an increased d-band width. As such, the occupied band states...
are shifted down in energy to conserve the net occupancy of the d-band, and therefore, the weighted center of the band is lowered in energy. Furthermore, it is expected that the Ru core should promote a noteworthy "ligand effect," wherein the electron density is withdrawn from the Pt d-band toward the Ru core.

In terms of catalysis, the lower weighted center of the d-band contributes to a lowered CO affinity as a result of a weakening of the overlap between the Pt d-orbitals and the CO π*-orbitals. Indeed, the fundamental problem of CO oxidation in Pt@Ru core−shell catalyst architectures has been studied from both theoretical and experimental perspectives to establish the basis for a new generation of materials and architectures for use as DMFC anode electrocatalysts. Specifically, the theoretical work performed by Nørskov et al. on mixed metal Pt MLs atop an Ru substrate revealed that Pt MLs containing non-noble metals such as Fe, Co, Rh, Sn, and Ni should maintain an improved catalytic performance as compared with PtRu alloys alone. Moreover, the presence of the added transition metal not only is expected to measurably increase the electronic and structural effects imparted by the Ru core on the Pt ML shell, thereby further increasing the CO kinetics beyond that of Pt−Ru architectures alone, but also could lead to a change in the mechanistic pathway of MOR itself.

4.3. Pt-Coated Pd$_{1-x}$Cu$_x$ NWs. For this system, we demonstrated a concerted effort to couple and combine the benefits of small size, anisotropic morphology, and tunable chemical composition to devise a novel “family” of functional
architectures. In particular, we fabricated ultrathin 1D Pt-coated Pd$_{1-x}$Cu$_x$ (i.e., Pt$\sim$Pd$_{1-x}$Cu$_x$) core–shell hierarchical nanostructures with readily tunable chemical compositions by utilizing a facile, surfactant-based, wet chemical synthesis coupled with the Cu UPD technique.

Our group of Pt$\sim$Pd$_{1-x}$Cu$_x$ NWs consistently outperformed not only commercial Pt NPs but also ultrathin Pt NWs by several fold orders of magnitude for both MOR and EOR in alkaline media. The variation of the MOR (Figure 8A,B) and EOR (Figure 8C,D) performance with the chemical composition of our ultrathin Pt$\sim$Pd$_{1-x}$Cu$_x$ NWs was also discussed; the values of measured catalytic activities appeared to rise with increasing Cu content.

The “optimal” chemical composition for MOR was deduced to be Pt$\sim$Pd$_{7}$Cu$_{3}$, which is in excellent agreement with CO stripping results, as CO is the intermediate species for MOR on Pt sites. Pt$\sim$Pd$_{7}$Cu$_{3}$ exhibited a surface area activity of 23.2 mA/cm$^2$, which is over 3-fold higher than that of commercial Pt NPs (i.e., 6.94 mA/cm$^2$) and analogous Pt ultrathin NWs (i.e., 7.45 mA/cm$^2$). Though there was no clear discernible composition trend, analogous EOR activities of all as-prepared Pt$\sim$Pd$_{1-x}$Au ultrathin NWs yielded a notable and perceptible improvement with respect to both pure Pt ultrathin

Figure 10. (A) Hexagonal 2.2 nm-diameter [(111)$_0$ (200)$_2$] NW models with various Au distributions. (a) Pd$_9$Au@Pt NWs, (b) Pd$_8$Au$_2$@Pt NWs, and (c) Pd$_7$Au$_3$@Pt NWs. Upper panel: (i) Pd$_{(1-x)}$Au$_x$@Pt NWs. Middle panel: (ii) Pd$_{(1-x)}$Au$_x$@Pt$_{(1-z)}$@Au$_z$@Pt$_{(1-z)}$ NWs. Lower panel: (iii) Pd$_{(1-x)}$Pt$_z$@Au$_x$@Pt$_{(1-z)}$ NWs. For clarity, eight supercells along the axis and bases at both ends are displayed. (B) Theoretical ESA activity (black) and MA (red) for various chemical compositions in a range of Pd$_{(1-x)}$Pt$_z$@Au$_x$@Pt$_{(1-z)}$ NWs. (C) High-resolution STEM imaging and (D) cross-sectional EELS analysis for the as-synthesized Pt$\sim$Pd$_{1}$Au ultrathin NWs. (E) Experimental results of ORR activities for a series of as-prepared Pt$\sim$Pd$_{1-x}$Au NWs. Reproduced from ref 114.
NWs and commercial Pt NPs. In particular, the SA of our core–shell nanostructured samples was measured to be ~10–12 mA/cm², denoting a quasi-3-fold higher enhancement with respect to reported values for our controls. Interestingly, the corresponding CA measurements (Figure 8E,F) for both reactions also confirmed that the optimized Pt–Pd,Cu₇ composition outperformed all of the other chemical compositions tested. Specifically, this carefully tailored system yielded not only the maximum peak current density but also the best long-term stability measured.

