

# Engineering Interface and Surface of Noble Metal Nanoparticle Nanotubes toward Enhanced Catalytic Activity for Fuel Cell Applications

CHUN-HUA CUI AND SHU-HONG YU\*

*Division of Nanomaterials & Chemistry, Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemistry, CAS Key Laboratory of Mechanical Behavior and Design of Materials, the National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230026, People's Republic of China*

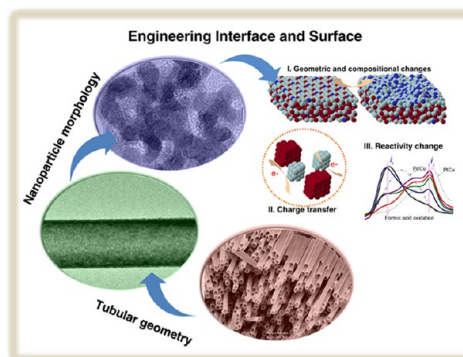
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## CONSPECTUS

In order for fuel cells to have commercial viability as alternative fuel sources, researchers need to develop highly active and robust fuel cell electrocatalysts. In recent years, the focus has been on the design and synthesis of novel catalytic materials with controlled interface and surface structures. Another goal is to uncover potential catalytic activity and selectivity, as well as understand their fundamental catalytic mechanisms. Scientists have achieved great progress in the experimental and theoretical investigation due to the urgent demand for broad commercialization of fuel cells in automotive applications. However, there are still three main problems: cost, performance, and stability. To meet these targets, the catalyst needs to have multisynergic functions. In addition, the composition and structure changes of the catalysts during the reactions still need to be explored.

Activity in catalytic nanomaterials is generally controlled by the size, shape, composition, and interface and surface engineering. As such, one-dimensional nanostructures such as nanowires and nanotubes are of special interest. However, these structures tend to lose the nanoparticle morphology and inhibit the use of catalysts in both fuel cell anodes and cathodes. In 2003, Rubinstein and co-workers proposed the idea of nanoparticle nanotubes (NNs), which combine the geometry of nanotubes and the morphology of nanoparticles. This concept gives both the high surface-to-volume ratio and the size effect, which are both appealing in electrocatalyst design.

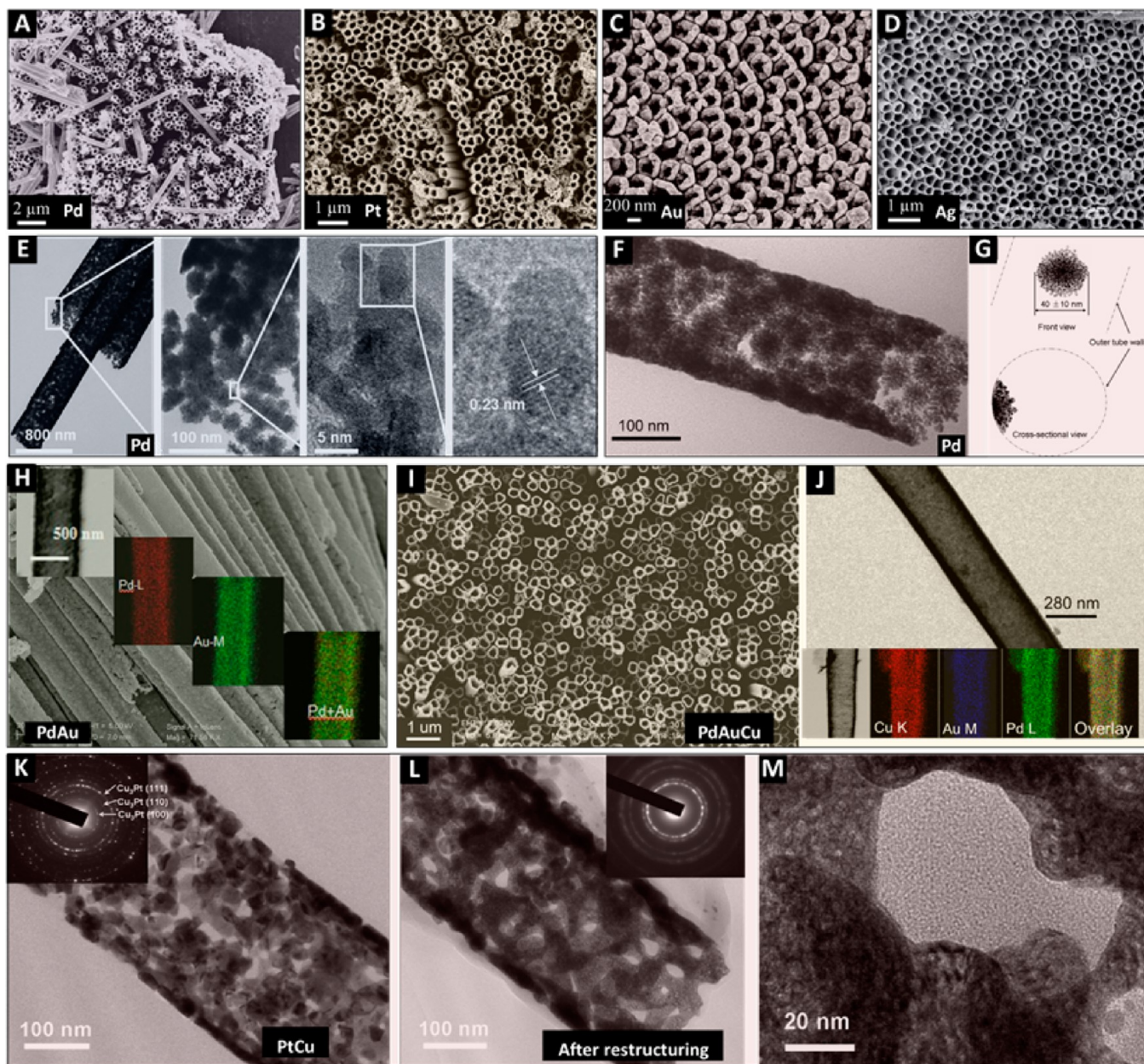
In this Account, we describe our developments in the construction of highly active NNs with unique surface and heterogeneous interface structures. We try to clarify enhanced activity and stability in catalytic systems by taking into account the activity impact factors. We briefly introduce material structural effects on the electrocatalytic reactivity including metal oxide/metal and metal/metal interfaces, dealloyed pure Pt, and mixed Pt/Pd surfaces. In addition, we discuss the geometric structure and surface composition changes and evolutions on the activity, selectivity, and stability under fuel cell operation conditions. We expect that these nanostructured materials with particular nanostructured characteristics, physical and chemical properties, and remarkable structure changes will offer new opportunities for wide scientific communities.



