Sonochemical preparation of nickel alumina nanotubes templated by anionic surfactant assemblies

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Abstract Nickel alumina nanotubes templated by dodecylsulfate assemblies have been successfully synthesized for the first time using a sonochemical process. These nanotubes were characterized by scanning electron microscope (SEM), a transmission electron microscope (TEM), X-ray diffraction (XRD). The formation mechanism of these nanotubes is also discussed. They were also calcined to study the change of the nanostructure morphology with the temperature. It was found that the nanotubes transformed from short nanotubes into dendritic structures of aggregations of nanoparticles into monodisperse nanoparticles, and these nanostructures hold high specific surface area.

Introduction

One-dimensional (1D) nanostructures, such as nanotubes, nanowires, nanorods, nanobelts and nanofibers, have currently become the focus of intense research, because they provide a good system to investigate the dependence of electrical, optical, and thermal transport or mechanical properties on dimensionality and size confinement [1–3]. Among the various morphologies reported, tubular architectures are of particular interest since they may find applications in catalysis, selective separation, drug release, sensors, containers, and conducting devices in nano-, opto-, or ionoelectronics [1–6]. The discovery of carbon nanotubes (CNT) in 1991 has sprawled the belief that other

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layered materials may also roll up into tubes just as the graphite sheets do [7]. This is reasonable because the layered structures tend to bend to eliminate dangling bonds by the intralayer linkage. As a result, the syntheses of many inorganic tubular nanostructures such as WS_2 [8], MoS_2 [9], BN [10], V_2O_5 [11] and $NiCl_2$ [12] nanotubes have been achieved. However, these nanotubes synthesis methods require either extreme conditions such as high temperatures or preformed templates. Therefore, it remains a challenge to find simple, mild and effective routes to synthesize tubular nanostructures of inorganic materials.

Nickel alumina have been widely investigated because of their lower cost and relatively high activity used as a catalyst; as favorable laser materials; as a well materials of anti-reflection coatings for solar absorbers and as functionally structural composite [13–17]. For example, it can be used as the anode material of a fuel cell, taking advantage of its catalytic properties [15, 16]. In addition, it holds good humidity sensing properties [18], and excellent magneto-optic properties [19]. Many methods such as sol–gel synthesis [20], electrophoretic deposition [15], liquid-feed flame spray pyrolysis [16] and sonochemistry methods [22] were used to prepare nanostructured nickel alumina. However, Up to now, almost all as-prepared nickel alumina are either powders or amorphous nanoporous materials. The formation of nickel alumina nanotubes leads to increased surface area compared to nanopowers or nanoparticles and should prove to be extremely beneficial for those applications in nanotechnology, especially in catalysis, separation technology, biomaterials engineering, and fabrication of nanodevices.

In recent years, sonochemistry techniques have been extensively used in the synthesis of nanoscale materials [23]. Extremely high temperatures (>5000 K), pressures (>800 atm) and cooling rates (>10^{10} K/s) can be attained

during acoustic cavitation [24]. These conditions are responsible for a variety of chemical and physical effects. Such remarkable environments provide a unique platform for the growth of novel nanostructures. To the best of our knowledge, the preparation of nickel alumina nanotubes has not been reported in the literature yet. Herein, we demonstrate a simple solution-phase approach for the synthesis of nickel alumina nanotubes templated by anionic surfactant assemblies induced by ultrasound.

Experimental

Nickel alumina nanotubes were synthesized by homogenous precipitation method using urea. Nickel chloride hexahydrate and aluminum nitrate nonahydrate were nickel and aluminum source. Sodium dodecyl sulfate (SDS) was used as templates. The molar ratio of (Ni + Al)/SDS/urea/H_2O was 1:2:30:60. In a typical synthesis, the precursor solution was made by dissolving 0.624 g of $NiCl_2 \cdot 6H_2O$, 0.948 g of $Al(NO_3)_3 \cdot 9H_2O$, 2.975 g of SDS and 9.05 g of urea in 5.4 g of distilled water at 313 K. The molar ratio of Ni/Al was 1. These were stirred at 313 ± 1 K for 1 h. The suspension was then treated by 400 W ultrasound (KQ-400DB, Kunshan) for 20 min at 313 K to obtain a clean and stable sol precursor for the synthesis of nickel alumina nanotubes templated by anionic surfactant assemblies. The mixed solution was heated at 353 K and then kept at that temperature for 5 h and 20 h. The pH of the reaction mixture increased from 3.4 at its initial level to 5.0 after 5 h and 7.6 after 20 h, due to the enhanced hydrolysis of urea, while precipitation reaction occurred and developed. The resulting mixture was cooled to room temperature to prevent further hydrolysis of urea. The solids were filtrated using hot water a few times and then dried in vacuum at 353 K. The resulting samples were then calcined at 523, 673 and 1033 K for 5 h, respectively.

