Date:

Date: 26-06-12 17:36:01

European Journal of Inorganic Chemistry

DOI: 10.1002/ejic.201200236

# Gram-Scale Synthesis of Multipod Pd Nanocrystals by a Simple Solid–Liquid Phase Reaction and Their Remarkable Electrocatalytic Properties

Pages: 8

Suli Liu,<sup>[a]</sup> Min Han,<sup>[a]</sup> Yi Shi,<sup>[a]</sup> Chengzhi Zhang,<sup>[a]</sup> Yu Chen,<sup>[a]</sup> Jianchun Bao,<sup>\*[a]</sup> and Zhihui Dai<sup>\*[a]</sup>

Keywords: Palladium / Nanostructures / Electrocatalysis / Reaction mechanisms / Oxidation

In this paper, we describe how multipod Pd nanocrystals (NCs) have been synthesized on the gram scale by means of a simple solid–liquid phase reaction route (i.e., thermal reduction of solid  $Pd(CH_3COO)_2$  in the liquid mixture of dodecylamine, oleic acid, and 1-octadecene under a temperature-programmed mode). The nanostructure evolves from the initially generated larger polyhedral NCs into smaller ones and then into the final multipods. The dodecylamine acts as both a mild reductant and a promoter, which affects the reduction rate and decreases the size of the initially formed polyhedral PdNCs. The morphology of the final NCs, such as tri- and tetrapods, may be determined by the number of growing points on each polyhedral NC. According to the temperature-and time-dependent experiments, a multistep growth mechanism including digestive ripening, oriented attach-

## Introduction

Over the past decade, nanostructured materials, and especially metal nanomaterials, have attracted considerable attention because their fascinating properties can be effectively tuned by rationally tailoring their morphologies.<sup>[1–12]</sup> For example, the position of the transverse resonance peak of Ag nanobars (from light polarized along the short axis) stays in the blue region of the visible spectrum. In contrast, their longitudinal resonance peak shifts from the visible to the near-infrared as the nanobar aspect ratio increases.<sup>[2]</sup> Also, multioctahedral Pt nanocrystals exhibit improved specific activity and durability relative to a commercial Pt/C catalyst for the oxygen reduction reaction.<sup>[6]</sup>

Among the various possible morphologies that can be taken by metal nanocrystals (NCs) with a face-centered cubic (fcc) phase, branched morphologies are an exciting new class of nanostructures on account of their unique structures, physicochemical properties, and their great potential as catalysts, sensing materials, and building blocks for

ment, and fusion process is proposed. This simple solidliquid phase reaction route can be extended to prepare other multipod metal nanostructures. The multipod PdNCs are found to have a high electrochemically active surface area and possess excellent electrocatalytic performance toward the oxidation of formic acid. Relative to that of polyhedral Pd and commercial Pd black catalysts, the multipod PdNCs exhibit much higher catalytic activity and long-term stability, which may make them a good candidate catalyst for direct formic acid fuel cells. This developed synthetic strategy together with the provided fundamental understanding of heterogeneous nucleation and growth has great potential for contriving a rational route to the preparation of advanced nanomaterials with specific morphology for catalytic and other functional applications.

nanoscale devices.<sup>[13]</sup> To date, many strategies have been developed to fabricate various branched metal nanostructures including Pt,<sup>[14,15]</sup> Pd,<sup>[16]</sup> Au,<sup>[17,18]</sup> Ag,<sup>[19,20]</sup> Rh,<sup>[21]</sup> and so on. A few mechanisms, such as burst nucleation and burst growth, and self-aggregation-based nanocrystal growth, have been proposed to explain the formation of NCs. Despite this success, exploiting a simple approach to the fabrication of branched metal NCs remains a challenging task, and the formation mechanism needs to be further identified. Recently, heterogeneous seeded growth has been used as a powerful tool for controlling the morphology of bimetallic nanostructures;<sup>[22-24]</sup> however, reports on the synthesis of monometallic NCs by means of the heterogeneous reaction route are rare.<sup>[25–27]</sup> Furthermore, it is noted that, in most of the syntheses that have been reported so far, only sub-gram quantities of metal NCs have been synthesized. For metal NCs to be used in a wide range of practical applications, it is necessary to develop a facile and economical mass production method with controllable morphology.

In this work, multipod PdNCs have been synthesized on the gram scale by means of a simple solid–liquid phase reaction route. By designing the heterogeneous-phase reaction model and adjusting the reaction temperature, we have been able to control the growth and assembly to form multipod PdNCs. Based on the temperature- and time-dependent experimental results, a multistep formation mecha-

 <sup>[</sup>a] Jiangsu Key Laboratory of Biofunctional Materials, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210097, P. R. China Fax: +86-25-85891767

E-mail: baojianchun@njnu.edu.cn

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201200236.