## 1. Introduction

Rapid development of fuel cell technology in the past decade has stimulated intensive research in design, synthesis, and fundamental understanding of electrocatalysts. Generally, the size, shape, composition, and interface/surface engineering in catalytic nanomaterials are the key

parameters that are usually considered in synthesis to exhibit the rule of activity dependence.<sup>1</sup> Pt- and Pd-based nanoparticle catalysts with controlled geometric architectures, compositional profile, and surface microstructures have demonstrated highly enhanced catalytic properties. Abundant defect sites and low-coordination atoms on the



**FIGURE 1.** Morphology and structure controls of various NNs. (A) Pd, (B) Pt, (C) Au, and (D) Ag NNs.<sup>10</sup> (E) The stepwise magnified TEM and HRTEM images of the Pd NNs. (F) TEM image and (G) schematic sketch showed the hierarchical structure in the Pd NNs. (H) PdAu heterostructured NNs without alloying.<sup>9</sup> (I) SEM image of PdAuCu NNs. (J) TEM image of a single PdAuCu NNs shows the obvious tubular structure. Element mapping showed the uniform distribution of element Pd, Au, and Cu.<sup>8</sup> (K) TEM image of PtCu NNs after thermal annealing at 600 °C. (L) TEM image of porous PtCu NNs after electrochemical treatment in 0.1 M HClO<sub>4</sub> solution with 250 potential cycles. (M) The magnified TEM image shows the highly rough surface.<sup>6</sup>

nanoparticle surfaces are favorable active sites for organic small molecule electro-oxidation and water splitting but sometimes are inhibitors for the oxygen reduction reaction (ORR). The promising one-dimensional nanostructures such as nanowires and nanotubes have received special interest.<sup>2,3</sup> However, these one-dimensional structures lost the nanoparticle morphology and inhibited the wide use of catalysts in both fuel cell anodes and cathodes. In 2003, Rubinstein and co-workers proposed the concept of

nanoparticle nanotubes (NNs).<sup>4</sup> The combination of nanotube geometry with nanoparticle morphology can achieve both the high surface-to-volume ratio and the size effect, which are highly attractive in design of electrocatalysts. Nanoparticles as attractive building blocks can be used to assemble three kinds of tubular structures, that is, single-component NNs, heterogeneous multicomponent NNs, and well-alloyed NNs. Thus, based on these unique structures, the creation of a heterogeneous interface in nanotubes and



the formation of an alloy particle surface with controlled microstructures will contribute to the enhanced electrocatalytic performance.

The catalytic activity strongly correlates with the adsorption strength and adsorption configuration for reactive molecules on the NNs and their competitive adsorption with the intermediate and guest species. This adsorption surface chemistry is highly related to three main impact factors, i.e., ligand effect, geometric strain effect, and ensemble effect. *Ligand effects* are caused by electronic charge transfer between the atomic vicinity at the heterostructured interfaces and in the surfaces within one to four surface atom layers.<sup>5</sup> *Geometric strain effects* are caused by the differences of surface atomic arrangements or bond lengths in contrast to those in the core region. However, strain release sometimes produces surface roughness and surface atomic rearrangement from the core to the surface region.<sup>6</sup> *Ensemble effects* come from the dissimilar surface atom ensembles (small group of surface atoms). The ensemble effects usually result in changes of the adsorption configuration, adsorption energy, and adsorption repulsions for reactive molecules on active sites.

Another important issue is how to monitor and understand the surface microstructure and composition changes of the NNs in fuel cell operation conditions. In general, even single potential cycling can leach out the less-noble metal and make the metal atoms migrate in catalyst surfaces.<sup>7</sup> The structure and composition changes of NN catalysts should be the direct evidence for realizing the catalytic activity and degradation. Leaching of active metal, surface segregation (compositional restructuring), and surface geometric restructuring are three main issues for catalyst evolution in electrochemical conditions. Effective tracking of these changes of the catalysts will provide more chances for optimizing their catalytic performance.

## 2. Controlled Synthesis of Surfactant-Free Nanoparticle Nanotubes (NNs)

Conventional colloidal chemistry approaches have shown limited success in the synthesis of NNs. Rubinstein and co-workers reported a pioneering multistep synthesis of well-defined Au(Ag) NNs by assembly of Au(Ag) nanoparticles on the inner pore walls of a 3-aminopropyl trimethoxysilane pretreated anodic aluminum oxide (AAO) template.<sup>4</sup> Other multistep-template methods were used to prepare tubular structures, but sometimes they consist of single crystal tube walls rather than nanoparticles.

A general one-step electrochemical method has been developed to prepare the NNs with uniform particle size

and well-defined tubular structure.<sup>6,8–10</sup> Through simply tuning the precursor concentration and applied potential, we have synthesized different types of NNs with controlled features as shown in Figure 1. For example, single-component Pt, Pd, Au, and Ag noble metal NNs were obtained in dimethyl sulfoxide (DMSO) solvent without addition of any surfactants as shown in Figure 1A–E.<sup>10</sup> The diameter and the length of the NNs were controlled by the inner diameter of the template channel and the reaction time, respectively. The particle sizes of Au (Ag) are much bigger relative to the Pt (Pd) nanoparticles, which may be related to the reduction potential and the interaction between metal nanoparticle and DMSO. Specially, hierarchical structure has been revealed in Pt and Pd NNs, which consist of flocky-like hemispheres that include plenty of tiny nanocrystals, about 3–6 nm (Figure 1E–G).<sup>10</sup> Therefore, the NNs have a large diameter (~300 nm) but high surface area owing to the hollow and unique structural characteristics. Based on the successful synthesis of single-component noble metal NNs, bimetallic NNs such as PdAu can be synthesized. By adjustment of the ratio of Pd and Au ion concentrations in the electrolyte and applied potential, Pd/Au NN heterostructures with controlled composition ratio has been achieved.<sup>9</sup> Due to the differences of the redox potentials in aqueous solution, it is difficult to control the composition ratio in the synthesis of multicomponent catalysts.<sup>11</sup> The reduction potential rule may not be available in a nonaqueous solvent; thus, the reduction reaction can be tailed on a given component system. Ternary heterostructures, for example, PdAuCu, have been prepared in a similar system.<sup>8</sup>

