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FABRICATION OF BIMETAL OXIDE HOLLOW NANOSPHERE USING CORE-CORONA MICELLES AS SOFT TEMPLATE*

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Abstract

Currently, nanoparticles with controlled morphology have tremendously attracted attention due to their wide application in catalysis, energy storage, and biomedicine. It is well known that hollow nanospheres with controlled size and shape show better performance compared to the conventional dense nanoparticles. In this research, Co/Fe oxide hollow nanospheres with diameter around 27±2 nm have been fabricated by using polymeric micelles of poly (styrene-block-acrylic acid) (PS-*b*-PAA) as a template. The polymer forms spherical micelles with PS-core and PAA-corona in aqueous solutions. According to the transmission electron microscopic (TEM) result, the void space of the fabricated hollow nanospheres is around 17 ±1 nm. The prepared Co/Fe oxide hollow nanospheres became shrunk during calcination. Fourier transform infrared resonance (FTIR) measurements confirm that the template polymer was completely removed during calcination.

Keywords: Nanoparticles, hollow , dense, polymeric micelles, core, corona

Introduction

Compared with dense inorganic nanoparticles, hollow inorganic nanoparticles possess more beneficial properties, e.g., lower density, larger specific area, additional surface permeability, etc. These advantages have intrigued in numerous studies on synthesis and applications of various nanosized inorganic hollow materials. Recently, polymeric micelles have been explored for the synthesis of nanoparticles because the size and morphology of the micelles can

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be tuned by adjusting block size and polymer combination (Chockalingam, 2015). The commonly used polymeric micelles exclusively contain a core-corona architecture formed by AB diblock or ABA triblock copolymers (Bastakoti, 2014). We have reported a facile template for inorganic hollow nanospheres by using ABC triblock polymers as a template, which core-shell--corona structured micelles (Zhai *et al*., 2013). In our method, each domain of the core-shell-corona micelle has its own function. The core acts as a template of the void space of the inorganic hollow nanosphere, the shell serves as reaction field for the precursor of the inorganic material and the corona prevents secondary aggregation of intermediate composite particles of polymeric inorganic material. However, synthesis difficulties and high cost make the triblock copolymer inconvenient to use in scale-up production. To avoid such problems a diblock copolymer poly- (styrene-b-acrylic acid) has been synthesized and used as template for the synthesis of Co/Fe hollow nanospheres. Among inorganic nanoparticles, those of ferrites are materials which combine several remarkable physical properties along with chemical stability and low production cost. In form of nanomaterials, ferrites may have superparamagnetic properties and are currently used in magnetic data storage, magnetic imaging, drug delivery and microwave devices (Segneanu, 2014). In the present contribution, we have synthesized Co/Fe oxide hollow nanospheres using a diblock copolymer, poly(styreneb-acrylic acid) (PS-*b*-PAA), as a template. This diblock polymer forms core-corona type micelles in which the core acts as a template of the void space and the corona acts as reaction site for Co/Fe formation. The synthesized nanospheres have been thoroughly characterized by transmission electron microscopy (TEM), Fourier transformed infrared spectroscopy (FTIR) and Energy Dispersive X Ray spectroscopy (EDX).

Materials and Methods

Materials

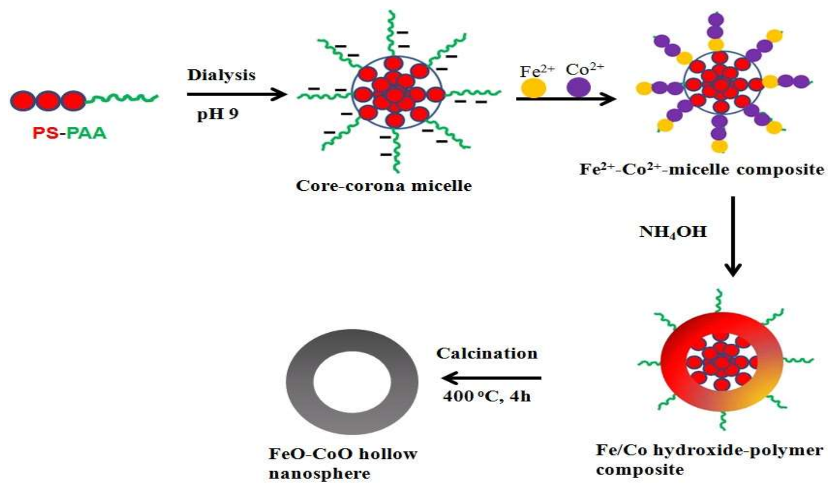
The di block polymer poly(styrene-*block*-acrylic acid) ($PS_{(20000)}$-*b*- $PAA_{(7800)}$) has been kindly supported by Professor Yusa, Department of Materials Science and Chemistry, University of Hyogo, Shosha, Himeji, Japan. The number inside parentheses represents the molecular weight of each block. Ferrous sulphate and cobalt sulphate have been purchased from Sigma Aldrich and Wako Chemicals, respectively. All chemicals were used without any treatment.

