

Temperature-tunable catalytic property of Pd–M (Ag, Cu) bimetallic nanoparticles stabilized by thermal-sensitive PDEAm-g-PAN/PSt polymeric microspheres



Shi Dongjian, Sui Jing, Duan Fang, Chen Mingqing*, He Bingxiao

The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, 214122 Wuxi, PR China

ARTICLE INFO

Article history:

Received 12 November 2012
Received in revised form 6 May 2013
Accepted 15 May 2013
Available online 23 May 2013

Keywords:

Polymeric microsphere
Thermal-sensitive
Bimetallic nanoparticle
Catalytic property

ABSTRACT

Thermal-sensitive poly(*N,N*-diethylacrylamide) grafted poly(acrylonitrile/styrene) (PDEAm-g-PAN/PSt) polymeric microspheres were prepared from PDEAm macromonomer, St and AN by dispersion copolymerization. The polymeric microspheres had raspberry-like morphology with large surface area. Palladium–metal (Pd–M) (M: copper, Cu, silver, Ag) bimetallic nanoparticles were stabilized on the surface of the PDEAm-g-PAN/PSt microspheres via the coordinate interaction between amide groups in PDEAm and metal ions with the reduction of the corresponding ions. Transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and thermogravimetry analysis (TGA) results confirmed the size and composition of the immobilized Pd–M nanoparticles. The Pd–M bimetallic nanoparticles showed superior catalytic efficiencies for the reduction of 4-nitrophenol (4-NP) than the monometallic nanoparticles. The catalytic activity of the Pd–M bimetallic catalysts could be controlled by the molar ratio of Pd and M ions and composition of Pd–M nanoparticles. Moreover, the catalytic property of the Pd–M nanoparticles could be regulated by temperature and increased with increasing the temperature above lower critical solution temperature (LCST). Furthermore, the Pd–M nanoparticles could be easily recycled and reused to catalyze 4-NP for five times without loss of activity. These bimetallic nanoparticles possess great potential in future practical application in catalytic technology.

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1. Introduction

Noble metals, including palladium (Pd), platinum (Pt), gold (Au), and so on, have been under increasing investigation as novel materials for the past few decades, due to their potential applications in chemical separation, catalysis, sensing, and diagnosis and treatment of some cancers [1,2]. The noble metallic nanoparticles (NPs) with several nanometers are of greater properties, which are significantly different from the corresponding bulk materials. Among the metallic NPs, Pd NPs play an important role in the hydrogenation of organic compounds [3], and facilitate a range of coupling reactions such as Heck, Mizoroki–Heck and Suzuki reactions [4,5]. To enhance the activity of Pd NPs, Pd-based bimetallic NPs have been developed by addition of a second metal. They show higher activity and selectivity than monometallic [6–8], due to the existing of coordination effect between the two metals. Moreover, the second metal can modify both the hydrogen availability and the strength of diene or alkyne complexation, improve the selectivity to alkene and extend the lifetime of the catalyst. However, these

NPs have some limitations in use, such as oxidation, agglomeration, and recycling.

Since the polymeric particles have high surface area and high surface energy, immobilization of the metallic NPs on polymeric particles can solve the problems effectively and provide the metallic NPs to be perfect features to their application in heterogeneous catalyst [9–13]. Many types of the stable bimetallic NPs, such as Pd–Au, Pd–Pt, and Pd–Rh, had been obtained to immobilize on the polymeric particles and showed well catalytic activities [14–17]. Liu group reported the preparation of polymer-stabilized Pt–Pd bimetallic colloidal nanocatalysts and characterization of their catalytic property in hydrodechlorination of chlorobenzene [18]. Zhang et al. prepared polymer-supported bimetallic Ag@AgAu nanocomposites, and the products could catalyze the reduction of 4-nitrophenol [19]. These bimetallic NPs showed superior activities and selectivities than the monometallic NPs in catalysis. However, in these examples, the employed noble metals are high cost to limit their practical applications, and the polymeric substrates are lack of environmental response.