Pages: 8

# FULL PAPER

nism (i.e., "digestive ripening," the oriented attachment and fusion process) is proposed. Additionally, the multipod PdNCs are used as electrocatalysts for formic acid oxidation. In comparison to the polyhedral and commercial Pd black catalysts, the multipod PdNCs possess a high electrochemically active surface area and excellent electrocatalytic activity toward formic acid oxidation, which shows their great potential for direct formic acid fuel cells (DFAFCs).

## **Results and Discussion**

#### Characterization of the Multipod PdNCs

Figure 1 (A) shows the XRD pattern of the Pd prepared under the typical reaction conditions. The diffraction peaks in the range of  $10 < 2\theta < 90^{\circ}$  can be indexed as (111), (200), (220), (311), and (222) planes of *fcc*-phase Pd, and the lattice parameter is a = 3.89 Å, which are all in good accordance with the American Society for Testing and Materials (ASTM) standard 65-2867. Energy-dispersive X-ray spectroscopy (EDS) analysis (Figure 1, B) shows that the sample is composed of Pd, C, and Cu. The observed C element might come from the adsorbed organic ligands or the carbon film on the TEM grid, and the Cu element originates from the TEM grid. TEM and HRTEM images of the Pd are shown in parts A and B of Figure 2. Part A of this figure shows that the Pd particles are multipod-shaped. The average diameter of the pod is about 4.6 nm and the



Figure 1. (A) XRD and (B) EDS patterns of the PdNCs synthesized under the typical reaction conditions.

pod length is mainly in the range of 8–10 nm. Further information on the microstructure comes from the HRTEM analysis (Figure 2, B). It shows that the multipod Pd structure is composed of associated quasi-spherical particles with lattice planes in between [marked with arrows (a) in Figure 2, B]. The lattice spacing was measured to be 2.30 Å, which corresponds to the interplanar separation between (111) lattice planes of the *fcc*-phase Pd. In addition, some defects exposed on the particle surface were also observed (marked with white circles in Figure 2, B; the magnified picture is shown in Figure S1 in the Supporting Information). which might be one of the important factors in their catalytic properties. The FTIR spectrum (Figure S2 in the Supporting Information) results reveal that the surfaces of the multipod PdNCs are covered with some organic ligands. Corresponding thermogravimetric (TG) analysis (Figure S3 in the Supporting Information) demonstrates that the weight percentage of the adsorbed surface ligands on multipod PdNCs is about 6%.



Figure 2. (A) TEM and (B) HRTEM images of multipod PdNCs.

# Growth Process and Formation Mechanism of the Multipod PdNCs

Different reaction routes such as homogeneous/heterogeneous, or aqueous/hydrophobic media, and even the reaction sequence,<sup>[28]</sup> will lead to different reduction kinetics and formation mechanism, thus obtaining the nanostructures with various morphologies. In most methods for metal NCs prepared in organic-medium-based media, metal precursors are often completely dissolved and the reaction systems are homogeneous. The majority of growth mechanisms abide by the classical mode (i.e., burst nucleation and burst growth). Li and co-workers unveiled a three-step "intermediate-formation/nucleation/growth" mechanism to explain the oleylamine-mediated shape evolution of PdNCs in toluene.<sup>[29]</sup> In the present case, a relatively weak reducing agent, dodecylamine (DDA), and a large amount of solid  $Pd(CH_3COO)_2$  were used. Due to its poor solubility in the mixed solvent, it is a solid-liquid phase reaction system. In

