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Shape-Controlled Synthesis of Monodisperse PdCu Nanocubes and Their Electrocatalytic Properties

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With increasing worldwide energy demand and environmental concerns, the need for sustainable sources is growing stronger and stronger. Among all attempts, fuel cells stand out as a practical and promising solution.^[1-3] At present, the state-of-the-art carbon-supported Pt nanocrystals are still the most commonly used electrocatalytic material for fuel cells because of both its activity and stability.^[4,5] However, the high cost of Pt is one of the most important barriers that limits the large-scale commercialization of fuel cells.^[6] Therefore, economical and effective Pt-free catalysts are required and an alternative solution is needed. Among the metal-based catalysts studied to date, Pd and Pd alloys have been the focus of recent research for catalyst alternatives to Pt for the oxygen reduction reaction (ORR) and direct alcohol oxidation. Therefore, Pd-based bimetallic nanocrystals, that is, Pd alloys with less expensive secondary transition metals, have been proposed as substitutes for the fuel-cell catalysts. It has been found that upon appropriate modification of their surface atomic structure, Pd-based nanomaterials can become promising electrocatalysts by simultaneously decreasing material cost and enhancing performance.^[7,8]

In recent years, there has been considerable progress on searching for Pd-based bimetallic electrocatalysts, such as synthesizing Pd–Pt nanocomposites,^[2,3] forming a Pd-monolayer on a second noble metal,^[9] or alloying Pd with less expensive 3d transition metals, including Fe,^[10] Co,^[11] Ni,^[12] and Cu,^[13–15]. Among the various bimetallic nanocrystals, PdCu nanocrystals have been intensively explored as catalytic materials for a variety of reactions such as generation of hydrogen, combustion, and CO oxidation.^[16,17] Such noble-metal–non-noble-metal alloy nanocrystals might be the best economical catalyst with the desired performance.^[18,19] Moreover, non-noble metallic Cu has received significant attention as an industrially important material and is considered as the ideal compromise between cost and excellent properties. Cu, with a full d band, has at-

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Herein, we describe a route to synthesize highly monodisperse PdCu nanocubes with an average size of 12 nm. PdCu nanocubes can be readily prepared by co-reduction of $PdCl_2$ and $[Cu(acac)_2]$ (acac = acetylacetonate), with oleylamine (OAm) as both a solvent and a reductant and trioctylphosphine (TOP) as a stabilizer. The carbon-supported PdCu nanocubes displayed substantially enhanced ORR activity compared to that of spherical PdCu nanoparticles, Pd nanoparticles, and commercial Pt/C catalyst.

The PdCu nanocubes were prepared from a 1:1 molar ratio of $PdCl_2$ and $[Cu(acac)_2]$ in OAm as solvent and with TOP as stabilizer (see the Supporting Information for details). A typical scanning electron microscopy (SEM) image shows that the ob-



Figure 1. a) SEM image and b, c) low- and high-magnification TEM images of the PdCu nanocubes. d) TEM image of PdCu nanocubes supported on commercial carbon (Vulcan XC-72). e) HRTEM image of one single PdCu nanocube and f) SAED pattern of the PdCu nanocubes.

tained product consists of about 12 nm (side length) PdCu nanocubes (Figure 1 a). Representative transmission electron microscopy (TEM) images of the as-made PdCu nanocubes are illustrated in Figure 1 b and c, which shows that the PdCu nanocubes are monodisperse and relatively uniform in size. To turn the unsupported nanocubes into a practical electrocatalyst, the PdCu nanocubes were supported on a commercial carbon material (Vulcan XC-72) with a high surface area. The TEM image in Figure 1 d evidences a fairly uniform distribution of the PdCu nanocubes on the commercial carbon support.

The nanocube composition has been extensively investigated by using various techniques including inductively coupled plasma mass spectrometry (ICP–MS) and energy-dispersive Xray spectroscopy (EDS), and the obtained consistent results suggest that the Pd/Cu molar ratio is 1:1. Moreover, only Pd and Cu could be detected (the Mo and carbon peaks originate from the carbon-coated TEM grid; the Supporting Information, Figure S1). The high resolution TEM (HRTEM) image of a single



Figure 2. XRD pattern of the as-synthesized nanocubes.

