Nanomaterials for Proton Exchange Membrane Fuel Cells

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Abstract The development of fuel cell technology, especially the proton exchange membrane fuel cell, is progressed through the use of nanomaterials. This chapter introduces the recent development of nanostructured electrocatalysts for fuel cell applications. An overview of various synthesis methods for nanostructured electrocatalyts is first presented. The morphology control of the electrocatalysts is then discussed, including zero-dimensional, one-dimensional, multi-dimensional, and hollow structures. Multi-component electrocatalysts with improved durability and activity for various fuel cell reactions are also introduced. Finally, the advantage of using carbon nanotubes as electrocatalyst support and noncovalent functionalization of nanotube surface is discussed in detail.

1 Introduction of Proton Exchange Membrane Fuel Cell(PEMFC)

The fuel cell, a device that converts chemical energy directly into electrical energy, involves an electrochemical reaction, like the conventional battery [1–4]. The difference is that fuel cells have an external and continuous supply of fuels and therefore do not require a time-consuming charging process. Fuel cells have attracted much attention in the past few decades due to their advantages over conventional internal combustion engines, such as low pollutant emissions, high efficiency, and high theoretical power output density.

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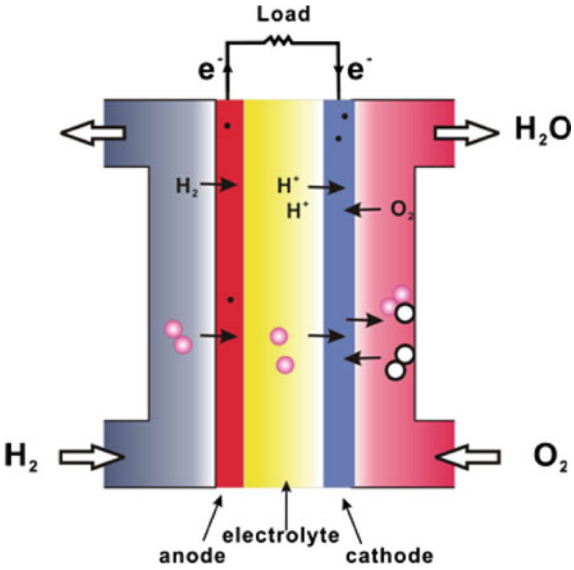


Fig. 1 Illustration of a proton exchange membrane fuel cell

An anode, electrolyte, and cathode are the main components of a fuel cell. Among the various members in the fuel cell family, PEMFCs are the most attractive candidate for automotive and portable applications [1, 4]. Figure 1 shows the main components of a PEMFC. The output voltage of a single cell is limited by the Nernst potential of the two half-cell reactions occurring on the two electrodes. Electrochemical oxidation of fuels such as hydrogen and small organic molecules (SOMs, such as methanol, ethanol, and formic acid) occurs on the anode and the electrochemical reduction of the oxidant takes place on the cathode. Ions generated from the electrochemical reduction or oxidation processes are transported through the electrolyte, which is ionically conductive but electronically insulating. During the reaction, the generated electrons will flow through the external circuit, producing electrical energy, while the ions will flow through the electrolyte from one side to the other side of the electrode, completing the overall fuel cell reactions. Depending on the fuels used, PEMFCs can be categorized as hydrogen/oxygen fuel cells, direct methanol fuel cells (DMFCs), and direct formic acid fuel cells (DFAFC) etc. [2, 5, 6].

In the various components of PEMFCs, nanotechnology is frequently employed to improve cell performance, increase durability, and reduce the cost. For example, the precious metal electrocatalysts used are reduced to the nanoscale, ensuring a high catalytic surface area and minimizing the amount of precious metal used to maintain high performance. Meanwhile, carbon nanomaterials are typically utilized as catalyst supports due to their high conductivity, good thermal and chemical stability, and excellent mechanical properties. Not limited to the catalyst, some nanosized materials such as carbon nanotube and silica oxide nanoparticles are also employed in the membrane to enhance its self-humidifying ability and mechanical properties. Therefore, nanomaterials have found extensive use in fuel cell system and will continue to be of research interest. Therefore, in this chapter, we will discuss the applications of nanomaterials in fuel cell systems. Specifically, we will focus on nanostructured electrocatalysts and their supports in PEMFC devices.

2 Synthesis Methods of Nanosized Electrocatalysts for PEMFC

Platinum-based metal nanoparticles supported on carbon are the most commonly used electrocatalysts for various reactions in PEMFCs. However, the high cost of this precious metal is a major barrier to a large-scale commercialization of PEMFCs. In order to reduce Pt usage without sacrificing cell performance, a great deal of effort must be devoted to improving the electrocatalyst utilization efficiency and enhancing the intrinsic catalytic activity of the electrocatalysts. One approach is to use high surface area carbon materials (e.g., carbon nanotube and carbon black) as supports to enhance the dispersion and distribution of metal nanoparticles and to improve their utilization efficiency [7]. The dispersion of metal electrocatalyst nanoparticles on carbon supports strongly depends on the interaction between them, and intrinsic properties of the supports. On the other hand, electrocatalytic activity is highly dependent on the morphology and particle size of metal electrocatalysts. Metal electrocatalysts exhibit shape, size, and dimension dependent catalytic properties, which have made controlling the morphology an active and prolific research area.

To date, various synthesis methods have been investigated to prepare supported metal electrocatalysts. These methods include impregnation, potential step electrodeposition, colloidal processing, and microwave-assisted polyol techniques [8]. The impregnation method, also called the electroless deposition method, is widely used to prepare highly-dispersed metal nanoparticles deposited on carbon supports. This approach involves the pre-mixing of carbon supports and metal precursors followed by the addition of reducing agents (such as sodium borohydride, ethylene glycol, and formic acid). The average particle size, dispersion, and distribution of the metal nanoparticles strongly depend on the properties of carbon supports and reducing agents. The synthesis and deposition of Pt nanoparticles by the electrodeposition is realized by pasting the carbon supports onto the working electrode and subsequent pulse deposition in an electrolyte containing metal precursors. However, such an electrodeposition method is not suitable for large-scale production. The colloidal route involves the pre-formation of metal nanoparticles followed by the deposition onto carbon supports. In this case, organic materials, such as polymers or surfactants, are used to stabilize metal nanoparticles to avoid aggregation in the colloidal dispersion. After the nanoparticles are deposited on the supports, these stabilizers should be removed from the metal surface. Otherwise, they can hinder the interaction between the reactant molecules and the active catalyst sites. Usually, a heat treatment or solvent rinse is used to remove the

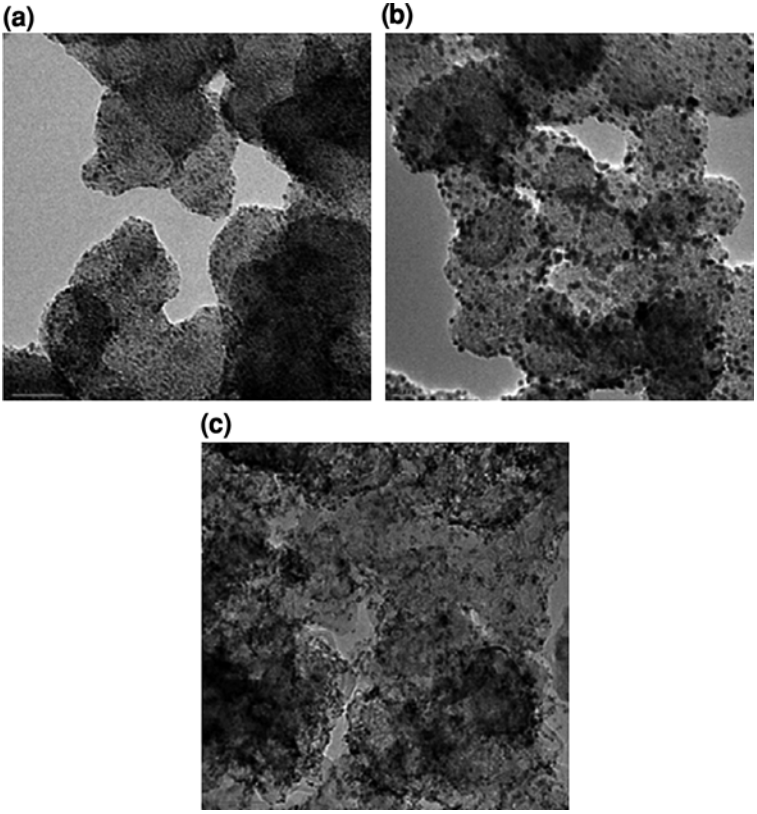


Fig. 2 TEM images of 6 wt% Pt and 3 wt% Ru catalysts deposited on Vulcan XC-72R. The PtRu catalysts were synthesized in ethylene glycol solutions with the following NaOH concentrations: 0.1 M (**a**), 0.075 M (**b**), and 0.068 M (**c**). The bars in (**a**) and (**b**) indicate a 20 nm scale, and the bar in (**c**) indicates a 50 nm scale. Reprinted with permission from Bock et al. [8] American Chemical Society

stabilizer molecules. However, it is difficult to completely remove them with a simple solvent rinse. On the other hand, the heat treatment method usually leads to the aggregation of metal nanoparticles, resulting in low utilization efficiency of the electrocatalysts and alteration of the surface composition of the catalysts if multi-component alloy catalysts are involved.

To date, the most commonly used chemical reduction method is the polyol reduction method. For this method, ethylene glycol is used as the solvent, reducing agent, and stabilizer. The formation of metal nanoparticles involves the reduction of metal precursor salts by ethylene glycol, which, in turn, is oxidized. It has been proposed that the oxidation of ethylene glycol mainly results in glycolic acid or glycolate anions, depending on the pH value of the solution. The stabilization of the metal nanoparticles by ethylene glycol system is realized by the electrostatic repulsion of the attached glycolate anions on the surface of the metal colloids.

The concentration of glycolate anions in the synthesis solution can be adjusted by controlling the pH of the solution. As the concentration of glycolate anions affects the stabilization behavior of the metal nanoparticles, the metal nanoparticle size can be easily tuned by controlling the pH of the synthesis solution. Bock et al. [8] performed such an investigation. As shown in Fig. 2, the average particle size and distribution of metal nanoparticles on carbon black can be adjusted by the concentration of NaOH. They concluded that the increase of the pH of the solution leads to smaller particle size. Such a strategy allows for the synthesis of highly-dispersed metal nanoparticles with tunable particle size on various substrates [8].

More recently, the microwave-assisted polyol reduction method has been developed to synthesize highly-dispersed metal nanoparticles deposited on carbon supports with much smaller particle size. Microwave irradiation facilitates the fast reduction of metal precursors to metal atoms and uniformly distributes heat in the reaction solution [9]. The creation of a high level of supersaturation within very short time range leads to fine particle size.

3 Morphology Control of Nanostructured Electrocatalysts

Extensive efforts have been directed toward the synthesis of morphology-controlled nanomaterials because of their extraordinary morphology-dependent properties and their wide application in various fields, such as catalysis, opto-electronics, biolabeling, chemical sensors, and fuel cells. To date, various forms of nanostructures have been developed, ranging from highly monodispersed spherical and cubic nanoparticles to various anisotropic nanostructures such as nanowires, nanorods, and nanotubes. Herein, we will review the recent progress of the morphology-controlled synthesis and its effect on the catalytic activities of metal nanomaterials [8, 10–14].