In our previous researches, we reported that large amount of Pt NPs could load on the surface of poly(*N*-isopropylacrylamide) grafted poly(acrylonitrile/styrene) (PNIPAAm-g-PAN/PSt) polymeric microspheres (MPs) [20–22], which had uniquely

* Corresponding author. Tel.: +86 510 85917019.

E-mail address: mqchen@jiangnan.edu.cn (C. Mingqing).

follower-like morphologies and were of much larger surface area than the usual microspheres with smooth surface. Herein, novel thermosensitive poly(*N,N*-diethylacrylamide) (PDEAm) grafted poly(acrylonitrile/styrene) (PDEAm-*g*-PAN/PSt) MPs was prepared to form microspheres with unusual morphologies (Scheme 1). The amide groups in the PDEAm chains could coordinate with metal ions for stabilizing the metallic NPs. Copper (Cu) and silver (Ag), which are low cost and have electrocatalytic properties, were employed as the second metals to prepare Pd-*M* (Ag, Cu) bimetallic NPs by immobilizing on the surface of PDEAm-*g*-PAN/PSt MPs. Pd-*M* bimetallic NPs were characterized by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). Their catalytic efficiency for the reduction of 4-nitrophenol (4-NP) was detected. Moreover, the factors, such as the amount of the immobilized Pd-*M* NPs, molar ratio of Pd and *M* ions, temperature, and recycle times, effects on the catalytic activity were investigated in detail.

2. Experimental

2.1. Materials

N,N-diethylacrylamide (DEAm, Wako Pure Chemical Industries, Ltd.) was purified by vacuum distillation. Azobisisobutyronitrile (AIBN, ShiSiHeWei Chemical Co., Ltd., Shanghai) was recrystallized from ethanol before use. Styrene (St), acrylonitrile (AN) and tetrahydrofuran (THF) were brought from Sinopharm Chemical Reagent Co., Ltd. and purified by vacuum distillation. Acryloyl chloride and 4-nitrophenol (4-NP) were purchased from Aladdin Chemistry. Palladium chloride (PtCl₂, Wako Pure Chemical Industries, Ltd.), 2-mercaptoethanol (Chemedir Biopharm-tech. Co., Ltd.), ethanol, sodium borohydride (NaBH₄), silver nitrate (AgNO₃) and cupric chloride (CuCl₂) (Sinopharm Chemical Reagent Co., Ltd.) were used as received.

2.2. Preparation of PDEAm-*g*-PAN/PSt MPs

PDEAm-*g*-PAN/PSt MPs were prepared according to the reported method [23]. Firstly, PDEAm macromonomer with a double bond end group was synthesized by radical polymerization of DEAm monomer using 2-mercaptoethanol as chain transfer agent and then condensation reaction with acryloyl chloride in THF (Scheme 1a). The number-averaged molecular weight of the macromonomer was 4780 by gel permeation chromatography (GPC, Waters Co., USA) with DMF as mobile phase. Then, a certain amount of the PDEAm macromonomer (0.9 mol% to total monomer), St, and AN were added into a ethanol/water mixed solvent ($v_{\text{EtOH}}/v_{\text{H}_2\text{O}} = 7/3$). The reaction system was sealed off after flushed with nitrogen and then kept at 60 °C for 24 h. Afterward, the as-prepared polymer microspheres were centrifuged and lyophilized (Scheme 1a).

The chemical structure of the product was confirmed by Fourier transform infrared spectroscopy (FTIR, 2000-104, ABB Co., USA) and proton nuclear Magnetic Resonance Spectrometer (¹H NMR AVANCE III 400 MHz, Bruker Co., Germany). The lower critical solution temperature (LCST) was characterized by UV-vis spectra (UV-1100, Beijing Rayleigh Analytical Instruments Co.). The morphology and size of the PDEAm-*g*-PAN/PSt polymer microsphere were characterized by scanning electron microscope (SEM, S4800, Hitachi, Japan) and DLS (Zeta PALS Zeta potential and particle size analyzer, DB-525, Brookhaven Co., USA).

