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Novel MoO_3 and WO_3 hollow nanospheres assembled with polymeric micelles

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ABSTRACT

Novel β-MoO_3 and WO_3 hollow nanospheres were synthesized using a soft template of polymeric micelle with *core–shell–corona* architecture. Poly(styrene-*b*-[3-(methacryloylamino)propyl] trimethylammonium chloride-*b*-ethylene oxide) micelles (PS-PMAPTAC-PEO) with cationic *shell* block effectively produce *core/shell* composite particles through electrostatic interaction with anionic precursors WO_4^{2-} and MoO_4^{2-}. Transmission electron microscope (TEM) images of β-MoO_3 and WO_3 have confirmed the hollow structure with average outer diameter of 42 ± 2 and 46 ± 2 nm, respectively; the hollow cavity diameters were found to be 16 ± 1 nm and 14 ± 1 nm for β-MoO_3 and WO_3, respectively. The combination of nitrogen adsorption/desorption analyses and TEM observation confirmed the presence of disordered mesopores in the shell domain of β-MoO_3 and WO_3 hollow particles.

1. Introduction

Transition metal oxides with diverse morphological structure have a wide range of potential applications. In particular, nano-structured transition metal oxides are of significant interest due to their applications in the fields of sensors, photocatalysis, electrochromic-, field-emission-, and solar energy devices [1,2]. Molybdenum trioxide is widely used in electrochemical devices and displays because their layered structure facilitates the formation of Mo(VI)/Mo(V) couple [3]. It is also an important catalyst for olefin metathesis reactions. Among the various morphological structures, hollow particles [4], especially those with a uniform size and shape have attracted much attention because of their low density, large specific area, and mechanical/thermal stabilities [5,6]. Although dense MoO_3 nanoparticles are reported so far [7,8], no hollow nanosphere has been reported. Tungsten oxide also finds potential applications in the areas of visible light responsive photocatalyst [9], electrochromic material [10], and gas sensor [11], and many studies have been focused over the dense oxide particles. In contrast to MoO_3, however, a few studies have been focused over micron sized WO_3 hollow particles. Ye and co-workers synthesized micrometer-sized hollow WO_3 particles by Ostwald ripening technique [12]. However, these microspheres were obtained under severe experimental conditions or on special substrates. Therefore, the organization of MoO_3 and WO_3 into well-defined uniform hollow nanospheres under mild experimental conditions still remains a challenging task.

For assembly of nanostructures, templates are often indispensable because they not only stabilize these nanoparticles, but also arrange them into the desired superstructures. So far, *core–corona* type micelles (AB diblock and ABA symmetric triblock copolymers) were commonly employed as templates [13,14]. However, these micelles become unstable when the precursors of desired materials are sorbed into the corona domain. In order to alleviate this difficulty, micelle with *core–shell–corona* architecture has been employed in our laboratory [15]. In this type of micelles, the *core* acts as a template of the cavity of the hollow nanoparticles, the *shell* plays the role of a reservoir as well as reaction site and the *corona* stabilizes the template-precursor hybrid particles to prevent the formation of secondary aggregates. Recently, we have reported the uses of *core–shell–corona* type micelles in the synthesis of Nb_2O_5, CeO_2 and V_2O_5 hollow nanospheres [16]. Herein, we report novel β-MoO_3 and WO_3 hollow nanospheres using a new triblock copolymer, poly (styrene-*b*-[3-(methacryloylamino)propyl] trimethylammonium chloride-*b*-ethylene oxide) (PS-PMAPTAC-PEO). This triblock copolymer forms a micelle with PS-*core*, PMAPTAC-*shell* and PEO-*corona* in aqueous solutions. The *shell*-forming block (PMAPTAC) is soluble in water at any pH, and thus plays the role of a reservoir and reaction site for the precursors under a wider range of conditions.

2. Experimental

The synthesis and characterization of triblock copolymer PS-PMAPTAC-PEO are reported elsewhere [17] (see supplementary materials, Scheme S1 and Figure S1). Appropriate amounts of $Na_2WO_4 \cdot 2H_2O$ or $Na_2MoO_4 \cdot 2H_2O$ were mixed with 5 mL of the polymeric micelle solution (1 g L^{-1}) followed by stirring for 3 days. The contents were acidified using dilute HCl to obtain tungstic or

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molybdic acid precipitate and further aged for 2 more days without agitation. The precipitate was separated by centrifugation, washed thoroughly with distilled water, and dried in an oven at 50 °C. To obtain hollow spheres, the dried powder was calcined at 500 °C for 4 h in air to remove the polymeric template. Zeta-potential was calculated from the electrophoresis mobility (Otsuka ELS-800). Transmission electron microscope (TEM) images were obtained using a JEOL JEM-1210 electron microscope at an accelerating voltage of 80 kV. Powder X-ray diffraction patterns were recorded using a Rigaku powder diffractometer with CuKα radiation. FTIR spectra were recorded on a Jasco FTIR-7300 spectrometer using KBr pellet technique. TG and DTA analyses were carried out using MAC Science TG–DTA 2100. The textural properties such as BET surface area and mesopore-size information of samples were evaluated using nitrogen adsorption/desorption isotherms with a Bel Japan Inc. BELSORB Mini instrument.