3.1 Zero-Dimensional Nano-Electrocatalysts

Fuel cell electrocatalysts are normally used in the form of zero-dimensional nanoparticles with small particle size, since small particles feature a high surface area to volume ratio, which is essential for surface catalysis applications [15]. Other than the surface area, the electrocatalytic activities are significantly affected by the surface properties of metal nanoparticles that could be tuned via size and shape-controlled synthesis. For example, Arenz et al. [16] investigated the size effect of Pt nanoparticles on the electrocatalytic activities for adlayer and bulk CO oxidation and found that the removal/oxidation of adsorbed CO on the Pt surface is sensitive to the surface properties of Pt nanoparticles. As shown in Fig. 3, the onset potential of adlayer CO oxidation is almost independent of the particle size, but the rate of CO_2 production decreases with the decrease of the particle size. They suggested that the removal/oxidation of CO is mainly controlled by the number of defects on the Pt surface. Large particles have “rougher” surfaces and therefore more defects than small particles, which have fairly smooth (111) facets. In contrast to CO adlayer oxidation, smaller particles are more active for bulk CO oxidation than larger particles because of the increased oxophilicity. Sun et al. [17] conducted shape-controlled synthesis of Pt nanoparticles. Polyhedral (3 nm), truncated cubic (5 nm), and cubic (7 nm) Pt nanoparticles were prepared, with dominating lattice fringes of Pt (111), Pt (100), and Pt (100) respectively, as shown in the TEM images in Fig. 4. The electrochemical investigation revealed that Pt (100)-dominated nanocubes are more active for the oxygen reduction reaction (ORR) in 0.5 M H_2SO_4 than the other two catalysts (polyhedral and truncated cubic nanoparticles). It is believed that such a shape-dependent ORR activity can be ascribed to the different adsorption properties of Pt surface. Therefore, these two examples demonstrate that the catalytic activities of the zero-dimensional nanoparticles could be efficiently tuned through the size and shape control.

3.2 *One-Dimensional Nano-Electrocatalysts*

In parallel, recently a lot of attention has been given to one-dimensional or branched metal nanostructures, such as nanorods, porous nanoparticles, multipods, nanowire networks, and dendritic nanoparticles. Zhuang et al. [18] successfully prepared one-dimensional Pd nanorods (Fig. 5) and zero-dimensional nanoparticles with electrochemical deposition technique by simply changing the precursor concentration. The electrochemical characterization indicated that Pd nanorods exhibited an unexpectedly higher area-specific activity toward the ORR than nanoparticles, which is close to that of bulk Pt. The electrochemical fingerprint experiment on CO stripping shows that the surface of Pd nanorods is dominated by Pd (110) facets, on which the adsorption of O is found to be exceptionally weak by subsequent density functional theory (DFT) calculations. It is believed that such a weak adsorption is the reason for the superior activity of Pd nanorods toward ORR. Another example of one-dimensional nanostructured electrocatalysts is the Pt nanotubes developed by Lu et al. [19]. The Pt nanotubes (Fig. 6) were synthesized via a redox replacement reaction in the presence of cetyltrimethylammonium bromide (CTAB). Improved catalytic activity toward methanol oxidation was observed compared to that of the nanowires, which is due to the high surface area and high preferential crystal facets of Pt nanotubes.

Using similar redox replacement reaction method, Yan et al. [20] successfully synthesized supportless Pt and PtPd alloy nanotubes (Fig. 7). As shown in Fig. 8, the as-synthesized PtPd alloy nanotubes not only exhibit significantly enhanced catalytic activities toward ORR, but also demonstrate an improved durability/stability, compared to monometallic Pt nanotubes, Pt black, and commercial Pt/C catalysts. The improved durability was explained by (1) the elimination of support

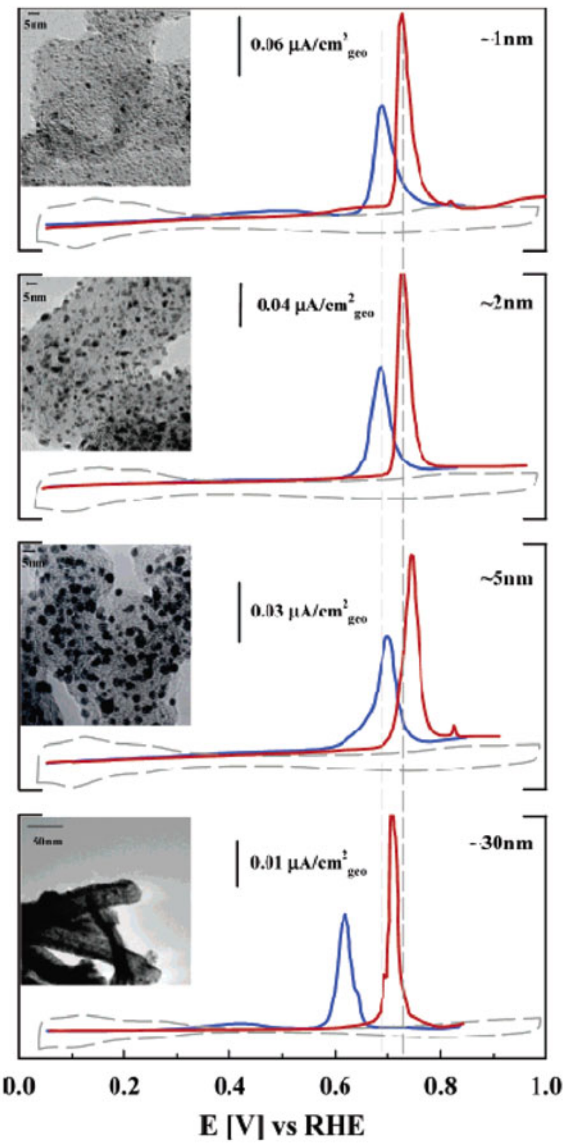


Fig. 3 Comparison of CO-stripping curves in 0.1 M HClO4 solution purged after CO adsorption with argon for 30 min at 0.05 V; scan rate 1 mV/s; dashed gray curves show the respective base voltammograms; the blue curves show the CO-stripping curves after oxide-annealing and the red curves after CO-annealing. Reprinted with permission from Arenz et al. [16] American Chemical Society

corrosion problem and (2) the one-dimensional nanostructure has a length on the order of microns, which makes it less vulnerable to dissolution, Ostwald ripening, and aggregation during fuel cell operation than the platinum nanoparticles. Additionally, the anisotropic morphology of the one-dimensional nanostructures also improves the mass transport properties and catalyst utilization efficiency for the electrocatalytic reaction. If properly assembled (e.g., cubic or hexagonal close-packing and vertical alignment on a Nafion® membrane), they can also lead to a

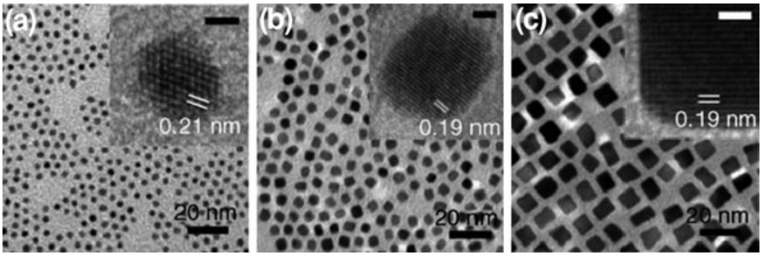


Fig. 4 TEM images of (**a**) the 3 nm polyhedral (**b**) the 5 nm truncated cubic, and (**c**) the 7 nm cubic Pt Nanoparticles. The insets are the representative HRTEM images of corresponding single particles, showing (**a**) Pt (111), (**b**) Pt (100), and (**c**) Pt (100) lattice fringes. All scale bars in the insets correspond to 1 nm. This is the pre-peer reviewed version of the following article: Wang et al. [17] Angewandte Chemie-International Edition 47:3588–3591

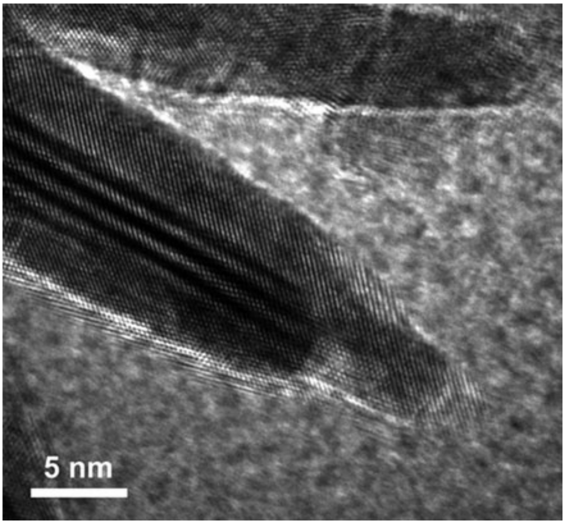


Fig. 5 A TEM image of Pd-NR deposited on carbon powder. Reprinted with permission from Xiao et al. [18] American Chemical Society

thin catalyst layer, further improving the mass-transfer characteristics within the catalyst layer [20]. On the basis of the above works, it can be concluded that, the electrocatalytic activity and durability of metal nanostructures can be controlled by changing the structure.

3.3 Two and Three-Dimensional Nano-Electrocatalysts

The increase in dimension of the metal nanostructures of electrocatalysts to two or three may produce other unexpected catalytic activities. Ding et al. [21] developed a simple method to fabricate a novel nanotubular mesoporous (NM) PdCu bimetallic catalyst with a nanoporous shell based on low-temperature dealloying in

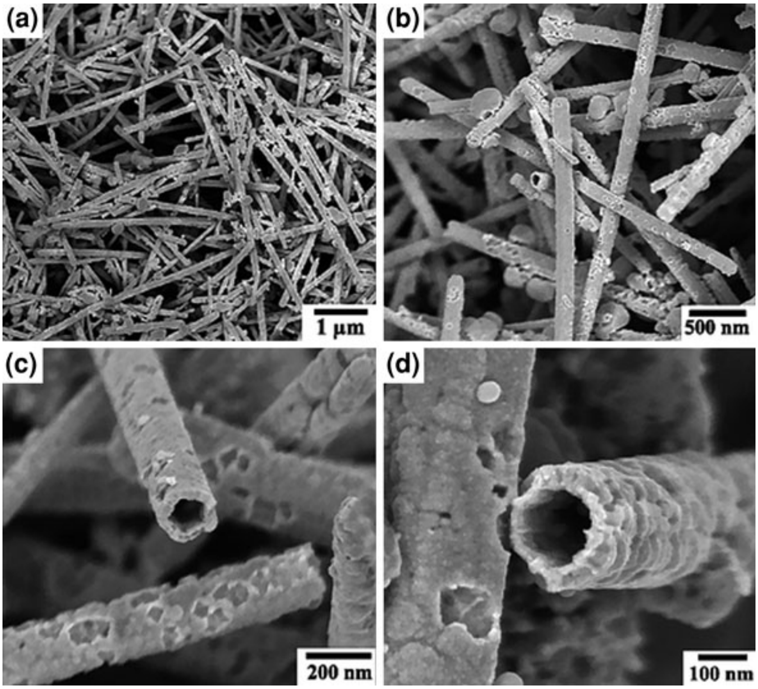


Fig. 6 (**a**–**d**) SEM and FE-SEM images of the platinum nanotubes. Reprinted with permission from Bi et al. [19] American Chemical Society

