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Nanotubes in Si-doped titanium dioxide

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Silicon-doped metal oxide nanotubes are formed in Si-doped titanium dioxide prepared by a sol–gel technique.

The discovery of novel properties of carbon nanotubes, which are different from both graphite and fullerene, aroused great interest in the studies of carbon nanotubes and related materials.[1–3] Several techniques have been developed recently for fabricating the nanotubular materials, such as arc discharge,[4] chemical vapour deposition,[5] laser ablation,[6] templating,[3] replication[7] and so on. However, methods for the fabrication of metal oxide nanotubes are very limited. TiO_2 and silicon-doped titania have many useful properties[8,9] and the fabrication of their nanotubes may have implications for creating high activity catalysts, effective deodorants and adsorbants. TiO_2 nanotubes with diameter of 70–100 nm were reported to be produced by using the replication method.[10] The preparation of TiO_2 nanotubes with smaller diameters has proved very difficult by using the replica technique because it is not easy to control the pore size of a mold such as alumina. Very recently, TiO_2 nanotubes with a diameter of 8 nm were obtained by controlling the chemical treatment conditions.[11,12] In this paper, we report the formation of nanotubes in silicon-doped TiO_2 prepared by a sol–gel technique.

Butanediol (> 98%, Merck) was added to a beaker containing tetraethyl orthosilicate (> 98%, Merck) according to the required silicon amounts of 0%, 1 at.%, 2 at.%, 3 at.%, 4 at.%, 5 at.% , 6 at.% and 10 at.% (mole percentage), labeled as TS0, TS1, TS2, TS3, TS4, TS5, TS6 and TS7 respectively. Then tetrapropyl orthotitanate (98%, Aldrich) was added at room temperature by stirring and a homogeneous transparent liquid was produced (butanediol : tetrapropyl orthotitanate = 2 : 1). The mixture was aged at ambient temperature for a few days. During these days the fluid became progressively viscous and a dry gel eventually resulted. Crystallization was achieved by subsequent calcination of the dry gel at different temperatures for 1 h by using the same heat-treatment program (5 °C min^{-1}) in air.

XRD results show that the phase transformation temperature of doped samples has a sensitive relationship with the silicon content. The evolution of both anatase and rutile starts at higher temperatures for silicon-doped samples. For example, only 1 at.% silicon dopant is able to cause a remarkable increase in the coexistence range of anatase and rutile between 640 and 830 °C, much higher than that of pure TiO_2 which is between 630 and 700 °C. XRD patterns belonging to silica or related phases are not found.

The surface area is increased greatly for the doped samples (Table 1). The pure titanium dioxide calcined at 600 °C for 1 h heavily sinters together and the surface area is 1.9 m^2 g^{-1}. It is worth noting that just 1 at.% silicon dopant causes an increase in surface area to 16.5 m^2 g^{-1} (TS1), and the surface area of TS7 (10 at.%) reaches 110 m^2 g^{-1} after calcination at 600 °C for 1 h by using the same heating program (5 °C min^{-1}). On the other hand, the pore size is decreased when the silicon content is increased. It is manifest that the silicon doping remarkably influences the sintering process. As a result of heavy restraint of the grain growth, which usually happens during the heat treatment of nanosized titania particles at high temperatures, the silicon-doped samples show much higher surface areas than that of pure titanium dioxide when heated using the same heating program. Silicon dopant suppresses grain growth of the nanoparticles, inducing a large increase in surface area for the doped samples.

Transmission electrom microscopy (TEM) results show that a lot of nanotubes coexist with nanoparticles in some samples calcined at 600 °C for 1 h in air, especially in the samples of TS5 (5 at.%) and TS6 (6 at.%). Small amounts of nanotubes were found in TS4, while the nanotubes can be observed everywhere in sample TS5. In TS6 the nanotubes can still be observed, but their content is less than that in TS5. However, only nanoparticles are observed in either TS7 or pure titanium dioxide. Fig. 1 presents the TEM nanotube images of TS5 (5 at.%) calcined at 600 °C for 1 h in air. The outer diameter of the tubes is around 13 nm and the inner diameter is 3 nm. EDX (mounted on the TEM) mapping images reveal that titanium and silicon are homogeneously distributed in the nanotubes, suggesting that

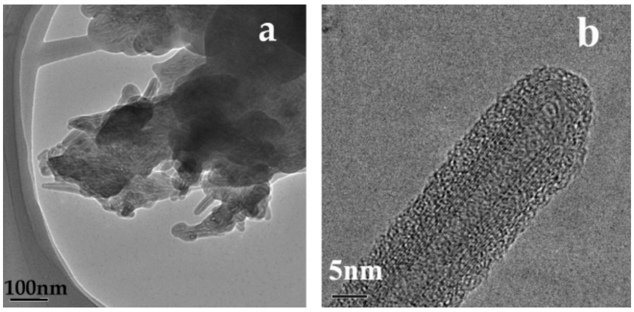

Fig. 1 TEM micrographs of nanotubes formed in silicon-doped titanium dioxide (TS5) calcined at 600 °C for 1 h in air. Heating program is 5 °C min^{-1}.

Table 1 The surface area and pore size of pure and silicon-doped titanium dioxide

Silicon content (at.%)	Temperature/°C	Time/h	Surface area/m^2 g^{-1}	Pore diameter (desorption)/nm	Pore diameter (adsorption)/nm
0	400	3	79	3.7	1–10
0	500	1.5	7.03	3.7	1–13
0	600	1	1.9	—	—
1	600	1	16.5	3.7	1–8
5	600	1	87.96	3.5	1–5
6	600	1	96.11	3.25	3.3
10	600	1	110.66	2.0	2.1

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the nanotubes are constructed from homogeneous silicon-doped titania.

The above experiments were repeated and the same results were observed. It is evident that the content of silicon dopant plays a key role in the formation of nanotubes. At present the mechanism of formation of the nanotubes is not clear. Further investigations are in progress.

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