The morphology and structure of the prepared samples were analyzed by a scanning electron microscope (FE-SEM, 1530VP, LEO), a transmission electron microscope (TEM, Technai 20, FEI), X-ray diffraction (XRD, Bruker D8 Advance X-ray powder diffractometer), Fourier-transform infrared absorption spectra (FTIR, NEXUS 670, Nicolet), Nitrogen adsorption and desorption experiments were carried out at 77 K on a Micromeritic ASAP 2010 system. Thermogravimetric analysis (TGA) was performed on Perkin-Elmer 7 Series thermal analysis system. Specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method [25] and pore size distribution was determined by the Barrett–Joyner–Halender (BJH) method [26] using the desorption branch of the isotherm.

Results and discussion

When sodium dodecyl sulfate (SDS) was used as a templating agent, $NiCl_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were used as precursors, precipitation of nickel alumina nanotubes occured when urea decomposes and released NH_3 after ultrasound irradiation for 20 min. Figure 1a–c provides a set of transmission electron microscopy (TEM) images of a solid nanotubes synthesized by sonication for 20 min and then after a reaction time of 20 h at 80 °C. A low magnification TEM image of the nanotubes is shown in Fig. 1a. The outer diameter of the nanotubes is about 50 nm, while the inner diameter is around 10–15 nm (shown in Fig. 1b–c). Figure 1c shows that the hollow interior nanotube is clearly visible.

Figure 2 shows field emission scanning electron microscopy (FESEM) images of the as-prepared nickel alumina synthesized in the presence of dodecyl sulfate assemblies. From Fig. 2a, it is evident that the nickel alumina product mainly consists of disordered morphology. However, the product (shown in Fig. 2b) prepared by sonochemistry is micrometer spherical particles composed of nickel alumina nanotubes. It is clearly seen the abundant tubular structures (shown in Fig. 2a, c and Fig. 1). These nanotubes often grow closely together. The typical Energy dispersive X-ray (EDS) spectroscopy analysis (shown in Fig. 2d) indicated that the synthesized nanotubes were

