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Preparation of ZnO nanoparticles localized on $SiC@SiO_2$ nanocables by a physical templating method

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Abstract

Impregnation of interlaced $SiC@SiO_2$ nanocables (SiC NWs sheathed by SiO_2 coatings) into a ZnO sol at 0 °C yielded, after thermal treatment up to 600 °C under argon, $SiC@SiO_2@ZnO$ nanostructures. These novel nanostructures consist in $SiC@SiO_2$ nanocables covered by numerous agglomerated ZnO nanoparticles. The latter are less than 5 nm in diameter. This result is to our knowledge the first example of a physical templating technique involving SiC-based nanowires. Moreover, we have obtained localized ZnO nanoparticles. This localization can be of interests for a further study of their physical properties. When a similar experiment was conducted with pure SiC nanowires, there was no interaction between the nanowires (NWs) and the solution, resulting in the formation of agglomerated ZnO NPs embedded into the 3D NWs network.

Keywords: SiC; ZnO; Nanowire; Nanocable; Nanoparticle; Physical templating

1. Introduction

An increasing number of works have been recently devoted to the preparation, characterization and utilization of inorganic 1D nanostructures. Among these materials, zinc oxide has attracted much interest due to its unique combination of valuable chemical and physical properties. Indeed, ZnO is a wide band gap (3.37 eV) semi-conducting material which exhibits interesting optical,[1] electronic, catalytic and photochemical properties. These properties allow envisaging applications in various domains[2] ranging from ultraviolet lasing applications[3] to catalysis[4] and gas sensing material.[5] Various kinds of ZnO nanostructures have been prepared in the last decade, such as for instance nanoparticles, nanowires, and nanotubes.[2,6–9] Another interest in ZnO lies in the fact that it is one of the few oxides that shows quantum confinement effects in an experimentally accessible size range.[10]

Moreover, a breakthrough in the mass production of highly long SiC-based nanostructures has been recently performed in our group. We reported a simple and cheap method, based on a vapor–solid (VS) growth mechanism, allowing the fabrication of large amounts of interlaced SiC nanowires and $SiC@SiO_2$ nanocables.[11,12] The NCs can be seen as coaxial nanostructures made of SiC nanowires (NWs) sheathed by one or several coatings, and forming coaxial nanocomposites. Since it is now possible to produce amounts of SiC-based nanostructures compatible with industrial applications, we are now exploring the possible applications of these nano-objects. Indeed, we investigate in the present paper the possibility to use the 3D isotropic network of interlaced SiC-based nanowires as a template for the production of more complex nanostructures *via* a replication process. To our knowledge, this technique, which has been named as the physical templating route by other group,[13] has never been applied to SiC-based nanowires. The principle of this method is very simple and involves the deposition of a nanometric coating onto the surface of existing nanostructures; the template may be eliminated in a further step revealing nanotubes.

Based on a synthetic technique reported for the formation of ZnO nanoparticles with particle size <10 nm, we investigate in the present paper the possibility of preparing ZnO-based 1D

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nanostructures from SiC-based NWs by the physical templating method.

2. Experimental procedure

2.1. Preparation of a ZnO sol

A transparent ZnO sol was prepared according to the simple method described by Meulenkamp.[8] This author has simplified the technique previously reported by Spanhel and Anderson.[14] First, anhydrous zinc acetate ($Zn(Ac)_2$, 1.53 g, 8.3 mmol) was dispersed into 74 mL of dry ethanol. Second, KOH (1.582 g, 28.2 mmol) was dissolved into 20 mL of ethanol, and then this solution was slowly added to the Zn-containing one under vigorous stirring at 0 °C. After addition, the solution became transparent and was stored under 4 °C in order to prevent any nanoparticle growth.

2.2. Fabrication of SiC nanowires and SiC@SiO_2 nanocables

Samples of pure intermixed SiC nanowires or SiC@SiO_2 nanocables were prepared as starting materials by the vapour–solid growth mechanism and according to a procedure described elsewhere.[11] The intermixed nanowires have the macroscopic aspect of cotton-like foams with a blue colour in the case of SiC and a white colour in the case of SiC@SiO_2.

2.3. Impregnation of the foams by the ZnO sol

In a typical experiment, foam containing pure SiC or SiC@SiO_2 nanowires was dipped into the alcoholic ZnO sol at 0 °C. After 1 min of immersion, the treated foam was removed from the solution and let to dry at rt under ambient lab atmosphere. The ensuing sample was subsequently heated under argon during 2 h up to 200 °C, 400 °C then 600 °C (heating rate 60 °C h^{-1}).

All the nanostructures depicted in this paper were analyzed by the means of scanning electron microscopy (SEM, Model S800, Hitachi), high-resolution transmission electron microscopy (HRTEM, TOPCON 002B), and XRD analysis using a Philipps PW 3040/60 X'Pert PRO X-ray diffraction system (Cu kα radiation; λ = 1.5406 Å at 40 kV and 30 mA).

