Chinese Chemical Letters 27 (2016) 843–846

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

Gold nanoparticles/carbon nanotubes composite microspheres for catalytic reduction of 4-nitrophenol

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ARTICLE INFO

Article history:
Received 19 October 2015
Received in revised form 1 December 2015
Accepted 5 January 2016
Available online 27 January 2016

Keywords:
Carbon nanotubes
Gold nanoparticles
Microsphere
Catalytic activity

ABSTRACT

The layer-by-layer assembly of polyethyleneimine and carbon nanotubes is carried out through the electrostatic interactions on colloidal polystyrene templates. The successful spherical growth of polyethyleneimine/carbon nanotube multilayers could be investigated by SEM. The subsequent in situ preparation and deposition of gold nanoparticles on the core–shell composites could yield novel microsphere complexes, which are characterized by SEM, TEM, EDX and XRD. The functional hierarchical microspheres with gold nanoparticles exhibit good catalytic activity in the reaction of reducing 4-nitrophenol to 4-aminophenol.

1. Introduction

The construction of materials in different dimensions is always the significant topic in the field of material science. For example, the carbon-based spherical structures have attracted tremendous attention owing to the potential applications in adsorption, catalysis, energy conversion and storage, *etc.* [1]. In recent years, the fabrication of composite microspheres involving carbon nanotubes (CNTs) has also been widely studied, aiming to develop novel hierarchical composite materials with fascinating properties [2]. In general, the layer-by-layer (LbL) assembly, an efficient technique in fabricating multilayer films with controllable thickness and components [3], is one of the most commonly used methods in the preparation of CNTs composite spheres with core–shell structures. In a typical process, CNTs modified with carboxylic groups and the corresponding polyelectrolyte (PE) are alternately deposited on the colloidal templates through the electrostatic interactions. The thickness of the CNTs/PE multilayer shell on the template could be controlled by the number of the LbL cycles. By etching or dissolution of the template core, hollow CNT microspheres or microcapsules could be obtained [4–9].

So far, the fabrication of CNT-based core–shell structures or capsules has got considerable progress, whereas the applications of such CNTs composites were barely investigated. Hao *et al.* reported the electrochemical behaviors of CNT-embedded microcapsules, indicating the potentials in the fields of biosensors and catalysis [8]. Actually, the introduction of functional components in these core–shell composites might afford the CNTs microspheres new applications. For example, electrode modified with spherical complexes incorporating metal nanoparticles and CNTs composite microspheres could exhibit satisfactory electrocatalytic performance [10]. In this letter, LbL assembly of multi-walled carbon nanotubes (MWNTs) and branched polyethyleneimine (PEI) is carried on the spherical polystyrene (PS) templates to fabricate (PEI/MWNTs)/PS composite microspheres. Thereafter, gold nanoparticles (GNPs) are deposited on the core–shell microspheres to prepare novel functional spherical GNP(PEI/MWNTs)PS complexes, which show good performance in the catalytic reduction of 4-nitrophenol.

2. Experimental

The pristine MWNTs (CVD method) were oxidized in nitric-sulfuric acid with the aid of sonication for 6 h to attach carboxylic acid groups on the nanotubes. The monodisperse polystyrene (PS) microsphere templates, with the diameter of about 4 μm, were prepared by a dispersion polymerization method [7]. In a typical LbL assembly of PEI/MWNTs on the PS microspheres, 10 mg of PS microspheres in 20 mL of aqueous PEI solution (2.0 mg/mL) was slightly stirred for 1 h before removing excess PEI by repeated centrifugation and water wash. Then a poly(sodium 4-styrenesulfonate) (PSS) layer and another PEI layer were deposited by

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http://dx.doi.org/10.1016/j.cclet.2016.01.019
1001-8417/

using the same procedure. Thereafter the positively charged microspheres were stirred in 20 mL of aqueous MWNT suspension (1.0 mg/mL) for 30 min before collected by centrifugation. After rinsed with deionized water, the microspheres covered by a layer of MWNTs were immersed in 20 mL of aqueous PEI solution (2.0 mg/mL) for 30 min, followed by the same rinsing process as described above. By repeating the assembly steps for MWNTs and PEI alternately, the PEI/MWNTs multilayers were deposited on the PS microspheres.

The loading of GNPs on the microspheres was carried out as follows. 10 mg of $(PEI/MWNTs)_3PS$ microspheres was dispersed in 20 mL of PEI solution (2.0 mg/mL), and then 0.3 mL of 30 mmol/L $HAuCl_4$ solution was added into the mixture before stirred at 70 °C for 2 h. Finally, the resulting dispersion was treated through centrifugation and water wash for three times, which yielded $GNP(PEI/MWNTs)_3PS$ composite microspheres.

To test the catalytic activity of the composites, 1.5 mL of aqueous 4-nitrophenol solution (0.87 mmol/L) and 10 mL of freshly prepared aqueous $NaBH_4$ solution (0.015 mol/L) were mixed at room temperature. Then 3 mg of $GNP(PEI/MWNTs)_3PS$ microspheres was added into the stirred solution to catalyze the transformation of 4-nitrophenol to 4-aminophenol, which was monitored by UV–vis absorption spectrophotometer in the reaction process.