Fig. 1 TEM images of the as-prepared nickel alumina nanotubes templated by dodecyl sulfate assemblies by sonication for 20 min and then after a reaction time of 20 h: (**a**) low-magnification image, (**b**) high resolution image of single nanotube, (**c**) high resolution image of the hollow interior structure
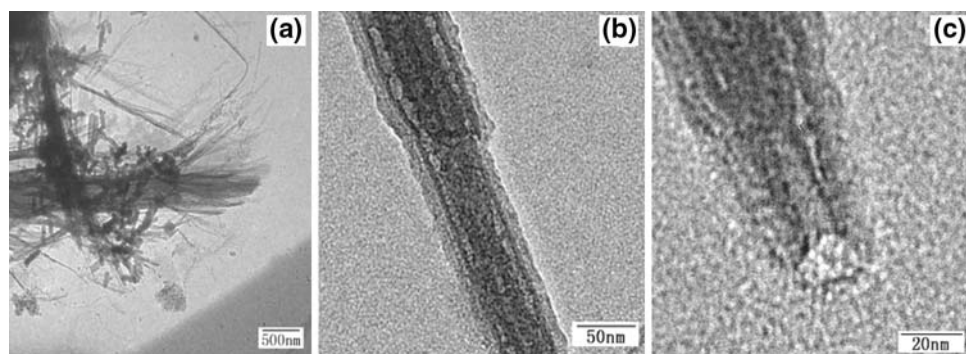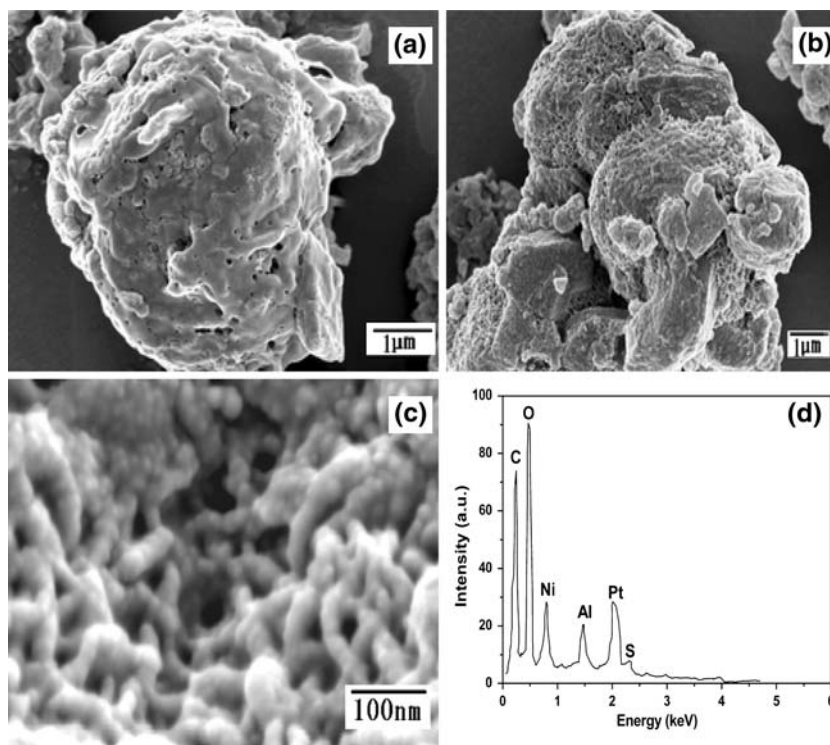
Fig. 2 FESEM images of nickel alumina samples treated without sonication (**a**) and with sonication (**b**); (**c**) Local magnification image obtained from (**b**); (**d**) EDX spectra obtained from (**c**)

composed of Ni, Al, O, C, S, which gave an atomic ratio of Ni: Al $\approx$ 1. The Pt peak was originated from the Pt coating in SEM sample processing.

The as-prepared samples synthesized by sonochemistry were also examined using powder X-Ray Diffraction (XRD). It can be seen from Fig. 3a that the XRD pattern of the solid after a reaction time of 5 h was characterized by their major peaks attributable to the 100, 200 and 300 reflections based on a layered strucuture. XRD pattern of the solid after a reaction time of 20 h was characterized by a major peak near $2\theta = 2.1$ (d = 4.2 nm) (shown in Fig. 3b). Such low angle peaks at $2\theta < 5°$ were not
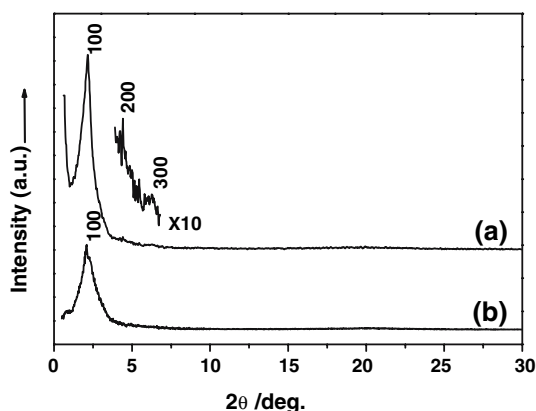
observed in silica and titania nanotubes with a small (about 5 nm) outer diameters [27]. This means that the present nanotubes are more uniform in their framework diameters than the others [27]. This result also shows layered nanophases have form nanotubes by means of layered rolling/wrapping by sonochemistry, which is similar to the principle of rare earth oxide nanotubes' synthesis without sonochemistry reported by Yada et al. [27]. However, we cannot find tubular nanostructures without sonochemistry. The possible reason is that ultrasounic radiation enhanced the interface curvature of the solution, which results in layered nanophases rolling into tubular nanostructures.

