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Morphology and control of Pd nanoparticles

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Abstract

Polymer-stabilized Pd nanoparticles synthesized by reduction of Pd salt with methanol are of various geometric shapes besides spherical. The TEM micrographs show that most of the triangular particles are plate-like although some tetrahedral particles are also observed. The four-sided rhombohedral and square particles and some of the hexagonal particles are plate-like as well. The pentagonal particles are decahedra formed from multiple twinning with imperfection. Most of the hexagonal particles and the icosahedral particles are imperfectly twinned. Extensive multiple twinning are observed under other synthesis conditions. Growing crystals were captured at intermediate stage of the particle formation. The proportion of the different morphologies could be varied by changing the conditions of the synthesis including the molar ratio of precursor salt: polymer, reducing agent, stabilizing polymer, reducing temperature and time, pH of the solution as well as average molecular weight of the polymer. A mechanism is proposed for the particle growth.

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1. Introduction

The catalytic activity and selectivity of metallic nanoparticles are strongly dependent on the particle size. It is also expected that the shape of the particles would affect the catalytic activity due to the changes of the surface-to-volume ratio and in the number of edges, corners and faces, as the morphology is varied [1]. Most nearly, monodispersed nanoparticles with sizes ranging from 1 to 20 nm assume near-spherical shape [2–4] as lower surface energy is associated with such geometry, although different morphologies have been detected.

Among the noble metal nanoparticles, the morphology of Pt has been most extensively studied. Mix structures of cubic, tetrahedral, irregular prismatic, icosahedral, octahedral [5,6], triangular, hexagonal as well as concave cubic [7], and nanowires Pt nanoparticles have been prepared. Spherical, rod-like and dendritic Ag nanoparticles as well as cubic Au and Ag nanoparticles have been prepared by pulse sonoelectrochemical method [8,9]. It is possible to prepare Cu particles with spherical to rod shapes [10]. For other protected noble metal colloidal nanoparticles without support, only sponge-like Ru [11], wire- and sponge-like Pd [12,13] decahedral, icosahedral, cuboctahedral, needle-like, flat-hexagonal and wire-like Ag [9,14,15] as well as decahedral, flat-triangular, rod- and plate-like Au particles [15–17] have been described.

Turkevich et al. discovered that colloidal Au particles were in plate forms rather than spheres [18]. Later, they reported that both the Pt and Pd particles can have plate-like structure with holes in the center and sharp edges [19]. However, the synthesis conditions for the regular plates were not reported. Sodium polyacrylate-stabilized Pd particles with large average diameter of 45 nm, prepared by reduction of palladium chloride solution with sodium formate, has been published but without description of their morphology and structures [20]. In addition, mixed structures of cuboctahedral, icosahedral, truncated decahedral or single twinned Pd particles have been reported [21–23]. We have previously reported [24] a preliminary study on the possibility of controlling the morphology of Pd nanoparticles in

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colloidal solution. In this paper, we describe in more detail the different morphologies of Pd colloidal nanoparticles and their control, prepared via chemical reduction in an aqueous environment using the polymer, PVP, as the stabilizing matrix.

2. Experimental

2.1. Materials and method

Palladium chloride (59% $PdCl_2$, Merck, Germany), chloroplatinic acid hexahydrate (40% $H_2PtCl_4 \cdot 6H_2O$, Merck, Germany and Beijing Chemicals), polyvinylpyrrolidone (PVP, average molecular weight, $M_w = 10{,}000, 40{,}000$ and $360{,}000$, Sigma, St. Louis), polyvinylcholoride (PVC, higher molecular weight, Sigma, St. Louis), polymethacylic acid sodium salt (PMAANa, 30 wt.% in H_2O, $M_w = 6500$, Aldrich, USA), sodium borohydride (Sigma, St. Louis) and sodium hydroxide (BDH, UK) were used as purchased. Methanol, ethanol, *n*-propanol, *i*-propanol, *N*,*N*-dimethylformamide (DMF) and hydrochloric acid (37%) (R&M, UK), aqueous ammonia (25 wt.%), were analytical grade reagents and used without further purification.