PdCu nanocube (Figure 1e) shows clear lattice fringes with an interfringe distance of approximately 2.97 Å. Correspondingly, the X-ray diffraction (XRD) pattern in Figure 2 displays an intensive diffraction peak at $2\theta = 30.033^{\circ}$ (i.e., d = 0.2973 nm). Compared with the powder-diffraction file (PDF)-database of the International Centre for Diffraction Data (ICDD) and calculations performed by using the MDI/JADE 6.0 program (the Supporting Information, Table S1) revealed that the PdCu nanocubes exhibited a new crystalline structure in a primitive cubic system with space group Pm3m; the unit-cell parameters were a=b=c=2.97 Å, and $\alpha=\beta=\gamma=90^{\circ}$, which correspond to a crystal structure similar to the standard CuZn pattern (JCPDS 02-1231). The structure was further validated by measuring a selected area electron diffraction (SAED) pattern (Figure 1 f), which was well indexed in comparison with the results of the simulated XRD pattern. In addition, no single-component peak from either Pd or Cu was detected, thus confirming the presence of only single-phase PdCu alloy.

Among all the experimental parameters, the amount of TOP appears to be the key for successful nanocube preparation (the Supporting Information, Figure S2). In the absence of TOP

or in the presence of 0.25 mL TOP only spherical nanoparticles are produced. Addition of TOP (0.75 mL) to the system results in bigger nanocubes with a size range of 40-80 nm. If the amount of TOP is increasing to 1 mL, the final product is composed of spherical nanoparticles and bigger polyhedral nanoparticles. Therefore, TOP plays the most important role in controlling the size of the PdCu nanocubes. We propose that the P atom from TOP can effectively stabilize the {100} faces of the PdCu nanocubes, and this stabilization lowers the total surface energy of the {100} faces and induces the evolution of nanocubes. Additionally, we found that the temperature also played a significant role (the Supporting information, Figure S3). Decreasing the reaction temperature to 210°C, the final product is composed of spherical nanoparticles and bigger nanocubes with a size range of 20-40 nm. As temperature was increased to 230 or 270°C, the side lengths of the resulting nanocubes were 30 and 40 nm, respectively. However, when the temperature was increased to 280 °C, only spherical nanoparticles were obtained. In addition to the cooperative effect of TOP and temperature, the morphology is also strongly affected by the molar ration of Pd/Cu (the Supporting Information, Figure S4). When the molar ratio of Pd/Cu was changed to 1:2 or 2, bigger and irregular nanocubes were obtained. When the molar ratio of Pd/Cu was changed to 1:3 or 3, only spherical nanoparticles were obtained, which has been reported previously.[17]

To evaluate the electrocatalytic ORR activities of the PdCu nanocubes, the PdCu nanocubes were loaded onto a carbon support (Vulcan XC-72R). OAm was removed by immersing the nanocubes in acetic acid for 10 h at 70 $^\circ\text{C}.^{\text{[22]}}$ Figure S5 in the Supporting Information illustrates that the structure and phase were almost the same before and after acetic acid treatment. However, EDS data confirmed that the Cu content was slightly decreased. Therefore, we studied the surface composition of the acid treated carbon-supported PdCu nanocube catalyst by XPS. The atom ratio of Pd/Cu on the surface was about 10:1, suggesting that the PdCu nanocube catalyst had a Pd-rich surface, which was favorable for enhancing the electrocatalytic activity. After treated with acetic acid, there was little OAm remaining on the PdCu surfaces, as illustrated by the Fourier transform infrared (FTIR) spectra (the Supporting Information, Figure S6). To provide references for activity, we also synthesized monodisperse PdCu (\approx 8 nm) nanoparticles and Pd nanoparticles (\approx 12 nm). The low- and the high-magnification TEM image of the PdCu nanoparticles and Pd nanoparticles indicate that both of them have a narrow size distribution (the Supporting Information, Figures S7 and S8). All diffraction peaks in the XRD patterns of the PdCu nanoparticles and Pd nanoparticles could be indexed to the (111) planes of face-centered cubic-structured PdCu and Pd, respectively (the Supporting Information, Figure S9). The catalytic activities of the obtained PdCu nanocubes, PdCu nanoparticles, and Pd nanoparticles toward ORR were evaluated in an electrochemical measurement system and compared with that of a commercial Pt/C catalyst (20 wt%, Johnson Matthey).

