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Controlled synthesis of pompon-like self-assemblies of Pd nanoparticles under microwave irradiation

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ABSTRACT

Pd nanoparticles with uniform, self-assembled pompon-like nanostructure were synthesized by thermal decomposition of palladium acetate under microwave irradiation with methyl isobutyl ketone (MIBK) as a solvent in the presence of a little amount of ethylene glycol (EG) and KOH without using any special stabilizers. The as-synthesized Pd nano-pompons were characterized by transmission electron microscopy, X-ray photoelectron spectroscopy and X-ray powder diffraction. The results show that the as-prepared Pd nano-pompons with the average diameters in the range of 28–81 nm were self-assemblies organized by hundreds of smaller primary nanoparticles with an average dimension of about 2.4 nm. The sizes of Pd nano-pompons can be well controlled by adjusting the concentration of palladium acetate. A little amount of EG and KOH also plays an important role in controlling the size, uniformity and dispersion of Pd nano-pompons. The Pd nano-pompons can be easily supported on γ-Al_2O_3 and their catalytic activity was examined preliminarily.

1. Introduction

Considerable attention has been paid to metal nanoclusters for decades owing to their potential applications in many fields such as catalysis [1,2], microelectronics [3,4], photonics [5], optoelectronics [6,7], plasmonics [8,9], information storage [10], optical sensing [11], biological labeling [12], and among others [13–15]. The properties of metal nanoparticles are strongly dependent on their size and shape, as well as their composition, crystallinity and structure [16–19]. So, special nanostructure with uniform size and well-defined shape is required to regulate their properties for various applications. Many techniques have been developed for the preparation of nanosized metallic materials, and different reducing agents and stabilizing compounds were employed to control particle size and shape [20–24].

As one of the most studied metallic nanoparticles, Pd has attracted much interest because of its extraordinary properties. It has been widely used as the catalysts for some organic reactions [25,26] and the low-temperature reduction of pollutants exhausted from automobiles [27,28] due to its exceptional sensitivity towards hydrogen [29]. Pd nanoparticles were also used as electrocatalysts for direct alcohol oxidation in alkaline media [30]. Since the catalytic efficiency of Pd nanoparticles highly depends on both its size and its shape, attempts have been made to obtain uniform Pd nanoparticles with a controlled mean size and a narrow distribution as well as special morphologies. For instance, polyvinylpyrrolidone (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 [31]. 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) [32]. The solvent-stabilized Pd colloids with average particle diameters from 7 to 260 nm were obtained by thermal decomposition of palladium acetate dissolved in various organic solvents [33]. So far, however, stable Pd nanoparticles self-assemblies with secondary nanostructures have not been obtained without using any special protecting 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 [34,35]. In this paper, microwave irradiation was employed to synthesize Pd nanoparticles by thermal decomposition of palladium acetate with methyl isobutyl ketone (MIBK) as a

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solvent in the presence of a little amount of EG and KOH. The as-synthesized Pd nanoparticles with self-assembled pompon-like microstructures were characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction (XRD). The catalytic activity of pompon-like Pd self-assemblies was also examined preliminarily by the hydrogenation of Pd nano-pompons/γ-Al$_2$O$_3$ for cyclohexene.

2. Experimental

Palladium acetate (Shanghai Senhao Fine Chemicals Co., LTD.), MIBK and EG (Acros Chemicals), and other chemicals were all analytical grade and used without further purification. Deionized water was used throughout. KOH was dissolved in EG and palladium acetate was dissolved in MIBK to make up a certain concentration of the corresponding solution prior to use, respectively.

In a typical synthesis, 0.02 mL of 1.67 mM KOH solution in EG and 9.98 mL of 1 mM palladium acetate solution in MIBK were added into a 50 mL round-bottle flask. The total volume of the reaction solution was kept at 10 mL. The mixture 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 dark brown, indicating the formation of Pd nanoparticles.

A certain amount of commercial γ-Al$_2$O$_3$ was added into the as-prepared Pd colloids (10 mL). After being oscillated for 12 h, the mixture was filtered and then the supported Pd catalyst was obtained. The Pd nanoparticles supported on γ-Al$_2$O$_3$ was examined by Flame Atomic Absorption Spectrometry (FAAS).

Catalytic hydrogenation of Pd pompons/γ-Al$_2$O$_3$ catalyst for cyclohexene to cyclohexane was conducted. In a typical run, 12.2 mg of freshly prepared Pd pompons/γ-Al$_2$O$_3$ were dissolved in 8 mL of methanol and then was added into a grass reactor attached to a thermometer, a condenser and a hydrotreator (including a hydrogen cylinder, hydrogen flowmeter and valves). After replacing the air in the reactor with highly pure nitrogen completely, the catalyst was activated with hydrogen for 1 h. Then, 2.0 mL of cyclohexene solution in methanal (1:1 by volume) was added. The reaction mixture was kept at 35 °C and stirred vigorously with a magnetic stirrer. The reaction time and hydrogen consumption were recorded.