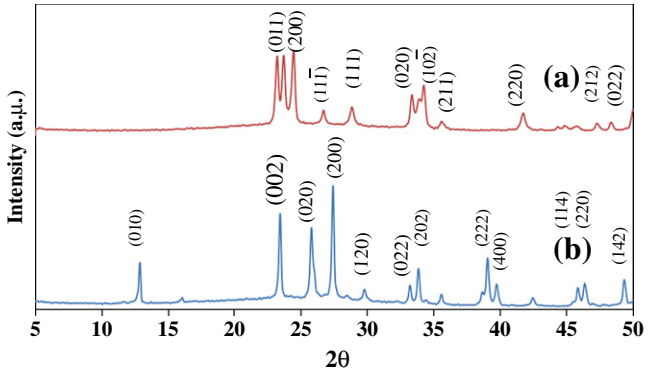


Fig. 1. XRD patterns of (a) hollow MoO_3 and (b) hollow WO_3 nanoshperes.

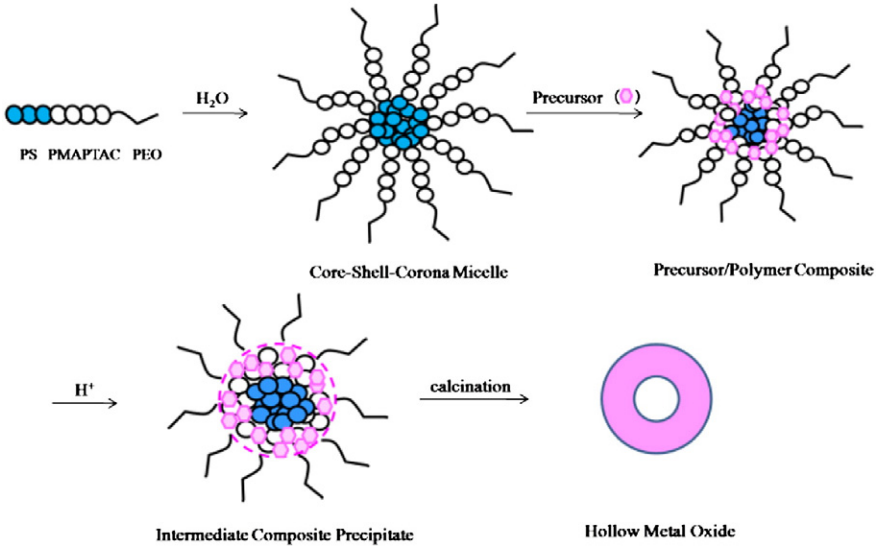
3. Results and discussion

Scheme 1 shows the schematic representation of the formation of hollow β-MoO_3 and WO_3 nanospheres. On addition of tungstate ions, the zeta potential (ξ) gradually decreased from 67.3 to ~0 mV indicating charge neutralization of positive charge of the PMAPTAC by the tungstate anions (see supplementary material, Figure S2). Thus the zeta-potential measurement indicates an optimum WO_4^{-2}/PMAPTAC ratio of 1.5 at a polymer concentration of g L^{-1}. Similarly, the minimum concentration of the sodium molybdate precursor required for complete charge neutralization was found to be 1.25.

The dried composite particles were then calcined at 500 °C for 4 h to remove the polymeric templates as well as crystallize the shell structure of hollow particles. The obtained XRD pattern (Fig. 1a) of molybdenum oxide corresponds to β-MoO_3 with cell parameters a = 7.12 , b = 5.38 , c = 5.55 and β = 91.9° (JCPDF 47-1081) and is in good agreement with previous report [18]. The WO_3 exhibited characteristic orthorhombic lattice (PD-32-1394) structure. Thermal analysis of composite particles revealed the presence of about 22% of polymeric templates. The complete removal of the polymeric template was also confirmed by the FTIR spectra (see supplementary material, Figure S3); the –C=C– bond vibration of the phenyl group (1600–1430 cm^{-1}) and the CH_2 vibration of the polymer backbone (3000–2800 cm^{-1}) were completely disappeared suggesting the effective removal of templates during heat treatment.

Fig. 2 shows TEM images of WO_3 hollow nanospheres and nearly all the particles have a uniform spherical hollow structure with a similar wall thickness. The average particle's size was found to be 46 ± 2 nm with cavity size of 14 ± 1 nm, and wall thickness is approximately 16 ± 1 nm. The WO_3 hollow spheres can be smoothly obtained with WO_4^{-2}/PMAPTAC ratios of 1.5 to 5 as evident from Fig. 2. However, at higher ratio, the aggregation of hollow particles is rather more pronounced due to deposition of precursors outside the micelles domain. Fig. 3 shows the TEM images of MoO_3 hollow nanospheres with different MoO_4^{2-}/PMAPTAC ratios from 1.5 to 5. From the TEM image, we calculated the cavity diameter of approximately 16 ± 1 nm and the wall thickness of about 13 ± 1 nm; whereas the average particle size was found to be 42 ± 2 nm. Similar to the WO_3 hollow spheres, aggregation is slightly increased when an excess of sodium molybdate (MoO_4^{2-}/PMAPTAC = 5) was used.

It should be noted that both hollow WO_3 and MoO_3 nanospheres were synthesized from the same template micelle, but the former has a relatively smaller cavity size (14 ± 1 nm) than the latter (16 ± 1 nm). Since the same PS core acts as the template of the cavity for the hollow nanospheres, one should expect the same cavity size for both WO_3 and MoO_3. However, a "shrinking" process during the calcination needs to be taken into account. Different hollow metal oxides might shrink to



Scheme 1. Fabrication of hollow nanospheres using PS-*b*-PMAPTAC-*b*-PEO micelle.