Gaseous adsorbate involved thermal annealing is highly effective to synthesize Pt- or Pd-enriched shell structures. Upon thermal treatment under flowing mixed hydrogen and argon, the electrodeposited pristine materials such as PtCu ripened into a tubular structure, which consisted of well-alloyed 40 nm sized core/shell PtCu/Pt nanoparticles, where the Pt atoms migrated to the surface region and accordingly the Cu atoms in the surface region migrated to the core.<sup>6</sup> In addition, for ternaries such as PtPdCu, both Pd and Pt migrated to the surface and Cu migrated to the core.<sup>12</sup> This surface compositional restructuring is driven by the heat of segregation, the surface mixing energy, and the high adsorption energy of hydrogen on Pd and Pt in contrast to Cu.<sup>6</sup>

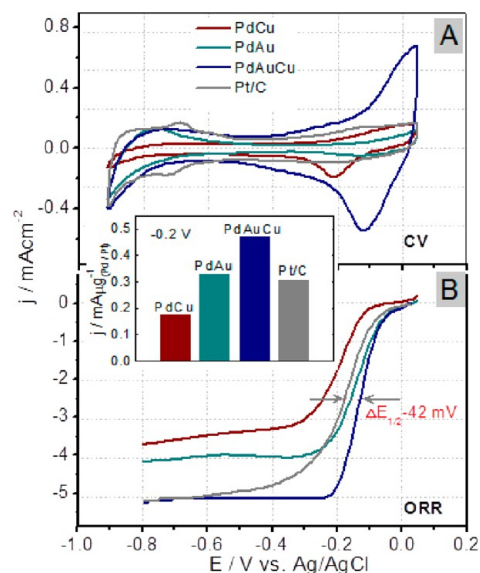
Electrochemical post-treatments have been considered as encouraging approaches to modify the catalyst surface. After thermal annealing, the NNs containing large particles result in the loss of the surface active area owing to Ostwald

ripening. Low surface area per Pt mass makes these catalysts lose mass activity and limited the utilization of costly Pt. Electrochemical potential cycling (dealloying) has been employed to modify the surface structures of PtM (M = Cu, Co, Ni) catalysts by Strasser and co-workers.<sup>7</sup> Potential cycling on M-enriched nanoparticle surface leached away a mass of active metal M that allowed the formation of skeleton rough surface and, finally, improved the surface active sites. We have used this strategy to modify the surface of our catalysts, especially on PtCu and PtPdCu NNs with Pt-enriched surface. Pt- or PtPd-enriched surface demonstrated high surface compressive strain, produced by the lattice mismatch between the Pt- or PtPd-enriched shell and the alloy core owing to a reduced Pt–Pt or Pt–Pd bond distance on the surface.<sup>13</sup> We found that potential cycling on Pt- or PtPd-enriched surface resulted in the release of surface compressive strain and caused the formation of rough surface owing to adsorbate-induced geometric restructuring, during which only a few active metal M atoms were leached from the surface<sup>6,14</sup> (Figure 1K–M). On the other hand, for ternary PtPdCu, besides the geometric restructuring induced rough surface, an interesting surface compositional restructuring was detected, that is, the Pt/Pd ratio increased with increasing the potential cycling in the topmost layer.<sup>14</sup>

Heterostructures such as Pd–Au and Pd–Au–Cu NNs, well-alloyed PtCu and PtNi NNs, porous PtCu NNs, or Pt- or PtPd-enriched PtPdCu NNs have been synthesized based on electrodeposited single- and multicomponent NNs. We can manipulate the surface compositional and geometric changes to understand the catalytic activity changes and *in situ* track the catalyst degradation.

### 3. Interface Effects on the Catalytic Reactivity

**3.1. Metal Oxide–Metal Interfaces.** Supported metal catalysts are among the most important materials in heterogeneous catalysis. Before the 1980s, metal oxide supports were only used as very attractive support materials for preventing the agglomeration of metal catalysts. After that, scientists discovered the strong bonding between the support and the metal.<sup>15</sup> This bonding could make the electrons transfer from the valence atoms to the supported metal particle and this electron transfer usually changes the electronic structure of the metallic surface. For example, a dumbbell-like Pt/Fe<sub>3</sub>O<sub>4</sub> catalyst owing to the change of the binding energy through electron transfer from Fe<sub>3</sub>O<sub>4</sub> to Pt demonstrated its 20-fold increase in mass activity toward the ORR relative to Pt catalyst.<sup>16</sup> In addition, metal oxide–metal interfaces change the adsorption configuration for

