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Synthesis of Monodisperse Pt Nanocubes and Their Enhanced Catalysis for Oxygen Reduction

Chao Wang,[†] Hideo Daimon,[‡] Youngmin Lee,[†] Jaemin Kim,[†] and Shouheng Sun*,[†]

Department of Chemistry and Division of Engineering, Brown University, Providence, Rhode Island 02912,
and Technology & Development Division, Hitachi Maxell, Ltd., 6-20-1 Kinunodai, Tsukubamirai,
Ibaraki 300-2496, Japan

Received January 20, 2007; E-mail: ssun@brown.edu

Synthesis of platinum (Pt) nanoparticles with controlled sizes and shapes is one of the most attractive goals in developing highly active Pt catalysts for fine chemical synthesis.[1] Well-dispersed Pt nanoparticles are also an important catalyst for fuel cell reactions: they catalyze hydrogen (or alcohol) oxidation at an anode and oxygen reduction at a cathode.[2] Pt nanoparticles are commonly prepared by reducing a Pt salt with hydrogen,[3] an alcohol,[4] sodium borohydride,[5] or hydrazine.[6] The syntheses have also achieved partial control of nanoparticle shape in cube,[3,4b,5b] multipod,[4c,7] and one-dimensional nanostructure,[8] among which Pt nanocubes are of particular interest in catalysis due to the presence of (100) dominant faces on the particle surface. Studies on oxygen reduction in acid electrolytes show that Pt (100) planes are more active than the (111) ones.[9] Using Pt nanocubes as catalyst, one would expect that less Pt is needed in the fuel cell reaction—a goal that has long been sought for commercialization of the fuel cell technology.[10] Despite the synthetic progresses made in the past, a reliable process for producing monodisperse Pt nanocubes with controlled sizes is still not available to date.

Here we report a simple high-temperature organic phase synthesis of monodisperse Pt nanocubes and study their catalysis for oxygen reduction in a fuel cell reaction condition. We recently reported the synthesis of monodisperse FePt nanocubes by simultaneous decomposition of iron pentacarbonyl, $Fe(CO)_5$, and reduction of platinum acetylacetonate, $Pt(acac)_2$, in the presence of oleic acid and oleylamine.[11] Oleic acid and oleylamine were used not only for nanoparticle stabilization but also for nanoparticle shape control. Sequential addition of oleic acid and oleylamine facilitated the formation of FePt nanocubes. Our further synthesis revealed that, regardless of the addition sequence of oleic acid and oleylamine, nearly monodisperse Pt nanocubes could be separated as long as a trace amount of $Fe(CO)_5$ was present during the reaction. Self-assembly of these nanocubes gave a (100) textured array, indicating a very narrow shape distribution in cubic Pt nanoparticles. Electrochemical studies showed that the Pt nanocubes catalyzed oxygen reduction in a 1.5 M H_2SO_4 aqueous solution with specific activity over 2-fold higher than that from the commercial Pt catalyst.

Monodisperse 8 nm Pt nanocubes were synthesized by dissolving $Pt(acac)_2$, oleic acid, and oleylamine in 1-octadecene (ODE) at room temperature and heating the solution at 120 and 200 °C in the presence of $Fe(CO)_5$ solution in ODE.[12] Figure 1A shows the typical transmission electron microscopic (TEM) image of the as-synthesized 8 nm nanocubes (the lower-resolution TEM image is also given in Figure S1). They are nearly 100% in cubic (or cube-like) shape. High-resolution TEM (HRTEM) image of a single Pt nanocube (Figure 1B) shows the Pt lattice fringes with the inter-fringe distance measured to be 0.19 nm, close to the lattice spacing of the {100} planes at 0.196 nm in the face-centered cubic (fcc) Pt crystal. Energy dispersive spectroscopic (EDS) analysis on the nanocube assembly shows no evidence of Fe in the nanocubes (Figure S2), indicating that the trace amount of Fe in the synthesis does not have measurable effect on the particle composition. The crystal structure of the Pt nanocubes was characterized by X-ray diffraction (XRD). Figure 1C shows the XRD pattern of the fcc structured 8 nm Pt nanocubes. Slow evaporation of the hexane dispersion (30 min) of the 8 nm Pt nanocubes on a silicon substrate led to a textured assembly, as shown in Figure 1D. The strong (200) peak in the diffraction pattern indicates that the Pt nanocubes align flat on the substrate. This further proves that the nanocubes have a very narrow shape distribution.