The size and morphology of the as-synthesized or the supported Pd nanoparticles were determined on a FEI Tecnai G^2 20 transmission electron microscopy operated at 200 kV. The sample for TEM observation was prepared by placing a drop of the colloidal dispersion onto a copper grid coated with a perforated carbon film, followed by evaporating the solvent at ambient temperature. The average particle size and the distribution were determined from the enlarged micrographs on the basis of the measurement of about 300 particles.

Ultraviolet–visible (UV–vis) absorption spectra were measured with a Unicam SP1750 UV–visible spectrophotometer. XRD was performed on a Bruker D8 Advance X-ray diffractometer employing Cu Kα radiation with 40 kV and 50 mA. The sample for XRD measurement was as follows: the Pd nanoparticles were deposited after centrifugation and then coated on a glass plate, followed by vacuum drying. XPS was recorded on a VG Multilab 2000 X-ray photoelectron spectrometer using Mg Kα radiation under a vacuum of 8×10^{-7} Pa. All binding energy values were determined with reference to carbon, C1s = 284.6 eV.

3. Results and discussion

3.1. Formation of Pd nanoparticles self-assemblies

Fig. 1 shows the time-dependent UV–vis absorption spectra during the formation of Pd nanoparticles. As shown in Fig. 1, at the beginning the reaction solution showed one strong characteristic absorption peak at around 342 nm, corresponding to ligand metal charge transfer transition of Pd(II) ions. It can be seen that, with the increase of irradiation time, the base line uplifted due to plasmon scattering of nanoparticles. The plasmon scattering arose and enhanced with increasing the irradiation time, indicating the formation of Pd nanoparticles. When the reaction solution was irradiated for 50 s, the plasmon scattering reached to the maximum. Furthermore, when the irradiation was prolonged to 60 s, the plasmon absorption declined slightly. It is well known that the frequency of the localized surface plasmon resonance of the nanoparticles is influenced by the size, shape, and dielectric environment of the particles. So, the decline of the plasmon absorption may be ascribed to an increase of the nanoparticle size or a gathering of the primary nanoparticles. The plasmon absorption kept unchanged after 60 s and this indicated that the reduction finished completely at 60 s. After 60 s, the ligand metal charge transfer peak of Pd(II) ions disappeared with the appearance of a weak tail. The presence of weak tail of electronic absorption band confirmed the formation of self-assemblies of Pd nanoparticles.

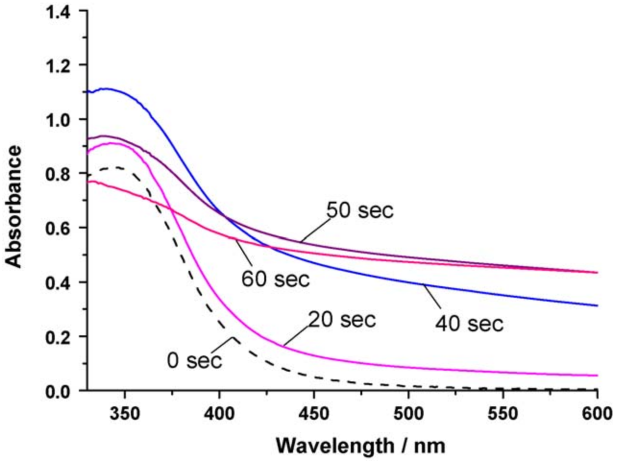

Fig. 1. UV–vis absorption spectra during the formation of palladium nanoparticles.

3.2. Effect of the precursor concentration

Fig. 2 shows TEM images of the typical Pd nanoparticles prepared with different concentrations of the precursor in the presence of 0.2% (by volume) of EG with the same molar ratio of Pd(II)/KOH of 150/1 by microwave heating for 60 s. As can be seen, the pompon-like self-assemblies of Pd nanoparticles were obtained in all cases, and their porous structures can be well observed. Obviously, the sizes of pompon-like self-assemblies (nano-pompons) of Pd nanoparticles are strongly dependent on the concentration of the precursor, palladium acetate. With the increase of the precursor concentration, the mean size of Pd self-assemblies increased. When the concentration of palladium acetate was 0.1, 0.5, 1.0 and 2.0 mM, the mean size of the as-prepared pompon-like self-assemblies was 27.6 ± 4.4, 36.2 ± 4.5, 44.4 ± 5.3, and 81.3 ± 5.4 nm, respectively, as shown in Fig. 2(a), (b), (c) and (d). It should be noted that when the concentration of the precursor is 0.1 mM, Pd nanochains were formed due to the adhesion of the pompon-like self-assemblies with each other, while in the other three cases the dispersion improved. Especially, when the precursor concentration was 1.0 mM, Pd self-assemblies with uniform and well-dispersive pompon-like nanostructure were obtained. This may be explained as: at a low precursor concentration, fewer primary Pd nanoparticles were produced by thermal decomposition of palladium acetate under microwave irradiation, so that there were