

Zirconia nanotubes

C. N. R. Rao,* B. C. Satishkumar and A. Govindaraj

Solid State and Structural Chemistry Unit and CSIR Centre of Excellence in Chemistry, Indian Institute of Science, Bangalore 560 012, India

Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560 064, India

Hollow nanotubes of zirconia as well as of yttria-stabilized zirconia are successfully prepared by first coating the carbon nanotubes appropriately with the oxidic material and then burning off the carbon of the template.

Preparation of hollow nanotubes of ceramic metal oxides is an important and challenging problem. Hollow nanotubes of silica have been recently prepared by the hydrolysis of tetraethylorthosilicate (TEOS) in a mixture of ethanol, ammonia, water and tartaric acid.¹ We were able to prepare silica nanotubes by calcining acid-treated carbon nanotubes coated with TEOS and then oxidizing the carbon at higher temperatures. The silica comprising the nanotubes was however amorphous. We considered that it would be most rewarding if we could prepare hollow nanotubes of important ceramic oxides. Here we report the first successful preparation of hollow nanotubes of both zirconia and yttria-stabilized zirconia through the use of carbon nanotubes as templates.

The procedure employed by us for preparing zirconia nanotubes is as follows. In a typical preparation, 200 mg of multi-walled carbon nanotubes (prepared by the arc evaporation of graphite² and subjected to heat treatment at 973 K in air for

20 min to remove other forms of carbon³) were refluxed in nitric acid (16 M) for 12 h to create acidic sites on the surface.^{4,5} The acid-treated carbon nanotubes were reacted with 2 ml of $Zr(OPr^n)_4$ in an argon atmosphere, sonicated for 2 min and the mixture was stored in a desiccator for 48 h. The product was then washed with dilute HF (48%) followed by dry methanol, to remove the excess alkoxide, followed by drying at 373 K and calcination at 723 K in air for 12 h. This procedure yielded zirconia-coated carbon nanotubes. Fig. 1(a) shows a typical scanning electron microscope (SEM) image of carbon nanotubes coated with ZrO_2 in this manner. A transmission electron microscope (TEM) image of a zirconia-coated nanotube is shown in Fig. 1(c). The ZrO_2 -coated carbon nanotubes were heated at 973 K in air for 48 h to oxidize the carbon. Thermogravimetry indicated that the carbon is oxidized around 973 K. By this means, we could obtain pure zirconia nanotubes as revealed in the SEM and TEM images of Fig. 2(a) and (b), respectively. The tube diameter is generally *ca.* 40 nm and the wall thickness is *ca.* 6 nm. The hollow nature of the nanotubes is clearly indicated by the TEM image. Electron and X-ray diffraction patterns showed the material to be composed of a 50 : 50 mixture of monoclinic and tetragonal phases. Heating to

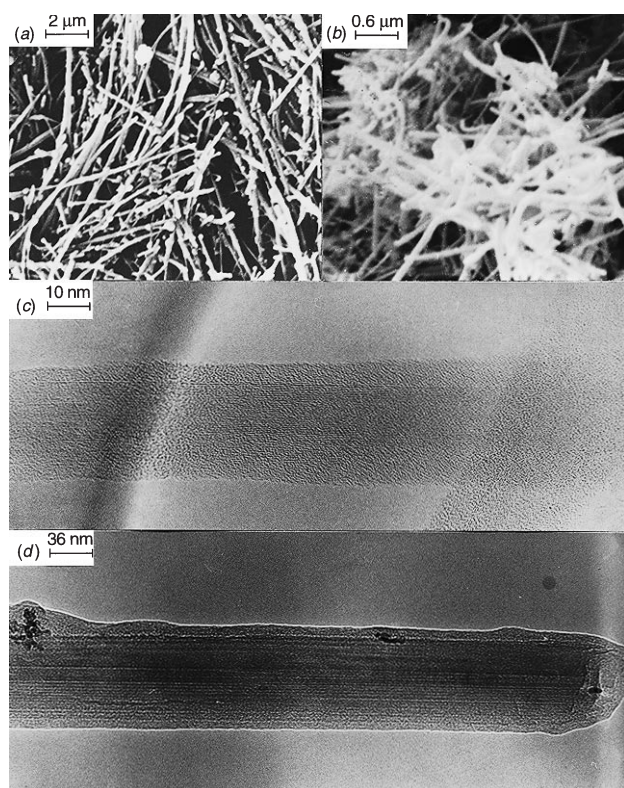


Fig. 1 (a) SEM image of zirconia-coated carbon nanotubes, (b) SEM image of carbon nanotubes coated with stabilized zirconia, (c) TEM image of a zirconia-coated carbon nanotube and (d) TEM image of a carbon nanotube coated with stabilized zirconia