Pages: 8



#### Gram-Scale Synthesis of Multipod Pd Nanocrystals

such a heterogeneous-phase system, because the undissolved solid precursor provides nucleation centers or sites, the nucleation barrier can be reduced relative to that of a homogeneous-phase system, thus leading to the relatively easy nucleation. The reaction phenomena elucidate this hypothesis. At room temperature, the solid precursor is deposited at the bottom of the reactor and the liquid layer is colorless. When the reactor is heated to 60 °C (6 °C min<sup>-1</sup>), the color of the surface of the solid gradually changes from reddish brown to black gradually and emits a few bubbles, thereby indicating that the solid  $Pd(CH_3COO)_2$  is reduced by DDA to form Pd particles. Upon further increasing the reaction temperature, the solid Pd(CH<sub>3</sub>COO)<sub>2</sub> is continuously reduced by DDA. To understand the formation process of the branched Pd nanostructure better, the intermediates produced at different reaction temperatures were investigated by TEM. Figure 3 shows the morphological and size evolution of Pd particles with the reaction temperature. As the reaction temperature was raised to 70 °C, polyhedral Pd particles with the size mainly in the range of 5-12 nm were formed (Figure 3, A). When the temperature reached 120 °C, those large nanoparticles evolved into small, irregular PdNCs 5-8 nm in size (Figure 3, B). Upon further increasing the temperature to 150 °C, the size of the Pd nanoparticles became close to 5 nm with a relatively narrow size distribution, and the most regular polyhedral particles (tetrahedral) were formed (Figure 3, C). The average size is about 5.2 nm. Figure 3 (D) shows the HRTEM analysis of the polyhedral Pd particles shown in Figure 3 (C). The measured d spacing corresponds to 0.23 nm, which can be assigned to the fcc Pd (111) plane. There are two points that should be noted for this part of the reaction. (i) The size change with temperature is different from the cases reported in some previous literature.<sup>[30,31]</sup> For example, Chen et al. reported that the size of the Ag particles prepared using AgNO<sub>3</sub> as a silver source in the oleylamine-liquid paraffin system increased as the temperature was increased from 100 to 140 °C.[31] The reason why the size of the particles decreases with the increase in the reaction temperature in the present case might be due to digestive ripening/ oxidative etching. In our experiment, the surfactant is DDA, which is in an excess amount and is beneficial to the "digestive ripening" process.<sup>[32-34]</sup> This also indicates that the present solid-liquid reaction and cool injection have a clear effect on the size and morphology of the nanostructures. (ii) These results imply that the multipod structure is formed, which results from the following ripening process. This is different from the case of Pt multipods prepared from 2,4-pentanedionate in organic solvent. The higher the reaction temperatures are, the earlier Pt multipods form and the sooner they evolve into spheres.<sup>[35]</sup>

To gain further insight into the formation process of the multipod PdNCs, the other two samples were examined after ripening at 150 °C for 2 and 6 min, respectively. The corresponding TEM images are shown in Figure 4. Compared with the case in Figure 3 (C), after ripening for about 2 min, some branched embryonic particles began to appear (Figure 4, A). Upon further ripening for about 6 min, the population of the branched particles increased. When ripening for 20 min, the branched particles (tri- and tetrapods) shown in Figure 2 (A) were obtained. It was also found that after ripening for 1 or 2 h, the size and morphology of the Pd did not change further. In addition, although the polyhedral particle evolved into the branched nanostructure, the diameter of branches was similar to that of the polyhedral



Figure 3. TEM images of PdNCs when the reaction temperature is (A) 70, (B) 120, and (C) 150 °C. (D) HRTEM image of the PdNCs in (C).



Figure 4. TEM images of the Pd particles after ripening at  $150 \text{ }^{\circ}\text{C}$  for (A) 2 and (B) 6 min, respectively; (C) HRTEM image of the particles after ripening for 2 min at  $150 \text{ }^{\circ}\text{C}$ .

Pages: 8

# FULL PAPER

particles, thereby implying that the formation of the multipod might be the oriented-attachment process (see discussion below).

Crystal structure anisotropy is considered to be the main driving force for the anisotropic growth of nanostructures. For fcc metals, polyhedra are widely accepted as thermodynamically stable morphologies, so this multipod Pd structure is relatively unexpected. The formation of anisotropic morphologies from fcc metals generally requires (i) kinetically controlled growth conditions, (ii) twinning in the nanoparticle nuclei, and (iii) the selective binding or nonbinding of surfactant molecules to different facets of the growing nanocrystal to lead to the anisotropy.<sup>[36-41]</sup> For example, Pt tetrapods and octapods were obtained in the polyol process through the manipulation of reduction kinetics.<sup>[40]</sup> Icosahedral nuclei were used to prepare podlike structures in Pt and Pd.<sup>[42]</sup> Recently, wormlike PdNCs were prepared by reverse micelles or phase-transfer reactions.<sup>[43]</sup> It is considered that, when using DDA as the stabilizing/ coating agent, the formation of wormlike particles is not related to the synthesis modes but mainly to the weak attachment of the coating agent, it being a diffusion-limited aggregation. This is an indication that the factor that affects the anisotropic growth is not simply related to the three types of conditions mentioned above. The primary nanoparticle-to-wire or -nanoring transformation has been observed for the oriented growth of some semiconductor NCs, in which the dipole moment is the driving force.<sup>[44-48]</sup> Though metals are not expected to form long-lived dipoles on their surface, the formation of metal nanowires based on the oriented-attachment mechanism is also observed. For instance, Au nanowires were obtained through oriented attachment by reacting chloroauric acid in oleylamine (OLA) under reflux conditions.<sup>[49]</sup> In the present case, the formation of the multipod PdNCs from a polyhedral Pd nanostructure should be interpreted as an oriented-attachment process, which is further confirmed by the HRTEM analysis. Figure 4 (C) shows the HRTEM image of the particles after ripening for 2 min at 150 °C. The growth is observed at multiple points on each polyhedral NC, most at the corners (marked with letters a, b, and c in Figure 4, C), thereby resulting in the podlike structure. Such assertive evidence for growth of multipod PdNCs has rarely been reported. This is rather similar to the Pt growth reported in the work of Sun and co-workers, in which secondary Pt grew at the cube vertices to form the nanopods.<sup>[9]</sup> It also implies that the morphology of the final NCs, such as tri- and tetrapods, might be determined by the number of growing points on each polyhedral intermediate.