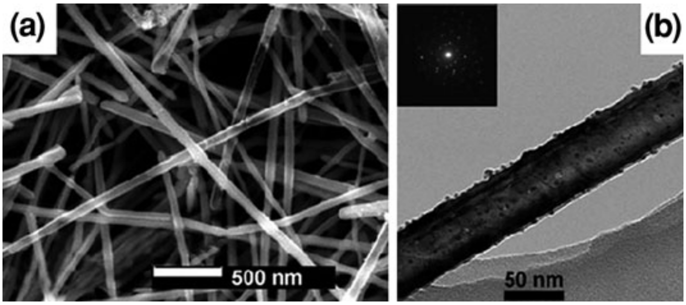


Fig. 7 **a** SEM image of PtPd nanotubes. **b** TEM image and electron diffraction pattern (*inset*) of PtPd nanotubes. This is the pre-peer reviewed version of the following article: Chen et al. [54]

an aqueous solution and a subsequent in situ galvanic replacement reaction. The as-prepared PdCu bimetallic catalyst exhibits a superior ORR activity, as shown in Fig. 9. The authors claimed that trimodal hollow bimetallic structure in the PdCu nanostructures play a crucial role in the enhancement of ORR activity. Another two-dimension example, Jiang et al. [22] fabricated Pd nanowire arrays (NWA) by the anodized aluminum oxide (AAO) templated electrodeposition

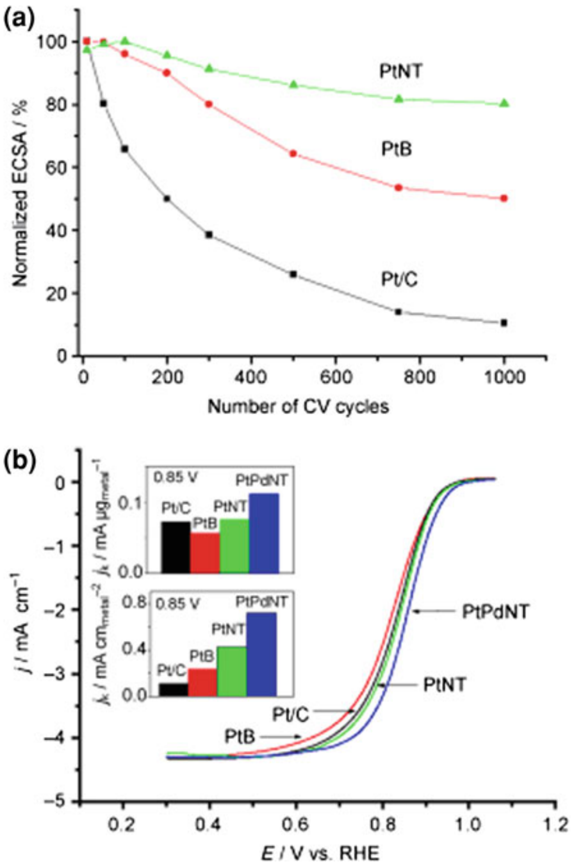


Fig. 8 **a** Loss of electrochemical surface area (ECSA) of Pt/C, platinum-black (PtB), and Pt nanotube catalysts with number of CV cycles in Ar-purged 0.5 M H_2SO_4 solution. **b** ORR curves in O_2-saturated 0.5 M H_2SO_4 solution. Inset: Mass activity (*top*) and specific activity (*bottom*) for the four catalysts at 0.85 V. This is the pre-peer reviewed version of the following article: Chen et al. [54]

method (Fig. 10). The Pd nanowire arrays have large amounts of electrochemically active surface area. The electrocatalytic activity and stability of the Pd nanowire array for ethanol electrooxidation are not only significantly higher than those of conventional Pd film electrodes, but also higher than those of commercial E-TEK PtRu/C electrocatalysts. The utilization efficiency and electrocatalytic activity of the Pd nanowire array electrode strongly depend on the length and structure of the Pd nanowires. The nanometer-sized gaps or pores between the nanowires in the array are straight and short, acting as effective transport channels to and from the electrode/electrolyte interface for the liquid fuel and products formed during the electrooxidation of ethanol [22].

Furthermore, Chen et al. [23], by use of a low-cost, one-step hydrothermal method, successfully prepared three-dimensional nanoporous PtRu networks (Fig. 11). The precursors Ru^{3+} and Pt^{4+} ions were reduced simultaneously by the reduction agent formaldehyde, resulting in the formation of PtRu alloys. The composition of the PtRu networks can be easily changed by varying the concentration of the Ru and Pt precursors. The surface characterization and

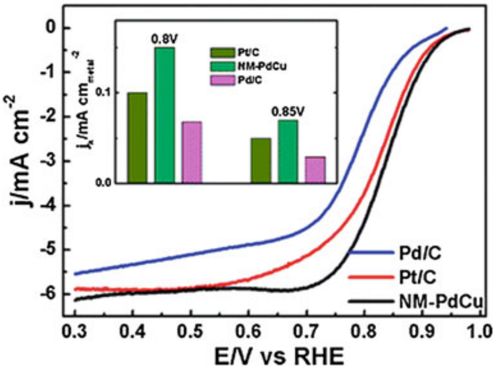


Fig. 9 Polarization curves for the ORR on NM-PdCu and Pd/C, Pt/C nanoparticles in an O_2-saturated 0.1 M $HClO_4$ at room temperature at 1600 rpm. Scan rate: 5 mV s^{-1}. The inset is the specific activity for NM-PdCu, Pt/C, and Pd/C catalysts at 0.8 and 0.85 V, respectively. Reprinted with permission from Xu et al. [21] American Chemical Society

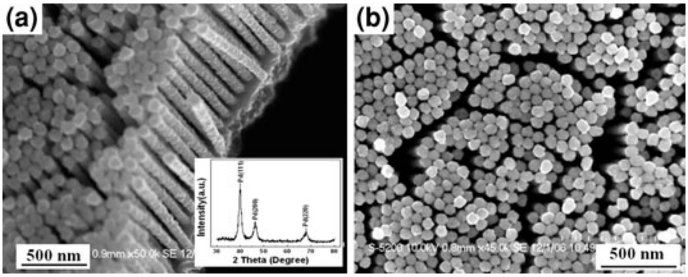


Fig. 10 SEM images of (**a**) cross section and (**b**) surface of Pd NWAs. Inset in (**a**): XRD pattern of Pd NWAs. This is the pre-peer reviewed version of the following article: Xu et al. [22]

electrochemical studies show that the active surface area of the synthesized novel nanoporous PtRu networks is much higher than that of the polycrystalline platinum electrode, and that the nanoporous PtRu networks have much higher activity for the electrochemical oxidation of methanol and CO.

In light of the potential benefits that multi-dimensional nanostructures possess, there is a pressing need to develop efficient approaches for the fabrication of multi-dimensional nanostructures with controllable morphology. A variety of approaches including chemical vapor deposition, laser assisted synthesis, electrochemical deposition, and hard or soft templating have been extensively attempted. The hard template method, e.g. using mesoporous silica, generally produces low metallic interconnectivity due to poor continuity of precursors in the mesoporous templates. Additionally, to remove the silica template, hydrofluoric acid, a serious environmental and safety hazard, is required. The template method based on the AAO is also limited by the channel diameter of the AAO available. On the other hand, low-temperature soft-template approaches based on wet-chemistry offer enormous process flexibility to assemble nanoscale building blocks into variety of nano-architectures. For example, metal nanowires can be synthesized using micelles, polymer-mediated nanoparticle assembly, and surfactant-stabilized water-in-oil microemulsions. Recently, a self-assembly soft-template method has been

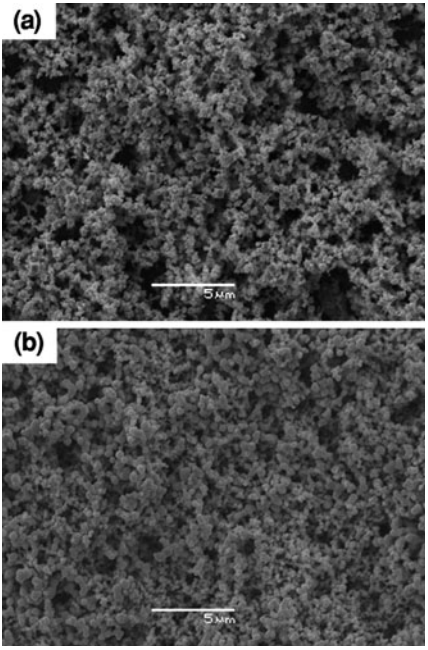


Fig. 11 SEM images of: (**a**) nanoporous Pt surface; and (**b**) typical nanoporous Pt-Ru electrode. Magnification: 5000×. This is the pre-peer reviewed version of the following article: Koczkur et al. [23]

developed to effectively synthesize Pd nanowire networks (NWNs) as electrocatalysts for formic acid oxidation [24]. The principle of the tunable synthesis of Pd nanostructures via the polysodium-p-styrenesulfonate (PSS) polyelectrolyte-mediated self-assembly process is shown in Fig. 12. Self-assembly occurs between positively charged Pd^{2+} ions and negatively charged SO_3 function groups attached to the pendent aromatic ring of PSS, forming anisotropic Pd^{2+}–PSS networks in solution. The reaction rate is controlled by pH. If the nucleation rate of Pd nanoparticles along the PSS molecular chains is fast, the crystallization and growth of Pd(0) would adopt the anisotropic Pd^{2+}-PSS network, forming Pd NWNs. The assembly and formation of Pd nanoparticles and NWNs occurs simultaneously. On the other hand, if the nucleation rate of Pd nanoparticles along the PSS polymeric chain is slow, the grain growth of Pd nanoparticles would dominate. The random nucleation and grain growth would disturb the anisotropic Pd^{2+}–PSS network in solution and form isolated Pd nanoparticles instead. This principle is confirmed by the TEM images shown in Fig. 13.

3.4 Hollow Metallic Electrocatalysts

The proper design of core–shell nanostructured electrocatalyst reduces the cost of precious metal electrocatalysts and improves their electrocatalytic activity. Meanwhile, hollow nanostructured electrocatalysts with empty cores have also

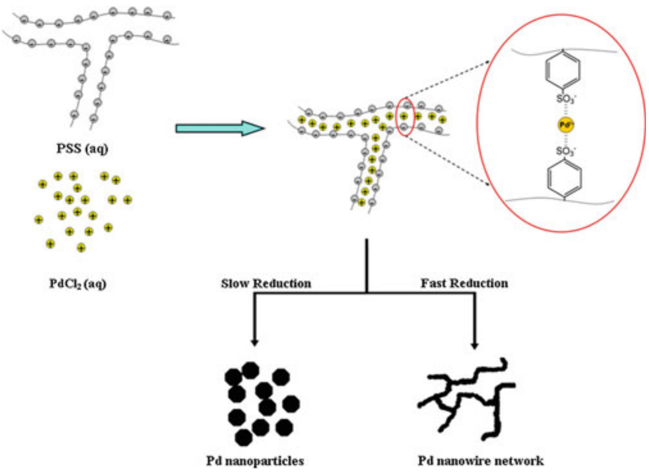


Fig. 12 A schematic illustration of the templateless and PSS-mediated self-assembly of Pd NWNs and nanoparticles. Reprinted with permission from Wang et al. [24] Copyright 2008 IOP Publishing Ltd

