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Novel Au–Pd bimetallic core–shell nanocomplex and its catalytic activity modulation

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ABSTRACT

A novel kind of polymer supported bimetallic nanocomplex was synthesized by a 'two-step' method. In this kind of complex, gold nanoparticles, which were stabilized by the tri-block copolymer chains, acted as the core and the Pd nanoparticles were in the shell. The gold nanoparticles and the Pd nanoparticles were connected by a kind of temperature sensitive polymer, poly(*N*-isopropylacrylamide) (PNIPAM). The bimetallic nanocomplex exhibited excellent catalytic activities in the reduction reaction, and also, the catalytic activity of the nanocomplex could be easily tuned by changing the weight ratio of two metallic particles. Because of the temperature sensitivity of PNIPAM block, the distance between gold nanoparticles and the Pd nanoparticles could be changed or tuned by changing the temperature of its aqueous solution. This novel property would be widely used in the area of testing and microelectronic devices.

1. Introduction

Bimetallic nanoparticles have attracted great attention in the past decades for that they have specific chemical and physical properties, that is much different from those of bulk metal and their monometallic counterparts [1–8]. The properties of the bimetallic nanoparticles can be well controlled or tuned by changing the morphologies or the sizes of both kinds of particles [6–10]. Monodispersed Mn–Pt bimetallic nanoparticles with the size between 2 and 9 nm got much higher coercivity values [7]. Core–shell Rh–Pd and Pt–Pd nanoparticles catalysts with well controlled core–shell morphology exhibited excellent physicochemical properties [10]. It is well known that the metallic nanoparticles performed much higher catalytic activity than bulk metal [11–19]. Because of the synergetic effect, bimetallic nanoparticles usually displayed higher catalytic activity than the monometallic ones [11–14]. Pt-core bimetallic Pt/Au-shell (Pt@Pt/Au) nanoparticles, which were prepared by multi-step reduction of $HAuCl_4$ and H_2PtCl_6 alternately, have shown much higher catalytic activity than the Au nanoparticles [20]. In the oxidation reaction of HCOOH, both kinds of bimetallic nanoparticles, Au-modified Pt (Au@Pt) and Pt-modified Au (Pt@Au) nanoparticles were found to be more active toward the oxidation of HCOOH compared to bare Pt nanoparticles, and they exhibited the maximum activity at Pt fraction between 0.15 and 0.25 with the enhancement factor of more than two orders of magnitude [21].

However, most of the bimetallic nanoparticles were alloy or having a core–shell structure with one kind of metal inside and another kind of metal outside [22–25]. Both the morphology and the structure were hard to be tuned or controlled after its formation [26–29]. Furthermore, the peculiar catalytic properties of metal nanoparticles were considered to be attributed to their high specific surface area and special surface structure [8,30–32], and this high specific surface area would leads to the common tendency of agglomeration of the metal nanoparticles. Scientists have tried many methods to stabilize the bimetallic nanoparticles in the solution [8,30–34]. The PdPt and PdRh bimetallic nanoparticles, which show promising catalytic activities for the hydrogenation of 1-hexene, can be well stabilized by a fourth generation amine-terminated poly(amidoamine) dendrimers [35]. The bimetallic nanoparticles can also be well stabilized by the polymer or the polymeric micelles, but the structure or the properties still cannot be easily controlled or changed by these stabilizers.

In this experiment, a new kind of 'core–shell' Au/Pd bimetallic nanocomplex, stabilized by the environmental sensitive tri-block copolymer, were synthesized through a two-step method. Au nanoparticles were in the 'core' and Pd nanoparticles were in the 'shell'. This new kind of 'core–shell' bimetallic nanoparticles exhibited high catalytic activity in the reduction reaction. Because of the temperature sensitive PNIPAM block, which was the connection of the core and the shell, the distance of Au and Pd nanoparticles could be changed or tuned by changing the temperature of its aqueous solution. This novel property of the inorganic/polymer

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hybrid materials would bring it into widely applications as testing and microelectronic devices and so on.

2. Materials and methods

2.1. Materials

Polyethylene glycol monomethyl ether (CH_3OPEG_{113}–OH) [$\overline{M_n}$ = 5000 and the polydispersity index (PDI) = 1.10] was purchased from Fluka and dried in the vacuum oven overnight before use. The monomer of 4-vinylpyridine (4VP) was purchased from Aldrich and purified according to Refs. [35,41–43]. The monomer of *N*-isopropylacrylamide (NIPAM, Acros Organics) was purified by recrystallization in a benzene/hexane mixture and dried carefully in vacuum. 2,2′-Azobis(isobutyronitrile) (AIBN) (DuPont) was recrystallized two times from ethanol prior to use. Tetrahydrofuran (THF) (99%; Saarchem) and toluene were distilled under reduced pressure. The following reagent was used as received: sodium metal (Merck), absolute ethanol (98.8%; Sigma Aldrich), hydrochloric acid (32 wt.%; Merck), benzyl bromide (98%; Fluka), anhydrous magnesium sulfate (Merck), $HAuCl_4$, $PdCl_2$, $NaBH_4$, carbon disulfide, sodium hydroxide, diethyl ether, maleic anhydride (MAh), dichloromethane (DCM), dimethyl ether and CCl_4.