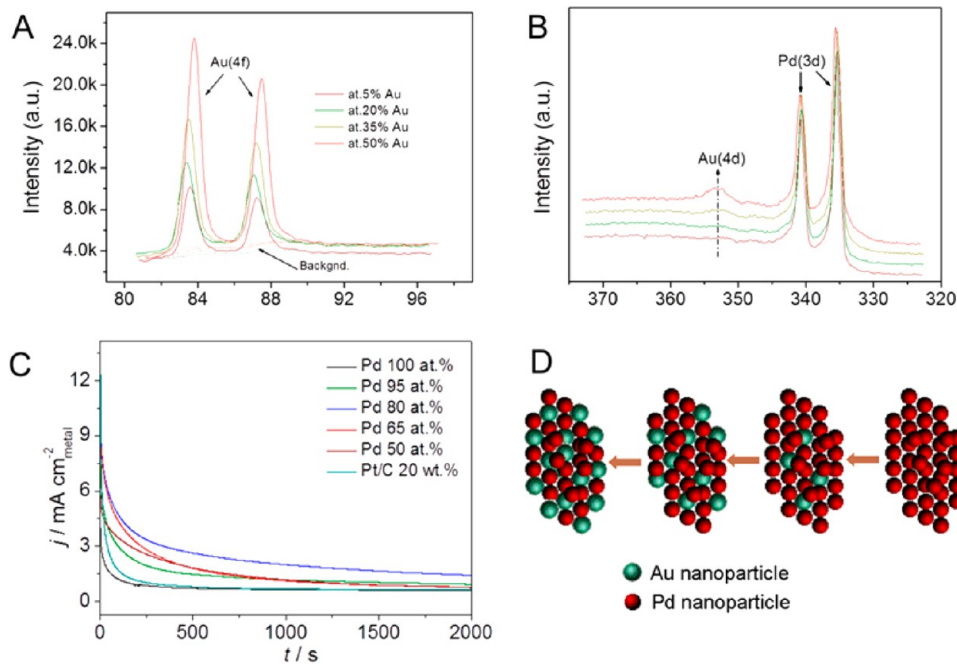


**FIGURE 2.** (A) CV curves of heterostructured PdAuCu NNs recorded in Ar-purged 0.1 M KOH solution at 50 mV s<sup>-1</sup>. (B) ORR polarization curves for PdCu, PdAu, PdAuCu NNs, and Pt/C catalysts. Inset shows the mass activity at -0.2 V for these four catalysts.<sup>8</sup>

reaction molecules. El-Deab et al. reported a composite nano-MnO<sub>x</sub>/Pt electrode that demonstrated a significant positive shift of onset potential for the ORR.<sup>17</sup> The enhancement was explained as the increased end-on adsorption orientation modes (higher adsorption amount for oxygen) in contrast to the bridged orientation at the bare Pt electrode, like an ensemble effect. Therefore, metal oxide–metal interfaces can provide various possibilities for modifying the metal catalytic surface.

The highly improved catalytic activities of ternary PdAuCu NNs have been investigated relative to binary PdCu and PdAu for both the ORR and H<sub>2</sub>O<sub>2</sub> reduction in alkaline solution (Figure 2).<sup>8</sup> In the binary PdCu system, the surface Cu was easily oxidized to Cu(I) at a given potential range. Specially, after Au was introduced in PdCu, the surface Cu can be oxidized to Cu(II). We found that the Cu(II) species can serve as a promoter to improve the ORR activity. In this case, the presence of Au may change the redox potential of Cu and favor the formation of active Cu(II) species through the potential difference in the Au/Cu system. The possible reason for the activity enhancement may be similar to the high activity for the H<sub>2</sub>O<sub>2</sub> reduction in the Au/Fe<sub>3</sub>O<sub>4</sub>, where there is an interaction between Au and Fe<sub>3</sub>O<sub>4</sub> from the Au polarization toward the support at the interface.<sup>18</sup>

Another galvanic cell method was developed for the synthesis of heterostructures. High-quality semiconductor Te nanowires acted as a facile template to prepare highly active heterostructured catalysts.<sup>19,20</sup> Te/Pt heterostructures



**FIGURE 3.** (A) Au(4f) and (B) Pd(3d) and Au(4d) spectra of the PdAu NNs with different molar ratios of Au (at. %). (C) Chronoamperometric curves for ethanol electro-oxidation at 0.3 V versus Hg/HgO on PdAu or Pd NNs and Pt/C catalyst. (D) Simplified schematic illustration of the interface increase with increasing of the Au ratio.<sup>9</sup>

have been easily synthesized by galvanic replacement. Interestingly, the downshift of the d-band center of Pt weakens the chemisorption with oxygen-containing species, such as  $\text{OH}_{\text{ad}}$  and  $\text{CO}_{\text{ad}}$ , and therefore, has a lower oxophilicity and favors the methanol oxidation reaction.<sup>21</sup>

**3.2. Metal–Metal Interfaces.** Although the distinctive catalytic activity of dispersed metal NPs supported on oxides has been extensively investigated and the interface effects have already been revealed, limited works presented have already been revealed, limited works presented metal–metal interfaces. For example, a carbon-supported Pt surface with deposited Au clusters prevents the oxidation–dissolution of Pt because oxidation of Pt in Pt–Au catalyst requires higher potentials relative to unmodified Pt nanoparticles.<sup>22</sup> Otherwise, the Au decorated Pt–Au catalysts by electrostatic self-assembly exhibit significantly enhanced activity toward formic acid oxidation because of the efficient spillover of HCOO from Au to the surrounding Pt NPs.<sup>23</sup> In addition, Pt–Pd binary heterostructure is also a promising catalyst for formic acid and ethanol oxidation.<sup>24</sup> However, constructing a metal–metal interface in a tube is quite difficult. A pioneering work was the double-wall Sn/Pt tube, which demonstrated attractive heterostructured interface sites and showed remarkably enhanced activity toward methanol oxidation by lowering its overpotentials.<sup>25</sup>

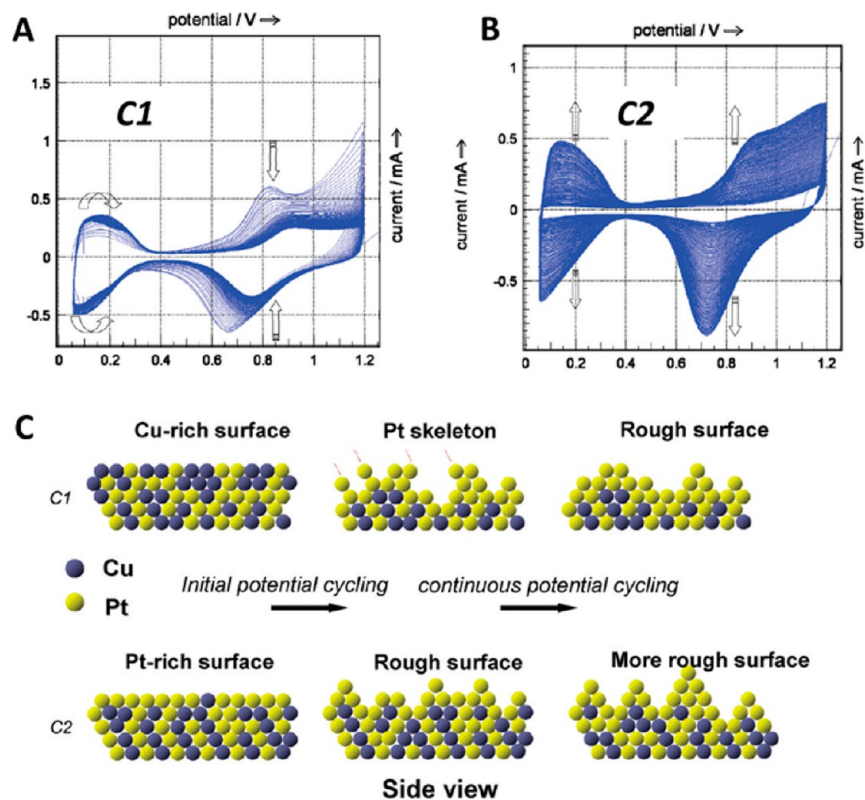
A Pd/Au bimetallic nanoparticle tubular structure with tunable interface sites has been designed to illustrate the

