



Tunable fabrication of hierarchical hybrids via the incorporation of poly(dopamine) functional interlayer



Ting Xu, Xin Zhao, Junxian Zhang, Jie Dong, Qinghua Zhang*

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, PR China

ARTICLE INFO

Article history:

Received 27 November 2015
Received in revised form 13 January 2016
Accepted 1 February 2016
Available online 3 February 2016

Keywords:

Au nanoparticles
Polydopamine
Core-shell conducting spheres
Polymer microspheres

ABSTRACT

Two kinds of ternary hybrids were prepared by anchoring different shapes and loadings of Au nanoparticles (NPs) on poly(dopamine) (PDA) functionalized polystyrene (PS) microspheres with two different strategies, i.e., in situ reduction and self-assembly approach. PDA coatings were firstly introduced to functionalize the hydrophobic PS surface with sufficient amino and hydroxyl groups, which enhanced the interaction between Au NPs and the polymer spheres. Thus, Au NPs could be easily immobilized onto the surface of the PDA/PS microspheres, and the hierarchical composite microspheres exhibited a well-defined core/shell structure without sacrificing the spherical PS morphology. PS/PDA/Au-R and PS/PDA/Au-A microspheres fabricated by in situ reduction and self-assembly approach showed different distinct Au nano-shell morphology with the corresponding optical, catalytic and electrochemical properties. Field emission scanning electron microscopy and transmission electronic microscopy verified these hierarchical structures with the ultrathin PDA film incorporating between the inner PS core and the outer Au NPs shell. X-ray diffraction and X-ray photoelectron spectroscopy confirmed the presence of PDA and Au layer on the surface of the composite particles. These green and facile methods with mild experimental conditions can extend to fabricate other polymer or inorganic substrates coated by various noble metals.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Tailoring interfacial properties with polymer/metal hierarchical assemblies supplies unlimited possibilities for the preparation of composite materials with specific properties and functions that could have potential applications in diverse fields, including catalysis, biomaterials, electronic, sensing and optics [1–6]. Compared with bulk polymer or metal separately, the combination of polymer/metal composite with proper interfacial properties can offer new chances to finely control the functionality of the obtained composite materials. Core-shell structure with individual components spatially separated has received considerable attention, not only because of the large scale range of geometries and morphologies tunable, but also because of enabling polymer/metal composites with multifunctional properties unavailable to their symmetrical counterparts [7–10]. The key issue of core-shell structure is how to design appropriate interface to modify the surface of polymer or/and metal with improved interesting properties and performances [11–14]. Although there are different existing methods used

for the modification of the material surfaces such as layer-by-layer assembly [15], hydrolysis [16], plasma treatment [17] and so on, these methods are typically time-consuming, multistep processing and harsh treatments.

Many efforts emphasized in this field drive to search for an efficient and facile coating approach to any surface. Previous study has demonstrated that the incorporation of soft polymeric coatings with sufficient functional groups could overcome the limitations of weak interaction between hydrophobic polymer core and novel metal and thus improve the distinct properties of hierarchical hybrids due to the synergistic effects. In this regard, some ternary systems with core/shell/shell structure, such as PS/polypyrrole/Au [18], SiO₂/polyethylene glycol/Au [19], Fe₃O₄/polypyrrole/Au [20], PS/polypyrrole/Ni [21,22], PS/polyelectrolyte/Au [23], PS/polypyrrole/Pd [24,25], PS/PDA/Ag [26,27], etc., have been fabricated and investigated to achieve desirable properties. Metallic nanoparticles (NPs) have presented their most flexible nanostructures owing to the strongly reliance on their size, shape, crystallinity, nature of the protecting organic shell, and surrounding media, as well as the resulting tenability of their optoelectronic and physicochemical properties [28]. Compared with other metallic NPs, noble metal NPs, especially Au NPs, are widely studied due to their facile preparation and unique applications. The high price,

* Corresponding author.

E-mail address: qzhzhang@dhu.edu.cn (Q. Zhang).

easily aggregation and poor dispersibility of Au NPs limit the application of Au NPs in further widespread fields [29,30]. Therefore, Au NPs combined with a polymer/inorganic core are commonly studied to improve the stability and high surface-area-to-volume ratios of the hybrids [31,32]. Meanwhile, the utilizing of polymer core can decrease the density of composites materials and improve the controllability [33].

Dopamine, which is enlightened by the composition of extraordinarily robust adhesion in mussels, is found to form surface-adherent polymer films with controllable thickness and durable stability [34]. The Polydopamine (PDA) films can easily attach to virtually all types of organic and inorganic substrates, even including superhydrophobic surfaces [35]. The valuable feature of polydopamine is that, it can introduce many functional groups to materials surface which can serve as reactive points for covalent modification with desired molecules and the anchors for the fixation of metal ions or metal NPs [36]. Thus, polydopamine has unsurprisingly presented a new opportunity to the modification of various material surfaces and has stimulated extensive research [37].

Few literatures have been reported on the fabrication of PS/Au microsphere with core/shell multilayer structure by the modification of bio-inspired PDA coatings [38,39]. In this work, we emphasized on using PS/PDA microspheres as supporters, which should be beneficial for the rational design of novel mental shell hierarchical hybrids with unique properties. In detail, PDA was firstly coated on the PS spheres by pH-induced polymerization of dopamine. The incorporation of PDA coating serves as an interlayer for the immobilization of metal NPs and the functionalization of polymer surface. PDA modified PS microspheres used as a template to anchoring different shapes of Au NPs by in situ reduction and self-assembly approach. Two kinds of ternary hybrids with different distinct Au nano-shell morphology exhibit the corresponding optical, catalytic and electrochemical properties. These green methods avoid multistep processing and harsh treatments to damage the spherical morphology.

