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Heterophase polymer dispersion: A green approach to the synthesis of functional hollow polymer microparticles

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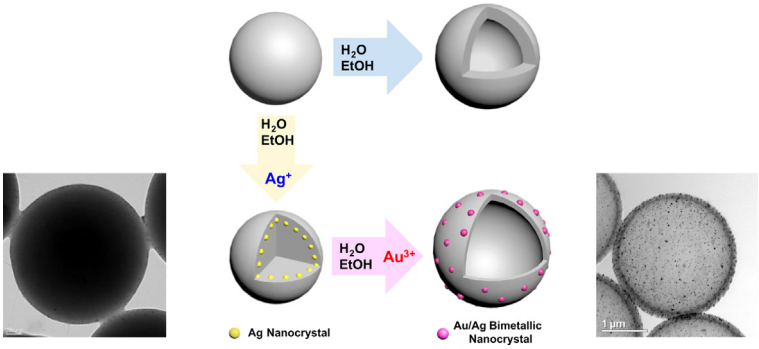
HIGHLIGHTS

- Easy-to-use method was developed for synthesizing functional hollow microparticles.
- The synthetic procedures involved environmentally acceptable "green" chemistry.
- The hybrid microparticles showed excellent catalytic activity and reusability.

GRAPHICAL ABSTRACT



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ABSTRACT

Hollow nanostructured polymer microspheres have various potential applications; however, the development of a facile method to synthesize such particles has proved challenging. In the current work, an easy-to-use, green and low-cost method adopting a heterophase polymer dispersion strategy was developed to produce monodisperse hollow microparticles with well-defined nanostructures. When polystyrene (PS) seed microparticles prepared using modified dispersion polymerization were dispersed in an ethanol-water mixture at 70 °C, they transformed into hollow PS microparticles as a result of uptake of the continuous phase by the particles. Via consecutive heterophase polymer dispersion processes involving the addition of metal precursors, hollow PS microparticles covered with bimetallic nanocrystals were obtained. That is, metal nanocrystals were produced *in situ* from metal precursors on the polymer particles. Based on our results and observations, we propose plausible mechanisms for the formation of these hollow microparticles. The hollow PS microparticles covered with bimetallic nanocrystals exhibited high catalytic activity at a low concentration and excellent reusability when used as catalysts for the reduction of 4-nitrophenol to 4-aminophenol using sodium borohydride as the reducing agent.

1. Introduction

Polymeric nanostructured hollow microspheres exhibit unique physicochemical properties and new functionalities. As a result of these properties, such structures have garnered considerable attention due to their potential applications as vehicles for drug delivery, dielectrics for electronics, photonic crystals [1–8]. To produce hollow polymer microparticles with well-defined nanostructures, various manufacturing

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techniques have been developed, including dynamic swelling, osmotic swelling, hard and soft templating and polymeric micelle methods. However, most of these methods are based on template-directed synthesis [9–15]. By using a sacrificial template, the cavity size of the hollow microparticles can be easily controlled; however, preparation of core-shell particles requires long processing times and continuous attention and effort. Furthermore, removal of cores to form hollow structures entails the use of dissolving or drying processes that require harsh processing environments and specialized equipment [16–18].

The inclusion of metal nanocrystals embedded in the surfaces of hollow polymer particles with controlled nanostructures should impart beneficial properties and extend the potential uses of such particles to applications such as antimicrobial agents, separation materials, and catalysts [19–21]. Generally, metal nanocrystals have been immobilized on the surfaces of solid supports by first forming metal nanocrystals and then depositing those nanocrystals on polymer particles [22,23]. To define and direct metal nanocrystals onto the polymer particle surface, surface pretreatments have usually been necessary to enhance the interaction between the metal nanocrystals and the polymer surface [24]. However, these *ex situ* processes require a great deal of processing time and continuous attention and effort, which complicate the synthetic procedures [25]. Efforts to synthesize supported metal nanostructures based on *in situ* reduction of metal precursors have been hampered by a lack of relevant easy-to-use synthetic methods.