3. Results and discussion

3.1. Impregnation of pure intermixed SiC nanowires by the ZnO sol

In a preliminary experiment, blue foam consisting in a 3D network of intermixed pure SiC nanowires (NWs) was prepared according to an experimental procedure established by our group.[11–12] The growth of the SiC nanowires was achieved *via* a vapor–solid mechanism. Fig. 1 shows a typical SEM image of the blue foam. The SiC nanowires exhibited diameter of ∼40 nm for lengths up to several hundreds of micrometers. Further analysis indicates that the nanowires are composed of the cubic form

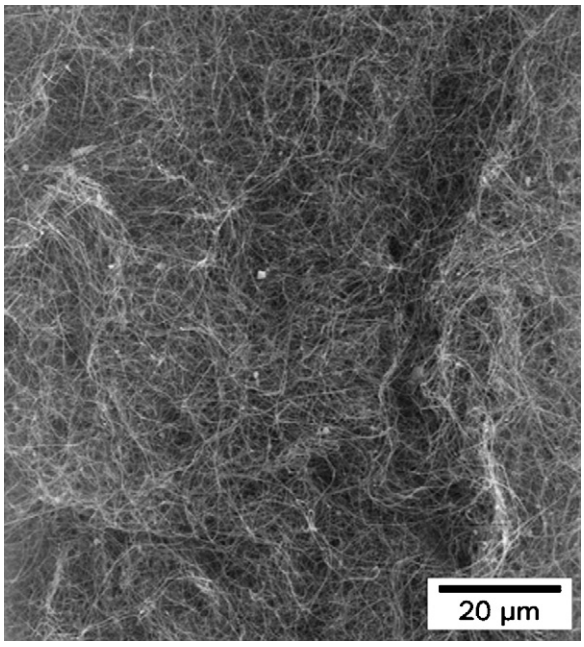

Fig. 1. Typical SEM image of pure intermixed SiC nanowires.

of SiC. The HRTEM image depicted in Fig. 2 underlines that the SiC nanowires are free of silica or carbon coatings onto their surface.

Second, a transparent ZnO sol was prepared according to a method described by Spanhel and Anderson,[14] and optimized by Meulenkamp.[8] Starting from an ethanol solution of anhydrous zinc acetate, addition of an ethanol solution of KOH under vigorous stirring at 0 °C yielded a transparent ZnO sol. The latter is well known to give ZnO nanoparticles with diameters in the range of 2–7 nm.[8] The sol was kept under 4 °C during the whole experiment in order to prevent any spontaneous nanoparticles growth.

In a typical experiment, the SiC NWs-containing foam was dipped into the ZnO sol at 0 °C. After 1 min of immersion, the foam was removed from the solution and dried at rt under ambient lab atmosphere. After 48 h of drying, the crude product was analyzed by SEM. Fig. 3 shows a SEM image of the sample.

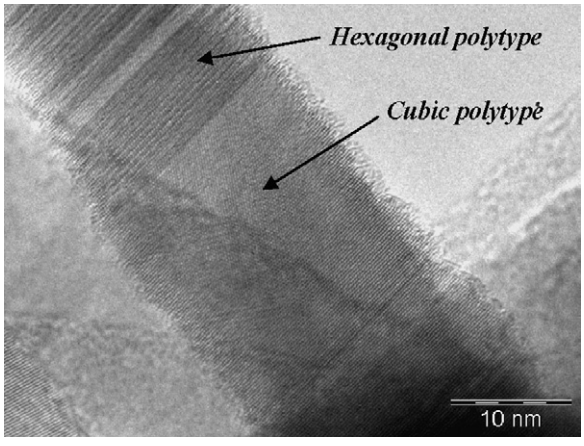

Fig. 2. HRTEM image of a SiC nanowire.

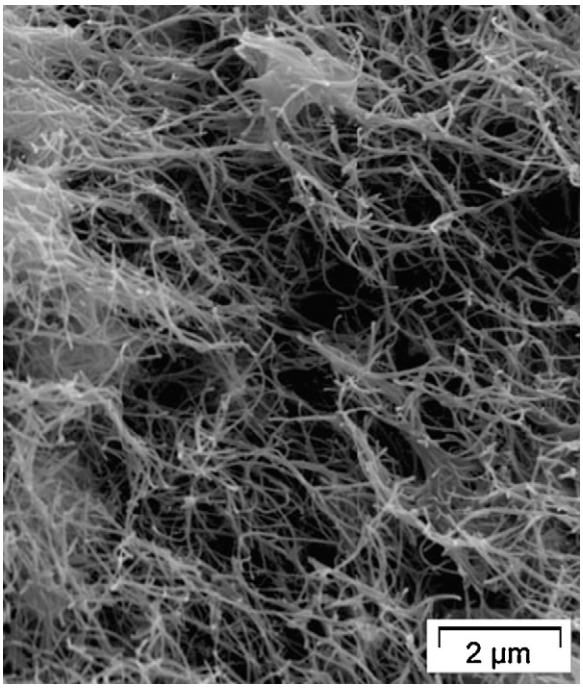

Fig. 3. SEM image of the SiC NWs-based foam impregnated by the ZnO sol.