2.3. Preparation of Pd-*M* (Ag, Cu) bimetallic NPs

A typical procedure for preparation of Pd-Cu bimetallic NPs was as follows: PdCl₂ (0.005 mmol), CuCl₂ (0.005 mmol) and the PDEAm-*g*-PAN/PSt polymer microspheres (20 mg, 0.15 mmol as PDEAm monomeric unit) were dissolved in 20 mL ethanol/water mixed solvent ($v_{\text{EtOH}}/v_{\text{H}_2\text{O}} = 7/3$), and then the solution was refluxed at 90 °C. In the period of 30 min, the color of the mixture changed from pale yellow to light grey. After reaction for 8 h, a dark grey homogeneous dispersion containing polymer microsphere-stabilized Pd-Cu bimetallic NPs was obtained. Finally, Pd-Cu NPs immobilized MPs were separated from the mixture by centrifugation (10,000 rpm, 5 min) for several times.

The size and morphology of the Pd-*M* NPs was characterized by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) (JEM-2100, Hitachi, Japan) after dropping the composite solutions onto a collodion-coated copper mesh grid, drying at ambient condition, and then carbon sputtering. X-ray diffraction (XRD) measurement was performed on a Japan Rigaku D/max X-ray diffractometer equipped with graphite monochromatized high-intensity Cu-K radiation ($\lambda = 0.15418$ nm). The weight percent of the stabilized Pd-*M* NPs was determined by thermogravimetry analysis (TGA, 1/1100SF, Mettler Toledo Co., Switzerland).

2.4. Catalytic reduction of 4-NP

The reduction of 4-NP in aqueous solution was performed to detect the catalytic activity of the bimetallic NPs. A 0.5 mL sample of NaBH₄ solution (0.7 mol/L) was added into 2.5 mL of 4-NP solution (0.15 mmol/L). Then, a given amount of the Pd-*M*/(PDEAm-*g*-PAN/PSt) composite was added into the mixture. After the addition of the bimetallic NPs, the sample was measured in each 80 s by UV-vis spectrum to detect the conversion of 4-NP.

3. Results and discussion

3.1. PDEAm-*g*-PAN/PSt MPs

The PDEAm-*g*-PAN/PSt MPs were prepared according to the reported method [23]. Their structures were confirmed by ¹H NMR spectrum (Fig. S1), and the result showed successful preparation of the MPs. Fig. 1 shows SEM image of the PDEAm-*g*-PAN/PSt MPs. From the image, MPs have uniquely raspberry-shape

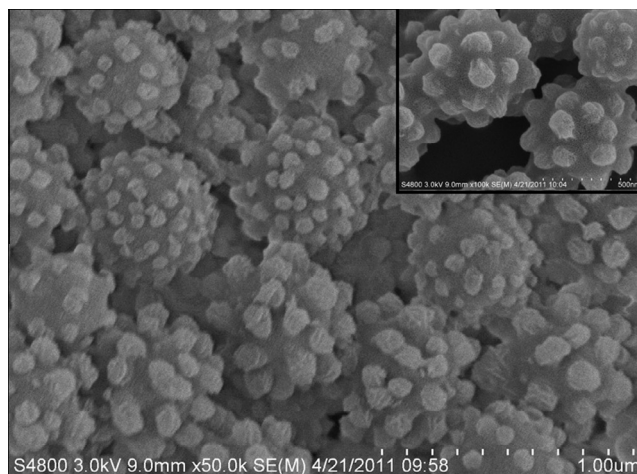


Fig. 1. SEM image of the PDEAm-*g*-PAN/PSt polymeric microspheres.

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