4.4. Pt-Coated Pd₀.₉₀Ni₀.₁₀ NWs. Because ultrathin Pd₀.₉₀Ni₀.₁₀ NWs proved to be a promising catalyst for ORR, we subsequently investigated the ORR performance of analogous ultrathin Pt-shell Pd₀.₉₀Ni₀.₁₀-core NW motifs.²⁵ Figure 9A shows the CV results of Pd₀.₉₀Ni₀.₁₀ NWs and Pt–Pd₀.₉₀Ni₀.₁₀ NWs. Presumably, after the Cu UPD process, a ML of Pt atoms was deposited onto the surface of the Pd₀.₉₀Ni₀.₁₀ NWs. We found that the CVs of Pt–Pd₀.₉₀Ni₀.₁₀ NWs exhibited Pt-like features, whereas on the basis of the polarization curves (Figure 9B), their ORR kinetics measured at 0.9 V were noticeably enhanced (Figure 9C). In effect, the Pt–Pd₀.₉₀Ni₀.₁₀ NWs yielded a SA and a corresponding MA of 0.62 mA/cm² and 1.44 A/mgPt, respectively. Figures 9D and E highlight the cycling data associated with ascertaining the durability of our optimized Pt–Pd₀.₉₀Ni₀.₁₀ NW sample. To summarize, when comparing both activity and durability trends of our series of tested samples, the “best” performance was clearly observed with Pt–Pd₀.₉₀Ni₀.₁₀ NWs, as compared with PdNi NWs, PdNi NPs, and commercial Pt NP controls.

4.5. Pt-Coated PdₐAu NWs. In prior studies, we have shown that (i) the as-prepared PdₐAu NWs maintain significantly enhanced ORR activity (0.40 mA/cm²) as compared with not only elemental Pt NW/C (0.12 mA/cm²) but also Pt NP/C (0.20 mA/cm²) and (ii) upon deposition of a Pt ML, the Pt–PdₐAu NWs maintained an optimal surface area and mass-normalized activities of 0.98 mA/cm² and 2.54 A/mgPt, respectively. Whereas it was obvious that the chemical composition played a major role in the observed trends, the precise spatial distributions of Pt, Au, and Pd elements within the core–shell motif (Figure 10C,D) were important but unknown variables. For example, we could not effectively differentiate between Pt and Au atoms using data from the EDS spectra alone.

We sought to address these issues experimentally and theoretically. Using density functional theory (DFT), for Pt–PdₐAu NWs incorporating various Pd-to-Au ratios, we simulated three possible geometric (Figure 10A) variations to obtain a precise picture, concerning the spatial elemental distribution of Au atoms within these ultrathin NWs. Scenario 1 had all of the Au atoms concentrated within the core; scenario 2 highlighted a portion of Au atoms segregated at the edge of the Pt shell. By contrast, scenario 3 confined and localized all of Au atoms within the Pt shell.²⁴ It turned out that the binding energy of oxygen on these metal surfaces could be used as a proxy for electrochemical performance, and could be directly correlated with the corresponding ORR kinetics and activities. Out of all three models analyzed, the model advocating complete Au surface segregation (i.e., scenario 3) yielded a theoretical ORR activity trend that matched well with the experimental results (Figure 10B,E).

In effect, combining complementary and supportive results from (a) in situ X-ray absorption spectroscopy (namely Pt and Au L edge data), (b) DFT calculations, and (c) electrochemical data into a comprehensive and substantive analysis enabled a more thorough understanding of the physicochemical structure of functionally relevant and active catalytic nanostructures. The overall analysis supported the idea that the catalytically active structure of our ternary NWs could actually be attributed to a PtAu–Pd motif, consisting of a PtAu binary shell coupled with a pure inner Pd core. Moreover, the plausible origin of the observed Au surface segregation could likely be ascribed to the external potential used (i.e., potential range of 0.5–0.8 V) during the Cu UPD process used to create the core–shell motif in the first place.