On the basis of the experimental results and analysis mentioned above, we can be sure that the Pd nanostructure evolves from the initially generated larger polyhedral NCs into smaller ones and then into the final multipods. A multistep growth mechanism that includes digestive ripening, an oriented attachment, and a fusion process can be proposed to explain the formation of multipod PdNCs.

In addition, several control experiments were carried out to learn additional information about the reduction reac-

tion. In the present strategy, DDA is used as a reducing reagent. When DDA is substituted with oleylamine, the reaction also leads to the formation of a multipod Pd nanostructure, thus indicating that such long-chain amines are beneficial to the formation of the branched structure. When using terpineol instead of DDA, flocculated Pd particle aggregates composed of small-sized particles of about 6 nm are obtained (Figure 5, A). The diameter of Pd aggregates is mainly in the range of 100-130 nm. This might result from the relatively fast reaction rate due to the stronger reducibility of terpineol than that of DDA and the structure of terpineol. In addition, we also find that the use of oleic acid (OA) is important in obtaining branched Pd nanostructures with good dispersivity but it is not essential for the formation of the multipod particles. The reaction in the absence of OA also gives multipod particles, but they are a little aggregated (Figure 5, B), thereby suggesting that the main role of OA is to protect and disperse the Pd particles. This is different from the case reported by Tilley and coworkers, in which a podlike Pd nanostructure was obtained by using only a surfactant mixture of 1:1 OLA and OA at room temperature.<sup>[50]</sup> Such differences might result from the variation of reaction conditions such as temperature and reaction mode (solid-liquid phase reaction), thereby leading to the different reaction kinetics.



Figure 5. TEM images of Pd prepared (A) using terpineol instead of DDA and keeping other typical synthesis conditions constant, and (B) in the absence of OA and keeping other typical synthesis conditions constant.

It is worth noting that this simple solid–liquid phase reaction route can be extended to prepare other branched metal nanostructures. For example, when using Ni-(HCOO)<sub>2</sub> instead of Pd(CH<sub>3</sub>COO)<sub>2</sub>, a temperature around 250 °C, and keeping other reaction conditions constant as in the case for multipod PdNCs, the complicated hierarchical Ni nanostructures assembled by small-sized multipod NiNCs (Figure 6) were obtained at a yield of 90%. To see clearly, the corresponding field-emission scanning electron Date: 26-06-12 17:36:01

Pages: 8

microscopy (FESEM) images of the hierarchical Ni nanostructures are shown in Figure S4 in the Supporting Information.



Figure 6. TEM image of the hierarchical Ni nanostructures stacked by small-sized multipod NiNCs.

#### **Catalytic Properties**

## Determination of the Electrochemically Active Surface Area of Pd Catalysts

The multipod PdNCs were tested as electrocatalysts for formic acid oxidation. For comparison, the electrocatalytic activities of polyhedral Pd nanostructures (approx. 5.2 nm) and commercial Pd black catalyst (>20 nm, Figure S5 in the Supporting Information) were also measured. Firstly, the electrochemically active surface areas (ECASA) of those three kinds of Pd catalysts were calculated from the hydrogen-adsorption/-desorption cyclic voltammograms (CV) on Pd-catalyst surfaces.<sup>[51-54]</sup> Figure 7 shows their CV curves recorded in 0.1 M HClO<sub>4</sub> solution without formic acid. The peak between -0.25 and 0 V can be ascribed to the adsorption/desorption of hydrogen onto the Pd surface, as well as adsorption of a small fraction of hydrogen into the Pd lattice.<sup>[28,55,56]</sup> A well-defined cathodic peak at about 0.35 V is attributed to the reduction of Pd oxide formed in the positive potential scan. According to the Coulombic amount (Q) associated with the reduction peak area of Pd(OH)<sub>2</sub>, the ECASA values of those three kinds of Pd catalysts are estimated from Equation (1).

$$ECASA = Q/(m \cdot C) \tag{1}$$

C is the reduction charge for a unit area of monolayer Pd nanocrystal on the Pd surface ( $420 \ \mu C \text{ cm}^{-2}$ ), and *m* is the mass of Pd on the catalyst surface. By calculation, the ECASA of multipod PdNCs, polyhedral Pd nanostructures, and commercial Pd catalysts are 21.05, 2.90, 1.67 m<sup>2</sup>g<sup>-1</sup>, respectively. The largest electrochemical specific surface for multipod PdNCs catalyst might be attributed to its special structure (i.e., the way the pods are spatially separated from each other) and small particle size (4.6 nm) of each pod. Because the multipod PdNCs possess the largest ECASA, they have the strongest affinity for  $-OH_{ads}$  species generated in the positive potential scan, thereby letting their reduction peak shift to a more negative potential than that of polyhedral PdNCs and commercial Pd catalyst. A similar phe-



