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A novel approach for synthesis of hierarchical mesoporous Nd_2O_3 nanomaterials

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Abstract: A novel route to the fabrication of hierarchical mesoporous Nd_2O_3 nanostructures including nanospheres and nanoporous network was described. Their structure and morphology evolution of the as-synthesized materials were determined by various techniques such as scanning electron microscopy, transmission electron microscopy, high-resolution transmission electron microscopy, X-ray diffraction, energy-dispersive X-ray spectroscopy, Fourier transforminfrared spectra, nitrogen adsorption/desorption isotherm, and a formation mechanism was proposed. The results revealed that the Nd_2O_3 nanospheres had the diameter of 300 nm, which were composed of small primary nanoparticles (NPs) with the size of 10 nm. The nanoporous structure also formed the NPs of *ca*. 10 nm which were connected with each other to form a three-dimensional (3D) texture. This simple and mild approach to fabricate hierarchical mesoporous Nd_2O_3 nanostructures could be easily scaled up and potentially extended to synthesize other oxide hierarchical structures.

Keywords: Nd_2O_3; hierarchical nanostructures; nanospheres; nanoporous network; rare earths

The synthesis of metal oxide particles with control over size, shape has been made and developed over the past two decades[1]. The metal oxide NPs play a pivotal role in many research fields such as electronics, chemical reactivity, energy conversion and optics because they can exhibit unique physicochemical properties originating from their limited size and a high density of their corner or edge surface sites associated with the shape effect[2–4], which differ from those of corresponding bulk materials. On the other hand, the metal oxide nanoparticle colloids can behave like elementary units to build secondary nanoarchitectures with new collective properties from the interparticle arrangement that could offer the inspiration for design of new materials[5]. The complex three-dimensional hierarchical structures show well-aligned porous structures with a rich variety of tunable physiochemical properties[6]. Das et al. demonstrated that mesoporous sulfated zirconia materials, which were formed by arrangement of highly crystalline primary ZrO_2 nanoparticles, exhibited excellent catalytic efficiency for monoalkylated products[7]. The mesoporous TiO_2 nanoparticles were built form monodisperse anatase titania nanoparticle precursor, which showed excellent catalytic activity in the photodegradation of dyes Methylene blue and Rose Bengal under UV-visible light irradiation[8].

Among various rare earth oxides, neodymium oxide is well known as one of the most interesting oxides due to its excellent and unique optical and electrical properties[9–12]. It has been utilized in promising applications such as in lung cancer treatment[13], gas sensors[14], catalysis[10,15], luminescent materials[16], biocompatibility material[17]. Various morphologies of Nd_2O_3 nanostructures have been successfully synthesized by several methods such as sol-gel auto-combustion[18], sol-gel[19], hydrothermal[20–22], microemulsion system[23] and so on. Therein, the Nd_2O_3 with porous structure is of great interest for important application. For instance, Michel et al. reported that the nanoporous Nd_2O_3 nanospheres exhibited a reproducible and reliable sensor for detection of CO, CO_2 and ethanol[14]. Umesh et al. observed that the porous Nd_2O_3:Ni^{2+} has been promising material for radiation dosimetry applications[24]. Similarly, the Co^{2+} doped Nd_2O_3 with porous structure is suitable for radiation dosimetry[25]. However, till now, very limited numbers of synthetic routes have been documented in literature to prepare hierarchical porous neodymium oxide. Thus, the development of a reliable and simple way for preparation of hierarchical nanostructured Nd_2O_3 is of great importance because their properties strongly depend on the morphology, crystal size and accessible surface area as a result of the interparticle arrangement.

In this work, we used two-phase approach for controllable synthesis of the hierarchical mesoporous neodymium oxide nanostructures with high surface area through the self-assembly of tiny primary Nd_2O_3 NPs. The possi-

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ble formation mechanisms of the materials were subsequently proposed and discussed.

1 Experimental

1.1 Materials

All chemicals were used as received without further purification. Neodymium (III) nitrate hexahydrate ($Nd(NO_3)_3{\cdot}6H_2O$), potassium oleate ($C_{18}H_{35}COOK$), and *tert*-butylamine [$(CH_3)_3CNH_2$, 98%], toluene, and ethanol were purchased from Sigma-Aldrich.

