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Fabrication of hollow spheres of metal oxide using fructose-derived carbonaceous spheres as sacrificial templates

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ABSTRACT

In this report, fructose-derived carbonaceous spheres were utilized as sacrificial templates for the fabrication of metal oxide hollow spheres (MOHSs) by a facile hydrothermal approach. Hollow spheres of a series of crystalline metal oxides (α-Fe_2O_3, Cr_2O_3, Co_3O_4, NiO, and ZnO) have been fabricated, utilizing the metal chloride as the oxide precursors. Heating of an aqueous solution of the metal chloride and fructose to moderate temperature in an autoclave affords a spherical composite consisting of a metal precursor shell sheathing a carbonaceous core. Subsequent removal of the interior carbonaceous cores by thermal treatment through oxidation in air produces free-standing crystalline oxides hollow spheres. The MOHSs were characterized by means of SEM, TEM, XRD, IR spectroscopy, energy dispersive X-ray (EDX) and sorption measurements. The results show convincingly that using fructose as a sacrificial template after application of a hydrothermal synthesis route could be a favourable sacrificial template for the fabrication of various MOHSs.

1. Introduction

Metal oxide hollow particles have shown to be promising as inorganic containers and vehicles in various applications, such as catalysis, Li-ion batteries, water treatment, photonic devices, chemical sensors, prosthetic materials and controlled release applications [1–6]. To date, inorganic hollow particles have been fabricated by using various novel mechanisms [7–11].

Indeed, in the last decades, the research activity for the fabrication of oxide hollow micro- and nanoparticles has increased largely due to their unique and enhanced properties, such as low density, hollow cores and large specific surface area combined with the various functions of oxides. For instance, it has been shown that hollow particles can be readily fabricated by using the nanoscale Kirkendall effect [12]. In addition, a well-known physical phenomenon of crystal growth – Ostwald ripening – has been applied for the fabrication of hollow materials [13]. As another synthesis mechanism, Messing et al. reported the formation of hollow particles with different morphologies using a variety of spray pyrolysis techniques [14]. Caruso et al. introduced the colloidal templating synthesis of hollow spheres for the first time in 1998 [15].

Among many synthesis mechanisms, sacrificial templating methods are considered as the most often used strategies. They are relying on the formation of core-shell composites and subsequent removal of the core by

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chemical or thermal means [16]. These methods have been developed considerably and the templates used are divided into:

- hard templates, including colloidal templates such as polymer [17] and silica spheres [18];
- soft templates, including surfactant vesicles and micro-emulsion droplets [16,19].

Xie et al. reported synthesized rutile-phase TiO_2 hierarchical hollow spheres using gas bubbles as a soft template [20]. Chen et al. reported the use of organic templates for the synthesis of silica hollow particles through sacrificial templating approach via the removal of the template by thermal treatment [21].

Latterly, carbohydrate-derived carbonaceous spheres, which are formed through the hydrothermal carbonization of aqueous solutions of saccharides, have been used successfully as sacrificial templates for the synthesis of hollow inorganic particles [22–24]. These sacrificial cores possess surface functionalities that facilitate the adsorption of the desired materials precursors onto their reactive surfaces, as shown by Li et al. [23] and Thomas et al. [24] for different hollow materials.

Among the potential saccharides that can be used as sacrificial templates for the synthesis of inorganic hollow structures, fructose is one of the most promising materials, as it is by far one of the most inexpensive and widely available saccharides. Although many researchers reported using carbohydrates as sacrificial templates for the synthesis of inorganic hollow particles [22–26], to the best of our knowledge, no one has employed fructose as the sacrificial template for the fabrication of hollow spheres by means of hydrothermal carbonization.

In the present contribution, we report a facile hydrothermal approach for the fabrication of series of oxide hollow spheres (α-Fe_2O_3, Cr_2O_3, Co_3O_4, NiO and ZnO) using fructose as the sacrificial template. The synthesis method shows some advantages, which likely make it attractive for the fabrication of other oxide hollow spheres, include:

- the use of inexpensive fructose as sacrificial template;
- fructose-derived carbonaceous spheres, formed by the hydrothermal hydrolysis of fructose, inherit surface O-functionalities, such as –C=O and–OH groups [27] – therefore, there is no need for prior surface modifications;
- only the template and the metal precursor are used for the fabrication of the hollow oxide spheres, thus, there is no need for any chemical additives;
- the fabrication method is a simple strategy that can be readily analyzed and manipulated in comparison to complex multi-step strategies with many procedures and a variety of chemical additives.

2. Materials and methods

2.1. Materials

Iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), chromium(III) chloride hexahydrate ($CrCl_3{\cdot}6H_2O$), cobalt(II) chloride hexahydrate ($CoCl_2{\cdot}6H_2O$), zinc(II) chloride ($ZnCl_2$) and nickel(II) chloride ($NiCl_2$) were obtained from Merck (Darmstadt, Germany). Commercial fructose ($C_6H_{12}O_6$) was bought from dm-drogerie markt, Germany. All mentioned chemicals were analytical grade and employed without further purification. Distilled water (conductivity $\sim 1.7\ \mu s{\cdot}cm^{-1}$) was used.

2.2. Fabrication of the metal oxide hollow spheres (MOHSs)

The major process step applied in the present work starts with heating the metal chloride with fructose in a closed system resulting in in situ formation of hybrid particles, due to the incorporation of the metal ions on the surface layers of the fructose-derived carbonaceous spheres. Finally, calcination of the hybrid spheres leads to the formation of the MOHSs.

In a typical synthesis experiment, 2252 mg (12.5 mmol) of fructose were dissolved in 20 mL of distilled water. The water-soluble metal chloride during the hydrothermal carbonization was added to satisfy the fructose/metal chloride molar ratio 20:1. The mixture was heated in a 100-mL Teflon-lined stainless steel autoclave at 135 °C for 6 h. The products were filtered off, washed three times with distilled water, and finally dried in a vacuum oven at 60 °C for 5 h. Thereafter, the metal oxide–carbon composites were calcined in the air at 500 °C (with a heating rate of 2 °C min^{-1}) for 5 h to remove the carbonaceous core, thus leading to the metal oxide hollow particles.

2.3. Characterization

The products were characterized by various techniques. Infrared (IR) spectra were obtained using IFS 88 from Bruker. XRD patterns were obtained by X-ray powder diffraction (X'Pert MPD, Pananalytical, Cu Kα radiation) operating in Bragg–Brentano geometry [28]. The diffractometer was equipped with a graphite monochromator at the detector side. The sample holder was a single-crystal silicon plate. The energy dispersive X-ray (EDX) analysis was performed using Thermo Noran Voyager EDX system attached to a CamScan series 4 Scanning Electron Microscope from Cambridge Scanning Company Ltd.

The surface area was studied by nitrogen-sorption measurements, which were performed with the use of a Micromeritics ASAP 2020 gas sorptometer. The samples were degassed in vacuo at a pressure of 0.4 Pa for at least 3 h at 200 °C. The measurements were then carried out at 77 K over a wide range of relative pressures from 0.01 to 0.995. Specific surface areas were calculated by assuming Brunauer–Emmet–Teller (BET) conditions.

The morphology was visualized using a JEOL JSM-7500F field emission scanning electron microscope at an accelerating voltage of 5 kV. Hereford, samples were ground to a powder and then mounted on an aluminum stub with a conductive carbon tape and, for electrically nonconductive samples, a thin layer of platinum coating was applied before SEM analysis. Transmission electron microscopy (TEM) was conducted on a JEOL model JEM-3010 electron microscope operating at 300 kV. The samples were ground into powder and mounted by drop