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Synthesis of silica nanotubes from kaolin clay

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Silica nanotubes were synthesized from kaolin clay using surfactant intercalation, sulfuric acid and hydrothermal treatments.

Since the discovery of carbon nanotubes in 1991,[1] many other nanosized tubular materials have been synthesized.[2,3] Due to the outstanding structural versatility of nanotubes, significant attention has been focused on these materials with respect to possible applications in advanced catalysis, sensor/actuator arrays, energy storage/conversion and opto-electronic devices.[4] Recently, various preparation methods like sol–gel, template assisted, and replica process have been used to synthesize silica nanotubes.[5] However, compared to silica porous materials, silica nanotubes are not easy to synthesise and the final nanotube products usually are unstable. In this communication, we present a relatively easy and inexpensive synthesis procedure for silica nanotubes by converting layered kaolin clay, as a silica source, into stable nanotubes. Kaolin is a naturally occurring clay and is extensively used as a catalyst, in paints and as a filler for reinforcing polymers. Kaolin has a layered silicate structure, which can be easily intercalated and exfoliated by organic cations.[6] Using the above properties of kaolin, we have developed a new process for the synthesis of silica nanotubes.

The synthesis of silica nanotubes involved the following steps. The white colored kaolin powder was obtained by calcining the original kaolin (Jiangsu province, China) at 750 °C for 4 h in air. The soluble salts were removed by washing the above material with distilled water and dried at 100 °C. 5 g of the dried kaolin was mixed with 20 mL of 0.1 M CTAB aqueous solutions with vigorous stirring. This mixture was aged for 10 h while stirring. 2 mL of concentrated sulfuric acid was then slowly added to the mixture, and stirred for 20 h. The thus obtained suspension was heated to 120 °C in an autoclave for 24 h under autogenous pressure. After hydrothermal treatment, the resulting material was filtered, washed, dried and calcined at 550 °C for 6 h in air, which resulted in a white powder of silica nanotubes. The starting materials and silica nanotubes were characterised by XRD, HRTEM, MAS-NMR and TG-DTA techniques.

Fig. 1. Shows the XRD patterns of the kaolin, and of the materials at different steps in the synthesis, as indicated in the legend. The calcined material displays the typical layered silicate structure of kaolin.[7] After treatment with CTAB for 5 h, the material clearly shows a shift in d_{100} peak towards lower 2θ values, due to expansion of the silicate layers by intercalated CTAB. At the same time the material starts losing its ordered/crystalline structure. With further increase in CTAB treatment to 10 h, the characteristic sharp peaks of kaolin disappear and a broad peak is seen between $2\theta = 20$ to 40°, along with a significant decrease in intensity of the d_{100} peak (Fig. 1c). Notably, the sample treated with CTAB shows a broad peak typical of an amorphous material along with a very weak d_{100} peak after sulfuric acid and hydrothermal treatment (Fig. 1d). The above observations indicate that the layered structure was significantly destroyed by the intercalation of the surfactant followed by the sulfuric acid and hydrothermal treatments.

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After treatment with CTAB, H_2SO_4 and hydrothermal aging, the well-defined structure of silica nanotubes is clearly seen in TEM images (Fig. 2), which show irregular rod-shaped hollow tubes (Fig. 2a). High-resolution TEM images (Fig. 2b, c) show tubular structures with open ends, due to peeling off of the outer layers, an inner diameter of about 50 nm and an outer diameter of 80 nm, and a length of less than 1 µm on average.

The solid-state ^{29}Si MAS-NMR spectra of the kaolin, and of the products at different steps in the synthesis, provide additional evidence of the conversion of the layered silicate structure of kaolin to a more condensed structure (Fig. 3). The observed MAS-NMR signals between $\delta p = -80$ to -120 ppm are due to different environments of Si. Q2 (-97 to -98 ppm), Q3 (-101 to -102 ppm) and Q4 (-110 to δp -111 ppm) species, which represent the Si structure as depicted in Fig. 3, are formed during various treatments.[8] Kaolin shows a sharp signal typical of Q2 species, indicating that all the Si elements are present in a similar environment (Fig. 3a). During CTAB exchange, the intensity of Q2 species decreases, while that of Q3 and Q4 species appears and increases with treatment time (Fig. 3b, c). All the Q2 species disappear on sulfuric acid treatment, and a dominating signal corresponding to Q4 species is observed (Fig. 3d), indicating the change of the layered to a condensed amorphous structure.[9] Moreover, our data are in agreement with those reported in the literature for silica nanotubes prepared from amorphous SiO_2, after hydrothermal treatment, where a similar spectrum was observed.[5] The XRD, MAS-NMR and HRTEM observations complement each other. The elemental analysis by ICP-AES showed that the final products only contain pure SiO_2.