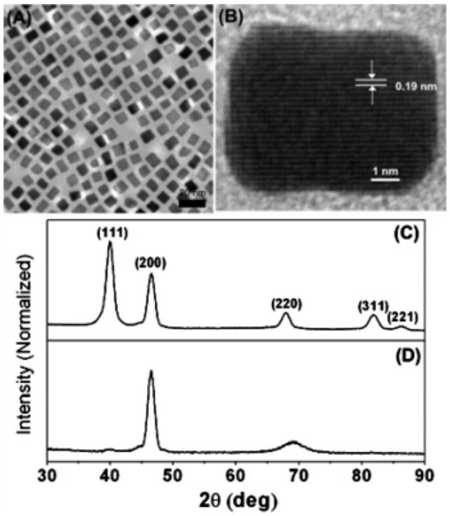

Figure 1. (A) TEM image of the 8 nm Pt nanocubes; (B) HRTEM image of a single Pt nanocube; (C) XRD pattern of the 8 nm Pt nanocube array; and (D) XRD pattern of the self-assembled 8 nm Pt nanocubes showing (100) texture.

The Pt nanocubes were synthesized by high-temperature (200 °C) reduction of $Pt(acac)_2$. The presence of the trace amount of $Fe(CO)_5$ was the key to achieve this shape control. Without $Fe(CO)_5$, Pt nanoparticles were still prepared, but the shape of the particles was much less controlled (Figure S3). In the presence of $Fe(CO)_5$, the cubes were obtained by controlling the heating rate at 3−5 °C per minute to 200 °C and heating at this temperature for 30 min.[12] TEM image of the reaction intermediate separated from the mixture 15 min after the addition of $Fe(CO)_5$ shows the presence of ~3 nm nanoparticles with polyhedral shapes (Figure S4). This suggests that Pt nuclei produced in the presence of trace amount of $Fe(CO)_5$ have polyhedral shapes, and nanocubes evolve from the growth of these polyhedral Pt nuclei. The shape of the Pt particles was also controlled by the presence of oleylamine and

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[†] Brown University.
[‡] Hitachi Maxell, Ltd.

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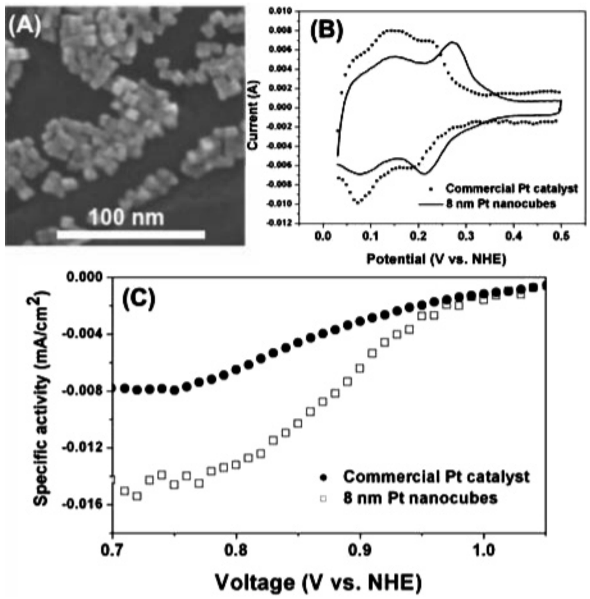

