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Short Communication

Size controlled synthesis of Pd nanoparticles inspired from the Wacker reaction and their catalytic performances

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ABSTRACT

A novel and facile strategy for the synthesis of size-controlled Pd nanoparticles employing C_2H_4 as the reducing agent was inspired from the Wacker reaction. Uniform Pd nanoparticles with the size ranging from 3 nm to 50 nm were successfully synthesized by using different types of capping agents and optimizing the synthesis parameters. Pd nanoparticles with different sizes exhibit a size-dependent catalytic performance in the aerobic oxidation of benzyl alcohol that could be reasonably attributed to the surface blocking effect exerted by the capping agent chemisorbed on their surfaces and the likely electronic effect.

1. Introduction

The controlled synthesis of uniform metal nanoparticles with well-defined morphologies has recently achieved great progresses [1–4]. Meanwhile, the morphology (size and shape)-dependent properties of metal nanoparticles have also been much revealed. Catalysis is one of the properties of metal nanoparticles that most sensitively depend on the morphology, and thus tailoring the size and shape of metal nanoparticles is now becoming a novel strategy to innovate efficient catalysts [5–9].

Pd nanoparticles are of specific interest due to their ability to catalyze a wide arrange of heterogeneous catalytic reactions [10–14] and electric chemical reactions in fuel cells [15–17]. Therefore, synthesis of Pd nanoparticles with controlled morphologies is one of the most critical issues. During the last decade, efforts have been devoted to the morphology-controlled synthesis of Pd nanoparticles by using a number of synthetic strategies such as polyol processes, aqueous phase synthesis methods, and template-assisted syntheses [18–29]. Monodispersed Pd nanoparticles with different sizes were fabricated by thermal decomposition of Pd-surfactant complexes [19] and by changing the alkyl length in employed surfactants [20]. Hexagonal Pd nanoparticles [21], Pd platelets [22], Pd cubooctahedra [23], Pd nanoboxes and nanocages [24], and Pd nanocubes [27,29] have also been successfully synthesized.

In this communication, we report a novel and facile strategy for the synthesis of size-controlled Pd nanoparticles inspired from the Wacker reaction. The Wacker reaction is an industrial process of the liquid phase oxidation of ethylene (C_2H_4) to acetaldehyde (CH_3CHO) catalyzed by $PdCl_2$ and $CuCl_2$, and its reaction mechanism has been established to follow:

$$H_2C=CH_2 + H_2O + PdCl_2 \rightarrow CH_3CHO + Pd + 2\,HCl$$

$$Pd + 2\,CuCl_2 \rightarrow PdCl_2 + 2\,CuCl$$

$$4\,CuCl + O_2 + 4\,HCl \rightarrow 2\,CuCl_2 + 2\,H_2O$$

It can be thus seen that C_2H_4 can be employed as a reducing agent for the synthesis of Pd nanoparticles. By optimizing the reaction parameters including the concentration of $[PdCl_4]^{2-}$ and C_2H_4, the type and concentration of surfactant, and the reaction temperature, we have successfully synthesized uniform Pd nanoparticles with the size ranging from 3 nm to 50 nm. The catalytic performance of as-synthesized Pd nanoparticles in the aerobic oxidation of benzyl alcohol (BA) was evaluated, and a size-dependent catalytic performance was observed whose likely origins were also investigated.

2. Experimental section

In a typical synthesis experiment, a H_2PdCl_4 solution (0.223 mol/L) was firstly prepared by dissolving 0.9899 g (0.0056 mol) $PdCl_2$ in 25 mL HCl solution (0.447 mol/L), then 0.87 μL H_2PdCl_4 solution and a desirable amount of surfactant (0.0719 g polyvinylpyrrolidone (PVP),

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70 μL polyethyleneglycol 400 (PEG 400), 1.2504 g polyethyleneglycol 2000 (PEG 2000), 0.1098 g sodium dodecyl sulfonate (SDS)) were co-added in 50 mL deionized water. The solution was heated to 50 °C, and then 5% C_2H_4–Ar mixture was purged into the solution at a flow rate of 10 mL/min. The reduction reaction lasted 3.5 h. The system was under stirring during the course of sample preparation.

UV–Vis absorption spectra were acquired on a UV-2450 UV–visible spectrophotometer. Transmission electron microscopy (TEM) images were acquired on JEOL-2010 and JEOL-2010F transmission electron microscopes. X-ray photoelectron spectroscopy (XPS) spectra were measured on an ESCALAB 250 electron spectrometer using nonmonochromatized Al Kα excitation source ($h\nu = 1486.6$ eV). The binding energies in XPS spectra were referenced with respect to the C 1s binding energy of adventitious carbon at 284.5 eV to correct the likely charging of samples.

The aerobic oxidation experiments of BA were carried out directly in the solution where Pd nanoparticles were synthesized. After the synthesis of Pd nanoparticles, the pH value of the solution was adjusted between 9 and 10 by the addition of 0.5106 g (0.0048 mol) sodium carbonate. The solution was heated and kept at 60 °C under stirring, and then pure O_2 was purged into the solution at a flow rate of 13 mL/min and 1 mL (0.0097 mol) benzyl alcohol was injected into the solution to start the reaction. The BA:Pd molar ratio was 500 in our catalytic experiments. After 1 h, the products and unconverted reactants were extracted from the system with ethyl acetate and analyzed by a gas chromatograph equipped with a flame ionization detector. The turn-over frequency of Pd nanoparticles was calculated on the basis of the amount of total Pd atoms.

