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Well-dispersed gold nanoparticles anchored into thiol-functionalized hierarchically porous materials for catalytic applications

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ABSTRACT

In this work, we demonstrate a novel method that enables the fabrication of thiol-functionalized hierarchically porous materials (SH-HPMs) by combination of hyper-cross-linking and molecular templating of core-shell bottlebrush copolymers. Well-dispersed gold (Au) nanoparticles with an average size of 3.0 nm, synthesized by in situ reduction of $HAuCl_4$, were then anchored into the SH-HPMs support, which showed remarkable catalytic performances on the reduction reaction of 4-nitrophenol.

1. Introduction

Noble metal nanoparticles are often used for catalytic reactions due to their high surface-to-volume ratios. Gold nanoparticles (GNPs), especially with nanometer level dimension, have recently generated extensive interest due to their high catalyst activities at low temperatures [1,2]. However, just because of their ultra-small size, the tendency of aggregation driven by high surface energy is a considerable downside, which limits their catalytic activities and reuse life-time [3]. Thus, in order to prevent aggregation, a great variety of strategies to immobilize gold nanoparticles in or onto appropriate solid supports have been exploited [4–6].

It is well known that the porous nanomaterials (for example: zeolites and activated carbons) as catalysts supports have attracted significant attention because of their special structure features, such as high surface areas, large pore volume and various pore sizes distributions [5,7]. Especially, in recent years, some new porous organic materials like covalent-organic frameworks (COFs) [8], metal-organic frameworks (MOFs) [9,10] and amorphous porous organic polymers (POPs) [11,12] have been explored as catalysts supports owing to their high surface areas and their capability to incorporate multiple chemical functionalities into the porous framework. It is worth mentioning that the great stability of the porous organic materials is an essential requirement for their practical applications [13]. However, COFs and MOFs linked by reversible chemical bond, exhibiting relatively high sensitivity to moisture, especially in the presence of base or acid chemicals, which will hamper their practical applications. Whereas, POPs constructed by chemically stable covalent bonds show high chemical and hydrothermal stabilities compared to COFs and MOFs, which can withstand a wide range of reaction temperatures. Therefore, POPs have been one of the promising candidates of catalysts supports for development of heterogeneous catalysts [11]. However, among most of the outstanding POPs reported so far, few functionalization have been developed.

It is common knowledge that the pores dimension of porous materials contains a range from micropores (<2 nm) to mesopores (2–50 nm) and macropores (>50 nm). Although, for catalytic applications, nanoparticles loading into the pore channels of supports with a sole micropore can effectively increase catalytic selectivity, the relative small micropores might impede the diffusion of the reactants and products, leading to low catalytic activity [13]. To solve this problem, introducing meso/macropores into the sole microporous materials to form a hierarchically porous structure will be an effective way. Herein, we successfully demonstrate a facile route to construct thiol-functionalized hierarchically porous materials (SH-HPMs) by combination of hyper-cross-linking and molecular templating of core-shell bottlebrush copolymers. The

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ultrafine GNPs with well-dispersed distributions were anchored into the SH-HPMs by reducing the $HAuCl_4$ with $NaBH_4$ (Au-HPMs). In addition, the catalytic performance of the resulting Au-HPMs with expect to high efficiency and stability was also evaluated for the reduction reaction of 4-nitrophenol.

2. Experimental sections

2.1. Materials

All reagents were used as received unless stated otherwise. Glycidyl methacrylate (GM, Acros 97%) was distilled before use. Dichloromethane (DCM) and N, N-dimethylformamide (DMF) were dried using CaH_2 and distilled. Styrene (Aldrich 99%) was purified by passing over basic alumina. 2, 2-Azoisobutyronitrile (AIBN) and D,L-lactide were purified by recrystallization from methanol and ethyl acetate, respectively. S-1-Dodecyl-S'-(α,α'-dimethyl-α''-acetic acid) trithiocarbonate (TC) [14] and 2-cyanoprop-2-yl-4-cyanodithiobenzoate (CPD) [15] were synthesized according to literature procedures.

2.2. Measurements

All ^{1}H NMR spectra were recorded on a Bruker AVANCE III™ 500 spectrometer (500 MHz) by using $CDCl_3$ as a solvent. GPC data were obtained from Waters GPC system equipped with a Waters 1515 isocratic HPLC pump, a 2414 refractive index (RI) detector, and two Waters' HPLC columns. Tetrahydrofuran was used as the solvent for polymers and eluent for GPC with a flow rate of 1 ml/min at 30 °C. The GPC instrument was calibrated with narrowly dispersed linear polystyrene standards. Transmission electron microscopy (TEM) images were obtained using a JEM-2100F TEM instrument. Samples were prepared by dip-coating a 400 mesh carbon-coated copper grid from the dilute sample solution allowing the solvent to evaporate. A Quantachrome Autosorb IQ surface area and porosity analyzer was utilized to study the pore structure of the samples. Before measurements, the polymer samples were degassed for more than 10 h at 120 °C. The Brunauer-Emmett-Teller surface area and the micropore surface area were determined by the BET equation and the t-plot equation, respectively. The pore size distribution was analyzed by original density functional theory (DFT). X-ray photoelectron spectroscopy (XPS) spectra were obtained on an ESCALAB 250Xi spectrometer. The powder X-ray diffraction (XRD) pattern of the sample was collected using a D8 Advance X-ray diffractometer (Bruker AXS, Germany) with Cu K radiation. The infrared (IR) spectra were recorded using Thermo NICOLET is50. UV–Vis spectra were recorded using the SOPTOP UV2400 spectrophotometer. Elemental analysis data were obtained using an Elementar vario EL III instrument. TG analyses were carried out with a NETZSCH STA449F3 simultaneous thermal analyzer at a heating rate of 10 K/min from 30 to 800 °C in a nitrogen atmosphere.