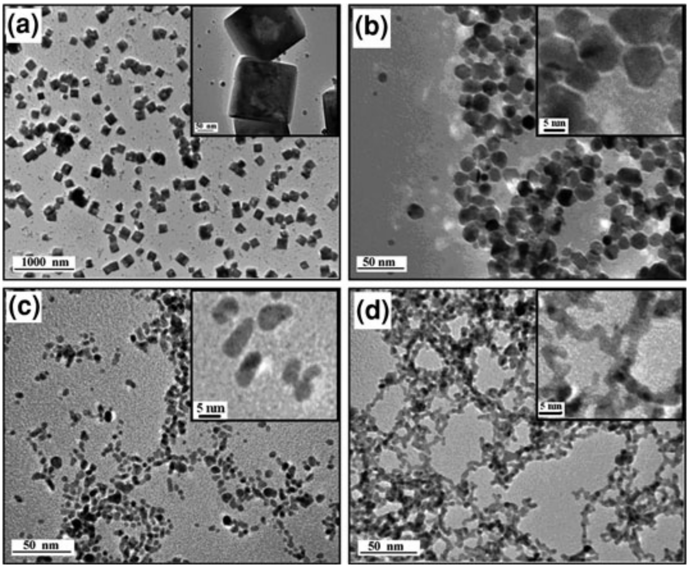


Fig. 13 TEM micrographs of Pd nanostructures synthesized in the presence of PSS polyelectrolyte. (**a**) Pd nanocubes synthesized at pH = 2, (**b**) Pd cuboctahedrons synthesized at pH = 6, (**c**) Pd nanorods synthesized at pH = 8, and (**d**) Pd nanowire networks synthesized at pH = 12. PSS/Pd ratio was 1:1 and ethanol was used as reducing agent. Inset is the high magnification TEM image. Reprinted with permission from Wang et al. [24] Copyright 2008 IOP Publishing Ltd

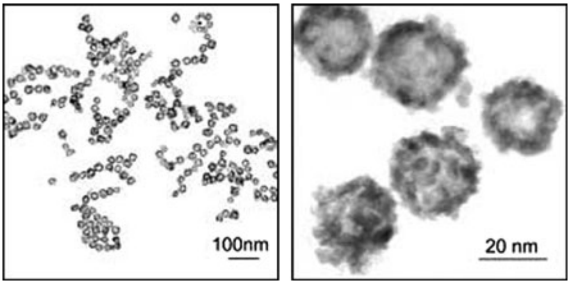


Fig. 14 TEM images of Pt hollow nanospheres (**a**) and (**b**). This is the pre-peer reviewed version of the following article: Liang et al. [27]

attracted much attention due to their unique properties. The hollow structure provides increased surface area and saves on material cost. It should be kept in mind that methodology is critically important to the preparation of a catalyst with a hollow structure. Template-based synthesis is the primary method to synthesize hollow metallic catalysts. Porous alumina, polystyrene spheres, silica spheres, and micelles have been employed as templates to prepare hollow metal nanostructures [25–28]. More recently, a galvanic replacement reaction-based template method was developed. This method uses a sacrificial Ag or Co nanoparticle as a template, which reduces aqueous metal ions, resulting in the formation of hollow metal nanostructures with various morphologies conformal to those of the templates. Bai and coworkers [27] developed a facile procedure for the synthesis of a Pt hollow nanosphere catalyst based on the replacement reaction between Co nanoparticles and H_2PtCl_6, as shown in Fig. 14. The as-prepared Pt hollow nanospheres had a very high surface area and therefore exhibited enhanced weight-normalized electrocatalytic performance. Based on this procedure, some bimetallic hollow nanospheres could also be synthesized. For example, Qiu [26] synthesized PtRu hollow nanospheres using Co as the sacrificial template and supported them on carbon nanotube support. The PtRu hollow nanospheres exhibited enhanced weight-normalized electrochemical performance for methanol oxidation compared with PtRu nanoparticles and commercial PtRu/C electrocatalysts due to the advantageous structural properties of the hollow structure.

4 Multi-component Electrocatalysts

Platinum is the best-known monometallic electrocatalyst for hydrogen oxidation and oxygen reduction reactions. However, at the anode side, Pt suffers from severe poisoning from fuel impurities, such as carbon monoxide (CO), and the electrocatalytic activity is quite low for other fuels like methanol or formic acid. Even for oxygen reduction at the cathode side, there exists a large overpotential. The enhancement of Pt electrocatalysts for fuel cell applications is usually realized by the appropriate design of multicomponent electrocatalysts with the introduction of another component, called the promoter.

4.1 Bimetallic Alloy Electrocatalysts

To overcome the low electrocatalytic activity of Pt toward fuels like methanol or CO containing hydrogen, the approach of incorporating other promoting metals has been investigated extensively, of which the most commonly used are ruthenium and tin. For example, it has been observed that the presence of Ru increases the rate of methanol adsorption and the maximum CO coverage of the surface is reached more rapidly at a PtRu surface than at a pure Pt catalyst at a given potential. A bifunctional mechanism originally proposed by Watanabe [29] is believed to be responsible for the activity improvement, where one metal (Pt) is available for the adsorption of the intermediate and the other metal on adjacent site acts as the adsorption site for oxygen-containing species. Since Ru can generate OH species from the water activation at lower potential than Pt [1, 12], the oxidation of the adsorbed CO species can be realized at lower potential.

PtSn bimetallic electrocatalysts have also been reported to show enhanced electrocatalytic activity for methanol oxidation in DMFCs [1]. It should be pointed out that the promotional role of a PtSn system is slightly different from that for PtRu electrocatalysts. The significant difference in electronegativity between Sn and Ru elements leads to different environments around the Pt sites in the two systems. Because of the small difference in electronegativity between Pt and Ru elements, the electronic effect of Ru on Pt is very weak and the bifunctional mechanism is responsible for the enhanced electrocatalytic performance of methanol oxidation on PtRu electrocatalysts. For PtSn electrocatalysts, Sn atoms donate electrons to Pt atoms due to Sn's smaller electronegativity. The charge transfer from Sn atoms to Pt atoms increases the electron density around Pt sites and downshifts their d-band center, which leads to weakened chemisorption energy with oxygen-containing species. Therefore, the enhancement of PtSn electrocatalysts is mainly due to the modification of electronic environment of Pt sites (electronic effect) [1].

At the cathode side, the ORR suffers from high polarization loss even with the use of the best catalyst Pt. There is an enormous impetus to find better and cheaper catalyst than Pt/C. Another consideration during the search of better electrocatalyst is its stability in highly corrosive and oxidizing environment in fuel cells. Throughout the effort to maintain the advantageous properties of Pt (i.e., relatively low overpotential, high stability) while simultaneously reducing the high Pt loading and searching for an improved ORR catalyst, a variety of binary and ternary Pt alloy systems have been investigated, with most of the alloyed metals being transition element metals, such as Co, Ni, Cu, Cr, Mo, and Fe. The main objective is to tune the ability of the metal to bond the key reaction intermediates in just the right way, either via the electronic effect or adjustment of the atomic distance between adjacent atoms. The appropriate chemisorption energy of O species with catalyst surface determines their electrocatalytic activity. An oxygen adsorption energy that is too high yields stable intermediates on the surface; if the interaction between oxygen and the surface leads is too weak, the adsorption is

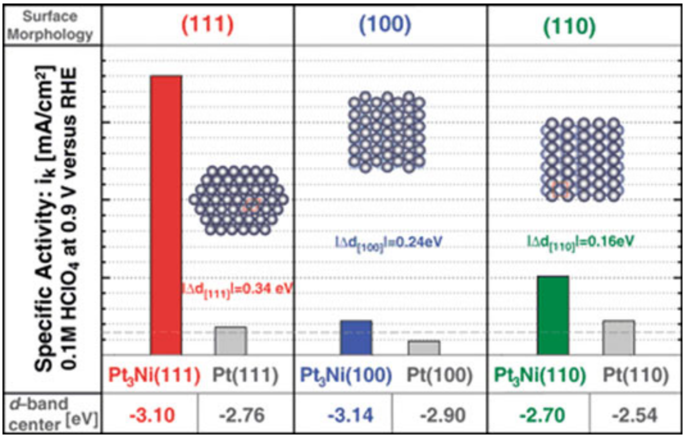


Fig. 15 Influence of the surface morphology and electronic surface properties on the kinetics of ORR. Specific activity is given as a kinetic current density i_k, measured at 0.9 V versus RHE. Values of d-band center position obtained from UPS spectra are listed for each surface morphology and compared between corresponding $Pt_3Ni(hkl)$ and Pt(hkl) surfaces. Reprinted with permission from Stamenkovic et al. [30] Copyright 2007 Science Magazine

also weak, thereby limiting the activity of molecular oxygen. To date, the most extensively investigated cathodic bimetallic electrocatalysts are PtNi and PtCo. Stamenkovic et al. [30] demonstrated that the Pt_3Ni (111) surface is 10-times more active for oxygen reduction reaction (ORR) than the corresponding monometallic Pt (111) surface, as illustrated in Fig. 15. They claim that the Pt_3Ni (111) surface has an unusual electronic structure (d-band center shift) and the distribution of surface atoms in the near-surface region. The downshift of the d-band center of Pt on the surface was caused by the electronic modification by the underlying Ni, resulting in weakened chemisorption with –OH (nonreactive oxygenated species) on Pt surface, leading to increased number of active sites for O_2 adsorption and reaction [30].

4.2 Bimetallic Core–Shell Electrocatalysts

Although alloying Pt with other transition metal elements can significantly enhance the electrocatalytic activity of fuel cells, these materials tend to dissolve from the electrocatalyst during fuel cell operation because of the strong favorability of transition metals to leave their metal alloy crystal and form ions in acidic and oxidizing environment. The leaching out of transition metals forms a Pt skin (less than 1 nm) on the electrocatalyst nanoparticles and has been proposed to be the main reason for the improved activity with the use of bimetallic alloy catalysts [31]. In order to overcome this problem, incorporating these transition metals into the cores of Pt nanoparticles is a promising way to reduce the cost. Such a

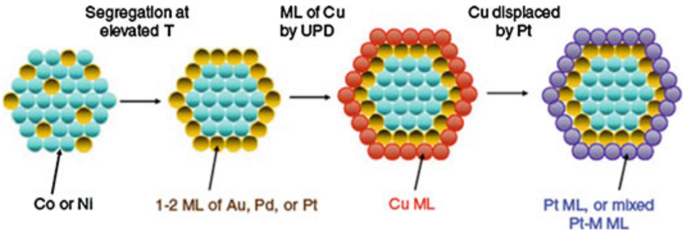


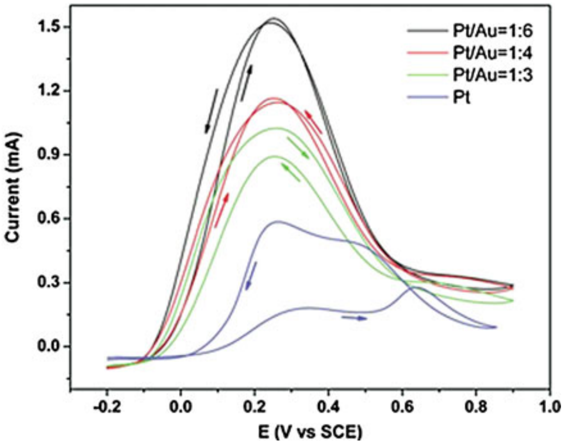
Fig. 16 Model for the synthesis of Pt monolayer catalysts on nonnoble metal-noble metal core–shell nanoparticles. Reprinted with permission from Zhang et al. [33] American Chemical Society

core–shell structure prevents the transition metals from dissolving out of the bimetallic structure and reduces the usage of precious Pt, since the catalytic reaction only occurs on the catalyst surface instead of inner core sites. Furthermore, the appropriate selection of inexpensive metal elements as the cores can modify the electronic structure of Pt shell, thereby improving the electrocatalytic activity of the Pt shell [32].

The first core–shell electrocatalyst for fuel cell reaction was reported by Adzic et al. [33]. They prepared a Pt monolayer on noble metal or nonnoble metal nanoparticles and examined them for O_2 reduction (see Fig. 16). These electrocatalysts showed a very high activity of O_2 reduction even though they contain only very small amounts of Pt. The Pt monolayer was prepared by galvanic displacement of a Cu monolayer deposited at underpotential condition. Geometric effects on the Pt monolayer and the effect of PtOH coverage, as revealed by electrochemical data, X-ray diffraction and X-ray absorption spectroscopy data, appear to be the sources of the enhanced catalytic activity. However, a full comparison to the common electrocatalyst Pt/C could not be obtained because of the large difference in the amount of active surface area. Moreover, from the viewpoint of mass production of the electrocatalyst, the electrochemical method used is less effective and less feasible compared to wet-chemistry approach [32].