3. Results and discussion

The LbL of MWNTs and PEI is realized through the electrostatic interaction between the carboxylic groups on the nanotubes and the amino groups of PEI, which is a typical process in the preparation of CNTs multilayer composites [11,12]. To facilitate the subsequent assembly of MWNTs, the PS templates are pretreated with PEI and PSS, which would afford more negative charges on the colloids. Then the alternative adsorption of PEI and MWNTs can be proceeded to fabricate the core–shell structured (PEI/MWNTs)/PS microspheres. The classic LbL assembly procedure on the planar substrate is usually monitored by UV–vis spectrometry. While for the assembly on spherical template, the stepwise growth of the multilayer could be clearly visualized through SEM. As shown in Fig. 1, with the increase of the assembly number, more and more MWNTs are successfully deposited on the PS microspheres. When the first layer of MWNTs is assembled, the microspheres are almost fully covered by nanotubes. After three LbL assembly cycles, the overlapped and entangled nanotubes endow the resulting $(PEI/MWNTs)_3PS$ microspheres with the rough and porous surfaces.

The incorporation of GNPs with the MWNTs composite microspheres is carried out through the *in situ* preparation of GNPs in the presence of $(PEI/MWNTs)_3PS$ microspheres in a PEI solution. Herein, PEI acts as both reducing reagent and protecting reagent, avoiding the introduction of other reagent [13]. Moreover, PEI in the PEI/MWNTs shell would anchor the GNPs, enhancing the stability of the $GNP(PEI/MWNTs)_3PS$ composite microspheres. Fig. 2a and b show the SEM images of the resulting sample at low and high magnification, respectively. Apparently, as seen in Fig. 2a, the deposition of GNPs seems to have little influence on the morphology of the microspheres. While from Fig. 2b, the location of GNPs could be clearly observed, which makes the surface of the nanotube much rougher. TEM characterization further exhibits the existence of GNPs on the microspheres. As shown in Fig. 2c, the GNPs are uniformly distributed on the nanotubes without obvious aggregation, with an average diameter of about 8 nm. The space fringes of the GNPs detected in the HRTEM image (Fig. 2d) is well matched with the (111) planes of Au. In addition, the SEM-EDX of $GNP(PEI/MWNTs)_3PS$ (Fig. 2e) also clearly demonstrates the presence of Au peaks, which confirms the formation of the functional core–shell composites. From the EDX data, the mass ratio of MWNTs and GNP could be roughly estimated as about 1:1, which implies the high efficiency of GNP deposition.

The structure of $GNP(PEI/MWNTs)_3PS$ microspheres is also characterized by X-ray diffraction (XRD), as well as PS microspheres and purified MWNTs for comparison. As shown in Fig. 3, PS microspheres present two characteristic peaks at 10.5° and 19.5°, respectively [14]. The peak of MWNTs at 26.2° is attributed to the (002) plane in the nanotube and the peak around 43° is assigned to reflections of impurities (iron phases) in the sample [15]. As for the patterns of $GNP(PEI/MWNTs)_3PS$, the absence of PS features indicates that the shell thickness is beyond the detection depth, while the peaks of MWNTs are obviously observed. The new peaks at 38.1°, 44.4°, 64.6° and 77.6° are ascribed to (111), (200), (220) and (311) reflections of crystalline Au, respectively [15].

It is well known that noble metal nanoparticles, such as Ag, Au, Pt and Pd, play critical roles in heterogeneous catalysis. However, such particles with the size of several nm, which provide highly active centers for the efficient catalysis, are apt to undergo aggregation under the reaction conditions, leading to decrease or loss of catalytic activity. In this case, the combination of nanoparticles and certain supports would solve this problem. In general, the supports with porous structure and high surface area could anchor the nanoparticles uniformly on the surface, which facilitates the catalytic activity of the catalyst without aggregation. Moreover, the catalyst recovery is easily performed through simple filtering or centrifuging [16]. Owing to their outstanding properties, CNTs are an ideal support for the metal nanoparticles [17]. Herein, the MWNTs-covered PS microspheres as the supports of GNP might present satisfactory catalytic behaviors. The catalytic reduction of 4-nitrophenol to 4-aminophenol with

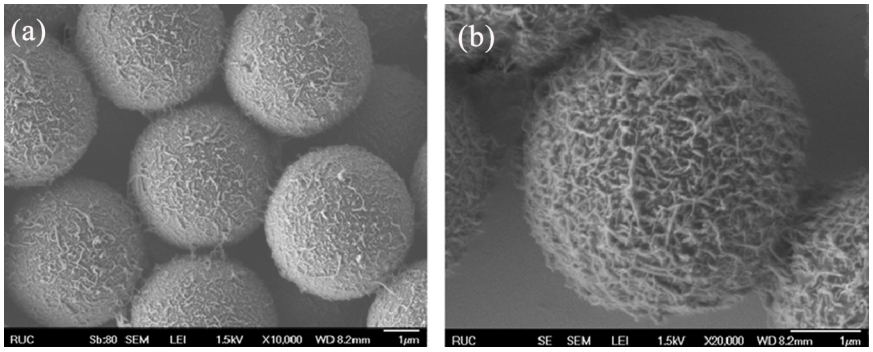

Fig. 1. SEM images of composite microspheres from the LbL assembly of PEI and MWNTs on the PS templates with one (a) and three (b) cycles. The scale bar is 1 μm for all images.