5. CHOICE OF CATALYST SUPPORT

5.1. Rationale. Carbon-based materials have usually been used as substrates for electrocatalysts, including carbon nanotubes (CNTs), carbon black (CB), graphene, carbon nanofibers, and fullerenes. In effect, carbon motifs possess the singularly favorable advantages of ubiquity, low price, high surface area, and excellent conductivity, all of which can contribute to the enhanced activity of the as-prepared catalysts.

Nevertheless, catalysts can sometimes aggregate and/or otherwise detach from the substrate, especially during reactions, an observation which may lead to decreased activity. One strategy for addressing this issue would be through chemical functionalization of the support, which would enable not only a more uniform dispersion of metallic catalysts but also protection from both dissolution and/or degradation.

As an example, theoretical DFT calculations have predicted that the presence of SH groups on CNTs can not only restrict particle migration but also enhance the oxidative resistance of Pt clusters attached onto these derivatized CNTs. Experimentally, the measured specific ORR activities of Pt NPs supported onto multiwalled CNTs (MWNTs) spanned a range from 0.3 to 0.6 mA/cm², depending upon the specific surface modifications of the supports, which were characterized by pendant –NH₂–COOH, –OH, and –SH functional moieties, respectively.

5.2. Functionalized CNTs. We chose to analyze ultrathin Pt NWs deposited onto a series of variously derivatized MWNT supports as well. However, a key difference in our studies, as compared with the previous work, was that we explored the impact of modifying not only the terminal ligand moiety but also the attachment approach. With respect to the latter issue, the problem with covalent functionalization is that robust treatment protocols, usually involving strong, destructive acids (such as HNO₃ and H₂SO₄ as illustrative examples), can lead to a loss of not only the structural integrity but also, consequentially, the favorable electronic properties of the CNTs, all of which could dramatically reduce both activity and long-term stability. Hence, our preference revolved around a less intrusive and less damaging noncovalent, physical sonicomediated approach. To highlight that both types of attachment methodologies are functionally equivalent, it is interesting to observe that the CVs of Pt NWs supported onto not only covalently functionalized COOH-terminated MWNTs (Figure 11A) but also analogous noncovalently functionalized COOH-derivatized MWNTs (Figure 11B) were essentially identical in nature. Specifically, a peak was observed at around 0.6–0.7 V, thereby confirming the redox activity of the surface carboxylic acid groups.

Indeed, our Pt NW@COOH-MWNT sample (Figure 11C) synthesized using the noncovalent method yielded the highest
activity measured of 1.54 mA/cm², which denoted not only a nearly 2.5-fold improvement as compared with Pt NW@raw-MWNTs (i.e., 0.60 mA/cm²) but also a 5-fold increase as compared with 0D@1D nanostructures, such as Pt NP@raw-MWNTs (i.e., 0.30 mA/cm²). To the best of our knowledge, our Pt NW@COOH-MWNT sample gave rise to the highest surface specific activity value measured, to date, using any carbon-based support, because it possessed a normalized Pt MA value of 0.68 A/mgPt, more than 4-fold higher than comparable data (i.e., 0.16 A/mgPt), measured for state-of-the-art commercial Pt/C systems. What made the key difference in our view was the favorable and synergistic metal-support combination of (1) using ultrathin Pt NWs instead of NPs, (2) employing a noncovalent derivatization method as opposed to a covalent-sonication-mediated method, (C) Bar graph highlighting the surface area activity of Pt NWs attached onto differentially functionalized CNTs. ORR activities have been normalized to their respective electrochemically active surface area values.

Figure 11. Cyclic voltammograms of Pt NWs supported onto various different types of functionalized MWNTs prepared by (A) a “covalent reflux” method and (B) a “noncovalent” sonication-mediated method. (C) Bar graph highlighting the surface area activity of Pt NWs attached onto differentially functionalized CNTs. ORR activities have been normalized to their respective electrochemically active surface area values.

6. SUMMARY AND OUTLOOK
To be effective and economically viable, catalysts should possess not only a high active surface area and corresponding favorable activity but also low cost and reasonable stability. Currently, Pt-based catalysts still represent the most widely used catalysts for applications in FCs mainly because of their high activity. Nevertheless, we and others have initiated a number of efforts toward optimizing (1) the intrinsic particle size of Pt nanostructures, (2) the production of novel morphological motifs, such as ultrathin NWs, and (3) the spatial distribution and dispersion of these nanoscale catalysts onto their underlying supports so as to transcend the traditional view of elemental Pt itself as the most important and best performing FC catalyst. As we have seen in this Perspective, Pt is scarce and expensive, and is moreover performance-limited in terms of both activity and stability.