3. Results and discussions

Pd nanoparticles synthesized with PVP, SDS, PEG400 and PEG2000 as the capping agent were denoted as Pd-PVP, Pd-SDS, Pd-PEG400 and Pd-PEG2000, respectively. Fig. 1 shows the UV–Vis absorption spectra during the synthesis of Pd-PVP. The peak at ~240 nm arising from $[PdCl_4]^{2-}$ [23] attenuates with the reaction proceeding and disappears after 150 min, indicating the complete reduction of $[PdCl_4]^{2-}$ by C_2H_4. The synthesized Pd nanoparticles were black and did not give an obvious surface plasmon resonance (SPR) peak in the UV–Vis spectra. Fine Pd nanoparticles exhibited SPR peak in the UV region that was difficult to be probed [30]. The reduction of $[PdCl_4]^{2-}$ by C_2H_4 employing SDS, PEG400 and PEG2000 as the surfactants under the same reaction condition was also demonstrated by UV–Vis absorption spectra.

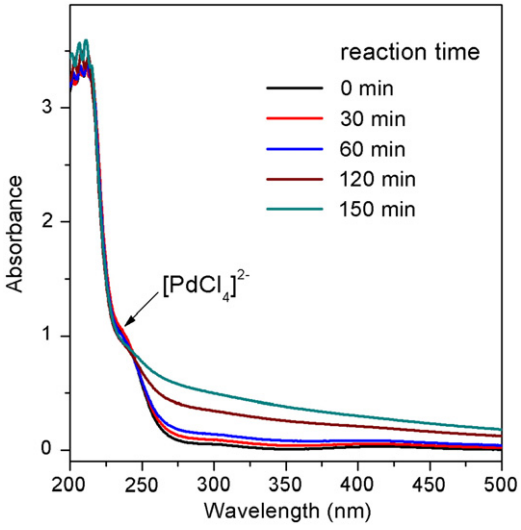

Fig. 1. UV–Vis absorption spectra of the reaction system for the synthesis of Pd-PVP nanoparticles at different reaction times.

Fig. 2 presents the TEM and HRTEM images of Pd-PVP, Pd-SDS, Pd-PEG400 and Pd-PEG2000 and their particle size distributions. Pd nanoparticles synthesized by the reduction of $[PdCl_4]^{2-}$ with C_2H_4

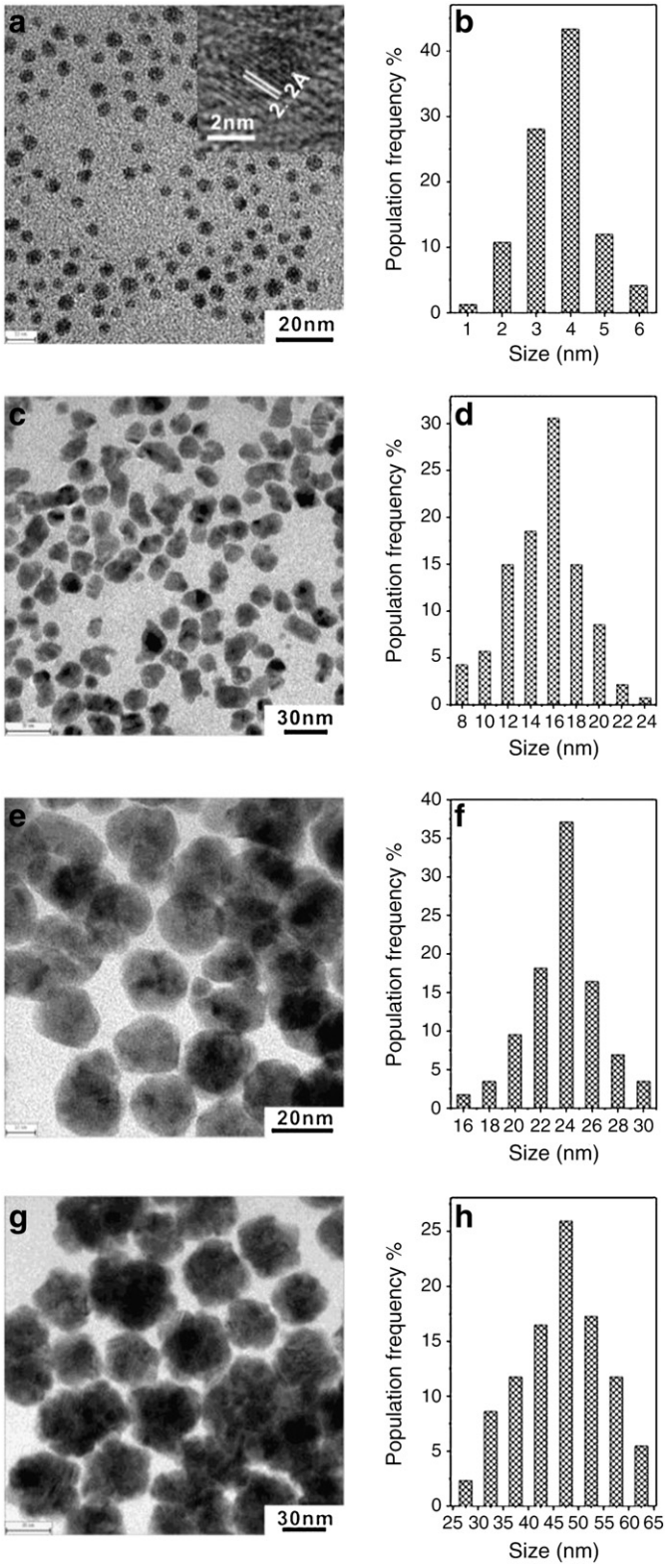

Fig. 2. TEM images and particle size distributions of Pd-PVP (a and b), Pd-SDS (c and d), Pd-PEG2000 (e and f), and Pd-PEG400 (g and h). The inset in Fig. 2a shows the HRTEM image of Pd-PVP.