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Formation of mesopores inside platinum nanospheres by using double hydrophilic block copolymers

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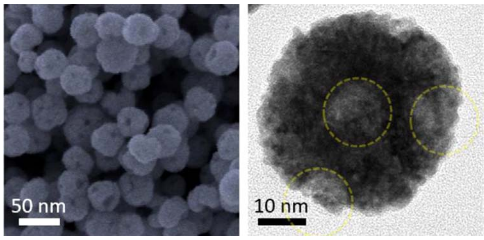
ABSTRACT

We report a simple and facile method for the formation of mesopores inside Pt nanospheres using double hydrophilic block copolymer poly(ethylene oxide-*b*-vinylpyridine) as template and structure directing agent. The dissolved Pt species strongly interact with the vinylpyridine and ethylene oxide units. The reduction of the Pt species in the presence of polymeric micelles leads to the formation of uniform mesoporous Pt nanospheres.



1. Introduction

Nanoarchitectured metals have attracted a great attention due to their performance in several catalytic reactions [1]. Many factors, such as shape, size, surface area, and crystallinity, influence their activity [2,3]. Several methods have been reported for controlling the shape and the size of metal nanoparticles. Pt/Cu nanocrystals with an average size of 50 nm were prepared by wet-chemical reduction of hydrophilic sources of Pt and Cu using N,N-dimethylformamide as both solvent and weak reducing agent [4]. Detsi et al. reported a one-step synthesis of porous Au/Ag nanoparticles by alloying during nanocrystal growth and dealloying through galvanic replacement reaction [5].

The use of macromolecules as capping agent for preparing metal nanoparticles with various shapes has become prevalent. Block copolymers have received a considerable attention to synthesize mesoporous metal nanoparticles. The self-assembly of certain block copolymers into several phase structures make them ideal templates for the synthesis of several metal nanostructures [6]. The hydrophobic block forms the pore and the hydrophilic block acts as a reactive unit for metal precursors. Several amphiphilic block copolymers have been utilized to synthesize porous metal nanoparticles of various shapes and sizes with different compositions using chemical reduction [7], solvothermal [8], electrochemical [9], and *in-situ* reduction on silica particles.[10] In particular, a core-shell-corona type triblock copolymer

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poly(styrene-*b*-2-vinylpyridine-*b*-ethylene oxide) (PS-*b*-PVP-*b*-PEO) with positively charged PVP units in acidic medium ($pH < 4$) has been successfully employed as a pore directing agent for the synthesis of mesoporous Pt with tunable pore size [7]. The length of the PS chain allows the fine-tuning of the mesopores. Cheng et al. also synthesized nanoporous gyroid platinum from double gyroid phase consisting of poly L-lactide (PLLA) networks in a polystyrene matrix of PS-*b*-PLLA templates [11].

The removal of the template can be achieved through solvent extraction and/or calcination. These methods are not viable for future commercialization because the solvent extraction requires a large amount of organic solvent to remove the polymeric template, while the calcination at high temperature destructs the original mesostructure. Using a double hydrophilic block copolymer (DHBC) is a suitable strategy to overcome the issues related to template removal. DHBCs are highly soluble in water and can be simply removed by washing with water, even if the molecules are strongly entrapped. Traditionally, DHBCs have been utilized for drug delivery and nanoparticles synthesis [12,13]. Here we focus on a new class of DHBC, poly(ethylene oxide-vinylpyridine) block copolymer (PEO-*b*-PVP). No organic solvents are required to dissolve this polymer because of the two hydrophilic blocks, the positively charged PVP^+ and the neutral PEO, make it highly soluble in acidic water. The dissolved Pt species can interact strongly with both the vinylpyridine and ethylene oxide units. After adding the Pt source, the micellization of PEO-*b*-PVP occurs. The formed polymeric micelles serve as a structure-directing agent for the formation of mesoporous Pt nanospheres.

2. Experimental

2.1. Synthesis of mesoporous Pt nanospheres

10 mg of $PEO_{(13,500)}$-*b*-$PVP_{(2100)}$ block copolymer (Polymer Source Inc.) was dissolved in 10 mL of water. The number inside parenthesis indicates the molecular weight of each block. The pH of the solution was maintained at 3 using 0.1 M HCl solution. 20 mg of K_2PtCl_4 was added into the polymer solution. Then, the solution was stirred for 2 h at room temperature. To reduce the Pt species, 0.1 mL of hydrazine was added into the solution and stirred for 15 min. The black precipitate was thoroughly washed with acidic water and dried at room temperature for further characterization.