Preparation of Co/Fe Oxide Hollow Nanospheres

The core-corona micelle of PS-*b*-PAA has been prepared according to the method described by Khanal *et al*., 2007. In a typical synthesis, 10 mL of micelle solution (1 g L^{-1}) was taken in a conical flask and the pH was adjusted to about 9 using dilute NaOH. It is known that about 90 % of COOH groups of PAA are deprotonated at pH 7 (Nakashima *et al*., 1999). Certain amount of ferrous sulphate and cobalt sulphate (1:1) is added into the micelle solution to make 150 % *DN* (degree of neutralization). *DN* is defined by the following equation,

$$DN\,(\%) = \frac{\text{Amount of added Co/Fe ion (equivalent)}}{\text{Amount of carboxylate ion in the polymer (equivalent)}} \times 100 \qquad (1)$$

The *DN* is kept at 150 % unless otherwise stated. Due to the electrostatic interaction between cationic Co^{2+}/Fe^{2+} and anionic COO^-, Co^{2+}/Fe^{2+} is preferentially attached to the PAA block. Required amount of dilute NH_4OH is added to the solution for precipitation. The precipitate of Co-Fe hydroxide/polymer composite was separated from the aqueous suspension by centrifugation. The solid product was repeatedly washed with water and ethanol followed by drying at 50 °C. Co/Fe oxide hollow nanospheres were obtained after the polymeric template was removed from Fe/Co hydroxide/polymer composite by calcination at 500 °C for 4 h. Scheme 1 shows the schematic representation of fabrication of Co/Fe oxide hollow nanospheres.



Scheme 1. Preparation of mixed metal oxide nanosphere using core-corona micelle as a template

Characterization of Hollow Particles

Transmission electron microscope (TEM) images were obtained using a JEOL JEM-1210 electron microscope at an accelerating voltage of 80 kV. Fourier transform infrared (FTIR) spectra were recorded on a Jasco FTIR 7300 spectrometer by using a KBr pellet technique. The elemental composition analysis was performed with Energy Dispersive X Ray (EDX) spectroscopy.

Results and Discussion

The formation of PS-*b*-PAA core-corona micelle has been confirmed by TEM. Figure 1 shows the representative TEM image of the core-corona micelle. It can be observed that the micelles are nearly spherical shape with a diameter around 23±2 nm. Similar results was observed by Alam *et al.*2015).

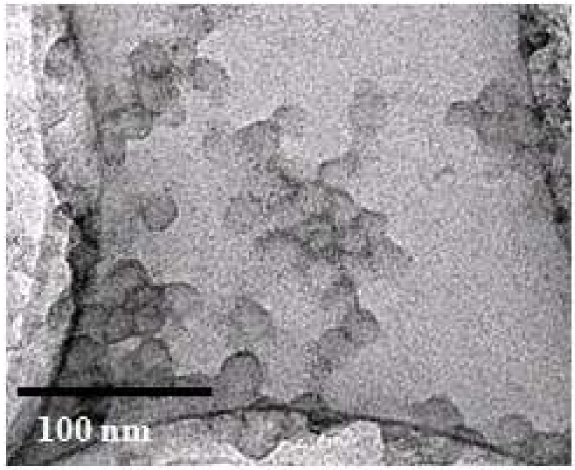


Figure 1. TEM image of the PS-*b*-PAA polymeric micelle stained with phosphotungstic

Figure 2 shows the TEM image of the Co/Fe oxide hollow nanosphere. Nanospheres are spherical shape with outer diameter of around 27±2 nm. The void space is around 17 ±1 nm. It should be noted that the void space is smaller than the core diameter of the micelle, which implies that the nanosphere shrinks during calcination. It can be observed from the TEM image that the some of the nanospheres are connected to each other, however, the morphology of the nanosphere resembles the template polymeric micelle.