2.3. Synthesis and catalytic application

2.3.1. Synthesis of PGM

GM (1 ml), CPD (9 mg), AIBN (1.2 mg) and benzene (1 ml) were mixed in a reaction vessel and degassed by 3 freeze-pump-thaw cycles. The polymerization was conducted at 60 °C for 14 h. The mixture was diluted with DCM, precipitated into methanol 3 times and dried under vacuum at room temperature for 24 h. Yield = 0.88 g (89%). GPC (PS standards): $M_n = 15{,}000$ g/mol, $M_w/M_n = 1.07$. ^{1}H NMR: n(GM) = 200.

2.3.2. Hydrolysis of PGM

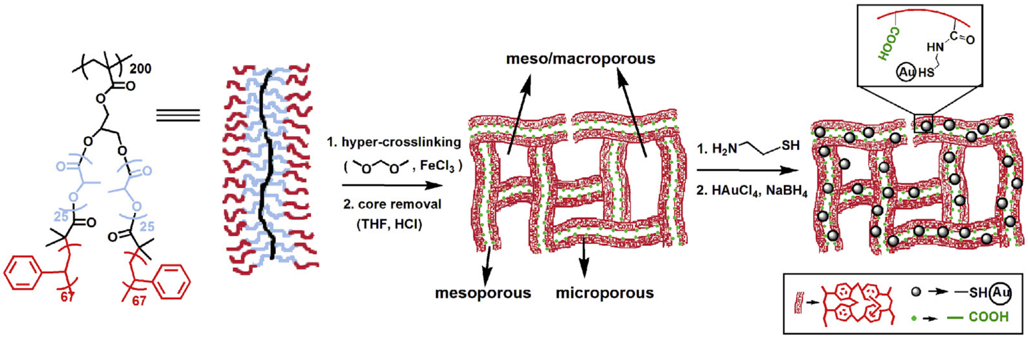
PGM (300 mg), THF (6 ml) and acetic acid (12 ml) were mixed in a 250 ml two-necked round-bottom flask. The reaction mixture was stirred and placed in an oil bath at 60 °C, followed by the slow addition of 18.5 ml water over the course of 1 h. After stirring for 24 h, the solvent was removed on a rotary evaporator. The isolated polymer was precipitated from methanol into diethyl ether 3 times and dried under vacuum at 25 °C for 24 h. Yield = 0.33 g (95%). ^{1}H NMR: Conversion = 95+%.

2.3.3. Synthesis of PGM-g-PLA

Hydrolyzed PGM (50 mg) and D,L-lactide (1800 mg) were added into a dried 50 ml round-bottom flask. Dry DMF (4.5 ml) was then added and the mixture was stirred until all polymer dissolved. 1,8-Diazbicyclo[5.4.0] undec-7-ene (DBU, 54 μL) was then injected into the flask. After stirring at room temperature for 1.5 h, the reaction was quenched by adding 162 mg benzoic acid. The resulting polymer was precipitated from THF into methanol/water (1:1) 3 times and dried under vacuum at 25 °C for 24 h. Yield = 1.25 g (75%). GPC (PS standards): $M_n = 190{,}000$ g/mol, $M_w/M_n = 1.11$. ^{1}H NMR: n (PLA) = 25.

2.3.4. Synthesis of PGM-g-(PLA-b-PS)

Hydroxyl end groups of the PLA brush were then modified to install trithiocarbonate (TC) functionalities as described in the literature [16]. PGM-g-PLA-TC (30 mg) was mixed with AIBN (0.24 mg), styrene (1.98 ml) and toluene (1.98 ml) in a reaction vessel and degassed by 3 freeze-pump-thaw cycles. The reaction was then conducted at 50 °C for 15 h and stopped by cooling to room temperature and opening the flask to air. The resulting reaction mixture was then precipitated from DCM to methanol 3 times and dried under vacuum at 25 °C for 24 h. Yield = 125 mg. GPC (PS standards): $M_n = 480{,}000$ g/mol, $M_w/M_n = 1.21$. ^{1}H NMR: n (styrene) = 67.



Scheme 1. Fabrication of thiol-functionalized hierarchically porous materials with well-dispersed GNPs.