More recently, Wang et al. [34, 35] developed an efficient wet-chemistry method to synthesize Au–Pt core–shell nanoparticles with controlled shell/core ratios for both methanol and formic acid oxidation. The synthesis process involves the pre-formation of Au seeds followed by the slow growth of Pt atoms on the Au cores in the presence of a weak reducing agent. Improved Pt utilization in terms of methanol oxidation is demonstrated with the core–shell structure. Furthermore, at very low Pt/Au molar ratios, incomplete Pt shells with decorated structures are formed. This catalyst not only significantly reduces the use of Pt via improved Pt dispersion, but also shows a high activity for formic acid oxidation as shown in Fig. 17. Compared to Pt/C, it undergoes a different reaction pathway by suppressing the formation of the CO intermediate where the Pt coverage on Au nanoparticles plays an important role. The origin behind this enhancement is proposed in Fig. 18. Formic acid oxidation on Pt generally follows a dual path mechanism. It is believed that the direct oxidation of formic acid on Pt surface (dehydrogenation) does not require the presence of continuous neighboring Pt

Fig. 17 CV of Pt/C and PtAu/C at 10 mV s21 in 0.5 M HCOOH + 0.5 M H_2SO_4. Reprinted with permission from Kristian et al. [35] Copyright 2007 The Royal Society of Chemistry



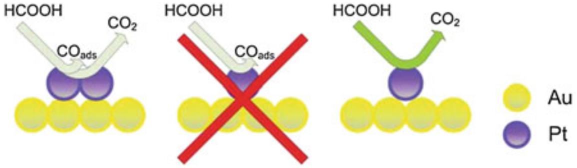


Fig. 18 Illustration of the catalytic reactions of formic acid oxidation (dissociative adsorption and dehydrogenation) on the Pt-decorated Au surface. Reprinted with permission from Kristian et al. [35] Copyright 2007 The Royal Society of Chemistry

sites, while the dissociative adsorption of formic acid to form CO requires at least two ensemble binding sites. A continuous decrease of Pt coverage on Au surface, i.e., decreasing the availability of Pt adjacent atoms, leads to a decrease in the dehydration rate and an eventual blocking of CO formation (the disappearance of the second oxidation peak at ~0.63 V), while the dehydrogenation reaction can still occur without being affected.

4.3 *Metal Oxide as the Promotional Component of Electrocatalysts*

The slow kinetics of the electrooxidation of methanol in PEMFCs is a large barrier to large-scale commercialization of fuel cells. As stated above, the most commonly used approach is to alloy Pt with other transition metals for use as catalysts. The detailed investigation on the electrocatalysis behavior of methanol oxidation on PtRu has shown that, in order to minimize the effect of the CO species, the cocatalyst, Ru should have a large fraction of oxide [36]. In such a case, CO tends to interact with the oxygenated species on oxide surface and converts to CO_2 at a relatively low potential via the classical bifunctional mechanism. On the basis of this concept, many researchers have been focusing on the promotional role of other metal oxides on the electrocatalytic reactions in fuel cells. Many metal oxides, such as TiO_2, CeO_2, SnO_2, ZrO_2, MgO, and MoO_2, have been extensively used as cocatalysts and found to play promotional role in alcohol oxidation or oxygen reduction either in acidic or alkaline media [20, 36–40]. Experimentally, researchers typically adopt two strategies to incorporate metal oxide into the catalyst system. One is to form a Pt-metal alloy, followed by the adjustment of the metal oxide component. Other researchers adopt a successive method; that is, loading metal oxide onto catalyst supports (such as carbon black and CNT/nanofiber), followed by the deposition of Pt nanoparticles onto the metal oxide/support composites.

Song et al. [36] prepared TiO_2 coated carbon nanotubes (TiO_2/CNTs) by a sol–gel method to act as Pt catalyst which support and enhance the electrooxidation of ethanol. The high-resolution TEM (HRTEM) images shown in Fig. 19 confirmed the successful coating of CNT and subsequent deposition of Pt nanoparticles with narrow particle size distribution. The electrochemical characterization for the ethanol oxidation and CO stripping demonstrates the promotional role of TiO_2/CNTs as Pt catalyst support. As shown in Fig. 20, the addition of TiO_2 significantly decreases the CO-stripping peak potential compared to Pt/CNTs and commercial Pt/C. This result shows that incorporating TiO_2 in the Pt/CNT catalyst system could enhance the electrochemical oxidation/removal of CO. It is believed that CO adsorption occurs only on the Pt surface and the bifunctional mechanism explains the promotional role of TiO_2. Plus, the addition of TiO_2 may enhance the durability of the catalysts because TiO_2 is very stable in acidic solution, which can hinder the corrosion of carbon nanotube supports. With a similar procedure, Peng et al. [41] synthesized MnO_2/CNT supported Pt and PtRu nanocatalysts for direct methanol fuel cells. It is concluded that the existence of MnO_2 on the surface of the CNTs effectively increases the proton conductivity of the catalyst, which remarkably enhances the electrochemical performance of the catalysts toward methanol oxidation.

In addition to mono-metal oxides as cocatalysts, multicomponent metal oxides are also used to enhance the electrochemical performance of ectrocatalysts in fuel cells. Qiu et al. [20] prepared Pt-$Ce_xZr_{1-x}O_2$/C catalysts with a co-precipitation method. This method involves the pre-mixing of zirconium nitrate and cerium nitrate with carbon black followed by the addition of an ammonia solution to prepare $Ce_xZr_{1-x}O_2$/C support composite. The deposition of Pt nanoparticles on the support composite completes the preparation of the catalysts. Figure 21 shows the typical CO-stripping voltammograms for the catalysts compared with Pt/C and PtRu/C. Catalysts with a metal oxide show much lower peak potential of CO stripping. The reason is that metal oxide favors the activation of water to produce the OH species on metal oxide surface, which subsequently interacts with poisonous CO adsorbed on Pt surface to generate CO_2 at lower potentials. The authors

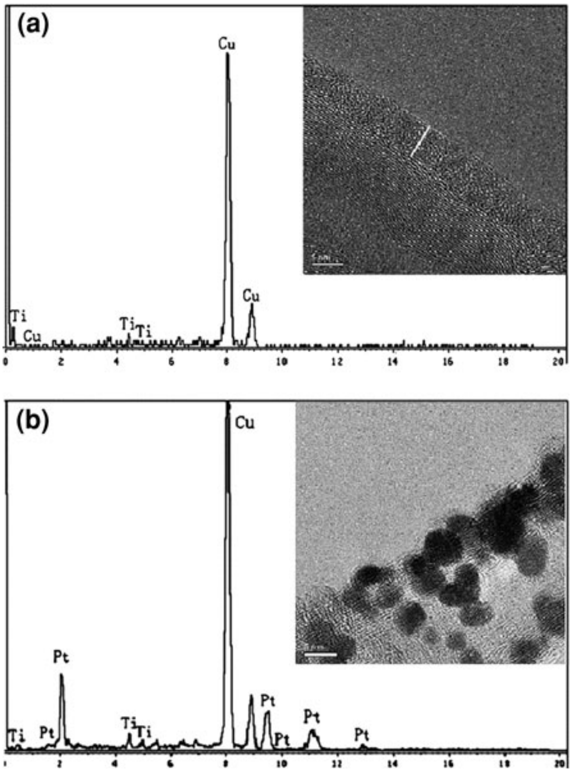


Fig. 19 HRTEM image and EDX spectrum of Pt–TiO_2/CNTs (1:1): (**a**) TiO_2/CNTs; (**b**) Pt–TiO_2/CNTs. The strong Cu-peak originates from the supporting HRTEM Cu grid. Reprinted from Song et al. [36] Copyright 2007 with permission from Elsevier

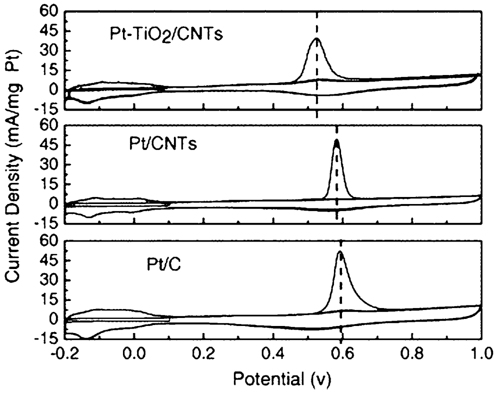


Fig. 20 CO stripping voltammograms in 1 M $HClO_4$ solutions with a scan rate of 10 mV s^{-1}. Reprinted from Song et al. [36] Copyright 2007 with permission from Elsevier

claimed that the peak potential of CO stripping depends on the content of ZrO_2 (1–x) in the catalysts and found that the peak potential increases with the increase of ZrO_2 content. The reason may be related to the different lattice structure of $Ce_xZr_{1-x}O_2$/C.

For the ethanol oxidation in direct ethanol fuel cells, the most serious barrier is the splitting of C–C bonds with the direct oxidation to CO_2. Recently, Adzic et al.

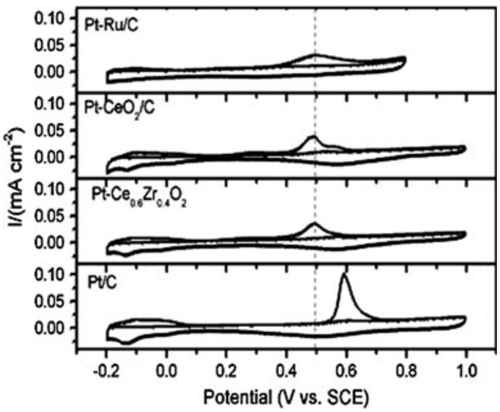


Fig. 21 The CO-stripping voltammograms recorded in 1 M $HClO_4$ solutions at 10 mV s^{-1} on Pt-CeO_2/C, Pt-$Ce_{0.6}Zr_{0.4}O_2$/C, PtRu/C, and Pt/C catalysts. Reprinted from Bai et al. [20] Copyright 2007 with permission from Elsevier

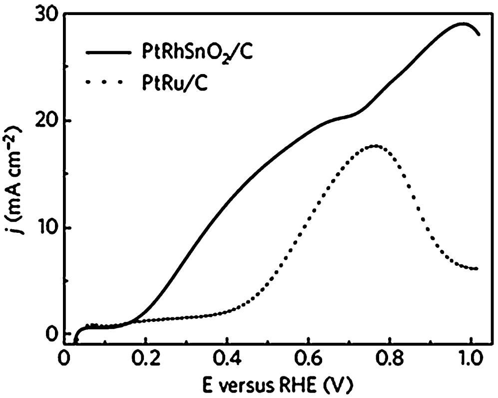


Fig. 22 Polarization curves of the oxidation of ethanol on PtRhSnO_2/C and PtRu/C (20% PtRu with 1:1 atomic ratio on C E-TEK). Reprinted with permission from Kowal et al. [42] Copyright 2009 Nature Publishing Group

[42] synthesized a ternary PtRhSnO_2/C electrocatalyst for ethanol electrooxidation by depositing platinum and rhodium atoms on carbon-supported tin dioxide nanoparticles. The as-synthesized electrocatalyst is capable of oxidizing ethanol with high efficiency and holds great promise for resolving the impediments to developing practical direct ethanol fuel cells. The electrochemical result shown in Fig. 22 demonstrates the significantly improved current density and lower onset potential of ethanol oxidation of PtRhSnO_2/C compared to the classical PtRu/C electrocatalysts. The PtRhSnO_2/C electrocatalyst effectively splits the C–C bond in ethanol at room temperature in acid solutions, facilitating its direct oxidation to CO_2 at low potentials, which has not been achieved with existing catalysts. It is concluded that the enhanced electrocatalytic activity is due to the specific property of each of the constituents, induced by their interactions. First, the addition of Rh effectively breaks C–C bonds based on interaction with Pt. Secondly, SnO_2, by strongly adsorbing water and interacting with the Pt and Rh, precludes the Rh and Pt sites from reacting with water to form M-OH, making them available for

ethanol oxidation. Also, SnO_2 activated with OH species facilitates CO removal from Rh active sites. Finally, Pt facilitates ethanol dehydrogenation and modifies the electronic structure of Rh to afford moderate bonding to ethanol, intermediates and products, leading to C–C bond splitting [42].