Figure 4a shows the fourier transform infrared (FTIR) spectrum of the as-prepared sample. The broad band at 3452 cm^{-1} can be attributed to the hydroxyl groups which are extensively hydrogen bonded. The two sharp peaks at 2850 and 2920 cm^{-1} are due to –CH$_2$– groups, and the shoulder peak at 2958 cm^{-1} is attributed to CH$_3$– groups. An additional broad band attributable to CO_3^{2-} appeared at 1300–1700 cm^{-1}, suggesting that carbonate species are also incorporated in the solid. Such incorporation of the carbonate species, originating from the hydrolysis of urea, was also observed for the hexagonal mesostructured and tubular rare earth oxides, alumina and gallium oxides [27–29]. The other broad peak in the range of 1000–1300 cm^{-1} may be attributed to –OSO$_3^-$. These results implied that dodecyl sulfate anions were incorporated in the nanotubular solid. In the calcined samples no peaks typical of
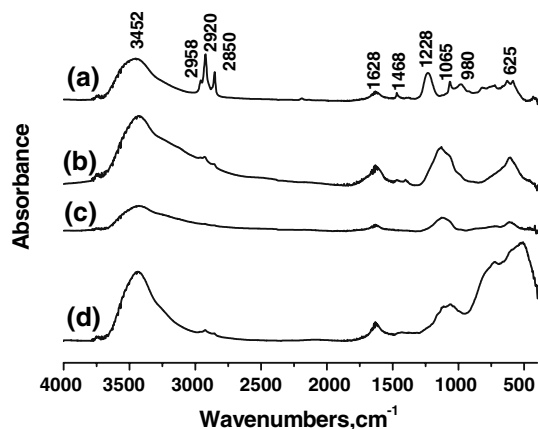

Fig. 3 XRD patterns of the as-prepared samples synthesized by sonication for 20 min and then reacting at different times (h): (**a**) 5; (**b**) 20

Fig. 4 FTIR spectra of the samples synthesized by sonochemistry: as-prepared sample (**a**); calcined samples at different temperatures (K): (**b**) 523, (**c**) 673, (**d**) 1033
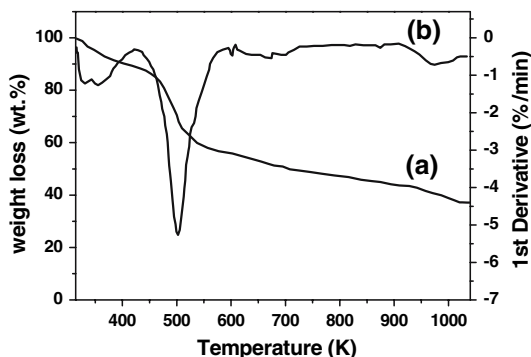

Fig. 5 Thermogravimetric analysis (TGA) of (A) as-prepared samples sonicated for 20 min and precipitated for 20 h and (B) corresponding differential thermal analysis (DTA)

C–H stretch vibrations corresponding to the alkyl tails of the surfactants were observed (shown in Fig. 4b–d).

Thermogravimetric differential thermal hydrolysis (TGA–DTA) curves of the solids synthesized by sonochemistry were shown in Fig. 5. The weight change curves exhibited a major weight loss at temperatures between 313 and 523 K, which is attributable to the elimination of water

and the decomposition of alkyl chain of surfactant. The weight losses in the 523–1033 K region are due to the desorption of carbonate species and sulfated groups and the elimination of H_2O formed by condensation of hydroxyl groups. The weight loss near 1023 K can be assigned to the complete desorption of SDS, which is consistent with TGA results of cerimum compound nanowires and nanorings reported by Yada et al. [30] and of a mesostructured alumina reported by Sicard et al. [31]. These results suggest a strong interaction between the sulfate head group and the nickel alumina framework.

