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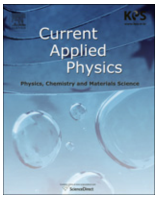

Synthesis of core–shell nanoparticles with a Pt nanoparticle core and a silica shell

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ABSTRACT

A method to prepare a core–shell structure consisting of a Pt metal core coated with a silica shell (Pt(in)SiO_2) is described herein. A silica shell was grown on poly(vinylpyrrolidone) (PVP)-stabilized Pt nanoparticles 2–3 nm in size through hydrolysis and condensation reactions of tetraethyl orthosilicate (TEOS) in a water/ethanol mixture with ammonia as a catalyst. This process requires precise control of the reaction conditions to avoid the formation of silica particles containing multiple Pt cores and core-free silica. The length of PVP molecules, water content, concentration of ammonia and Pt nanoparticles in solution were found to significantly influence the core–shell structure. By optimizing these parameters, it was possible to prepare core–shell particles each containing a single Pt nanoparticle with a silica layer coating approximately 10 nm thick.

1. Introduction

Metal nanoparticles have received much attention for their use in many promising catalytic and biomedical applications because they exhibit unique magnetic and catalytic properties that are not shown in bulk materials [1–3]. However, metal nanoparticles easily aggregate, which minimizes their surface area and surface energy, resulting in a loss of properties that are specific to nanostructures [4]. Therefore, it is important to develop a way of maintaining the size and shape of the nanoparticles. In this respect, silica coated metal nanoparticles have been extensively studied [5–8]. The silica shell functions as a physical barrier to prevent the aggregation of the metal nanoparticles. In addition, the silica coating has excellent properties for various applications, such as a high water solubility, non-toxicity and a controllable porosity. Hyeon et al. prepared silica shell nanocomposite particles with a magnetic core for biomedical applications including magnetic resonance imaging and drug delivery [9]. They found that silica-coated Fe_3O_4 nanoparticles were not only well-dispersible in water but also biocompatible. Moreover, the surfaces of silica coated nanoparticles can easily be functionalized for bioconjugation purposes. More recently, Somorjai et al. reported that mesoporous silica coated Pt nanoparticles are excellent nanocatalytic systems for high-temperature reactions [10]. Mesoporous silica shells were shown to prevent the sintering of Pt nanoparticles up to 750 °C and provided reaction gases direct access through the pores of the silica layers.

Most reported silica coating methods are based on the Stöber method, which typically involves amine-catalyzed hydrolysis and condensation of silicon alkoxide [11]. Kobayashi et al. found that parameters such as the concentration of water, ammonia and tetraethyl orthosilicate (TEOS) are critical factors in determining the morphology of the silica coated particles [12,13]. Konno et al. reported that the addition of ammonia to the gold colloid solution after the addition of TEOS is necessary to prepare silica coated particles with single gold cores [14]. Graf et al. developed a general method to coat various core materials with silica shells via a surface modification process of poly(vinylpyrrolidone) (PVP) [15].

In general, the properties of nanoparticles depend greatly on their size. Indeed, when the size of a metal nanoparticle catalyst decreases, its catalytic activity increases as a result of its enhanced active surface area [16–18]. However, the majority of silica coating processes are developed for particles larger than 10 nm, mainly because small nanoparticles are unstable and tend to form irregular silica particles with multiple cor`es [19–21]. Consequently, coating such small metal particles homogeneously with a silica layer is still a challenge. In this study, effects of the parameters, such as the molecular weight of PVP and the concentration of water, ammonia and Pt colloid in solution, were explored and optimized to form core shell structures that consist of Pt nanoparticles 2–3 nm in size coated with a uniform silica shell.

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2. Experimental

2.1. Chemicals

Platinum chloride ($PtCl_4$) was purchased from Alfa Aesar. Ammonia (29 wt% NH_3 in water), tetraethyl orthosilicate (TEOS 98%) and PVP with average molar masses of 55 kg mol^{-1} (PVP-55) and 10 kg mol^{-1} (PVP-10) were purchased from Sigma–Aldrich. PVP with an average molar mass of 3.5 kg mol^{-1} (PVP-3.5) was purchased from Acros Organics. All other chemicals were reagent grade and were used without further purification.

2.2. Preparation of silica coated Pt nanoparticles (Pt(in)SiO_2)

$PtCl_4$ was dissolved in 100 ml of de-ionized water, and then an ultrasonically blended PVP aqueous solution was added under vigorous stirring. After 1 h, a predetermined amount of an $NaBH_4$ aqueous solution was added quickly, and the reactant solution was then stirred for 24 h. The PVP-stabilized Pt nanoparticles were isolated by centrifugation and re-dispersed in an ethanol/water mixture. Silica was coated on the surface of the Pt nanoparticles to form Pt(in)SiO_2 through a modified Stöber process. A predetermined volume of TEOS was added to the Pt colloid solution. Thereafter, a silica coating was initiated by rapidly adding ammonia into the solution. The concentration of water and ammonia was varied from 3 to 40 vol.% and from 0.3 to 1.3 M with respect to the total reactant solution, respectively. Subsequently, the solutions were stirred at room temperature for 24 h, and then the Pt(in)SiO_2 was collected by centrifugation and thoroughly washed with ethanol. The obtained sample was dried in an oven at 80 °C. To examine its thermal stability, as-synthesized Pt(in)SiO_2 was heat treated at 400 °C for 30 min in air and then annealed further at 800 °C for 5 h under a continuous flow of Ar.