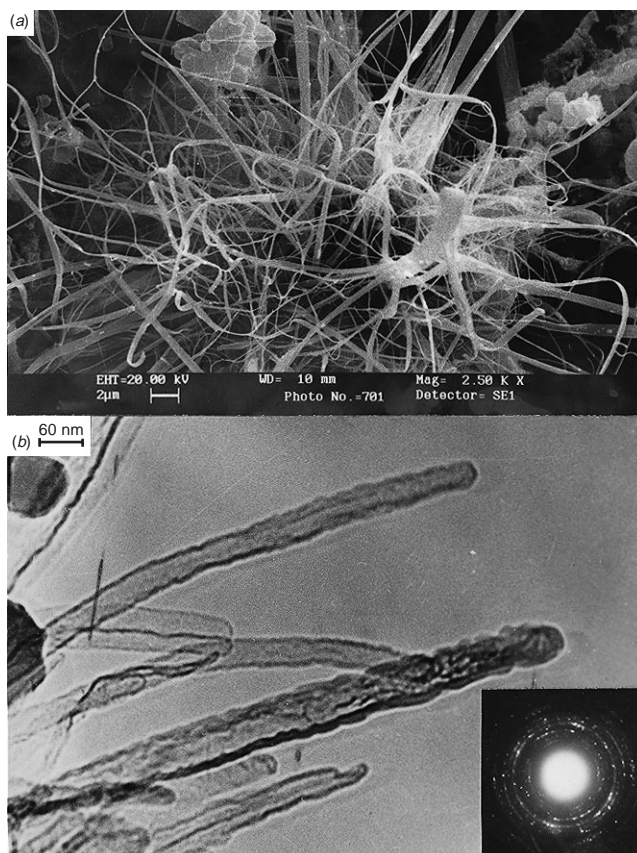


Fig. 2 (a) SEM image of zirconia nanotubes, (b) TEM image showing hollow nanotubes of zirconia. Inset gives the electron diffraction pattern.

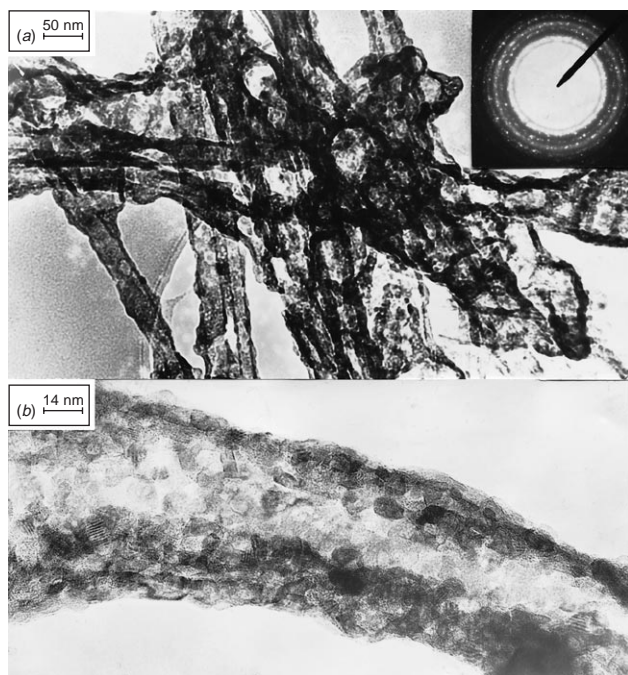


Fig. 3 TEM images showing hollow nanotubes of stabilized zirconia. The electron diffraction pattern is shown in the inset.

high temperatures to obtain monophasic nanotubes resulted in the collapse of the nanotubes, because of the first-order nature of the monoclinic–tetragonal transformation.⁶ Since this would not be a problem with stabilized zirconia, we proceeded to prepare the nanotubes of yttria-stabilized zirconia (0.92 ZrO₂–0.08 Y₂O₃) by a similar procedure.

In order to prepare the nanotubes of yttria-stabilized zirconia, 1.5 g of ZrOCl₂·8H₂O was dissolved in 10 ml of distilled water, to which 3 ml of a solution of 0.1 g of Y₂O₃ in 16 M HNO₃ was added. After cooling the solution to 273 K, the pH of solution was adjusted to 9 by the addition of ammonia, to obtain a gel. The gel was washed thoroughly with distilled water and dissolved in HNO₃ (1 M). 300 mg of acid-treated carbon

nanotubes were stirred with this solution for 24 h. The solvent was slowly evaporated in a hot air oven, the product dried at 373 K for 12 h and then calcined at 723 K in air for 12 h. This procedure yielded carbon nanotubes coated with stabilized zirconia. Thermogravimetry showed that the carbon in the coated tubes is oxidized completely around 970 K in air.

A typical SEM image of carbon nanotubes coated with stabilized zirconia is shown in Fig. 1(b) and a TEM image of one such nanotube is shown in Fig. 1(d). We have found it desirable to treat the nanotubes coated with stabilized zirconia with ethylene glycol followed by dilute HNO₃, before burning off the carbon, in order to stabilize the tubular structure of stabilized zirconia. After oxidizing the carbon at 973 K, we obtained hollow nanotubes of stabilized zirconia. The TEM images in Fig. 3 show the outer diameter to vary between 40 and 50 nm, and the wall thickness to be *ca.* 6 nm. The image in Fig. 3(b) shows the lattice fringes of the oxide in some regions. The hollow nature of the nanotubes is also revealed in the images. The electron diffraction and X-ray diffraction patterns showed the material to possess the known cubic structure of stabilized zirconia ($a = 5.1164 \text{ \AA}$). We believe that such hollow ceramic nanotubes may have several applications. We are now in the process of preparing such ceramic nanotubes starting with single-walled carbon nanotubes.

Footnote and References

* E-mail: cnrrao@sscu.iisc.ernet.in

- 1 H. Nakamura and Y. Matsui, *J. Am. Chem. Soc.*, 1995, **117**, 2651; H. Nakamura and Y. Matsui, *Adv. Mater.*, 1995, **7**, 871.
- 2 S. Iijima, *Nature*, 1991, **354**, 56.
- 3 C. N. R. Rao, R. Seshadri, A. Govindaraj and R. Sen, *Mater. Sci. Eng.*, 1995, **R15**, 209.
- 4 R. M. Lago, S. C. Tsang, K. L. Lu, Y. K. Chen and M. L. Green, *J. Chem. Soc., Chem. Commun.*, 1995, 135.
- 5 C. N. R. Rao, A. Govindaraj and B. C. Satishkumar, *Chem. Commun.*, 1996, 1525.
- 6 C. N. R. Rao and K. J. Rao, *Phase Transitions in Solids*, McGraw-Hill, New York, 1978.

Received in Cambridge, UK, 26th February 1997; 7/01354J