Diverse strategies for replacing Pt have revolved around the idea of not only minimizing Pt loading within unusual architectural configurations but also replacing Pt with more plentiful, less expensive, and potentially less hazardous alternatives such as Ni, Fe, and Cu through careful chemical manipulation. Therefore, with the goal of developing and understanding the behavior of novel electrocatalysts in the context of small-molecule reactions such as ORR, HOR, EOR, MOR, and FAOR, we and others have specifically emphasized the importance of synergistically tailoring, on a holistic level, tunable reaction parameters such as (a) size (i.e., nanoscale), (b) morphology (i.e., anisotropic motifs), (c) chemical composition (i.e., alloys), (d) the presence of a core–shell architecture (i.e., an outer Pt ML conformally coating a non-Pt containing core), and (e) the nature (i.e., chemically functionalized) of the underlying support, so as to maximize catalyst performance and minimize catalyst deactivation.

Specifically, some of the highest electrochemical activities reported to date have been obtained by deliberately tuning the morphologies (i.e., generation of core–shell motifs) and chemical compositions of Pt-based bimetallic nanostructures onto rationally tailored substrates. In doing so, improved durability metrics coupled with measured activities of over a magnitude higher than the state-of-the-art commercial Pt catalyst have been achieved. We and others have developed ambient synthetic methods to prepare morphology- and composition-tunable Pt-based 1D nanostructures possessing high structural uniformity and a homogeneous distribution of elements. In optimizing both the morphology and chemical composition, we have exploited the advantages of phenomena such as, but not limited to, the bifunctional mechanism, the ligand effect, and the lattice strain effect. Overall, these advances have been of relevance in terms of creating a cheaper, more stable, and more efficient family of novel catalytic materials that will also be inherently less susceptible to poisoning and degradation.

It should be noted that even though our laboratory has focused on 1D NW-based motifs, significant complementary efforts from a number of different groups on equally effective, Pt-free 2D-based structures are also worth mentioning. Theoretically, metal-free, heteroatom-doped graphene-based nanomaterials were predicted to evoke highly favorable electrocatalytic performance toward ORR, denoting results which were ascribed to their achievable active surface area, their mobility and transfer and therefore yielded a positive collective impact upon the observed electrochemical performance.
beneficial exposure of reaction sites for either oxygen adsorption or reduction, and their excellent thermal and electronic properties.129,130 Experimentally, Fe–N–C-based materials characterized by a graphitic-layered structure produced a current density of 44 mA/cm² at 0.85 V and a maximum power density of 490 mW/cm² at 1 bar O₂ when incorporated into FCs.131 In addition, porous boron carbon nitride nanosheets with a surface area of 817 m²/g yielded comparable ORR activity, better stability, and improved methanol durability as compared with their Pt/C (20% Pt loading) counterparts in both alkaline and acidic media.132

Nonetheless, apart from the experimental design of new and improved catalyst materials, a number of daunting challenges remain. Though initial efforts are promising, theoretical calculations still have not been able to fully correlate the nuances of the catalyst structure with the measured performance. Experimentally, it is still nontrivial (i) to probe the spatial and temporal evolution of the physical structure and chemical composition of these novel nanoscale architectures (whether they are ultrathin NWs or core–shell motifs) in an interpretable, routine, and/or convincing manner and (ii) to analyze these various electrocatalytic processes under realistic in situ conditions, using dynamic in situ characterization techniques.

The hope and expectation is that the strengths and attributes of these novel probes can be used to analyze and correlate local and subtle changes in factors such as (i) the chemical composition and physical structure, as manifested by variations in the atomic arrangement, degree of oxidation, defect concentration, and crystallinity, as illustrative examples, and (ii) electronic properties. These parameters strongly influence and ultimately dictate the nature of catalyst-support interactions during an evolving electrochemical reaction under a realistic operating environment, all of which have tangible consequences for the observed catalytic mechanism, activity, and performance. A number of recent and interesting studies have focused not only on in situ, synchrotron-based techniques such as, but not limited to, X-ray absorption spectroscopy, X-ray photoelectron spectroscopy, soft X-ray ptychography, and XRD133–136 but also single-molecule imaging approaches.137 All of these advances denote positive and forward looking steps in the right direction toward eventually achieving these important goals of clearly elucidating critical structure-property correlations.

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