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Shape-controlled synthesis of palladium nanocrystals by microwave irradiation*

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Abstract: The controlled synthesis of Pd icosahedra in tetraethylene glycol (TEG) with H_2PdCl_4 as a precursor and poly(vinylpyrrolidone) (PVP) as a stabilizer in the presence of an appropriate amount of KOH under microwave irradiation was demonstrated. TEG served as both solvent and reducing agent, and stable Pd icosahedra with uniform sizes and well-defined shapes could be prepared in a yield of over 90 % by microwave heating for 60 s. The sizes of Pd icosahedra can be well controlled by adjusting the concentration of the precursor H_2PdCl_4 .

Keywords: icosahedra; microwave polyol process; nanoparticles; palladium; tetraethylene glycol.

INTRODUCTION

To prepare metal nanoparticles with monodispersity and well-defined morphology is an endless endeavor, which is incited by the theoretical importance and the potential applications of nanostructured materials [1–4]. The chemical and physical properties of metal nanoparticles differ from those of bulk metals because of surface or quantum size effects [5,6]. They have been extensively investigated in the fields of catalysis [4,6,7], electronics [7,8], magnetic devices [9,10], photonics [11], optoelectronics [12], information storage [13,14], biological labeling [15,16], imaging [17], and sensing [18,19]. The intrinsic properties of metal nanoparticles are sensitive to their composition, size, shape, crystallinity, and structure. It has been realized that many metals can now be successfully synthesized with controllable sizes. However, the challenge of shape- or morphology-controlled synthesis of metal nanoparticles has been met with limited success. Recently, the intensive research motivations for the shape-controlled synthesis of metal nanoparticles are based on the fact that in many cases it allows one to fine tune the properties with a greater versatility than can be achieved otherwise [20-22]. For example, the surface plasmon resonance peaks of Ag and Au nanorods have shown great red-shifts with increasing aspect ratios [23,24]. With regard to catalysis, cubic nanoparticles of Pt with surfaces enclosed by the $\{100\}$ facets catalyze reactions involving hydrogen, while the reactivity of carbon monoxide is enhanced by the {210} facets of bulky ball-shaped nanoparticles [25,26]. In the case of Pd, calculations have indicated that the surface plasmon resonance peaks of Pd nanoparticles can be tuned from the UV (330 nm) to the visible (530 nm) region by tailoring their shape from cube to icosahedron and then triangular thin plate [27,28]. Thus, it can be expected that both Pd icosahedra and thin plates can serve as substrates

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for surface-enhanced Raman scattering detection with greatly improved activities [29,30]. Furthermore, due to its exceptional sensitivity toward hydrogen [31,32], Pd has been widely used as the catalysts for some organic reactions [33–36], the low-temperature reduction of pollutant gases [37,38], and the direct alcohol oxidations [39–42].

Pd nanoparticles with various morphologies have been prepared using many methods [43–45]. For instance, poly(vinylpyrrolidone) (PVP)-stabilized Pd colloidal nanoparticles coexisting with various geometric shapes such as triangular, pentagonal, hexagonal, square, and rhombohedral Pd as well as truncated cubes or octahedral, decahedra, and icosahedra were obtained by fast reduction of Pd salt with methanol [46]. Pd nanobars and nanorods could be prepared with high yields and good uniformity by using a modified polyol process in which $[PdCl_4]^{2-}$ was reduced by ethylene glycol (EG) [47]. However, multiply twinned particles (MTPs) such as Pd icosahedra have never been the major product of typical solution-phase syntheses conducted in air. The fast reduction of $[PdCl_4]^{2-}$ by EG produced 90 % truncated cubes or octahedral and only 10 % icosahedra [48]. The reason was thought to be that Pd MTPs are highly susceptible to an oxidative environment. The key to the success of Pd icosahedra formation is to eliminate oxidative etching. Recently, citric acid or citrate ions were introduced to block the oxidative etching, and then Pd icosahedra were selectively synthesized in a yield of 80 % at 90 °C for 26 h in aqueous solution [49]. So far, however, well-defined Pd icosahedra in a high yield have not been obtained by using the polyol process without any oxygen elimination agent.

Microwave dielectric heating has many advantages compared with conventional heating, such as prompt start up, uniform heating, very short heating time, easy heat control (on and off), low cost, etc. It has been extensively applied to the synthesis of metallic nanostructures [50,51]. Herein we report a simple method for high-yield synthesis of Pd icosahedra using microwave polyol process with tetra-ethylene glycol (TEG) as both a reducing agent and a solvent. Stable Pd icosahedra were formed in high yields in a short time in TEG solution with H_2PdCl_4 as a precursor and PVP as a stabilizer under microwave irradiation. The influences of the experimental parameters on the sizes and shape of Pd icosahedra were also investigated and discussed.