The formation process of silica nanotubes from kaolin could be explained as follows. CTAB in the first step helps in exfoliating the layered structure. Sulfuric acid removes the framework Al ions as $Al_2(SO_4)_3$, which results in many irregular exfoliated layered-silica/surfactant composites. This can be confirmed from TG-DTA (Fig. 4), which shows a weight

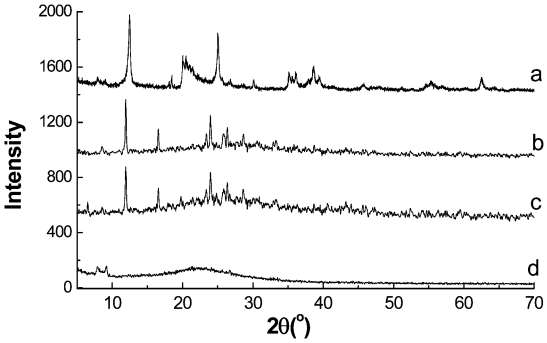

Fig. 1 XRD of (a) original kaolin, after CTAB exchanging for (b) 5 h, (c) 10 h, and (d) after sulfuric acid/hydrothermal treatment.

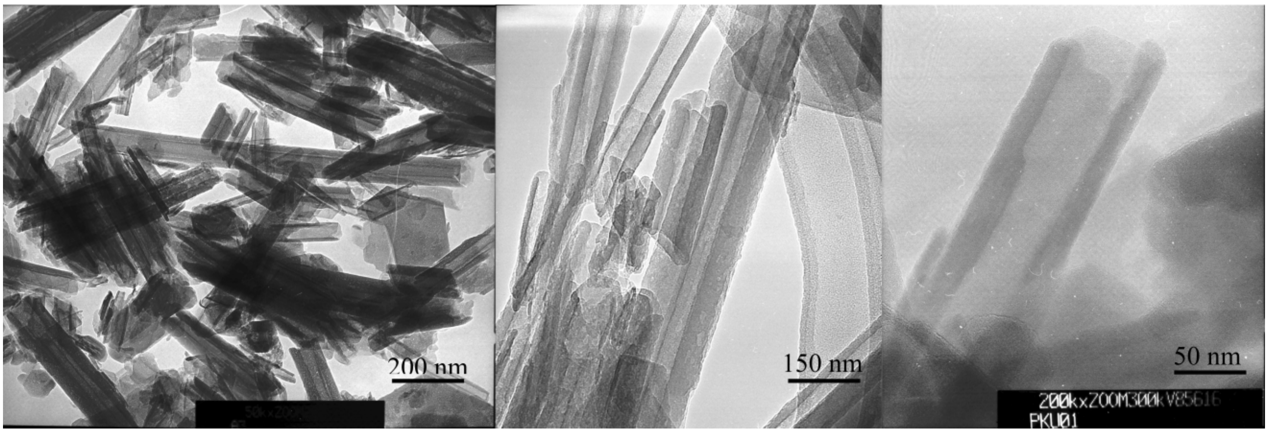

Fig. 2 TEM images of (a) final product, (b) and (c) high magnification of (a).

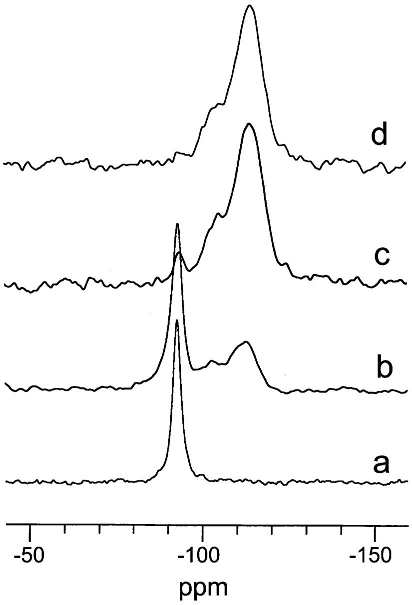

Fig. 3 ^{29}Si MAS-NMR spectra of the products at different reaction steps as indicated in the legend to Fig. 1.

loss of approximately 12% after heating washed, uncalcined samples from 118 °C to 510 °C, due to the removal of surfactant. Layered silica/surfactant composites easily curve under proper pH conditions.[10] Feng *et al*.[11] also observed curved surface morphologies resulting from disinclination and dislocation. After hydrothermal treatment, this curvature becomes even more pronounced. In summary, intercalation of surfactant, followed by acid and hydrothermal treatments, plays an important role in the conversion process, which is similar to the mechanism proposed by Lin and Mou.[10]

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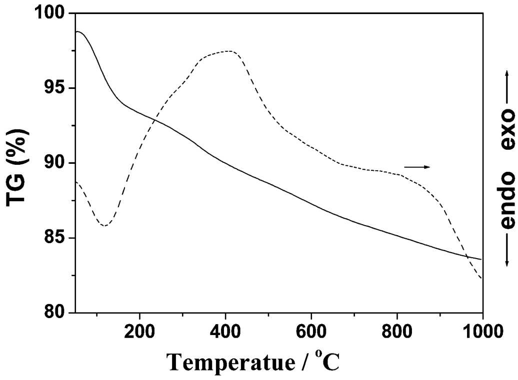

Fig. 4 TG-DTA of uncalcined silica nanotube.

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