interface effect on the activity for the ethanol electro-oxidation.<sup>9</sup> This heterostructure was synthesized by a surfactant-free route, thus there was no capping agent at the interface sites, avoiding the interference of adsorption molecules.<sup>10</sup> The interface sites of this bimetallic system have been finely controlled by tuning the proportion of Pd and Au NPs, which are homogeneously distributed in tubes. The results suggest that the catalytic activity is mainly relative to the interface sites and has no direct relation with individual metal components in this Pd/Au. When the atomic fraction of Au was increased to 20–35 at. %, the Pd/Au catalyst had the best activity for ethanol oxidation. Moreover, at this component ratio, significant shifts of the Au(4f) peaks toward lower binding energies were observed, indicating a modification of the electronic structure of the metal as shown in Figure 3.

## 4. Surface Effects on Catalytic Reactivity

**4.1. Fundamental Concepts for Catalytic Surface.** The low catalytic activity and poor stability of platinum-based electrocatalysts and their high cost for low-temperature fuel cell processes are critical issues that need to be addressed. One of the most attractive approaches is the synthesis of low Pt content binary and ternary alloy electrode materials by alloying a 3d transition metal. In the past decade, there emerged three electrocatalyst concepts, that is, Pt





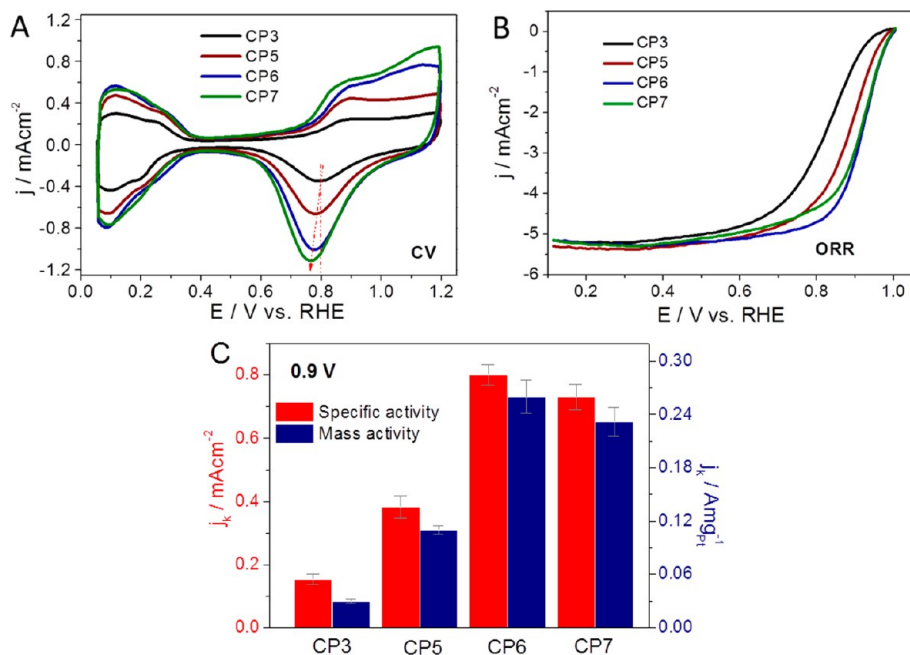
**FIGURE 4.** CVs for Cu-rich surface (A, C1) and Pt-rich surface (B, C2) of CuPt NNs. (C) Schematic of different surface structure evolutions between C1 and C2 surfaces.<sup>6</sup>

monolayer, Pt-skin, and dealloyed Pt. "Pt monolayer" catalysts consisted of a monolayer of Pt on a guest metal or alloy core and "Pt skin" catalysts contained a segregated single Pt surface layer from an alloy core. These two catalysts offered strain-induced d-band center shifts (geometric effect) and electronic coupling (ligand effect), which weakened the interactions between Pt and adsorbates such as  $H_{\text{upd}}$  and  $OH_{\text{ad}}$ . "Dealloyed Pt" catalysts with rough Pt surface were obtained by selectively leaching 3d transition metals such as Cu, Ni, and Co from the surface of alloy nanoparticles.<sup>7</sup> The Pt thickness of a dealloyed particle is much thicker (0.6–1.0 nm) relative to the Pt monolayer and the Pt skin structure.<sup>13</sup> Geometric strain effects are operative over a higher atomic depth.<sup>13</sup>

Beyond three ideal concepts on design of electrocatalysts, there still have been some other cases in the design and development of catalytic surfaces. In acidic or alkaline electrolytes, the catalysts are subjected to leaching and surface atom migration because the surface atoms tend to form a thermodynamically stable structure to adapt the electrochemical environments. The redox potential cycling at higher potential causes the adsorption of oxygenated species and at lower potential results in the adsorption of

hydrogen. These adsorbates on a catalyst during potential cycling drive the migration of surface metal atoms, cause catalytic surface faceting or surface roughening, in turn, change the surface morphology and microstructure. We called this process "geometric restructuring". On the other hand, potential cycling also can make the change of the surface composition. If the composition change results from active metal dissolution, it is called dealloying or leaching. Otherwise, it is described as "surface segregation" (compositional restructuring) owing to the atomic migration between the surface and core regions and the atomic redistribution on a mixed alloy surface. In this part, we mainly focus on the "restructured surface" or "rearranged surface". Developing this concept is to more easily understand the behaviors of catalysts in electrochemical environments not only for the catalyst treatments but also for the understanding of the degradation of alloyed catalysts.