Figure 7. CVs of (a) multipod Pd, (b) polyhedral Pd, and (c) commercial Pd black catalysts in 0.1 M HClO<sub>4</sub> solution at the rate of 50 mV s<sup>-1</sup>.

nomenon has been observed by Lee et al. in the electrooxidation of formic acid when using carbon-supported Pd nanoparticles as catalysts.<sup>[57]</sup>

#### Electrocatalytic Activity of Catalysts for HCOOH Oxidation

Figure 8 (A) displays the CV plots of those three kinds of Pd catalysts in 0.5 м HCOOH + 0.1 м HClO<sub>4</sub> solution at a rate of 50 mV s<sup>-1</sup>. With its remarkably high ECASA, the multipod PdNC-modified electrode exhibits a high mass activity in the electrocatalytic oxidation of formic acid. In the positive scan direction, the main oxidation peaks of formic acid by multipod PdNCs, polyhedral Pd nanostructures, and commercial Pd catalysts are located at 0.17, 0.19, and 0.23 V, respectively, which correspond to the direct oxidation of formic acid. The corresponding main oxidation peak currents on those three kinds of Pd catalysts are 170, 50, and 90 mA mg<sup>-1</sup> Pd, respectively. Meanwhile, their onset oxidation potential for formic acid is located near -0.15, -0.13, and -0.10 V, respectively. The largest oxidation peak current and the lowest onset oxidation potential suggest that the multipod Pd exhibits significantly better electrocatalytic performance than those of polyhedral Pd nanostructures and commercial Pd catalysts. To evaluate the longterm stability of catalysts, chronoamperometry tests were conducted. Figure 8 (B) shows their chronoamperometric curves in 0.5 м HCOOH + 0.1 м HClO<sub>4</sub> solution at a potential of 0.15 V. After 3000 s measurements, their oxidation peak currents were 31.68, 5.05, and  $6.72 \text{ mAmg}^{-1}$  Pd, respectively, thereby revealing that the durability of multipod PdNC catalyst is higher than those of the other two Pd catalysts. The remarkable enhancement of electrocatalytic performance in a multipod PdNC catalyst toward formic acid oxidation might be attributed to the following two reasons. (i) The ECASA of the multipod Pd catalyst is much higher than that of the polyhedral Pd and commercial Pd catalysts due to the way the multipods are spatially separated from each other, thereby leading to the highly favorable conditions for maximizing Pd surface area and surface permeability,<sup>[29,57,58]</sup> whereas polyhedral Pd and commercial Pd are easily found in a highly agglomerated form. (ii)

# **FULL PAPER**

The particular morphology of multipod Pd composed of small Pd nanoparticles results in the presence of a relatively high density of defects, which provides more active sites for formic acid oxidation and enhances the rate of the formic acid oxidation.<sup>[7,59,60]</sup>



Figure 8. (A) CVs and (B) chronoamperometric curves of (a) multipod Pd, (b) polyhedral Pd, and (c) commercial Pd black catalysts in 0.5 M HCOOH + 0.1 M HCIO<sub>4</sub> solution.

## Conclusion

In summary, we have synthesized multipod PdNCs in high yield by means of a developed solid-liquid phase reaction route in DDA and 1-octadecene (ODE) mixed solvent. Such a simple and effective reaction route, combined with a varying temperature mode, enables the size and the morphology of NCs to be controlled and their economical mass production to be achieved. The temperature- and time-dependent experimental results show that the nanostructure evolves from polyhedral particles to multipods with an increase in reaction temperature by growing on the vertices of polyhedral NCs. This can be described as the digestive ripening, oriented attachment, and fusion process. Relative to the polyhedral and commercial Pd black catalysts, the multipod PdNCs show a very high electrochemically active surface area and a significant increase in electrocatalytic activity toward formic acid oxidation, which makes them preferable catalysts for DFAFCs. This facile heterogeneous reaction method as well as the understanding of the growth process is of great potential toward the rational synthesis of advanced nanomaterials for catalytic and other functional applications.