2. Materials and methods

2.1. Materials

Styrene (St), poly(vinylpyrrolidone) (PVP), hydrogen tetrachloroaurate hydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), sodium citrate, and ammonium hydroxide (25–28%) was purchased from Sinopharm Chemical Reagent Co. Ltd. St was purified by treatment with 5 wt% aqueous NaOH solution to remove the inhibitor. 2,2-Azobisisobutyronitrile (AIBN) was supplied by Tianjin Guangfu Fine Chemical Research Institute. Dopamine hydrochloride was purchased from Aladdin Industrial Corporation. Alcohol (99.7%) was obtained from Yang Yuan Chemical Reagent Co. Tetrahydrofuran (THF) was obtained from Shanghai Lingfeng Chemical Reagent Co. Ltd. Deionized water was used for rinsing and preparation of all solutions.

2.2. Synthesis of monodispersed PS microspheres

The fabrication process of PS microspheres was reported in our previous work. Firstly, 22 mL ethanol was added to a 50 mL four-necked flask which was deaerated by bubbling highly pure nitrogen. Then, 10 g styrene and 0.11 g AIBN were added, following with the addition of 2 g PVP. The resulted solution was continued to stir at 75 °C for 24 h. Then the solution was diluted with deionized water and centrifuged for four times. Finally, the PS microspheres were obtained after drying the precipitate at 50 °C overnight.

2.3. Preparation of PS/PDA composite microspheres

Briefly, 40.0 mL distilled water was added in a 100 mL three-necked flask equipped with a mechanical stirrer followed by addition of the above PS microspheres (1 g) at room temperature. Next, 0.1 g dopamine hydrochloride and 10 mL ethanol were mixed under mild stirring. Then, the required amount of ammonium (3 mL^{-1} based on DI-water) was added into the above water-ethanol solution. The polymerization reaction was allowed to proceed for 24 h. The obtained particles were washed with ethanol and water, and finally, the products were dried at 50 °C in a vacuum oven.

2.4. Preparation of PS/PDA/Au-R and PS/PDA/Au-A composite microspheres

The incorporation of Au particles with PS/PDA hybrids was conducted by two different strategies, which are in situ reduction of Au^{3+} and self-assembly of Au particles. (I) In situ reduction approach. 1.2 mL HAuCl_4 solution (0.05 g/mL) was added into 40 mL aqueous solution containing PS/PDA microspheres. Then the mixture was placed in oil bath at 80 °C and 5 mg sodium citrate was dropped into with a vigorous stirring for 5 min. After the solution cooling down to room temperature, the obtained PS/PDA/Au-R spheres were separated by centrifugation. (II) Self-assembly approach. 1.2 mL HAuCl_4 solution (0.05 g/mL) was added to 75 mL deionized water at 80 °C. Then, 0.12 g sodium citrate was added under vigorous stirring for 5 min. After the solution cooling down, the PS/PDA microspheres were added to the as-synthesized Au colloid under stirring. The obtained PS/PDA/Au-A spheres were separated by centrifugation. The resultant product was filtered, washed and then dried at 60 °C vacuum for 24 h.

2.5. Characterization

The morphology of PS/PDA/Au composite microspheres was performed on field emission scanning electron microscopy (FESEM, Hitachi S-4800). Transmission electron microscopy (TEM) was carried out on a Hitachi H-800 electron microscope at an accelerating voltage of 10 kV. X-ray diffraction (XRD) measurements were conducted on a Rigaku D-max-2500 diffractometer (Cu K_{α} radiation, $\lambda = 0.15418 \text{ nm}$). X-ray photoelectron spectroscopy (XPS) experiment was taken on a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) with Al K_{α} radiation ($h\nu = 1486.6 \text{ eV}$). The hydrophilicity of the film surface was characterized on the basis of static contact angle measurement using a contact angle goniometer (OCA40, Dataphysics, Germany) equipped with a video capture. Thermogravimetric analysis (TGA) was performed under nitrogen with a Perkin-Elmer TGA2050 instrument at a heating rate of $10 \text{ }^{\circ}\text{C min}^{-1}$. Surface-enhanced Raman scattering (SERS) were measured on a LabRam-1B Raman spectroscope (He-Ne laser excitation) with 633 nm. Rhodamine 6G (R6G) as an analyte with the concentration of $1 \times 10^{-5} \text{ M}$ was added to suspension containing synthesized composite microspheres. The solution was excited with a 633 nm laser line to collect the SERS spectra. Electrochemical experiments were carried out in a three-electrode system. The working, counter and reference electrode were a glassy carbon electrode with a diameter of 3 mm, a platinum wire and a saturated calomel electrode (SCE), respectively. Cyclic voltammetry (CV) was measured using an Autolab (PGSTAT320N) electrochemical workstation. $2 \times 10^{-3} \text{ M K}_3\text{Fe}(\text{CN})_6$ and 0.1 M KCl solution at room temperature was used as the electrolyte. To investigate the catalytic reduction of 4-nitrophenol (4-NP) by NaBH_4 , the solution containing PS/PDA/Au composite spheres was added into 4-nitrophenol with the concentration of $1.5 \times 10^{-3} \text{ M}$. Then NaBH_4 solution was rapidly added under constant stirring. The concentration of 4-NP

Download English Version:

<https://daneshyari.com/en/article/5355215>

Download Persian Version:

<https://daneshyari.com/article/5355215>

[Daneshyari.com](https://daneshyari.com)