All the glass wares and magnetic bars were soaked with aqua-regia for a few days, then rinsed several times with distilled water and dried in an oven before used. The polymer-stabilized noble metal colloids were prepared according to a previously reported method [24]. An appropriate amount of the metal salt was dissolved in HCl solution, then, evaporated to dryness. The residue was again dissolved in an aqueous methanolic solution containing the stabilizing polymer to make up the required polymer:metal ratio. The resulting solution was refluxed or heated to an appropriate temperature to effect the reduction with or without addition of a 0.1 M methanolic NaOH.

2.2. Transmission electron microscopy (TEM)

The electron microscopy sample was prepared by placing a drop of the colloidal dispersion onto a copper grid followed by evaporating the solvent under ambient condition. The particle size and morphology were determined by TEM (Philips CM12 at 80–100 kV), while the crystalline structure of the metal nanoparticles was characterized with high-resolution TEM (HRTEM) (JEOL-2010 at 200 kV). Typically, the TEM micrographs of each sample were taken at multiple, random locations in the sample to ensure that the images reported are representative and at several magnifications, in order to obtain information about the sample in general as well as at closer visualization at higher magnifications and that the sample is not perturbed by the TEM beam. The average particle diameters were obtained by measuring >300 particles from the enlarged micrographs of each sample by using Image Analyst software (SIS Soft-Imaging Software, GmbH, Germany).

2.3. X-ray photoelectron spectroscopy (XPS)

XPS was recorded on an ESCALAB 2201-XL (VG Inc., Institute of Chemistry, Beijing) photoelectron spectrometer by using monochromatic Mg Kα radiation under vacuum at 2×10^{-6} Pa. The samples were dried under vacuum at room temperature prior to XPS measurement.

3. Results and discussion

Colloidal Pd nanoparticles were prepared by reduction of molar ratio of $PVP_{40\,K}$:Pd = 60:4 in aqueous methanolic solution at the refluxing temperature. XPS measurement showed only Pd $3d_{5/2}$ and $3d_{3/2}$ peaks at 339.6 and 334.4 eV, respectively, with reference to the C1s peak appearing at 284.6 eV, indicating that the Pd particles were in zero valence state. From the XRD diffraction pattern, the characteristic peaks for Pd at $2\theta = 40^\circ$, 47°, 68°, 82° and 86° corresponding to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) lattice planes, respectively, were observed. The d-spacing and lattice constant were ∼0.223–0.225 and 0.386–0.390 nm, respectively, indicating the resultant particles were of pure Pd with FCC structure, in excellent agreement with those previously reported [2].

3.1. Structures of the geometric particles

A typical TEM micrograph of the Pd nanoparticles at lower magnification is shown in Fig. 1(a), while the dark field image is shown in Fig. 1(b). As can be seen, the particles are well-dispersed. The mean size and relative standard deviation are 12.6 and 0.34 nm, respectively. These images show that most of the particles have definite geometric shapes and are mostly single crystalline (SCP) with morphologies identifiable as spherical, triangular, rhombohedral or square, pentagonal and hexagonal-faced particles, while the remainders are twinned particles. Their distributions are: triangular, 47%; pentagonal, 24%; hexagonal, 22%; spherical, 3%; square or rhombohedral, 2%.

The small spherical particles are flat and generally shapeless (Fig. 2(a-i and a-ii)). These apparently flat particles have no internal features as the atomic fringes are displayed across the entire plane of the particles. These flat particles may be the precursor [6] for the larger particles, the morphologies of which are described below.

3.1.1. Triangular and hexagonal particles

Triangular particles of alumina-supported Pt catalyst showed plate-like morphology after a sintering process [25]. Further, trigonal lamellar particles of both the Au and Ag hydrosols [26] and hexagonal platelet of PVP protected Cu particles [27] have also been reported. We have found that, in the Pd colloid prepared, not just the triangular, but some of the hexagonal-faced particles existed in plate-like forms with sharp edges. Fig. 2(b-i) shows the plate-like triangular-faced particles, while Fig. 2(b-ii) shows the plate-like hexagonal-faced particle consisting of six atomic layers. Their structures are also confirmed by WBDF imaging as shown in Fig. 1(b). Both the triangular (T) and hexagonal (H)-faced particles show one to two fringes at the outer part of the particles, while no fringe is observed at the center, which is consistent with those reported for flat Ag nanoparticles [15]. This indicates that such particles are not the tetrahedral and cubooctahedral [27] types but plate-like. Very often, these triangular-faced particles are truncated at corners, giving rise

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