5 Noncovalent Functionalization of Carbon Nanotubes as Electrocatalyst Supports

5.1 Motivation for Using Carbon Nanotubes as Supports

Platinum-based electrocatalysts normally exist in the form of nano-scaled particles deposited on catalyst supports with a high surface area [43]. The catalyst supports not only to prevent the nano-scaled electrocatalyst particles from aggregation, but also to play a significant role in transporting the electrons generated from and consumed by the electrochemical reactions [12]. It has been demonstrated that catalyst supports have great influence on the performance and durability of electrocatalysts. An ideal catalyst support should meet these requirements: (a) high surface area to improve the catalyst dispersion; (b) low combustive reactivity; (c) high conductivity; and (d) high electrochemical and thermal stability. Currently, the most popular support material is porous carbon black (XC-72) with high surface area, which leads to well-dispersed electrocatalyst nanoparticles [43]. Recently, developing novel catalyst supports for PEMFC application has attracted much attention, a large portion of which has been devoted to the investigation of using carbon nanotubes (CNTs) as catalyst supports [43–45].

CNTs have attracted much attention due to their promising physical and chemical properties, since their discovery in 1990s by Ijima in Japan. Nowadays, the synthesis of carbon nanotubes can be realized by three main approaches: chemical vapor deposition, laser vaporization, and arc-discharge evaporation. CNTs are categorized as multi-walled carbon nanotubes (MWCNTs), double-walled carbon nanotubes (DWCNTs), and single-walled carbon nanotubes (SWCNTs) on the basis of the number of graphitic layers in the structure. CNTs have attracted increasing interest in both fundamental physics and a plethora of applications, including mechanically reinforced composites, field-effect transistors, chemical/electrochemical sensors, hydrogen storage, catalysis, and electronic nano-devices [12, 43–45].

CNTs are widely investigated as support materials for Pt and Pt alloy catalysts in fuel cells due to their high surface area, good electronic conductivity, and high chemical and thermal stability [3, 45, 46]. Compared with carbon black, CNTs allow for a higher utilization of Pt due to their smooth surfaces, as opposed to conventional carbon black supports where a big portion of Pt nanoparticles are trapped in the pores. An additional advantage of CNTs over carbon black is increased durability, owing to their inert nature. Furthermore, the high electrical conductivity of CNTs and their unique interaction with metal electrocatalysts (more specifically, the interaction of the π-electrons of carbon nanotubes and the d-electrons of platinum) leads to enhanced electrocatalytic activity [43]. The deposition, dispersion, and size of metal nanoparticles supported strongly depend on the surface properties of the CNTs [47]. The electrocatalytic activity of metal nanoparticles is significantly affected by the nature of their interaction with CNTs. The synthesis process of CNTs usually generates bundles, especially for single-walled CNTs, which limits their utility [43]. Furthermore, pristine CNTs are chemically inert; therefore, it is necessary to activate the graphitic surface of the nanotubes to disperse them in solution and efficiently deposit catalyst nanoparticles [48]. Thus, a pre-functionalization process is required for the use of CNTs as support material.

At the early development stage of CNT functionalization, the chemical oxidation of CNTs is most commonly used. Typically, this method involves the ultrasonication or refluxing CNTs in a harsh acid mixture, e.g., a mixture of sulfuric acid and nitric acid, resulting in the formation of oxygen-containing functional groups (i.e., carboxyl groups) on the ends and side-walls of CNTs [49]. The presence of carboxyl groups introduced by the chemical oxidation enables the further functionalization of CNTs via the covalent coupling. Various functional groups could be obtained on CNTs through the synthetic chemistry design [49]. However, such a vigorous functionalization process leads to the damage of the perfect CNT structure, namely, opening the nanotube caps, generating holes in the CNT side-walls or even cutting CNTs. In addition, the introduced functional groups prefer to locate at the defect sites of CNTs, and thus the distribution of functional groups is not uniform.

Alternatively, a gentler and more facile noncovalent functionalization method has been developed. Surfactant aggregating, bifunctional molecule stacking, macromolecule immobilization, and polymer wrapping on CNTs are the four main strategies to noncovalently functionalize CNTs. Surfactants are amphiphilic molecules, in which the hydrophobic ends attach to the hydrophobic CNT surface and the hydrophilic ends are directed to the solvent (aqueous solution), forming aggregates. A bifunctional molecule containing aromatic groups can be efficiently stacked on CNT surface via π–π interactions [50]. For macromolecules like proteins, the hydrophobic regions in the proteins could be responsible for the adsorption onto CNTs. CNTs can be effectively functionalized by most water-soluble polymers via a wrapping technique. These noncovalent functionalization methods effectively and uniformly introduce specific molecules/functional groups to the CNT surfaces without any damage to their structures. Compared to the covalent method, the noncovalent methods are more facile and effective for the functionalization of CNTs [12].

5.2 Noncovalent Functionalization of Carbon Nanotubes with Bifunctional Molecules

Recently, Wang et al. [9, 24, 51] developed a noncovalent functionalization method to modify the surface of CNTs with bifunctional molecules as electrocatalyst supports. As illustrated in Fig. 23, it involves the adsorption of

1-aminopyrene (1-AP) molecules onto the surface of MWCNTs. 1-AP is a bifunctional molecule with a pyrenyl group and an amino functional group. The pyrenyl group, being highly aromatic, is known to interact strongly with the basal plane of graphite via π-stacking. In a similar manner, the pyrenyl group of 1-AP also strongly interacts with the side-walls of MWCNTs, immobilizing the molecule. When the pH of the solution is controlled at a slightly acidic level (e.g., pH 6.5), the amino groups of 1-AP immobilized on the MWCNT surface are protonated and gain a weak positive charge. This leads to the electrostatic attraction of the negatively charged $PtCl_6^{2-}$, followed by the subsequent self-assembly of positively charged Ru^{3+} on the 1-AP-MWCNTs. The microwave-assisted polyol treatment in the presence of ethylene glycol reduces the PtRu precursors, forming PtRu nanoparticles on the MWCNTs. These surface groups also serve as anchoring sites for the direct deposition of reduced metal nanoparticles, which are negatively charged. Differing from the acid-oxidized MWCNTs, where the harsh chemical acids are used to produce carboxylic acid sites on the surface, the 1-AP-functionalization treatment preserves the integrity and the electronic structure of MWCNTs. As shown in Fig. 24, fine metal nanoparticles with a narrow size distribution were deposited on 1-AP-CNTs with a uniform distributions, a result of the evenly-distributed functional groups on the surface of CNTs. The average particle size is 2 nm and no aggregation occurs, even with high PtRu loading. However, on acid-oxidized CNTs, PtRu nanoparticles tend to form aggregates of large particle size due to the poor distribution of functional groups introduced by the harsh acid oxidation. The density of PtRu electrocatalysts can be controlled by adjusting the feeding concentration of the metal precursors. As a result, PtRu nanoparticles on 1-AP-MWCNTs have higher electrochemical surface area, much better activity, and enhanced stability for methanol electrochemical oxidation in acid solution than those on AO-MWCNTs [9].

5.3 Non-covalent Functionalization of Carbon Nanotubes by Polymer-Wrapping

Polymer-wrapping techniques are also used to functionalize carbon nanotubes as electrocatalyst supports. Wang et al. [24] used poly(diallyldimethylammonium chloride) (called PDDA) to wrap CNTs in an aqueous solution. PDDA is a water-soluble quaternary ammonium with a positive charge. During the functionalization process, sodium chloride salt is added to allow the PDDA chain to adopt a random configuration, leading to high coverage of PDDA chains on MWCNTs (PDDA-MWCNTs). This noncovalent functionalization not only leads to a high density and homogeneous dispersion of surface functional groups on MWCNTs, but also preserves the intrinsic properties of MWCNTs without damaging their perfect surface structures. As illustrated in Fig. 25, because of the positive surface charge on MWCNTs, a large amount of negatively charged Pt precursor can be anchored onto the MWCNT surfaces via electrostatic interaction. The subsequent reduction

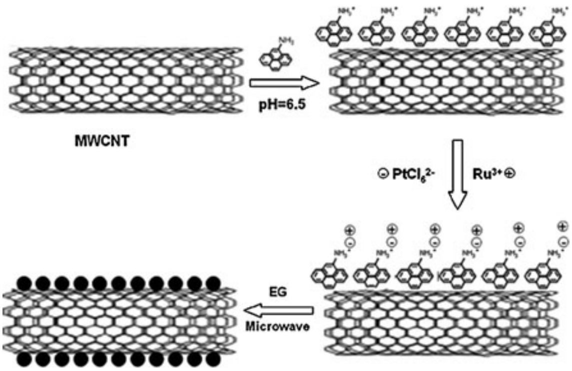


Fig. 23 Schematic diagram of the synthesis of PtRu electrocatalysts on 1-AP-functionalized MWCNTs. Reprinted with permission from Wang et al. [9] American Chemical Society

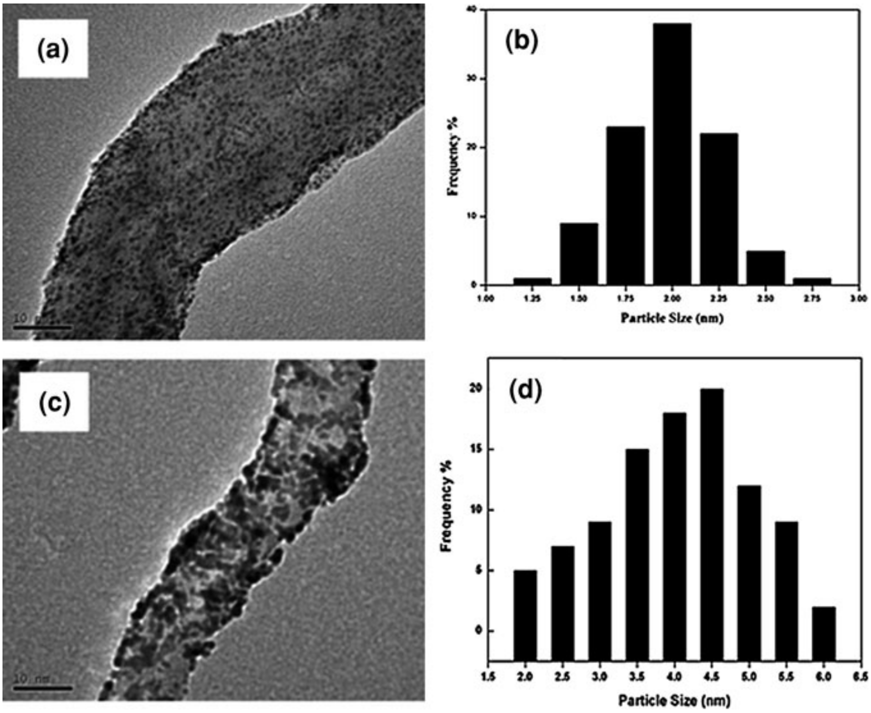


Fig. 24 TEM images and distribution histograms of PtRu nanoparticles on 1-AP-MWCNTs (**a** and **b**) and AO-MWCNTs (**c** and **d**). The PtRu loading was 40 wt%. Reprinted with permission from Wang et al. [9] American Chemical Society

by ethylene glycol (EG) yields Pt nanoparticles with uniform distribution and high density [12].