The nanotubes were also calcined to study the change of nanostructure morphology with temperature. The solid was calcined at a heating rate of 1 K min⁻¹ up to 523, 673 and 1033 K in air and then kept at those temperatures for 5 h. TEM images shown in Fig. 6, indicated that short nanotubes observed below 523 K, transformed into aggregations of nanoparticles above 673 K with dendritic structures. It is thus concluded that the collapse of nanotube structure is due to the transformation of the nickel alumina compound into Ni/γ–Al_2O_3 along with the degradation and/or desorption of carbonate, and hydroxyl species composing the wall structure. Monodisperse nanoparticles can be observed above 1033 K. Specific surface areas of calcined products for the 523, 673 and 1033 K were determined to be 95, 327 and 134 m² g⁻¹, respectively (shown in Fig. 7a). The pore size distributions calcined products for 523, 673 and 1033 K did indicate the existence of mesopores, which was shown in Fig. 7b.

Conclusion

In summary, nickel alumina nanotubes templated by dodecylsulfate assemblies with open-ended tips were for the first time synthesized by sonochemistry. In addition, the simplicity of homogeneous precipitation process, cheapness, and availability of raw materials are advantages favoring the scaling-up of nanotubes. The present results demonstrate the potential feasibility to synthesize

Fig. 6 TEM images of the calcined samples at different temperatures (K): (**a**) 523, (**b**) 673, (**c**) 1033
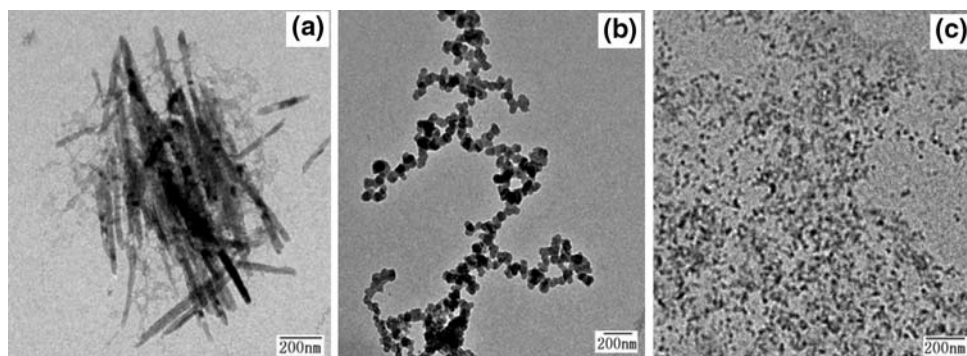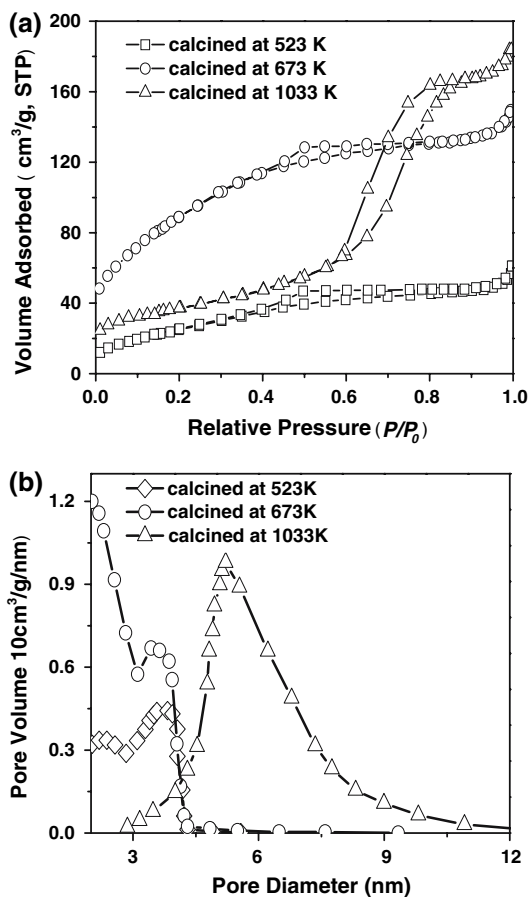
Fig. 7 (**a**) The adsorption/desorption isotherm of calcined samples at different temperatures (K) for 523, 673 and 1033. (**b**) BJH pore-size distribution curves of calcined sample at different temperatures obtained by the adsorption branches of the corresponding samples

one-dimensional metastable nanotubes by sonochemistry, showing that this route is a promising route for rationally and structurally designing nanomaterials.

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