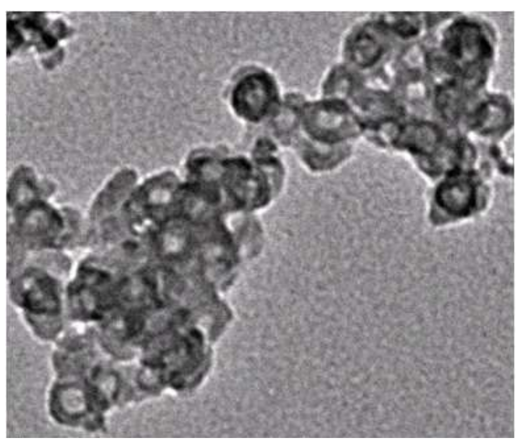


Figure 2. TEM image of the Co/Fe oxide hollow nanospheres after calcination

To confirm the removal of polymer template and the presence of Co/Fe oxide, FTIR analyses have been carried out. Figure 3 shows Co/Fe oxide hollow nanospheres before and after calcination (thick line) at 500 °C for 4 h. As shown in Figure 3, the disappearance of the vibrational bands of the polymer main chain (around 2900 cm^{-1}) and the C=C vibrational band of the phenyl ring (around 1650 cm^{-1}) after the calcination indicates the complete removal of the polymeric template. The presence of two strong M-O stretching and bending frequencies at 1,481 and 831 cm^{-1} shows phase purity of monodisperse one in the face-centered cubic surface.

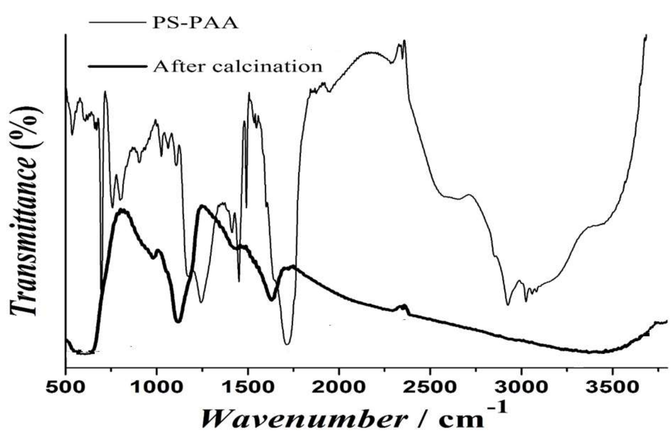


Figure 3. FTIR spectra of the PS-*b*-PAA polymer (thin line), Fe/Co oxide hollow nanosphere after calcination (thick line)

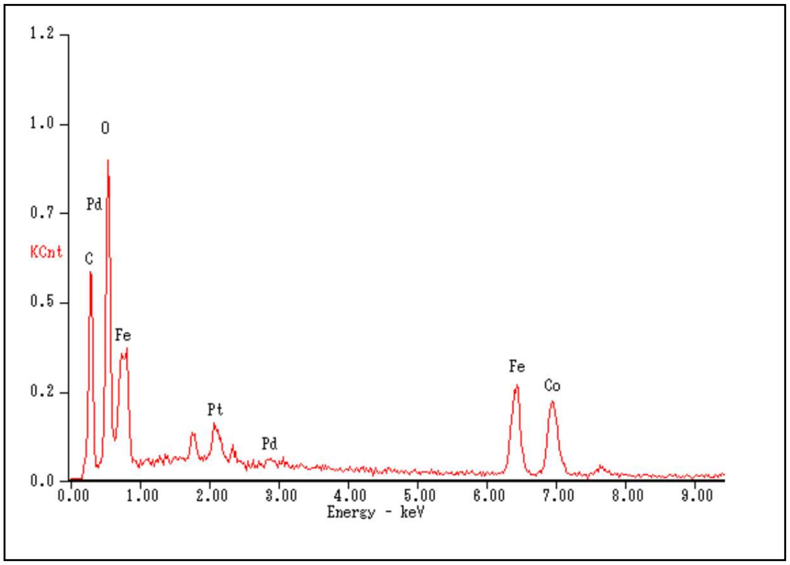


Figure 4. EDX spectrum of Fe/Co oxide hollow nanospheres

Figure 4 represents the EDX spectrum of Fe/Co oxide hollow nanospheres which indicate the existence of Co and Fe in the nanoparticles.

Conclusion

A facile way to fabrication of Co/Fe bimetal oxide hollow nanospheres has been explored by using a diblock copolymer PS-*b*-PAA as a template, which forms core corona micelles in aqueous media. PS-*b*-PAA polymeric micelles are spherical and the size of the PS-core is 23±2 nm. The Co/Fe hollow nanospheres have an outer diameter of 27±2 nm in which the void space diameter and the shell thickness are 17 and 5 nm, respectively. The synthesized Co/Fe nanospheres could allow varieties of applications especially early detection of tumors by magnetic resonance imaging (MRI) where iron oxide bond with various types of ligands such as proteins, peptides and small molecules demonstrate active targeting of tumors via specific molecular recognition.

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