Cyclic voltammograms were measured in Ar-saturated 0.1 $\rm M$ KOH solutions at room temperature between -0.8~V to 0.2 V

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Figure 3. a) Cyclic voltammograms recorded in Ar-purged 0.1 mu KOH solution at room temperature with a sweep rate of 50 mV s⁻¹. b) ORR polarization curves at a sweep rate of 20 mV s⁻¹. Inset: Mass activity at -0.15 V for these catalysts. [PdCu nanocubes (-----), PdCu nanoparticles (------), Pd nanoparticles (---------), and commercial Pt/C catalysts (--------)].

versus Ag/AgCl, as shown in Figure 3 a. It shows that the PdCu nanocubes result in redox peaks with a higher intensity than the Pd nanoparticles and a lower intensity than the smaller PdCu nanoparticles. The higher intensity of the redox peaks of the PdCu nanoparticles may be attributed to the smaller size. Typical current peaks associated with the oxidation/reduction of Pd were observed. During the cathodic sweep, the peak for the reduction of Pd oxide appeared at around -0.3 V versus Ag/AgCl for the PdCu nanocubes, of which the peak position was similar to the Pd-based nanostructures reported previously.^[23]

The catalytic activity of these catalysts for the ORR was measured in O2-saturated 0.1 м KOH solutions at room temperature using a glassy-carbon rotating disk electrode with a sweep rate of 20 mVs⁻¹ at 1600 rpm (Figure 3 b). For the PdCu nanocubes, PdCu nanoparticles, Pd nanoparticles, and commercial Pt/C catalysts, the metal loading of Pd or Pt was 10.2 μ g cm⁻². The PdCu-nanocube electrode exhibits an onset potential of 0.03 V, a shift of about 30 mV to more positive potentials than that of the commercial Pt/C, and the diffusion-limiting current from -0.8 V to -0.25 V is very steady. The PdCu nanoparticles show an onset potential similar to the commercial Pt/C, whereas the onset potential of the Pd nanoparticles is at -0.02 V. The half-wave potential of PdCu nanocubes catalysts is -0.123 V, which is more positive compared to that of PdCu nanoparticles, Pd nanoparticles, and the commercial Pt/C catalysts, indicating a greatly enhanced ORR activity. Furthermore, the PdCu nanocubes have the highest mass activity, 2 times higher than that of the commercial Pt/C catalysts and 1.6 and 3.6 times higher than that of PdCu nanoparticles and Pd nanoparticles catalysts, respectively (Figure 3b, inset). The excellent



Figure 4. a) ORR polarization curves for the PdCu nanocubes catalyst in 0.1 M KOH at room temperature with a sweep rate of 20 mV s⁻¹ at different 100 (—), 400 (—), 900 (—), 1600 (—), and 2500 rpm (—). b) The corresponding Koutecky–Levich plots (n = 4) for the PdCu nanocubes catalyst at -0.30 (**a**),-0.35 (**b**), and -0.40 V (**a**).

activity of the PdCu nanocubes catalyst for ORR should be attributed to their (100)-dominated cubic nanostructure, which is consistent with the phenomenon observed in Pt(hkl)-dependent^[24] and Pd(hkl)-dependent^[25-27] ORR activities for extended electrode surfaces.

Rotation-rate-dependent current density-potential curves of the PdCu nanocubes catalyst are shown in Figure 4. High rotational speeds result in an increase in O₂ diffusion to the electrode surface and remarkable catalytic reduction currents. The corresponding Koutecky–Levich plots (j^{-1} vs. $\omega^{-1/2}$) at various electrode potentials show good linearity and nearly parallel fitting lines, indicating first-order kinetics with respect to dissolved O₂ and similar electron-transfer numbers for ORR at different potentials. The Koutecky–Levich equation [Eqs. (1) and (2)] can be used to analyze the kinetic parameters:

$$\frac{1}{j} = \frac{1}{j_{k}} + \frac{1}{j_{d}} = \frac{1}{j_{k}} + \frac{1}{B\omega^{1/2}}$$
(1)

$$B = 0.62 n F C_0 D_0^{2/3} \eta^{-1/6}$$
⁽²⁾

where *j* is the measured current density, j_k is the kinetically limited current density, j_d is the diffusion-limited current density, ω is the electrode rotation rate, *n* is the overall number of electrons transferred in O₂ reduction, *F* is the Faraday constant, C₀ is the concentration of O₂ in the electrolyte (1.14× 10⁻³ mol L⁻¹), D₀ is the diffusion coefficient of O₂ (1.73×