2.2. Characterization

The dynamic light scattering experiment (DLS) measurements were carried out using an Otsuka ELS Z zeta-potential and particle analyzer. To measure the average sizes of the particles, the DLS measurement was repeated three times. All the measurements were carried out at 25 °C. The morphology of the sample was observed under field emission scanning electron microscope (SEM, HITACHI SU-8000) and transmission electron microscope (TEM, JEOL JEM-1210). The crystalline phases and crystallinity were measured by X-ray powder diffraction (XRD, SHIMADZU XRD-7000) analysis. N_2 adsorption-desorption isotherms were obtained with an Autosorb-1 (Quantachrome Instruments USA).

3. Results and discussion

The double hydrophilic block copolymer, PEO-*b*-PVP, was firstly dissolved in water. The pH was maintained at 3 using 0.1 M HCl solution. At pH 3, the PVP block is protonated and highly soluble in water. The polymer solution is completely transparent and no micelles are formed. Both neutral PEO and cationic PVP blocks are hydrophilic in acidic condition. The pyridyl group of PVP block is a Bronsted base with acid dissociation constant (*pKa)* value around 4 [14]. In acidic condition ($pH < 4$), the PVP chains are positively charged and work as collection sites for negatively charged species. After adding the Pt source, the $PtCl_4^{2-}$ species preferentially bind with the positively charged PVP^+ and develops hydrophobicity, resulting in the formation of micelles. While most of the Pt species become located inside the PVP cores, a certain amount also adsorbs inside the external ethylene oxide (EO) region of the micelles, because the coordinated water molecules around Pt ions usually interact with the EO groups [15]. The hydrodynamic diameter calculated from dynamic light scattering using Stokes-Einstein equation is around 30 nm (Fig. 1a) [16]. The $PtCl_4^{2-}$/PVP-*b*-PEO micelles observed on the TEM images reveal the presence of spherical particles with a diameter of 22 ± 3 nm and distributed homogeneously (Fig. 1b). The heavier element (Pt species) is located inside the core of the $PtCl_4^{2-}$/PVP-*b*-PEO micelles (encircled dark regions). The slightly smaller size in TEM compared with DLS measurement (average 30 nm) can be attributed to the exclusion of the PEO corona.

The interaction between the inorganic precursors and the polymeric micelles is critical in the soft-templating method [17]. In this study, an anionic metal precursor is used to strengthen the

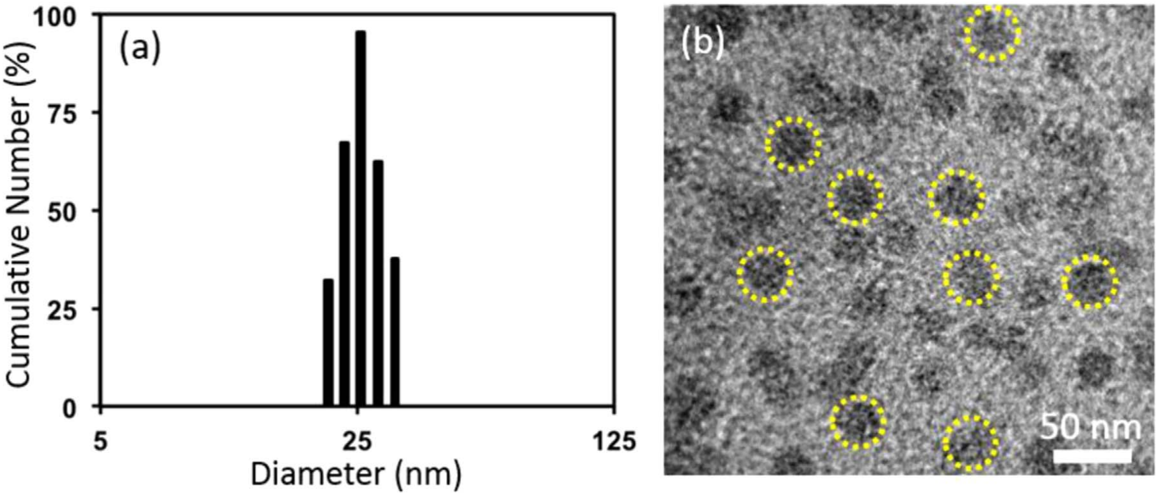

Fig. 1. (a) Hydrodynamic diameter distribution and (b) TEM image of the $PtCl_4^{2-}$/PVP-PEO composite micelles. Yellow circles indicate the cores with Pt species.