#### **Experimental Section**

Synthesis of Multipod PdNCs: All chemicals used in this work were used as received. In a typical synthesis, a solid sample of Pd(CH<sub>3</sub>COO)<sub>2</sub> (2.5 g), 1-octadecene (ODE) (10 mL), dodecylamine (DDA) (8 mL), and oleic acid (OA) (0.5 mL) were added to a 250 mL three-necked flask at room temperature. Subsequently, the reactor was heated to 150 °C at a rate of 6 °C min<sup>-1</sup> and kept at that temperature for 30 min. Finally, the reactor was naturally cooled to 30 °C. The crude product was separated and redispersed in heptane or hexane. Upon adding absolute ethanol (50 mL) into the dispersed solution, a large amount of precipitates was produced, which was separated by centrifugation and washed with heptane and absolute ethanol 2 to 3 times to remove byproducts. Finally, the precipitate was dried in vacuo for 4 h and used for further characterization and analysis. The yield of the multipod PdNCs was about 95% (the adsorbed surface ligands are not deducted). Thus, the detailed amount of multipod PdNCs that can be synthesized per batch is about 1.13 g.

**Physical Measurements:** X-ray diffraction (XRD) patterns were recorded on a powder sample with a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite-monochromated Cu- $K_{\alpha}$  radiation ( $\lambda = 1.54060$  Å) with  $2\theta$  ranging from 10 to 90°. The corresponding work voltage and current were 40 kV and 100 mA, respectively. MDI Jade 5.0 software was used to deal with the acquired diffraction data. The TEM images were taken with a JEM-200CX instrument (Japan) using an accelerating voltage of 200 kV. The HRTEM images were recorded with a JEOL-2100 apparatus at an accelerating voltage of 200 kV. The FTIR spectra were recorded with a NEXUS670 infrared spectrometer (USA). The thermogravimetric analysis was performed with a Perkin–Elmer TG/DTA synchronous thermoanalysis instrument. FESEM images were recorded with an S-4800 scanning electron microscope that operated at an accelerating voltage of 5 kV.

Electrocatalytic Measurement: Electrochemical measurements were performed in a conventional three-electrode electrochemical cell with a CHI 600 electrochemical analyzer (CH Instruments, Shanghai Chenghua Co.). A Pt plate auxiliary electrode and a saturated calomel reference electrode (SCE) were used. All potentials refer to SCE. Before the electrochemical measurements, N<sub>2</sub> was bubbled through the solution for 10 min to remove the dissolved O<sub>2</sub>. During the electrochemical experiments, a continuous N<sub>2</sub> flow was maintained over the solution. All the electrochemical measurements were carried out at  $(30 \pm 1)$  °C.

Before the electrochemical experiments, multipod PdNCs (4 mg) were dispersed in ethanol (2 mL) by ultrasonication for 30 min to generate a uniform suspension. The concentration of the multipod PdNCs suspension was about  $2 \text{ mgmL}^{-1}$ . The glassy carbon (GC) electrodes (3 mm in diameter) were polished to a mirrorlike finish with 1.0, 0.3, and 0.05 µm alumina slurry (Beuhler) followed by rinsing thoroughly with doubly distilled water. The electrodes were successively sonicated in 1:1 nitric acid, acetone, and doubly distilled water, and then allowed to dry at room temperature. The resulting suspension (5.0 µL) was laid on the surface of the precleaned GC electrode and allowed to dry at 40 °C. Finally, Nafion solution (3.0  $\mu$ L, 5 wt.-%) was dispersed on the electrode surface and dried again at 40 °C. Thus, the working electrode was fabricated, and the specific loading of metal Pd on the electrode surface was about 140 µg cm<sup>-2</sup>. For comparison, the polyhedral Pd nanostructures and commercial Pd-catalyst-modified GC electrodes were also prepared by using the same procedure. All the modified electrodes were pretreated by cycling the potential between -0.2

Date: 26-06-12 17:36:01

Pages: 8

Gram-Scale Synthesis of Multipod Pd Nanocrystals



and 1.2 V for several cycles in a 0.1 M HClO<sub>4</sub> solution prior to the electrochemical test.

**Supporting Information** (see footnote on the first page of this article): HRTEM image, FT-IR spectrum, and thermogravimetric plot of multipod Pd NCs; FE-SEM images of hierarchical Ni nanostructures and TEM image of commercial Pd black catalyst.

### Acknowledgments

This work was supported by the National Natural Science Foundation of China (NSFC) under the research projects 20901041, 21175069, and 21171096, the program for New Century Excellent Talents in University of Chinese Ministry of Education (NCET-09-0159), the Priority Academic Program Development of Jiangsu Higher Education Institutions, and the Program for Outstanding Innovation Research Team of Universities in Jiangsu Province (11KJA150003).