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10⁻⁵ cm²s⁻¹), and η is the viscosity of electrolyte (0.01 cm²s⁻¹).^[28] In the j^{-1} versus $\omega^{-1/2}$ plot, the slope is 1/*B*. By using the so-called *B* factor, the number of electrons transferred (*n*) can be obtained. The electron-transfer number was calculated from the slopes of Koutecky–Levich plots to be approximately 4 at -0.3-0.4 V, suggesting that the PdCu nanocubes catalysts favor a 4e⁻ oxygen-reduction process, which is higher than that of PdCu nanoparticles and Pd nanoparticles and similar to ORR catalyzed by a high-quality commercial Pt/C catalyst measured in the same 0.1 m KOH electrolyte (the Supporting Information, Figure S10);^[29,30] this suggests complete reduction of O₂ to H₂O on the carbon-supported PdCu cubic nanostructure catalysts.

In summary, we have demonstrated a facile route to synthesize highly monodisperse PdCu nanocubes with an average size of 12 nm. The carbon-supported PdCu nanocubes displayed substantially enhanced ORR activity compared with that of PdCu nanoparticles, Pd nanoparticles, and commercial Pt/C catalysts. The ORR catalytic activity of Pd nanocubes was 2 times higher than that of commercial Pt/C catalysts, 1.6 times higher than that of PdCu nanoparticles, and 3.6 times higher than that of Pd nanoparticles. Electrocatalytic experiments revealed that the PdCu nanocubes show highly improved activities compared with spherical PdCu nanoparticles, which confirms that their activities depend on the shape. This approach can potentially be extended to access other metal alloys to generate shape-controlled nanocrystals and thus superb catalytic activities towards ORR or small alcohol oxidation reactions in fuel cells.

Experimental Section

Materials: All chemicals are of analytical grade and were used as received without further purification.

Synthesis of monodisperse PdCu nanocubes: In a typical procedure, PdCl₂ (0.1 mmol), [Cu(acac)₂] (0.1 mmol), and OAm (5 mL) were loaded into a 25 mL three-necked flask while stirring. The mixture was heated under N₂ atmosphere to 100 °C and kept at this temperature for 30 min, after which TOP (0.5 mL) was injected into the solution. Then, the mixture was heated to 250 °C at a heating rate of 10 °Cmin⁻¹ and incubated at this temperature for 30 min, generating a black solution. After cooling down to room temperature, the black precipitate was centrifuged, washed three times with 20 mL ethanol, and redispersed in hexane.

Synthesis of monodisperse PdCu nanoparticles: In a typical procedure, PdCl₂ (0.1 mmol), [Cu(acac)₂] (0.1 mmol), and OAm (5 mL) were loaded into a 25 mL three-necked flask while stirring. The mixture was heated under N₂ atmosphere to 100 °C and kept at this temperature for 30 min. Then, the mixture was heated to 200 °C at a heating rate of 10 °C min⁻¹ and incubated at this temperature for 1 h, generating a black solution. After cooling to room temperature, the black precipitate was centrifuged, washed three times with 20 mL ethanol, and redispersed in hexane.

Synthesis of Pd monodisperse nanoparticles: In a typical procedure, PdCl₂ (0.1 mmol), OAm (5 mL), and TOP (1 mL) were loaded into a 25 mL three-necked flask under stirring. The mixture was heated under N₂ atmosphere to 100 °C and kept at this temperature for 30 min. Then, the mixture was heated to 300 °C at a heating rate

of 10 $^{\circ}$ Cmin⁻¹ and incubated at this temperature for 1 h, generating a black solution. After cooling to room temperature, the black precipitate was centrifuged, washed three times with 20 mL ethanol, and redispersed in hexane.

Synthesis of carbon-supported Pd-based catalysts (20% loading): To prepare the Pd-based catalysts, 10 mL hexane dispersion of 10 mg PdCu NCs, PdCu NPs, or Pd NPs was mixed with 40 mg Vulcan carbon (Vulcan XC-72R) and sonicated for 2 h, after which hexane was evaporated from the solution. The catalysts were then immersed in acetic acid for 10 h at 70 °C to remove OAm from the Pd-based nanostructures. The catalysts were washed with ethanol and dried under vacuum.

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