2.2. Synthesis of dithiobenzoic acid (DTBA)

Dithiobenzoic acid was prepared according to the method described by Ramachandran et al. [44]. The details can be described as follows. The Grignard reagent, obtained from the reaction of bromobenzene (5.6 g, 0.036 mol) with magnesium (0.82 g, 0.036 mol) in absolute diethyl ether (100 mL), reacted with carbon disulfide (2.7 g, 0.036 mol) in dry tetrahydrofuran (30 mL) at −5 °C for 1 h. The mixture was diluted with 50 mL diethyl ether and decomposed with ice-cold dilute hydrochloric acid (50 mL). The organic layer was separated and extracted with 10% ice-cold sodium hydroxide solution (30 mL × 3). The alkaline solution was washed with diethyl ether three times and acidified with 10% ice-cold hydrochloric acid solution, and then, extracted with diethyl ether. The ether solution was washed with distilled water three times. After evaporation of the solvent, pure DTBA was obtained, in 40% yield.

2.3. Synthesis of PEO macro-chain-transfer agent

PEO-OH (8.0 g, 1.6 mmol) was dissolved in dried toluene (30 mL), and then MAh (1.0 g, 10 mmol) was added. The mixture was stirred at 60 °C for 20 h. Then toluene was removed by distillation, and the residue was dissolved into CH_2Cl_2. The product was precipitated into diethyl ether to remove the unreacted MAh. PEO-MAh was purified by repeating the dissolving and precipitating process, and then it was dried in a vacuum oven at 40 °C.

A solution of PEO-MAh (5.0 g, 1.0 mmol) and DTBA (3.2 g, 20 mmol) in CCl4 (20 mL) was sealed in a degassed tube, and the addition reaction of DTBA with MAh end group was carried out at 65 °C for 48 h. Then, the resulting PEO, capped with a dithiobenzoate group, was obtained by precipitation in excess diethyl ether. The resulting product was dried in a vacuum oven.

2.4. RAFT reaction of P4VP

To synthesize PEO-*b*-P4VP di-block copolymer, a glass tube was charged with the calculated amount of PEO-SC(=S)Ph, AIBN, and 4-vinyl pyridine (4VP) in THF. It was then degassed by three freeze–evacuate–thaw cycles and sealed in vacuo. The polymerization was carried out at 100 °C for a prescribed time. PEO-*b*-P4VP was precipitated out in absolute diethyl ether, collected by filtration, and dried in a vacuum oven at 40 °C.

2.5. Synthesis of PEO-b-P4VP-b-PNIPAM tri-block copolymers

The procedure for synthesizing PEO-*b*-P4VP-*b*-PNIPAM was the same as that described above except that the PEO-*b*-P4VP-SC(=S)Ph was used as the macro-chain-transfer agent and the monomer was NIPAM here.

2.6. Preparation of polymer-grafted gold nanoparticles

$HAuCl_4$ and tri-block copolymer were first dissolved into ethanol and THF respectively. Then, under vigorously stir, 10 mL tri-block polymer (260 mg, 0.01 mmol) solution was added into 10 mL $HAuCl_4 \cdot xH_2O$ (37.9 mg, 0.1 mmol) solution (the molar ratio of polymer/$HAuCl_4 \cdot xH_2O$ was 1/10). The mixture was stirred for 30 min in an ice bath. Then, 1.0 mL $NaBH_4$ solution (1.0 M) in THF was added dropwise within 2 min. The mixture solution turned immediately purple and was kept in the ice bath for 4 h. The purification of nanoparticles was performed using centrifugation and dialysis against water. The aqueous dispersion was frozen and lyophilized.

2.7. Preparation of bimetal nanoparticles

To the vigorously stirred purple solution of polymer-grafted gold nanoparticles, $PdCl_2$ THF solutions with different concentrations were added. The mixture was stirred for 30 min in an ice bath. Then, 1.0 mL $NaBH_4$ solution (1.0 M) in THF was added dropwise within 2 min. The mixture solution was stirred in the ice bath for 4 h. The product was also centrifuged and dialyzed against water.

2.8. Characterization of the polymers

The molecular weight of the block copolymers were determined by the ^{1}H NMR on a Bruker AV300 spectrometer at room temperature. Gel permeation chromatography (GPC) analysis was carried out on a Waters 600E gel permeation chromatography analysis system equipped with a Waters 2414 refractive index detector at 30 °C, a Waters 1515 isocratic HPLC pump, and waters styragel HT columns, where THF/DMF was used as the eluent and linear polystyrene as the calibration standard.

2.9. Characterization of the nanoparticles

Dynamic laser scattering (DLS) measurements were performed on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT) at 532 nm at room temperature. The strength-average hydrodynamic diameters and the hydrodynamic diameter distributions of the micelles or complex were obtained at a measurement angle of 90°. Transmission electron microscopy (TEM) measurements were conducted by using a Philips T20ST electron microscopy at an acceleration voltage of 200 kV, whereby a small drop of micelle/composite solution was deposited onto a carbon-coated copper TEM grid and dried at room temperature and atmospheric pressure. UV–vis spectra were recorded on a TU-8110 UV–visible spectrophotometer equipped with two silicon diode detectors and a xenon flash lamp.

2.10. Measurement of the catalytic activity of gold nanoparticles and bimetallic nanocomplex

The catalytic reduction was conducted in a standard quartz cell with a path length of 1.0 cm. The $NaBH_4$ aqueous solution was first mixed together with *p*-nitrophenol aqueous solution (pH 10.0, ad-