**4.2. Geometric Restructuring in Electrochemical Environments.** Every catalyst under potential cycling (stability tests) experiences shape and size alternations. The surface atoms of a catalyst are energetic in electrochemical environments. Nanoparticle catalysts with small particle sizes such as commercial Pt/C catalysts lose the surface area under



**FIGURE 5.** (A) CVs of the CuPt NNs recorded in an Ar-saturated 0.1 M HClO<sub>4</sub> solution at 50 mV/s. (B) ORR polarization curves for CuPt NNs after 250 cycles in an O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution (20 mV/s, 1600 rpm). (C) Specific and mass activities of CuPt NNs at 0.9 V vs RHE. Specific and mass activities are depicted as kinetic current densities ( $j_k$ ) normalized to the ECSA and loading Pt mass, respectively.<sup>18</sup>

potential cycling and suffer from morphology changes.<sup>26</sup> In our group, potential cycling was used to transform the Pt oxide/Pt core/shell nanoparticles completely into highly active and stable pure Pt nanoparticles by surface atomic rearrangement.<sup>27</sup> For Pt-based alloys, however, it is quite difficult to clarify whether the morphology changes come from leaching of the less noble metal or the concomitant atomic restructuring. Strasser and co-workers reported size-dependent morphology in dealloyed bimetallic catalysts from 3 to 100 nm.<sup>28</sup> The particle upon dealloying is a single core-shell structure below 10 nm, multiple core-shell structures from 10 to 15 nm, and a porous structure above 15 nm. This result is further evidenced by Snyder et al. in PtNi nanoparticles.<sup>29</sup> Obviously, this key size about 15 nm is highly related to the surface kinetic processes (surface atomic diffusion coefficient). The morphology change induced by strong leaching of active metals is not within the topic of this Account, but the surface Pt atom rearrangements and faceting owing to the missing neighboring active metals are included in this subject.

Geometric restructuring has been studied in the tubular catalyst containing CuPt nanoparticles (~40 nm) with a Pt-rich shell and high lattice ordering.<sup>6</sup> After 250 potential cycles, the surface area increased about 10-fold higher relative to the initial surface and porosity was observed, indicating roughness (Figure 4B).<sup>6</sup> It must be noted that there

is less leaching relative to the dealloying processing on active-metal-enriched surfaces in the whole geometric restructuring process.<sup>30</sup> Thus, the highly enhanced surface area was attributed to surface restructuring that was driven by the potential-induced release of the surface strain, which came from the compressed Pt–Pt bonds in the surface in contrast to the Pt–Cu bonds in the core region (Figure 4). The strain release under potential cycling contributes to the rearrangement of surface atoms and the enhancement of surface area. However, for the Cu-enriched surface, the strong leaching benefits the formation of a highly rough surface with a large number of low coordination atoms and dangling bonds (Figure 4C). To minimize the surface free energy, the concomitant atomic rearrangement could decrease the surface active sites and smooth the surface. A similar trend has also been observed in PtNi and ternary PtPdCu alloy systems.<sup>12,31</sup> To further observe the surface roughness by electron microscopy, we thermally treated the PtPdCu NNs at 500 °C for 8 h in 5% H<sub>2</sub> balanced with Ar to obtain a near-extended flat metal surface. After 250 potential cycling treatments, obvious gully like contrast difference was observed compared with that before 250 cycling treatments, suggesting the formation of a rough surface upon potential cycling.<sup>12</sup>

The enhanced activity and stability for the ORR have been studied on PtCu bimetallic tubular electrocatalysts.

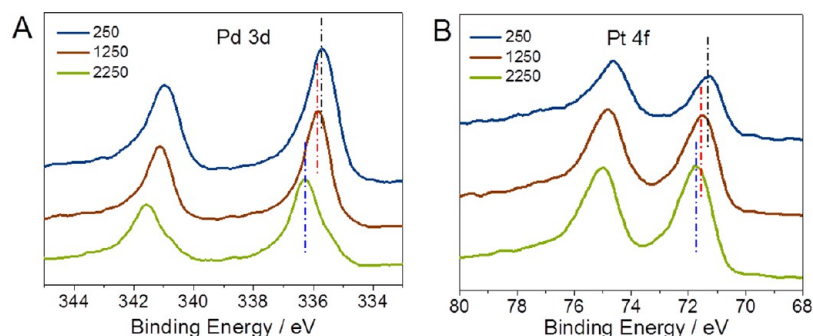


FIGURE 6. (A) Pd 3d and (B) Pt 4f core levels of the PtPdCu NNs after 250–2250 potential cycles.<sup>14</sup>

To reveal the surface morphology and composition changes and how these alternations influence the activity, we have synthesized a series of CuPt surfactant-free tubular electrocatalysts with sequential increased lattice ordering and surface atomic fraction of Pt.<sup>6</sup> The catalysts with a Pt-rich surface and high lattice ordering caused less Cu leaching, higher surface area, and higher activity and stability, and vice versa. The higher Cu composition in bulk increased the surface strain at the interface between Pt shell and CuPt alloy core. The compressive strain release upon potential cycling resulted in a rough surface, but the much rougher Pt surface with low coordination number favors the adsorption of oxidized species, such as hydroxyls. The regular negative shifts of the peak potentials on the backward sweep suggested the stronger bond energy with increasing the potential cycling number in Figure 5A. Thus, for the dealloyed Pt shell surface, the enhanced performance should be a balance between the Cu content at the core and the density of surface Pt sites with low coordination number.<sup>6</sup> This case helps one understand the correlation between lattice strain effect and strain release owing to the surface roughness. Rearranged rough surface demonstrated specific and mass activities of  $0.8 \text{ mA cm}_{\text{Pt}}^{-2}$  and  $0.232 \text{ A mg}_{\text{Pt}}^{-1}$  at  $0.9 \text{ V}$  for ORR in Figure 5C. Moreover, after a long-term stability test (10 000 cycles), the electrochemically active surface area (ECSA) of the rearranged surface can be restored to its initial value after another 250 cycles in  $\text{N}_2$  saturated electrolyte. Besides PtCu, the rearranged Pt–Ni surface of Pt-rich Pt–Ni NNs after potential cycling also demonstrated highly improved activity, stability, and resistance to poisoning for the methanol electro-oxidation.<sup>31</sup>