One of the most significant advantages of this noncovalent functionalization is the high density of functional groups introduced onto the CNT surface. Such high density allows for a high loading of metal nanoparticles. By combining the

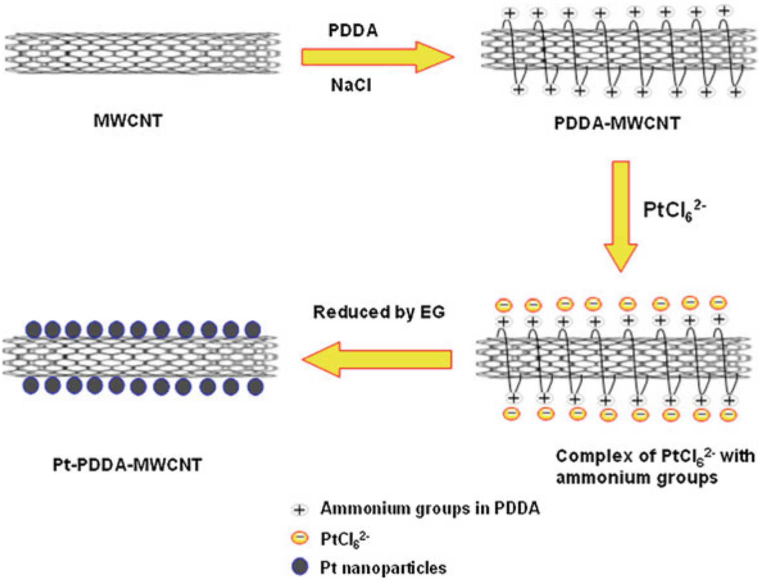


Fig. 25 Illustration of the synthesis of Pt nanoparticles on PDDA wrapped CNTs. Reprinted with permission from Wang et al. [24] Copyright 2008 IOP Publishing Ltd

noncovalent functionalization with polyelectrolyte and a seed-mediated growth method, Wang et al. successfully synthesized Pt/CNT electrocatalysts with various loadings ranging from 10–93 wt%, with the corresponding TEM images shown in Fig. 26. The correlation between the electrocatalytic activity and interconnectivity of Pt nanoparticles on CNT was further investigated. It was demonstrated for the first time that the electrocatalytic activities of Pt/CNTs catalysts are fundamentally correlated to the interconnectivity. The magnitude of the interconnectivity of Pt nanoparticles is a critical factor influencing their electrocatalytic activity, and the interconnected Pt nanoparticles are more active than the isolated Pt nanoparticles. The high electrocatalytic activity of highly interconnected Pt nanoparticles is considered to be related to the increased number of active grain boundaries, which promote the electrocatalytic activity of Pt nanoparticles. On the other hand, the interconnected Pt nanoparticles significantly weaken their chemical adsorption with oxygen-containing species (i.e., CO_{ad} and OH_{ad}), resulting in increased electrocatalytic activity for CO and methanol oxidation and oxygen reduction. The increase of interconnectivity of Pt nanoparticles also reduces the interface resistance among particles for electron transfer [12, 51].

Based on the same polymer-wrapping techniques, polyelectrolytes with various characteristic functional groups, to be used as interlinkers to catch Pt nanoparticles, were deployed to functionalize carbon nanotubes. The effect of

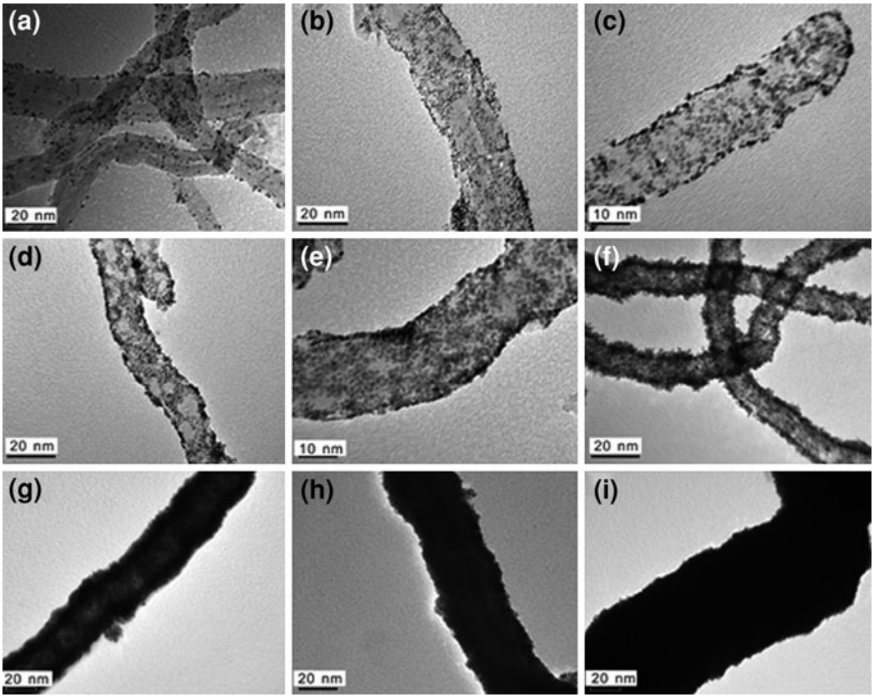


Fig. 26 TEM micrographs of Pt/MWCNTs catalysts with Pt loadings of (**a**) 10 wt%, (**b**) 20 wt%, (**c**) 30 wt%, (**d**) 40 wt%, (**e**) 50 wt%, (**f**) 69 wt%, (**g**) 81.6 wt%, (**h**) 86 wt%, and (**i**) 93 wt%. Reprinted with permission from Wanget al. [51] American Chemical Society

interlinkers between Pt nanoparticles and carbon nanotubes on the electrocatalytic activity for methanol oxidation was investigated by the same group. It was found that polyanions (e.g., poly(styrenesulfonic acid) (PSS) and poly(acrylic acid sodium) (PAA)) have a beneficial effect on methanol electrooxidation on Pt nanoparticles supported on CNTs. The effect is due to charge transfer from polyanions to Pt sites and supply of oxygen-containing species, as evidenced by X-ray photoelectron spectroscopy (XPS) results. The increased electron density around Pt sites via charge transfer causes partial filling of Pt 5*d*-bands, resulting in the downward shift of the *d*-band center and weaker chemisorption with oxygen-containing species (e.g., CO_{ad}). The weakened chemisorption of CO on Pt nanoparticles promotes methanol electrooxidation. However, polycations have a contrary effect on the electronic structure and chemisorption properties of Pt nanoparticles. On the other hand, the long-term stability testing shows that polycation-functionalized CNTs as Pt supports enhances their stability by the stronger interaction between Pt nanoparticles and CNTs contributed by the electrostatic attraction forces.

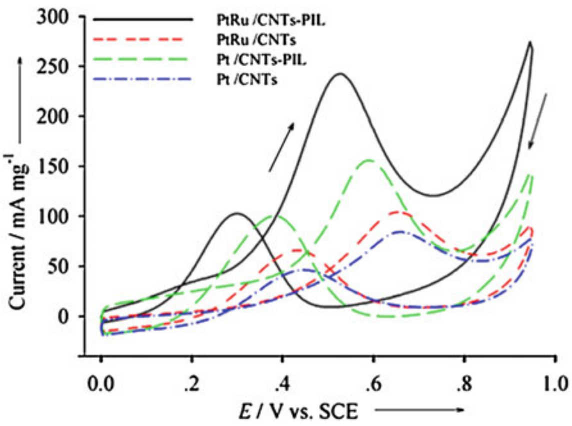
In addition to direct-stacking of bifunctional molecules and polymer wrapping, layer by layer self-assembly is another strategy to immobilize metal nanoparticles on the CNT surfaces. For example, Yang et al. [52] immobilized Pt nanocubes on CNT surface noncovalently using this technique. In this method, CNTs were first pre-functionalized with a negatively charged polyelectrolyte, PSS. Meanwhile, Pt nanocubes stabilized by a positively charged surfactant, CTAB, were synthesized separately. Mixing of the two batches leads to the deposition and immobilization of Pt nanocubes on CNT via electrostatic self-assembly. The Pt NC/CNT electrocatalyst shows relatively high catalytic activity toward the reduction of oxygen.

5.4 Noncovalent Functionalization of Carbon Nanotubes by Ionic Liquid

To develop another advanced strategy, Chen et al. [53] made use of an ionic liquid to functionalize CNT. This approach is based on free radical polymerization of the ionic-liquid monomer 3-ethyl-1-vinylimidazolium tetrafluoroborate via thermal-initiation to form ionic-liquid polymers (PIL) on the surfaces of the CNTs. This results in a large number of surface functional groups on the CNT with good dispersion. The introduction of the ionic species on the surfaces of CNTs provides positive charges to stabilize metal nanoparticles and prevents them from aggregating. Furthermore, the electrochemical performance of these catalysts was investigated by cyclic voltammetry in a nitrogen-saturated 0.5 M H_2SO_4 + 1.0 M CH_3OH solution, with the CV curves shown in Fig. 27. It was found that catalysts supported on ionic-liquid-functionalized CNTs show enhanced current density, reduced onset and peak potential, and improved CO tolerance, compared to those supported on conventional CNTs. This observation shows the advantage of ionic-liquid/CNT composites as electrocatalyst supports for fuel cell applications.

On the basis of the above examples, we conclude that noncovalent functionalization of CNTs effectively equips CNTs with specified functional groups with a high density and uniform distribution. These surface groups function as active sites to anchor metal precursors or metal nanoparticles, resulting in well-dispersed, narrowly-distributed, loading-controlled metal nanoparticles/CNT electrocatalysts. In addition to the physical role, these functional groups also interact with catalyst nanoparticles and affect their intrinsic electrochemical activities. To date, most strategies to tune the activity have been limited to the modification of Pt with other metals, while no specific attention has been paid to the anchoring groups connecting the metal nanoparticles and the support material, which may be equally important. This direction is certainly worthy further studying. Thus, the non-covalent functionalization strategy is an attractive method for the coating of CNTs with size and shape-controlled Pt-based nanoparticles and other nanocatalysts.

Fig. 27 Cyclic voltammograms of the different electrocatalysts in nitrogen-saturated 0.5 M H_2SO_4 +1.0 M CH_3OH at a scan rate of 50 mV s^{-1}. This is the pre-peer reviewed version of the following article: Wu et al. [53]



6 Conclusions

Nanoscale design of electrocatalysts provides a general approach to precisely control the composition, structure, and properties of electrocatalysts for fuel cells. It also furthers the fundamental understanding of electrocatalysis on various catalysts. For practical application in fuel cells, appropriate adoption of nanomaterials and nanotechnology has been shown to improve electrocatalytic activity, durability, and cost. Additionally, nanostructured materials are also being extensively used in other critical components of fuel cells.