Figure 2. (A) HRSEM image of a specific carbon fiber in the carbon paper showing the presence of 8 nm Pt nanocubes. (B) Cyclic voltammograms of the commercial Pt catalyst and the 8 nm Pt nanocubes with a scanning rate of 5 mV/s in 1.5 M H_2SO_4 under constant nitrogen bubbling. (C) Specific activity of oxygen reduction for (●) the commercial Pt catalyst and (□) the 8 nm Pt nanocubes.

oleic acid. If oleylamine was used alone, spherical Pt nanoparticles were obtained (Figure S5). Unlike the preparation of FePt nanocubes in which the addition sequence of oleic acid and oleylamine is important,[11] the synthesis of Pt nanocubes under the current reaction conditions does not need the sequential addition of these surfactants. This suggests that the presence of oleic acid, a weaker surfactant to Pt than oleylamine, facilitates the growth of the particles into cubes. Note that oleic acid alone cannot stabilize the Pt nanoparticles well—most of them form aggregates, but those suspended in hexane show cubic shape (Figure S6) even though the particles are polydispersed.

The catalytic activity of the 8 nm Pt nanocubes toward oxygen reduction was evaluated in an electrochemical measurement system[12] and compared with that of the commercial spherical Pt nanoparticle catalyst with a mean diameter of 3 nm (TEC10E50E from Tanaka Noble Metal Ltd., Japan). The catalysts were deposited on carbon paper (TORAY) (Figure S7) that had been sonicated in 1.5 M H_2SO_4 for 1 h at room temperature. It contains numerous carbon fibers for catalyst loading. The hexane dispersion of the 8 nm Pt nanocubes was dropped onto the carbon paper (2 × 2 cm), and hexane was allowed to evaporate, leaving nanocube deposition on the carbon fibers. Figure 2A is the high-resolution scanning electron microscopic (HRSEM) image of a specific carbon fiber in the carbon paper showing the presence of 8 nm Pt nanocubes. The nanocubes were treated with UV irradiation (wavelength at 185 and 254 nm in air for 24 h) to remove the surfactants and then sandwiched between two Teflon plates with Au to form a working electrode that was immersed into a 1.5 M H_2SO_4 aqueous solution (308 K) under constant gas bubbling. Ag/AgCl and Au wire were used as reference and counter electrodes, respectively. The potential was scanned from 1.0 to 0.2 V (vs normal hydrogen electrode, NHE) with a scan rate of 5 mV/s. Under nitrogen bubbling, the CV of both commercial Pt catalyst and 8 nm Pt nanocubes was measured, as shown in Figure 2B, and was used to estimate the surface area of the catalysts.[13] Unlike the commercial Pt catalyst, the CV of the 8 nm Pt nanocube assembly in Figure 2B shows a peak at 0.27 V which originates from the hydrogen desorption on the Pt (100) face.[14] This suggests that the (100) face is dominant in the 8 nm Pt nanocube assembly on the carbon paper. The specific catalytic activity (in mA/cm^2) was calculated by dividing the raw electrocatalytic current over the surface area of the catalyst. Figure 2C shows the specific activity for oxygen reduction (mA/cm^2) of the commercial Pt catalyst and the Pt nanocubes synthesized in this work. For potentials ranging from 0.9 to 0.8 V (typical potential range for oxygen reduction reaction), the activity of the Pt nanocubes is over 2 times as high as that of the commercial catalyst, indicating that the nanocubes indeed offer an enhancement in oxygen reduction. Note that the shape of the Pt nanocubes after electrochemical experiments was unchanged.

We have reported that the monodisperse Pt nanocubes can be synthesized by the reduction of Pt(acac)$_2$ in the presence of oleic acid and oleylamine and a trace amount of Fe(CO)$_5$. Self-assembly of these nanocubes results in a (100) textured array. The nanocubes on a carbon paper show an enhanced catalysis toward oxygen reduction, and their specific activity is over 2 times as high as that from the commercial Pt catalyst. Detailed studies on size- and shape-dependent catalysis of these Pt nanoparticles for oxygen reduction at a cathode and methanol oxidation at an anode are underway.

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Supporting Information Available: Pt nanoparticle synthesis and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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