MATERIALS AND METHODS

Chemicals

Palladium chloride (PdCl₂), potassium hydroxide (KOH) (Shanghai Chemicals Co., China), TEG (Acros Chemicals), PVP (average molecular weight, $M_w = 40\,000$, Fluka Chemicals) and other chemicals were all of analytical grade and used without further purification. H₂PdCl₄•*n*H₂O was prepared by treating PdCl₂ with concentrated hydrochloric acid (37 %) at 35 °C, in which the molar ratio of HCl/PdCl₂ was 2/1, and then evaporating to dryness. H₂PdCl₄•*n*H₂O was dissolved in TEG, the concentration of Pd(II) was kept at 0.03 mol⁻¹. Both KOH and PVP were also dissolved in TEG to make up a certain concentration of the corresponding solution in TEG, respectively.

Preparation of Pd nanoparticles

In a typical synthesis, 1 ml of 0.03 mol l^{-1} H₂PdCl₄ solution, 1 ml of 0.15 mol⁻¹ PVP (in monomeric unit) solution and 1.0 ml of 0.045 mol l^{-1} KOH solution were added to a 50-ml beaker placed in an icewater bath. Then, 7 ml TEG was added to keep the final volume of the mixture at 10 ml. After thorough mixing, the solution was then put into a modified domestic microwave oven (Galanz, 900 W) and heated for 60 s with 100 % output of the power. The color of the solution turned from pale yellow to brownish black, and PVP-stabilized Pd nanoparticles were obtained.

Characterization

UV–vis absorption spectra were measured on a Lambda BIO35 spectrophotometer. Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) images were taken on a JEOL JEM-2010FEF field-emission electron microscope operated at 200 kV. Diffractograms of HR-TEM were obtained by Fourier transformation. Scanning electron microscopy (SEM) images were taken on a KL30 S-FEG field-emission SEM operated at 10 kV. X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 advance X-ray diffractometer employing Cu $K\alpha$ radiation with 40 kV and 50 mA. X-ray photoelectron spectroscopy (XPS) was recorded on a VG Multilab 2000 XPS using Mg $K\alpha$ radiation under a vacuum of 8×10^{-7} Pa. All binding energy values were determined with reference to carbon C_{1s} = 284.6 eV.

RESULTS AND DISCUSSION

UV-vis absorption spectra of the reaction system

Figure 1 shows the time-dependent UV-vis absorption spectra for Pd nanoparticle formation. As shown in Fig. 1, at the beginning the reaction solution showed two strong characteristic absorption peaks at around 286 and 334 nm, corresponding to those of $PdCl_4^{2-}$ ion. In addition, another peak at around 440 nm for $PdCl_4^{2-}$ ion was also observed but too weak to identify. It can be seen that no obvious change for the absorption peaks was observed at 20 s. When the reaction proceeded for 40 s, the peak at 334 nm disappeared almost completely and the absorption spectrum exhibited a typical surface plasmon scattering, indicating the formation of the Pd nanoparticles. The plasmon scattering further enhanced with increasing the irradiation time, due to the increase of Pd nanoparticles. When the reaction solution was heated by microwave irradiation for 60 s, the plasmon absorption reached to the maximum. Even though the heating was prolonged, the absorption was kept the same as that at 60 s. This confirmed that the reduction has finished completely at 60 s.



Fig. 1 UV-vis absorption spectra of the reaction system at different stages.

TEM characterization

Figure 2 shows TEM images of the as-prepared Pd nanoparticles with a molar ratio of $H_2PdCl_4/KOH/PVP$ of 1/1.5/5 by microwave irradiation for 60 s under the full output of power. As can be seen, nearly all of the projections of the Pd nanoparticles illustrate hexagonal shape with an average size of about 32 nm under TEM. According to the studies on this morphology, these particles should be considered

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Fig. 2 TEM and HR-TEM images of Pd nanoparticles. (a) TEM image, the inset is a cut of the SEM image; (b) HR-TEM image, the inset is an FFT image of the selected Pd nanoparticle.

as icosahedral [52]. Thus, an SEM image was further taken for the corresponding sample after treatment (the inset in Fig. 2a). SEM images reveal that the as-prepared Pd nanoparticles with hexagonal shape are actually uniform, well-defined icosahedra. Figure 2b displays a typical HR-TEM image of a Pd icosahedron with a three-fold axis parallel to the electron beam, which is consistent with the recent literature [49]. A six-fold symmetry of the twinning planes radiating out from a central axis shows that icosahedral Pd particles are MTPs. The inset shows a fast Fourier transform (FFT) pattern. In the FFT pattern, the 6 spots corresponding to the three-fold orientation can be clearly seen. The distance between the (111) planes is about 2.3 Å.

XRD pattern of Pd icosahedra

The XRD pattern of the Pd icosahedra obtained in the typical experiment above is shown in Fig. 3. Three peaks of Pd at $2\theta = 40.5^{\circ}$, 46.8° , 68.4° , corresponding to the (111), (200), (220) lattice planes, are observed. All the diffraction peaks can be well indexed to face-centered cubic (fcc) Pd according to the JCPDS card No. 05-0681, indicating that the as-prepared Pd icosahedra have a high purity and high crystallinity. The mean particle size is estimated by the Scherrer's equation to be about 31.7 nm, which is excellently consistent with the observation by TEM.



Fig. 3 XRD pattern of the typical icosahedral Pd nanoparticles.