- [1] T. K. Sau, A. L. Rogach, Adv. Mater. 2010, 22, 1781-1804.
- [2] B. Wiley, Y. G. Sun, Y. N. Xia, Acc. Chem. Res. 2007, 40, 1067– 1076.
- [3] A. Kisner, M. Heggen, E. Fernández, S. Lenk, D. Mayer, U. Simon, A. Offenhäusser, Y. Mourzina, *Chem. Eur. J.* 2011, 17, 9503–9507.
- [4] S. Shanmugam, U. Simon, Chem. Eur. J. 2008, 14, 8776-8779.
- [5] D. S. Wang, Q. Peng, Y. D. Li, Nano Res. 2010, 3, 574-580.
- [6] B. W. Lim, X. M. Lu, M. J. Jiang, P. H. C. Camargo, E. C. Cho, E. P. Lee, Y. N. Xia, *Nano Lett.* **2008**, *8*, 4043–4047.
- [7] L. Wang, H. J. Wang, Y. Nemoto, Y. Yamauchi, *Chem. Mater.* 2010, 22, 2835–2841.
- [8] A. X. Yin, X. Q. Min, W. Zhu, H. S. Wu, Y. W. Zhang, C. H. Yan, Chem. Commun. 2012, 48, 543–545.
- [9] M. N. Mankin, V. Mazumder, S. H. Sun, Chem. Mater. 2011, 23, 132–136.
- [10] S. J. Guo, S. J. Dong, E. K. Wang, ACS Nano 2010, 4, 547– 555.
- [11] C. J. Murphy, L. B. Thompson, A. M. Alkilany, P. N. Sisco, S. P. Boulos, S. T. Sivapalan, J. A. Yang, D. J. Chernak, J. Y. Huang, J. Phys. Chem. Lett. 2010, 1, 2867–2875.
- [12] Q. A. Yuan, X. Wang, Nanoscale 2010, 2, 2328-2335.
- [13] B. Lim, Y. N. Xia, Angew. Chem. 2011, 123, 78; Angew. Chem. Int. Ed. 2011, 50, 76–85.
- [14] X. W. Teng, X. Y. Liang, S. Maksimuk, H. Yang, Small 2006, 2, 249–253.
- [15] L. Wang, Y. Yamauchi, J. Am. Chem. Soc. 2009, 131, 9152– 9153.
- [16] J. Watt, N. Young, S. Haigh, A. Kirkland, R. D. Tilley, *Adv. Mater.* 2009, 21, 2288–2293.
- [17] H. G. Liao, Y. X. Jiang, Z. Y. Zhou, S. P. Chen, S. G. Sun, Angew. Chem. 2008, 120, 9240–9243.
- [18] Z. Q. Li, W. Y. Li, P. H. C. Camargo, Y. N. Xia, Angew. Chem. 2008, 120, 9799–9802.
- [19] J. Y. Chen, B. Lim, E. P. Lee, Y. N. Xia, Nano Today 2009, 4, 81–95.
- [20] M. J. Mulvihill, X. Y. Ling, J. Henzie, P. D. Yang, J. Am. Chem. Soc. 2010, 132, 268–274.
- [21] S. M. Humphrey, M. E. Grass, S. E. Habas, K. Niesz, G. A. Somorjai, T. D. Tilley, *Nano Lett.* 2007, 7, 785–790.
- [22] S. E. Habas, H. Lee, V. Radmilovic, G. A. Somorjai, P. D. Yang, *Nat. Mater.* 2007, *6*, 692–697.
- [23] P. H. C. Camargo, Y. Xiong, L. Ji, J. M. Zuo, Y. N. Xia, J. Am. Chem. Soc. 2007, 129, 15452–15453.
- [24] Z. Peng, H. Yang, J. Am. Chem. Soc. 2009, 131, 7542-7543.