2.3. Characterization

The morphology of the silica coated Pt nanoparticles was characterized by transmission electron microscopy (TEM). TEM was performed using a JEM-3010 microscope operated at 300 kV. To study the surface composition of the core shell structure, X-ray photoelectron spectroscopy (XPS) was obtained using a K-Alpha X-ray photoelectron spectrometer (Thermo VG, U.K.) with a monochromated Al X-ray source (1486.6 eV). The pressure of the analyzer chamber was maintained at 1.8×10^{-9} mb during the measurement. The survey scans were collected using pass energy of 200 eV. The size of the Pt nanoparticles before and after heat treatment was examined by X-ray diffraction (XRD). XRD patterns were recorded with a Rigaku Miniflex diffractometer using Cu Kα radiation at $\lambda = 1.541$ Å. The 2θ angular regions between 20° and 90° were explored at a scan rate of 2° min^{-1} with the angular resolution of 0.02° for all XRD tests. The adsorption/desorption isotherms of nitrogen at 77 K were measured with a Micromeritics ASAP 2020 apparatus. The specific surface area was calculated from the Brunauer-Emmett-Teller (BET) equation and the average pore size was calculated by Barrett–Joyner–Halenda (BJH) method based on the adsorption branch of the isotherms.

3. Results and discussion

For the preparation of a Pt(in)SiO_2 core–shell structure, it is critical to stabilize colloidal Pt particles during the shell growth

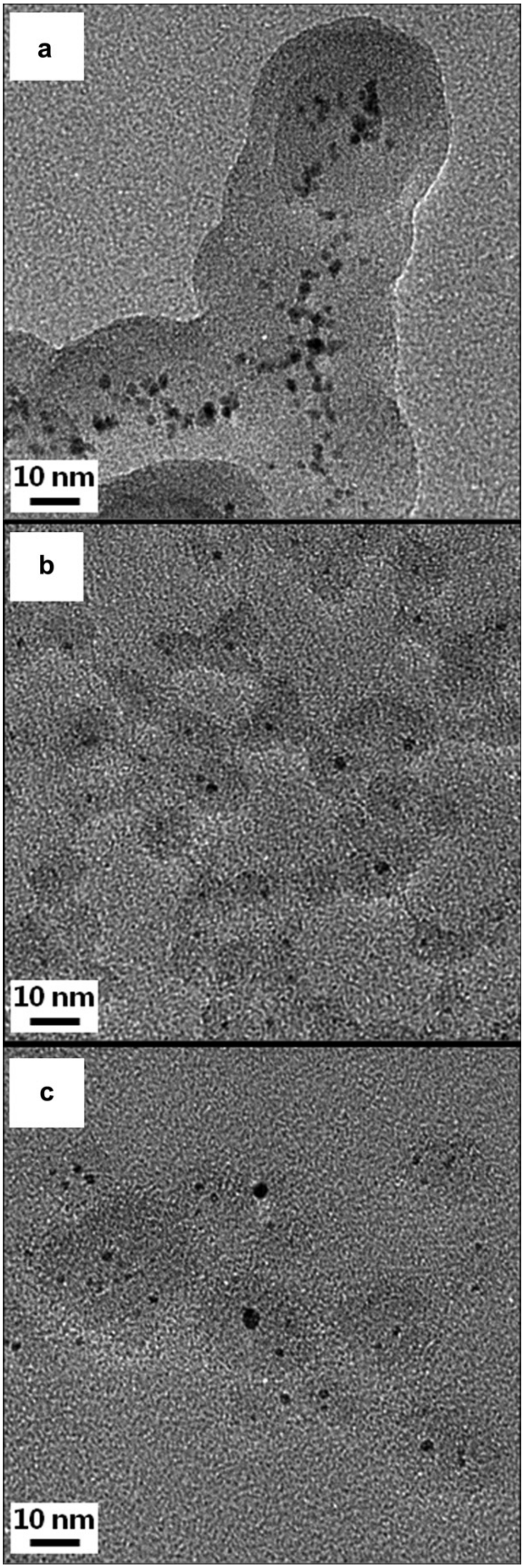

Fig. 1. TEM images of silica coated Pt nanoparticles prepared with (a) PVP-3.5, (b) PVP-10 and (c) PVP-40. The concentration of water, ammonia and TEOS were 3.5 vol.%, 0.8 M and 0.043 M, respectively.