**4.3. Compositional Restructuring in Electrochemical Environments.** Electrochemical dealloying could induce oxidation and dissolution of less noble metals in the surface, changing the surface composition. However, potential cycling also can induce surface segregation or compositional restructuring

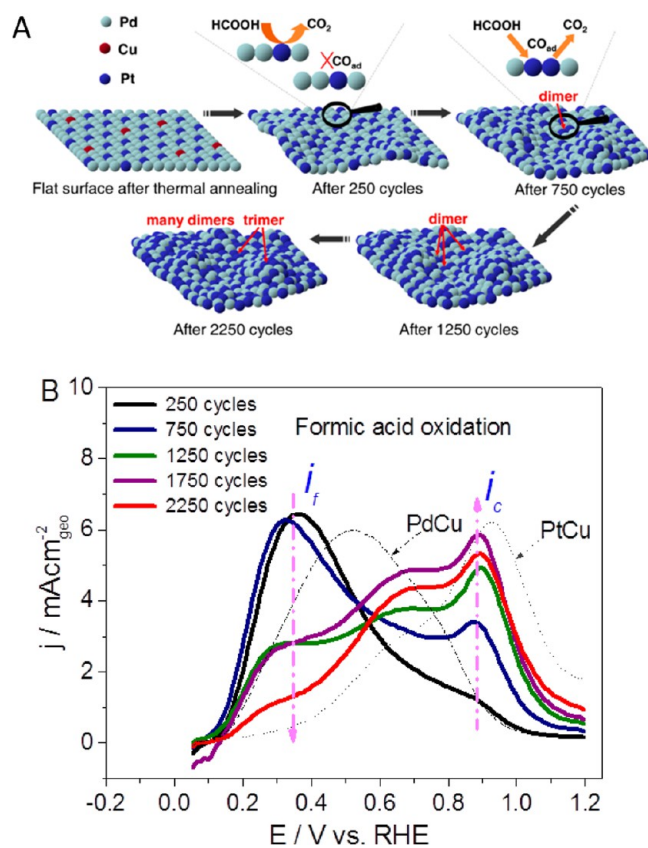
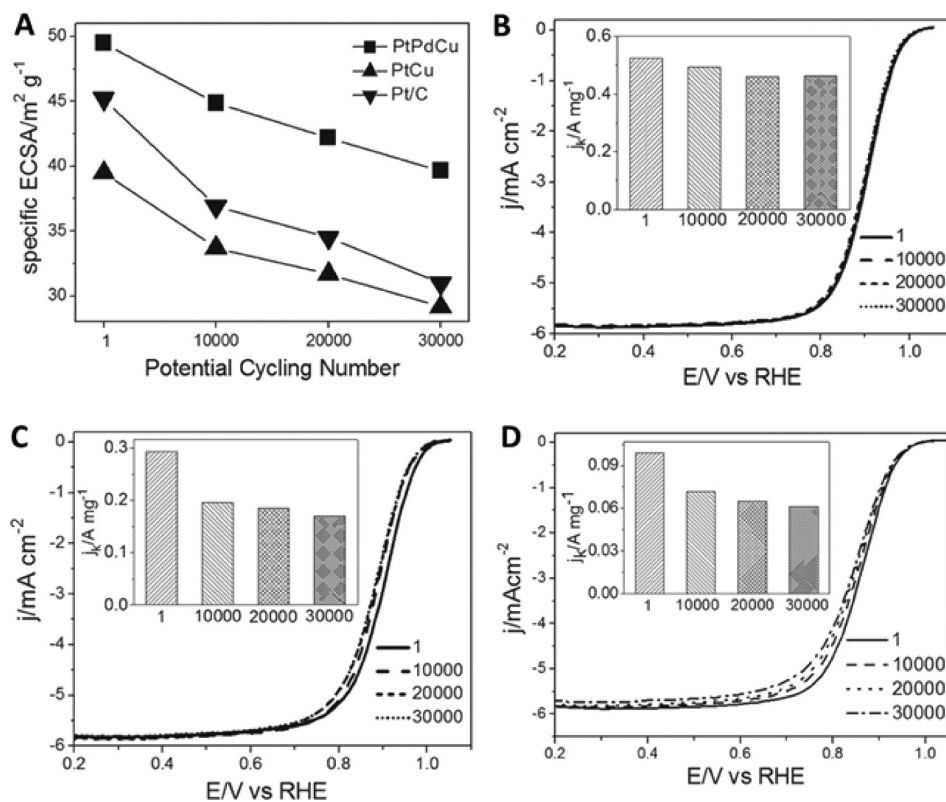


FIGURE 7. (A) Schematic of the surface-atomic redistribution of Pt and Pd in PtPdCu NNs during potential cycling. (B) CVs of the formic acid oxidation through the positive scan after different numbers of potential cycles;  $i_f$  represents the peak current intensities of direct oxidation of HCOOH to  $\text{CO}_2$  in pathway I, and  $i_c$  denotes the peak current intensities of oxidation to  $\text{CO}_2$  through the formation of an intermediate CO in pathway II.

without any dissolution of less noble metals.<sup>32</sup> This idea has been used to explain the catalytic degradation mechanism in electrocatalysis. This surface segregation usually is decided by adsorbate molecules. For example, for the PtCo alloy, in alkaline solution, the Co atoms segregated to the surface because of the stronger adsorption/desorption of oxygenated species on Co,<sup>32</sup> while in CO-saturated alkaline





**FIGURE 8.** (A) ECSAs of PtPdCu NNs, PtCu NNs, and commercial Pt/C catalysts during durability testing. ORR polarization curves recorded in oxygen-saturated 0.1 M HClO<sub>4</sub> solutions at 5 mV s<sup>-1</sup> at 1600 rpm for the PtPdCu NNs (B), PtCu NNs (C), and commercial Pt/C catalysts (D). Insets show the mass activity at 0.9 V versus RHE.<sup>34</sup>

electrolyte, the stronger CO adsorption on Pt compels the migration of Pt to the surface and constructs a Pt<sub>x</sub>Co<sub>y</sub>/Pt core/shell structure.<sup>33</sup> However, there is still a great challenge for the surface segregation study in acidic electrolytes.