- [25] M. Yamamoto, M. Nakamoto, J. Mater. Chem. 2003, 13, 2064– 2065.
- [26] X. Wang, J. Zhuang, Q. Peng, Y. D. Li, Nature 2005, 437, 121– 124.
- [27] Y.-H. Chen, H.-H. Hung, M. H. Huang, J. Am. Chem. Soc. 2009, 131, 9114–9121.
- [28] Y. W. Lee, M. Kim, S. W. Han, Chem. Commun. 2010, 46, 1535–1537.
- [29] Z. Q. Niu, Q. Peng, M. Gong, H. P. Rong, Y. D. Li, Angew. Chem. 2011, 123, 6439; Angew. Chem. Int. Ed. 2011, 50, 6315– 6319.
- [30] V. Mazumder, S. H. Sun, J. Am. Chem. Soc. 2009, 131, 4588-4589.
- [31] M. Chen, Y. G. Feng, X. Wang, T. C. Li, J. Y. Zhang, D. J. Qian, *Langmuir* 2007, 23, 5296–5304.
- [32] A. C. S. Samia, J. A. Schlueter, J. S. Jiang, S. D. Bader, C. J. Qin, X. M. Lin, *Chem. Mater.* 2006, 18, 5203–5212.
- [33] A. C. S. Samia, K. Hyzer, J. A. Schlueter, C. L. Qin, J. S. Jiang, S. D. Bader, X. M. Lin, J. Am. Chem. Soc. 2005, 127, 4126– 4127.
- [34] B. L. V. Prasad, S. I. Stoeva, C. M. Sorensen, K. J. Klabunde, *Chem. Mater.* 2003, 15, 935–942.
- [35] X. W. Teng, H. Yang, Nano Lett. 2005, 5, 885-891.
- [36] J. Watt, N. Young, S. Haigh, A. Kirkland, R. D. Tilley, Adv. Mater. 2009, 21, 2288–2293.
- [37] L. Y. Ruan, C. Y. Chiu, Y. J. Li, Y. Huang, Nano Lett. 2011, 11, 3040–3046.
- [38] S. Maksimuk, X. W. Teng, H. Yang, *Phys. Chem. Chem. Phys.* 2006, 8, 4660–4663.
- [39] X. W. Lou, C. L. Yuan, L. A. Archer, Chem. Mater. 2006, 18, 3921–3923.
- [40] J. Y. Chen, T. Herricks, Y. N. Xia, Angew. Chem. 2005, 117, 2645; Angew. Chem. Int. Ed. 2005, 44, 2589–2592.
- [41] S. H. Chen, Z. L. Wang, J. Ballato, S. H. Foulger, D. L. Carroll, J. Am. Chem. Soc. 2003, 125, 16186–16187.
- [42] S. Maksimuk, X. Teng, H. Yang, J. Phys. Chem. C 2007, 111, 14312–14319.
- [43] K. Naoe, C. Petit, M. P. Pileni, J. Phys. Chem. C 2007, 111, 16249–16254.
- [44] Z. Y. Tang, N. A. Kotov, Adv. Mater. 2005, 17, 951-962.
- [45] A. B. Panda, S. Acharya, A. Efrima, Adv. Mater. 2005, 17, 2471–2474.
- [46] K.-S. Cho, D. V. Talapin, W. Gaschler, C. B. Murray, J. Am. Chem. Soc. 2005, 127, 7140–7147.
- [47] A. P. Alivisatos, Science 2000, 289, 736–737.
- [48] R. L. Penn, J. F. Banfield, Science 1998, 281, 969–971.
- [49] A. Halder, N. Ravishankar, Adv. Mater. 2007, 19, 1854–1858.
  [50] J. Watt, S. Cheong, M. F. Toney, B. Ingham, J. Cookson, P. T.
- Bishop, R. D. Tilley, ACS Nano 2010, 4, 396-402.
- [51] L. Xiao, L. Zhuang, Y. Liu, J. T. Lu, H. D. Abruna, J. Am. Chem. Soc. 2009, 131, 602–608.
- [52] Z. Y. Bai, L. Yang, L. Li, J. Lv, K. Wang, J. Zhang, J. Phys. Chem. C 2009, 113, 10568–10573.
- [53] C. Batchelor-McAuley, C. E. Banks, A. O. Simm, T. G. J. Jones, R. G. Compton, *ChemPhysChem* **2006**, *7*, 1081–1085.
- [54] R. Pattabiraman, Appl. Catal. A 1997, 153, 9-20.
- [55] Y. Liang, Y. Zhou, J. Ma, J. Y. Zhao, Y. Chen, Y. W. Tang, T. H. Lu, *Applied Catalysis B: Environ.* 2011, 103, 388–396.
- [56] J. L. Haan, K. M. Stafford, R. I. Masel, J. Phys. Chem. C 2010, 114, 11665–11672.
- [57] W. J. Zhou, J. Y. Lee, J. Phys. Chem. C 2008, 112, 3789-3793.
- [58] L. Wang, Y. Nemoto, Y. Yamauchi, J. Am. Chem. Soc. 2011, 133, 9674–9677.
- [59] H. Chen, R. S. Liu, M. Y. Lo, S. C. Chang, L. D. Tsai, Y. M. Peng, J. F. Lee, J. Phys. Chem. C 2008, 112, 7522–7526.
- [60] W. P. Zhou, A. Lewera, R. Larsen, R. I. Masel, P. S. Bagus, A. Wieckowski, J. Phys. Chem. B 2006, 110, 13393–13398.

Received: March 7, 2012 Published Online: ■ **FULL PAPER** 

Date:

Multipod Pd nanocrystals were synthesized on the gram scale by means of a simple so-

lid–liquid phase reaction route. A multistep formation mechanism that includes digestive ripening, oriented attachment, and a fusion process is proposed. This Pd nanostructure exhibits excellent electrocatalytic activity and long-term stability toward the oxidation of formic acid.



Palladium Nanocrystals

ᆗ

S. Liu, M. Han, Y. Shi, C. Zhang, Y. Chen, J. Bao,\* Z. Dai\* ...... 1–8

Gram-Scale Synthesis of Multipod Pd Nanocrystals by a Simple Solid–Liquid Phase Reaction and Their Remarkable Electrocatalytic Properties

Keywords: Palladium / Nanostructures / Electrocatalysis / Reaction mechanisms / Oxidation