References

1. Arico AS, Srinivasan S, Antonucci V (2001) DMFCs: DMFCs: from fundamental aspects to technology development. Fuel Cells 1:1–29
2. Borup R, Meyers J, Pivovar B, Kim YS, Mukundan R, Garland N, Myers D, Wilson M, Garzon F, Wood D, Zelenay P, More K, Stroh K, Zawodzinski T, Boncella J, Mcgrath JE, Inaba M, Miyatake K, Hori M, Ota K, Ogumi Z, Miyata S, Nishikata A, Zyun S, Uchimoto Y, Yasuda K, Kimijima K-i, Iwashita N (2007) Scientific aspects of polymer electrolyte fuel cell durability and degradation. Chem Rev 3904–3951
3. Carmo M, Paganin VA, Rosolen JM, Gonzalez ER (2005) Alternative supports for the preparation of catalysts for low-temperature fuel cells: the use of carbon nanotubes. J Power Sources 142:169–176
4. Du B, Guo QH, Pollard R, Rodriguez D, Smith C, Elter J (2006) PEM fuel cells: status and challenges for commercial stationary power applications. JOM 58:45–49
5. Smitha B, Sridhar S, Khan AA (2005) Solid polymer electrolyte membranes for fuel cell applications—a review. J Membr Sci 259:10–26
6. Zhu YM, Khan Z, Masel RI (2005) The behavior of palladium catalysts in direct formic acid fuel cells. J Power Sources 139:15–20
7. Ralph TR, Hards GA, Keating JE, Campbell SA, Wilkinson DP, Davis M, StPierre J, Johnson MC (1997) Low cost electrodes for proton exchange membrane fuel cells — performance in single cells and Ballard stacks. J Electrochem Soc 144:3845–3857

8. Bock C, Paquet C, Couillard M, Botton GA, MacDougall BR (2004) Size-selected synthesis of PtRu nano-catalysts: reaction and size control mechanism. J Am Chem Soc 126: 8028–8037
9. Wang SY, Wang X, Jiang SP (2008) PtRu nanoparticles supported on 1- aminopyrene-functionalized multiwalled carbon nanotubes and their electrocatalytic activity for methanol oxidation. Langmuir 24:10505–10512
10. Han MY, Gao XH, Su JZ, Nie S (2001) Quantum-dot-tagged microbeads for multiplexed optical coding of biomolecules. Nat Biotechnol 19:631–635
11. Kim F, Song JH, Yang PD (2002) Photochemical synthesis of gold nanorods. J Am Chem Soc 124:14316–14317
12. Wang S (2010) Nanostructured electrocatalysts for proton exchange membrane fuel cells (PEMFCs). PhD Thesis, Nanyang Technological University, Singapore
13. Xu Z, Xiao FS, Purnell SK, Alexeev O, Kawi S, Deutsch SE, Gates BC (1994) Size-dependent catalytic activity of supported metal clusters. Nature 372:346–348
14. Zhang ZB, Sun XZ, Dresselhaus MS, Ying JY, Heremans J (2000) Electronic transport properties of single-crystal bismuth nanowire arrays. Phys Rev B 61:4850–4861
15. Hsin YL, Hwang KC, Yeh CT (2007) Poly(vinylpyrrolidone)-modified graphite carbon nanofibers as promising supports for PtRu catalysts in direct methanol fuel cells. J Am Chem Soc 129:9999–10010
16. Arenz M, Mayrhofer KJJ, Stamenkovic V, Blizanac BB, Tomoyuki T, Ross PN, Markovic NM (2005) The effect of the particle size on the kinetics of CO electrooxidation on high surface area Pt catalysts. J Am Chem Soc 127:6819–6829
17. Wang C, Daimon H, Onodera T, Koda T, Sun SH (2008) A general approach to the size- and shape-controlled synthesis of platinum nanoparticles and their catalytic reduction of oxygen. Angewandte Chemie-International Edition 47:3588–3591
18. Xiao L, Zhuang L, Liu Y, Lu JT, Abruna HD (2009) Activating Pd by morphology tailoring for oxygen reduction. J Am Chem Soc 131:602–608
19. Bi YP, Lu GX (2008) Facile synthesis of platinum nanofiber/nanotube junction structures at room temperature. Chem Mater 20:1224–1226
20. Bai YX, Wu JJ, Qiu XP, Xi JY, Wang JS, Li JF, Zhu WT, Chen LQ (2007) Electrochemical characterization of Pt-CeO$_2$/C and Pt-CexZr1 − xO$_2$/C catalysts for ethanol electro-oxidation. Appl Catal B-Environ 73:144–149
21. Xu CX, Zhang Y, Wang LQ, Xu LQ, Bian XF, Ma HY, Ding Y (2009) Nanotubular mesoporous PdCu bimetallic electrocatalysts toward oxygen reduction reaction. Chem Mater 21:3110–3116
22. Xu CW, Wang H, Shen PK, Jiang SP (2007) Highly ordered Pd nanowire arrays as effective electrocatalysts for ethanol oxidation in direct alcohol fuel cells. Adv Mater 19:4256
23. Koczkur K, Yi QF, Chen AC (2007) Nanoporous Pt-Ru networks and their electrocatalytical properties. Adv Mater 19:2648
24. Wang SY, Wang X, Jiang SP (2008) Controllable self-assembly of Pd nanowire networks as highly active electrocatalysts for direct formic acid fuel cells. Nanotechnology 19:455602
25. Guo DJ, Cui SK (2009) Hollow PtCo nanospheres supported on multiwalled carbon nanotubes for methanol electrooxidation. J Colloid Interface Sci 340:53–57
26. Guo DJ, Zhao L, Qiu XP, Chen LQ, Zhu WT (2008) Novel hollow PtRu nanospheres supported on multi-walled carbon nanotube for methanol electrooxidation. J Power Sources 177:334–338
27. Liang HP, Zhang HM, Hu JS, Guo YG, Wan LJ, Bai CL (2004) Pt hollow nanospheres: facile synthesis and enhanced electrocatalysts. Angewandte Chemie-International Edition 43:1540–1543
28. Zhao J, Chen WX, Zheng YF, Li X (2006) Novel carbon supported hollow Pt nanospheres for methanol electrooxidation. J Power Sources 162:168–172
29. Kotobuki M, Watanabe A, Uchida H, Yamashita H, Watanabe M (2005) Reaction mechanism of preferential oxidation of carbon monoxide on Pt, Fe, and Pt-Fe/mordenite catalysts. J Catal 236:262–269

30. Stamenkovic VR, Fowler B, Mun BS, Wang GJ, Ross PN, Lucas CA, Markovic NM (2007) Improve oxygen reduction activity on Pt3Ni(111) via increased surface site availability. Science 315:493
31. Toda T, Igarashi H, Watanabe M (1999) Enhancement of the electrocatalytic O_2 reduction on Pt-Fe alloys. J Electroanal Chem 460:258–262
32. Kristian N (2010) Study of Pt-M (M=Au and Co) nano-catalysts with low Pt loading for PEMFC applications. PhD Thesis, Nanyang Technological University, Singapore
33. Zhang J, Lima FHB, Shao MH, Sasaki K, Wang JX, Hanson J, Adzic RR (2005) Platinum monolayer on nonnoble metal-noble metal core-shell nanoparticle electrocatalysts for O_2 reduction. J Phys Chem B 109:22701–22704
34. Kristian N, Wang X (2008) Pt-shell-Au-core/C electrocatalyst with a controlled shell thickness and improved Pt utilization for fuel cell reactions. Electrochem Commun 10:12–15
35. Kristian N, Yan Y, Wang X (2007) Highly efficient submonolayer Pt-decorated Au nano-catalysts for formic acid oxidation. Chem Commun 353–355
36. Song HQ, Qiu XP, Li FS, Zhu WT, Chen LQ (2007) Ethanol electro-oxidation on catalysts with TiO_2 coated carbon nanotubes as support. Electrochem Commun 9:1416–1421
37. Hou Z, Yi B, Yu H, Lin Z, Zhang H (2003) CO tolerance electrocatalyst of PtRu-$HxMeO_3$/C (Me = W, Mo) made by composite support method. J Power Sources 123:116–125
38. Jayaraman S, Jaramillo TF, Baeck SH, McFarland EW (2005) Synthesis and characterization of Pt-WO_3 as methanol oxidation catalysts for fuel cells. J Phys Chem B 109:22958–22966
39. Jiang L, Colmenares L, Jusys Z, Sun G, Behm RJ (2007) Ethanol electrooxidation on novel carbon supported Pt/SnOx/C catalysts with varied Pt:Sn ratio. Electrochim Acta 53:377
40. Waki K, Matsubara K, Ke K, Yamazaki Y (2005) Self-organized Pt/SnO_2 electrocatalysts on multiwalled carbon nanotubes. Electrochem Solid State Lett 8:A489–A491
41. Zhou CM, Wang HJ, Peng F, Liang JH, Yu H, Yang J (2009) MnO_2/CNT supported Pt and PtRu nanocatalysts for direct methanol fuel cells. Langmuir 25:7711–7717
42. Kowal A, Li M, Shao M, Sasaki K, Vukmirovic MB, Zhang J, Marinkovic NS, Liu P, Frenkel AI, Adzic RR (2009) Ternary Pt/Rh/SnO_2 electrocatalysts for oxidizing ethanol to CO_2. Nat Mater 8:325–330
43. Shao YY, Liu J, Wang Y, Lin YH (2009) Novel catalyst support materials for PEM fuel cells: current status and future prospects. J Mater Chem 19:46–59
44. Wang JJ, Yin GP, Shao YY, Wang ZB, Gao YZ (2008) Investigation of further improvement of platinum catalyst durability with highly graphitized carbon nanotubes support. J Phys Chem C 112:5784–5789
45. Wang X, Li WZ, Chen ZW, Waje M, Yan YS (2006) Durability inestigation of carbon nanotube as catalyst support for proton exchange membrane fuel cell. J Power Sources 158:154–159
46. Liu ZL, Lin XH, Lee JY, Zhang W, Han M, Gan LM (2002) Preparation and characterization of platinum-based electrocatalysts on multiwalled carbon nanotubes for proton exchange membrane fuel cells. Langmuir 18:4054–4060
47. Tian ZQ, Jiang SP, Liang YM, Shen PK (2006) Synthesis and characterization of platinum catalysts on muldwalled carbon nanotubes by intermittent microwave irradiation for fuel cell applications. J Phys Chem B 110:5343–5350
48. Balasubramanian K, Burghard M (2005) Chemically functionalized carbon nanotubes. Small 1:180–192
49. Yu RQ, Chen LW, Liu QP, Lin JY, Tan KL, Ng SC, Chan HSO, Xu GQ, Hor TSA (1998) Platinum deposition on carbon nanotubes via chemical modification. Chem Mater 10: 718–722
50. Ou YY, Huang MH (2006) High-density assembly of gold nanoparticles on multiwalled carbon nanotubes using 1-pyrenemethylamine as interlinker. J Phys Chem B 110:2031–2036
51. Wang SY, Jiang SP, White TJ, Guo J, Wang X (2009) Electrocatalytic activity and interconnectivity of Pt nanoparticles on multiwalled carbon nanotubes for fuel cells. J Phys Chem C 113:18935–18945

52. Yang W, Wang XL, Yang F, Yang C, Yang XR (2008) Carbon nanotubes decorated with Pt nanocubes by a noncovalent functionalization method and their role in oxygen reduction. Adv Mater 20:2579–2587
53. Wu BH, Hu D, Kuang YJ, Liu B, Zhang XH, Chen JH (2009) Functionalization of carbon nanotubes by an ionic-liquid polymer: dispersion of Pt and PtRu nanoparticles on carbon nanotubes and their electrocatalytic oxidation of methanol. Angewandte Chemie-International Edition 48:4751–4754
54. Chen ZW, Waje M, Li WZ, Yan YS (2007) Supportless Pt and PtPd nanotubes as electrocatalysts for oxygen-reduction reactions. Angewandte Chemie-International Edition 46:4060–4063