1.2 Preparation of hierarchical mesoporous Nd_2O_3

Synthesis of hierarchical mesoporous Nd_2O_3 nanospheres. In this study, neodymium oleate was used as starting materials. To prepare neodymium-oleate complex, an organic solution was prepared by adding 20 mL of toluene into the ethanol solution (6.4 mL) containing potassium oleate (1.1 mmol). Subsequently, the organic phase was mixed with 12.8 mL of an aqueous solution of $Nd(NO_3)_3{\cdot}H_2O$ (0.36 mmol) and transferred to a flask. The two-phase mixture was then heated to 70 ºC for 60 min with stirring vigorously, and the organic solution turned light yellow after the reaction, indicating the occurrence of the coordinative reaction between Nd^{3+} and oleate anion for complex formation. The upper homogeneous toluene supernatant phase (20 mL) containing Nd-oleate complexes was isolated using a separatory funnel[26]. To form Nd_2O_3 nanospheres, we typically added 5 mL of oleyamine to the above-prepared $Nd(OA)_3$ complex solution (20 mL, 0.018 mol/L) under stirring for 10 min. The organic solution was then transferred to a 100 mL Teflon-lined stainless steel autoclave containing an aqueous solution (20 mL) of *tert*-butylamine (0.15 mL). The autoclave was seated and heated to the crystallization temperature at 180 ºC for 24 h[27]. After that, the products were precipitated from organic phase by adding an excess of ethanol further isolated by centrifugation.

Preparation of Nd_2O_3 porous network. The above obtained homogeneous dispersion was evaporated in a rotary evaporator and then to dry at 80 ºC for 12 h. The as-prepared samples were then heated at a constant rate of 10 ºC/min in air to 700 ºC, and kept at this temperature for 5 h to obtain Nd_2O_3 nanoporous network.

1.3 Characterization

The crystal structure of products were characterized by X-ray diffraction (XRD, D8 Advance, Brucker, Germany) with Cu Kα (λ=1.54 nm) radiation. Infrared spectra were recorded using a Nicolet 6700 FTIR spectrometer. The morphology and the average particle size of Nd_2O_3 nanostructures were investigated via scanning electron microscopy (SEM, Model JSM-5300LV), transmission electron microscopy (TEM, Model JEOLE-3432, Japan). High-resolution TEM images analysis were taken on a JEOL field emission transmission electron microscope (2100F). The nitrogen adsorption/desorption isotherms of the heat-treated samples were obtained using a Micromeritics at 77 K. The Brunauer-Emmett-Teller (BET) specific surface areas (S_{BET}) were calculated using the BET equation. Desorption isotherm was used to determine the pore size distribution using the Barrett-Joyner-Halenda (BJH) method.

2 Results and discussion

The surface morphologies of hierarchical neodymium oxide nanospheres were observed by SEM, TEM and HRTEM techniques. Low magnification SEM image (Fig. 2(a)) indicates the high homogeneousness of the sample. The as-obtained Nd_2O_3 consists of spherical particles with uniform size around 350 nm and a harsh surface. The high magnification SEM and TEM images show that the spherical particles are formed by numerous primary particles with average articles about 10 nm. Furthermore, HRTEM image further displays that the synthesized nanospheres are composed of numerous interconnected individual NPs, in good agreement with the SEM and TEM results. The presence of lattice fringes indicates the crystallinity of the particles.

The morphology of Nd_2O_3 nanoporous network material are shown in Fig. 2. The SEM result shows that Nd_2O_3 displays an irregularly sponge-like structure. The ligaments in nanoporous structure with diameters of approximately 10 nm were formed by Nd_2O_3 NPs agglomeration (Fig. 2(c) and (d)). The clear contrast between the dark skeletons and bright pores demonstrates the formation of three-dimensional porous structures. The result shows that since the NPs are protected by alkyl chains (oleic acid), subsequently their catastrophic aggregation can be prevented upon thermal treatment[28]. Because the long alkyl chain surfactants covering the NPs can act as sacrificial spacers between the NPs, which are removed during the thermal procedure, giving rise to a porous structure.

The phase and the crystal structure of the as-prepared Nd_2O_3 nanostructures were examined by XRD pattern (Fig. 3). All the distinguishable peaks were indexed to the cubic phase of Nd_2O_3 with lattice constant of $a=b=c=$ 1.107200 nm, corresponding to JCPDS No. 21-0579. Both samples have broad reflections with low intensities, suggesting that these structures are formed from the small size of Nd_2O_3 NPs[29]. The weaker diffraction lines of hierarchical Nd_2O_3 nanospheres suggest that the spherical particles were coated by amorphous capping agents. Besides, no obvious peaks corresponding to neodymium hydroxide or neodymium nitrate are observed, indicating the high purity of all the final products. This indicates that the hierarchical porous Nd_2O_3 nanostructures with