Noble metals such as Pt and Pd are relatively resistant to corrosion and dissolution in acidic electrolyte, which provides possibilities in the study of the surface segregation chemistry. Ternary PtPdCu porous tubes with a mixed PtPd alloy surface are a best-fit catalyst for this study. We uncovered the surface atomic redistribution upon electrochemical potential cycling.<sup>14</sup> After the leaching of the surface Cu atoms and following construction of the PtPd alloy surface, further potential cycling activated the migration of Pt to the topmost surface and subsequent changes in the surface electronic structure and the adsorbate-bond energy for the oxygenated species. Interestingly, the peak current potential during backward sweep after potential cycling treatment positively shifted about ~70 mV, which was strongly correlated with electronic structure changes as shown in Figure 6A,B and, thus, influenced the ORR catalytic activity.<sup>14</sup> This surface atomic redistribution could be considered as a major factor to explain the catalytic activity and durability.

On the basis of these findings, we have used this composition restructuring on the topmost layer to evidence the surface active site-dependent formic acid electro-oxidation. For the formic acid oxidation, it is well-known that the oxidation of HCOOH to CO<sub>2</sub> proceeds through two parallel pathways: direct oxidation to CO<sub>2</sub> (pathway I) and oxidation to CO<sub>2</sub> through the adsorption of a CO intermediate (pathway II). In pathway I, the HCOOH molecules are directly oxidized to CO<sub>2</sub>. Pathway II involves HCOOH dehydrogenation to form CO and subsequent electro-oxidation of the adsorbed CO to CO<sub>2</sub> at high potentials. The sites of a single Pt atom surrounded by Pd atoms favored the direct oxidation of formic acid through pathway I (Figure 7A). Active sites consisting of two or three neighboring Pt atoms (dimer or trimer of Pt atoms) were required for pathway II (Figure 7A). Potential cycling increased the density of dimers and trimers of Pt atoms on the topmost surface, which enhanced the adsorption of CO<sub>ad</sub> on the surface. This process favors pathway II and gives an increase of relative current density,  $i_c/i_t$ , between 0.35 and 0.9 V (Figure 7B).

Another galvanic replacement method has been utilized to synthesize PtPdCu NN catalysts in large scale. This catalyst

demonstrated comparable catalytic activity for the ORR relative to PtCu NNs after potential cycling but showed much higher catalytic stability.<sup>34</sup> As shown in Figure 8A, the ECSAs of PtPdCu, PtCu, and Pt/C catalysts decreased proportionally after stability tests, suggesting the comparable loss of the active sites. The loss of ECSA for PtPdCu NNs was ~20%, but the PtPdCu maintained ~90% of the initial mass activity relative to PtCu and Pt/C as shown in Figure 8B–D. These results suggested that the increased intrinsic activity compensated the loss of the surface active sites. After the stability test, the specific activity was even higher than that before stability test. Thus, the enhanced stability should be attributed to the improved activity per surface active site due to the surface atomic redistribution induced change of surface electronic structure.<sup>14</sup>

## 5. Concluding Remarks

Unsupported nanoparticle tubular catalysts with tailored unusual interfaces and surface nanostructures provide multiple synergic functions and modified physical and chemical properties relative to conventional nanoparticle catalysts. In this Account, we summarize recent achievements in design and synthesis of nanoparticle nanotube (NNs) fuel cell electrocatalysts. Enhancements of the catalytic properties are mainly determined by the inherent nature of catalysts and the adsorption properties of the catalytic surfaces. However, the research bottleneck and challenge in the field of fuel cell technology still meet with the high cost and low reactivity. To unfold the nanocatalysts such as unsupported NNs into a practical application, the dimensions should be extended. For example, thin films, spongy structures, network structures,<sup>26</sup> and even nano-sized assemblies are attractive choices for this target.

Surfactant-free colloidal chemical synthesis of the electrocatalysts still holds great potential for further improvement of the catalytic reactivity, because capping agent molecules adsorbed on the catalyst surface may block the exposure of the surface active sites. The surfactant-free NNs reported in this Account provide a possibility for the synthesis of nanoparticle catalysts. Moreover, carbon-supported surfactant-free shaped alloy nanoparticles have been synthesized and presented exceptional catalytic activity.<sup>35</sup> Developing surfactant-free synthesis of Pt-based alloy should be an alternative route for the activity enhancement. Another serious issue is that the leaching-induced composition and shape changes for alloyed catalysts depress the long-term activity. Thus, developing multicomponent alloys with a highly active surface integrated with synergic supports such as metal carbide should be a promising approach in the future.

Despite all the above success, till now, we still have very limited understanding of the changes of catalysts in reaction conditions. Tracking the shape and composition changes during the electrocatalysis will provide the references for understanding the surface area and activity loss mechanisms. Meanwhile, with the fast development of electron microscopy and other *in situ* analysis techniques, as well as computational chemistry, there are more chances to get the exact surface composition and structural information at an atomic scale.<sup>36</sup> These achievements will pave the way for the further development of fuel cell applications.

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## BIOGRAPHICAL INFORMATION

**Chun-Hua Cui** earned his Ph.D. in Nanochemistry under the supervision of Prof. Shu-Hong Yu from the USTC in 2011. He is currently a Postdoctoral research associate under Prof. Peter Strasser at the Technical University Berlin, Germany. His research interests focus on the design and synthesis of surfactant-free nanocatalysts and their applications in fuel cells.

**Shu-Hong Yu** received his Ph.D. in inorganic chemistry in 1998 from the University of Science and Technology of China (USTC). After he finished postdoctoral research in the Tokyo Institute of Technology and the Max Planck Institute of Colloids and Interfaces, he was appointed as a full professor in 2002 at the USTC and was awarded the Cheung Kong Professorship. His recent awards include the Roy-Somiyama Medal of the International Solvothermal and Hydrothermal Association (ISHA, 2010) and *Chem. Soc. Rev.* Emerging Investigator Award (2010). His research interests are focused on synthesis and self-assembly of new nanostructured materials and nanocomposites, functional nanostructures, and their applications. He serves as an associate editor for *CrystEngComm* and *Materials Research Bulletin*, and is an editorial advisory board member of *Chemical Science*, *Nano Research*, *Particle & Particle Systems Characterization*, and *Current Nanoscience*.

## FOOTNOTES

\*To whom correspondence should be addressed. E-mail: shyu@ustc.edu.cn. The authors declare no competing financial interest.

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