In this paper, we report a facile, green and low-cost synthetic approach for producing hollow polystyrene (PS) microparticles with well-defined nanostructures. This new synthetic route differs from and has advantages over previously reported procedures. First, the proposed method follows an easy-to-use protocol based on a template-free method adopting hetero polymer dispersion, without the need to form a sacrificial template in advance. Second, the synthetic procedures involve environmentally acceptable “green” chemistry. In contrast to most of the previously described studies on the synthesis of hollow PS particles, achieved by using a toxic organic solvent such as xylene and/or styrene monomer [11,18,26,27], in the proposed method, an environmentally benign solvent (a mixture of water and ethanol) is used and no additional toxic organic solvents are required. In addition, the proposed method is a direct transformation method that does not require an additional template removal process, which normally involves harsh environments using toxic organic solvents, corrosive mediums, acids and alkalis [28–32]. Third, in our method, simply adding the metal precursors into the dispersion medium results in the formation of polymer microparticles embedded with metal nanocrystals. That is, the metal precursors are converted into metal nanocrystals *in situ* on the polymer particles, without involving the formation of metal nanocrystals in advance or the pretreatment of the surfaces of the polymer particles. Moreover, the proposed protocol does not require toxic reducing agents such as $NaBH_4$, hydrazine, and DMF, and the nanocrystals are uniformly embedded in the polymer microparticle surfaces. Moreover, because galvanic replacement reactions are used to produce hollow polystyrene microparticles covered with bimetallic (Au/Ag or Pt/Ag) nanocrystals, the use of precious metals is decreased. Finally, due to the presence of air cavities, the hollow PS microparticles have high surface-to-volume ratios and low bulk density values, features suitable for supporting materials for catalysts. In addition, the size of the hollow PS microparticles means that they can be easily separated from the reaction system using centrifugation.

We monitored the morphological and structural changes during the formation of the hollow microparticles. Based on the observations and experimental results, we propose plausible mechanisms for the formation of the hollow microparticles. Our findings on the particle morphology and composition motivated us to explore the catalytic activities of the bimetallic (Au/Ag or Pt/Ag) nanocrystals covering the hollow PS hybrid microparticles. Their application as catalysts for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) using $NaBH_4$ as the reducing agent was investigated, with the results showing that the hollow hybrid microparticles with bimetallic nanocrystals showed good catalytic activity at low concentrations and could be reused several times.

2. Experimental

2.1. Chemicals and materials

Styrene (product No. S4972, 2.5 L), ammonium persulfate (APS), polyvinylpyrrolidone (PVP; Mw ≈ 55 kDa), ethanol (product No. 459844-1L), silver nitrate (product No. 209139, 100 g), gold (III) chloride trihydrate (product No. 520918, 1 g), and potassium tetrachloroplatinate (II) (product No. 323411, 1 g) were obtained from Aldrich (USA). All chemicals were used without further purification. Deionized (DI) water was obtained from SK Chemicals (product AH365-4, 4 L, Republic of Korea).

2.2. Synthesis of polystyrene (PS) microparticles

Spherical PS microparticles were synthesized by following our previously reported one-pot synthetic method [33]. A mass of 0.01 g of pre-weighed PVP and APS (15 mM) were first added to a 50 mL vial. Then, 25 mL of ethanol and 3 mL of deionized water were added. The resulting mixture was stirred with a magnetic bar for 10 min at room temperature, and styrene monomer (2.2 mL) was added to the stirred mixture. The vial was then placed in an oil bath at 70 °C. The reaction was carried out for 6 h, and then quenched by placing the vial in ice water for 30 min. The product was collected after centrifugation at 6000 rpm, and was washed repeatedly with DI water.

2.3. Fabrication of hollow PS microparticles

The synthesized PS microparticles (0.03 g) were dispersed in 1 mL of DI water. The PS microparticle dispersion was poured into a 20 mL vial. Then, 5 mL of ethanol was poured into the vial. The vial was then placed in an oil bath at 70 °C and stirred with a magnetic bar. After allowing the reaction to proceed for 24 h, the vial was placed in ice water for 30 min and the products were rinsed repeatedly with DI water.

2.4. Fabrication of Ag nanocrystal-embedded PS microparticles

Pre-weighed PVP (0.003 g) and 1 mL of an aqueous solution containing $AgNO_3$ (177 mM) were added to a 20 mL vial. A 1 mL aliquot of an aqueous dispersion containing 0.02 g of PS microparticles and 5 mL of ethanol were poured into the vial. The vial was then placed in an oil bath at 70 °C and stirred with a magnetic bar. After allowing the reaction to proceed for 24 h, the vial was placed in ice water for 30 min and the products were rinsed repeatedly with DI water.

2.5. Fabrication of hollow PS microparticles covered with bimetallic nanocrystals

A 0.3 mL aliquot of an aqueous solution of Ag nanocrystal-embedded PS microparticles and 5 mL of ethanol were poured into a 20 mL vial. Then, 0.2 mL of an aqueous solution containing 0.001 g of PVP and 0.5 mL of an aqueous $HAuCl_4$ solution (1 mM) were added to the vial. The vial was then placed in an oil bath at 70 °C and stirred at 400 rpm with a magnetic bar. After allowing the reaction to proceed for 24 h, the vial was placed in ice water for 30 min and the products were rinsed repeatedly with DI water. For the fabrication of hollow PS microparticles covered with Pt/Ag bimetallic nanocrystals, an aqueous K_2PtCl_4 solution (1 mM) was used instead of the aqueous $HAuCl_4$ solution.