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XPS spectrogram of the Pd nanoparticle

XPS was employed to obtain the information on the electronic state of the surface region of Pd nanoparticles. As shown in Fig. 4, XPS measurement indicates the binding energy of Pd3d_{5/2} and Pd3d_{3/2} at 335.08 and 340.35 eV, respectively, refer to $C_{1s} = 284.6$ eV, and the interval is 5.27 eV. The binding energy is coincident with the reference value (335.10 and 340.36 eV) [53], indicating that the as-prepared Pd nanoparticles is in a zero oxidation state.



Fig. 4 XPS spectrogram of the Pd nanoparticles, Pd 3d regions.

Effect of PVP on the synthesis of Pd icosahedra

The PVP/H_2PdCl_4 molar ratio plays an important role in controlling the morphologies of final Pd nanoparticles. It is believed that PVP serves mainly as a steric stabilizer to eliminate random agglomeration and direct the particles to grow into the well-defined icosahedral shape during the synthesis [48]. Especially, PVP can also be served as a reducing agent for syntheses of metal nanoparticles in some cases. Considering the amount of PVP is very low compared with the solvent, TEG, the reducing action of PVP can be neglected in the polyol process [54–56].

Figure 5 shows TEM images of Pd nanoparticles with different amount of PVP. As shown in Fig. 5a, an obvious agglomeration was observed without using PVP, though several hexagonal particles were formed. When PVP/H₂PdCl₄ molar ratio was 3/1, quite a few Pd icosahedra appeared with some large irregular Pd nanoparticles (Fig. 5b). In the optimum condition, PVP/H₂PdCl₄ molar ratio is 5/1, uniform hexagonal Pd nanoparticles (icosahedra) with a narrow distribution were produced (Fig. 5c). However, if excess PVP was used, it tended to form smaller spherical particles, as shown in Fig. 5d. The steric effect of PVP-stabilized particles from agglomeration. Different sections of the Pd icosahedron surface may have a different affinity with PVP. An adequate quantity of PVP would clear up this deference due to a sufficient coverage by PVP on the Pd particles surface, resulting in an isotropic growth for all different faces. However, the excess of PVP surrounding the particles or existing in solution may form a barrier to inhibit the further growth of Pd particles, hence smaller spherical nanoparticles become dominant. Thus, an appropriately low PVP/H₂PdCl₄ ratio is favorable for the formation of larger and uniform Pd icosahedra. For the formation of Pd icosahedra, experimental results indicate that the optimum H₂PdCl₄/KOH/PVP molar ratio is 1/1.5/5 when the concentration of H₂PdCl₄ is 9.0 mmol 1⁻¹.



Fig. 5 TEM images of Pd nanoparticles with different amount of PVP. PVP/H_2PdCl_4 molar ratio is 0/1, 3/1, 5/1, 10/1 for (a), (b), (c), (d), respectively. In all cases, the concentration of H_2PdCl_4 is 9.0 mmol l^{-1} and H_2PdCl_4/KOH molar ratio is 1:1.5.

Effect of the concentration of the precursor

Generally, the concentration of precursor plays an important role in controlling particle sizes. Figure 6 shows TEM images of Pd icosahedra obtained at three different H_2PdCl_4 concentrations, while keeping a molar ratio of $H_2PdCl_4/KOH/PVP$ the same at 1/1.5/5 in all cases. The sizes of Pd icosahedra are strongly dependent on the concentration of H_2PdCl_4 . When H_2PdCl_4 concentration was 3, 9, and 50 mmol l⁻¹, the mean size of the as-prepared Pd icosahedra was 16, 32, and 82 nm, respectively, and all demonstrated narrow distributions. Smaller icosahedra are preferentially produced at a low concentration of H_2PdCl_4 (Fig. 6a), while larger icosahedra are preferentially produced at a high H_2PdCl_4 concentration (Figs. 6c,d). These results indicate that the sizes of the as-prepared Pd icosahedra nano-structures increase with increasing H_2PdCl_4 concentration. An increase of the precursor concentration promotes the growth of Pd nanocrystals with the addition of more Pd atoms in a period of time. So, the sizes of the Pd icosahedra can be well controlled by adjusting the concentration of H_2PdCl_4 .



Fig. 6 TEM images of Pd icosahedra obtained at different concentrations of H_2PdCl_4 . The concentration of H_2PdCl_4 was (a) 3 mmol l^{-1} ; (b) 9 mmol l^{-1} ; both (c) and (d) 50 mmol l^{-1} , respectively. The inset of (c) shows a dark-field image of the corresponding Pd icosahedra. In all cases, the molar ratio of $H_2PdCl_4/KOH/PVP$ was kept at 1/1.5/5.

CONCLUSIONS

In summary, uniform and well-defined Pd icosahedra nanocrystals can be readily synthesized in a high yield of over 90 % by reducing H_2PdCl_4 in TEG with PVP as a stabilizer under microwave irradiation. TEG was used as both a solvent and a reducing agent in the reaction system for the selective synthesis of Pd icosahedra. The sizes of Pd icosahedra can be well controlled by adjusting the concentration of the precursor H_2PdCl_4 .

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