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Facile synthesis of Mn_2O_3 hollow and core–shell cube-like nanostructures and their catalytic properties

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ABSTRACT

Manganese carbonate ($MnCO_3$) hollow cube-like nanostructures were synthesized via a facile polyol process and then thermal converted to phase-pure manganese oxide (Mn_2O_3). Based on the structural analysis of $MnCO_3$ precursor obtained at different reaction times, a mechanism of inside-out Ostwald ripening was proposed to account for the formation of the hollow nanostructures. An annealing treatment at 500 °C with a ramping rate of 3 °C min^{-1} was utilized to convert the $MnCO_3$ precursor into Mn_2O_3. The manganese oxide powder products possessed mesoporosity and essentially preserved the pristine morphology of the $MnCO_3$ precursor. The products were characterized by X-ray powder diffraction (XRD), and field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Fourier transform infrared spectrometry (FT-IR), Thermal gravimetric analyze (TGA), X-ray photoelectron spectroscopy (XPS), and Brunauer–Emmett–Teller (BET). Furthermore, relative to Mn_2O_3 core–shell cube-like microstructures, the mesoporous hollow cubes exhibited a higher catalytic activity towards CO oxidation.

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1. Introduction

Recently, inorganic hollow micro/nanostructures with remarkable interior space have attracted considerable attention owing to a wide range of applications in chemical reactors, drug delivery, catalysis and sensors [1–4]. Because the properties of hollow structures could be tuned by tailoring their shape and crystallization, there has been increasing interest in the controlling synthesis of hollow structures with non-spherical morphologies such as polyhedra, ellipsoids and cones. Compared to spherical counterparts, the synthesis of hollow structures with well-defined non-spherical shapes remained a significant challenge to materials scientists [5]. Soft templates such as surfactant micelles and emulsion droplets, do not assume well-defined non-spherical shapes in order to minimize the interfacial energy. Even with hard templates, preparation of non-spherical hollow structures introduces additional challenges. These range from the difficulty in forming a uniform coating around surfaces with large variation in curvature to the paucity of available non-spherical templates for the synthesis. Due to these difficulties, reports on synthesis of non-spherical hollow structures are rare. Thus, the search for template-free, simple, mild, high-yield and environmentally friendly methods to synthesize different inorganic hollow structures is still a significant challenge. In the past decade, various physical phenomena such as oriented attachment [6], Ostwald ripening [7] and Kirkendall effect [8] have been employed in a number of one-pot template-free methods for fabrications of hollow inorganic nanostructures. Among them, mass transport via Ostwald ripening has been proven to be a facile approach to generate symmetric and/or asymmetric interior spaces for inorganic nanostructures [9–11].

Manganese oxides have been the subject of fascinating interest due to their unique properties and widespread potential applications such as dry-cell batteries [12,13], catalysts [14–18], water-purifying agents [19] and so on. Many novel synthetic routes have been employed to make micro/nanosized manganese oxides with different sizes, shapes and morphologies [19–26]. Among them, a two-step process is often adopted. Solid precursors containing Mn are first prepared and then converted to manganese oxide. In particular, $MnCO_3$ have been demonstrated to be effective precursors to synthesize manganese oxide. Zhao et al. synthesized nanoporous γ-MnO_2 via a facile route using a hydrothermal treatment and sequential thermal decomposition of $MnCO_3$ [27]. Fei et al. reported a simple controlled preparation of hierarchical hollow microspheres and microcubes of MnO_2 nanosheets through self-assembly with a $MnCO_3$ crystal-templating process [28]. Cao et al. synthesized various Mn_2O_3 hollow structures, such as spheres, cubes, ellipsoids, and dumbbells via a $MnCO_3$ precursor route [29]. We also prepared MnO2 and Mn2O3 hollow dumbbells using $MnCO_3$ hollow microstructures as a precursor template [30]. However, the number of reports on one-pot synthesis of non-spherical hollow structures of this class of compound intermediates is significantly limited because of the paucity of non-spherical templates and difficulty in forming uniform coatings around high-curvature surfaces. Herein, we developed a facile process for controlled synthesis of $MnCO_3$ hollow cube-like nanostructures using EG as the solvent. The as-obtained $MnCO_3$ can be thermal converted to phase-pure Mn_2O_3 maintaining their pristine shapes essentially unchanged. The formation mechanism of the hollow structures can be attributed to an inside-out Ostwald ripening process. As an example of potential applications, the as-obtained hollow nanostructures were used as catalyst in CO oxidation and exhibited relatively high activity.

2. Experimental

2.1. Preparation

All chemicals were of analytical grade and used as received without further purification. In a typical synthesis, $MnCl_2{\cdot}4H_2O$ (1.6 g), urea (0.5 g), deionized water (H_2O, 1 mL) and poly(vinyl pyrrolidone) (PVP, K-30; 0.4 g) were added to ethylene glycol (EG, 50 mL) in a 150 mL round flask. Then the mixture was stirred with a magnetic stirrer bar to give a clear solution and heated to refluxing temperature (ca. 190 °C) under the ambient pressure. About 20 min later, a white precipitate began to appear, indicating the formation of $MnCO_3$. The solution was heated for another 60 min to ensure the formation of