It appears clearly from Fig. 3 that few gel domains are embedded into the network of interlaced nanowires. This tends to support that there is clearly no interaction between the ZnO sol and the 3D network of interlaced SiC nanowires. Therefore, no physical templating effect has been observed in that case. We assume that this result has to be related to the low affinity of SiC with ethanol solution, *i.e.* to the hydrophobic feature of SiC nanowires. In order to bypass this drawback, similar experiments were conducted with a 3D network of SiC@SiO_2 nanocables.

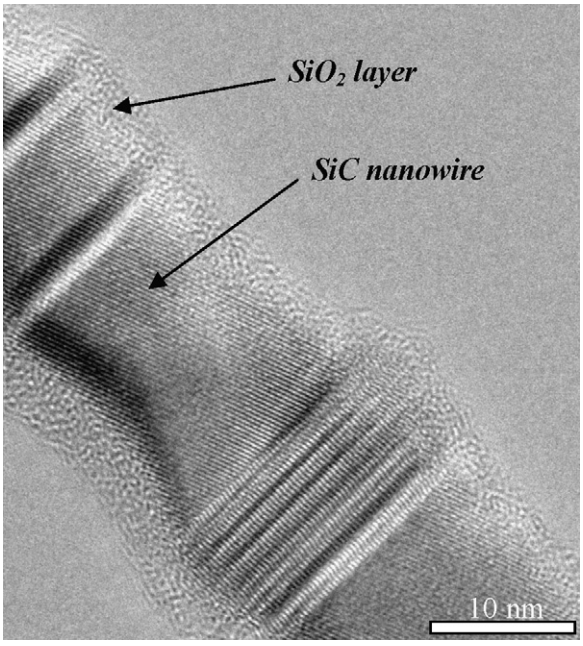

Fig. 4. TEM image of a typical SiC@SiO_2 nanocable.

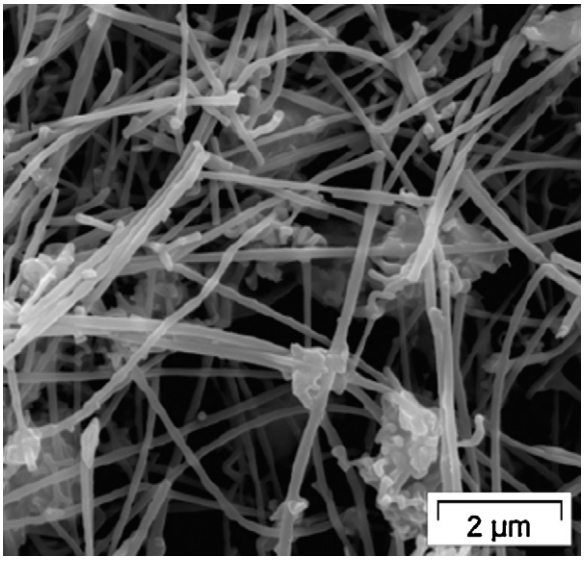

Fig. 5. SEM image of the cotton-like solid made of SiC@SiO_2 nanocables after immersion into ZnO sol and drying under ambient lab atmosphere.

3.2. Impregnation of pure intermixed SiC@SiO_2 nanocables by the ZnO sol

A 3D scaffold of interlaced SiC@SiO_2 nanowires was prepared as starting materials. For that purpose, foam made of SiC NWs was heated in air up to 600 °C during 2 h, yielding a white cotton-like solid. SEM image of the latter is similar to the one shown in Fig. 1. Fig. 4 displays a TEM image of a SiC@SiO_2 nanocable. As expected, cubic silicon carbide nanowires appeared to be coated by an amorphous silica coating. The SiC core is about 20 nm in diameter and the silica coating is about 3 nm in thickness.

As depicted above with the SiC NWs, the cotton-like solid was immerged into the ZnO sol at 0 °C. After drying at rt, the

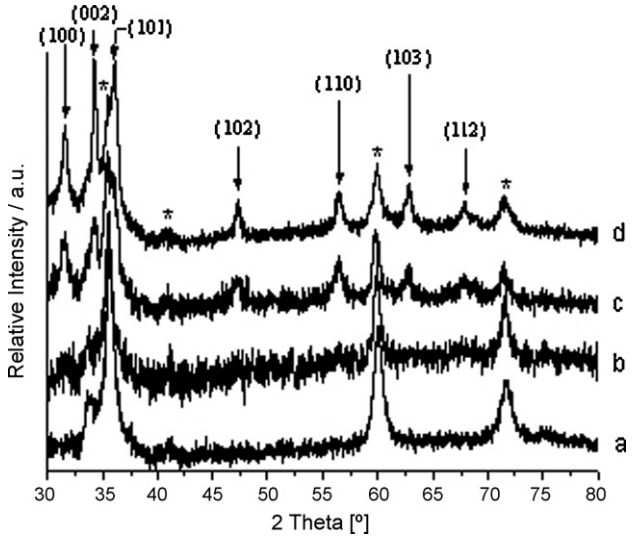

Fig. 6. XRD patterns of crude product derived from SiC@SiO_2 nanocables at RT and after heating up to 200 °C; 400 °C and 600 °C. Peaks corresponding to cubic-SiC are labeled (*) and peaks corresponding to hexagonal ZnO are indexed.

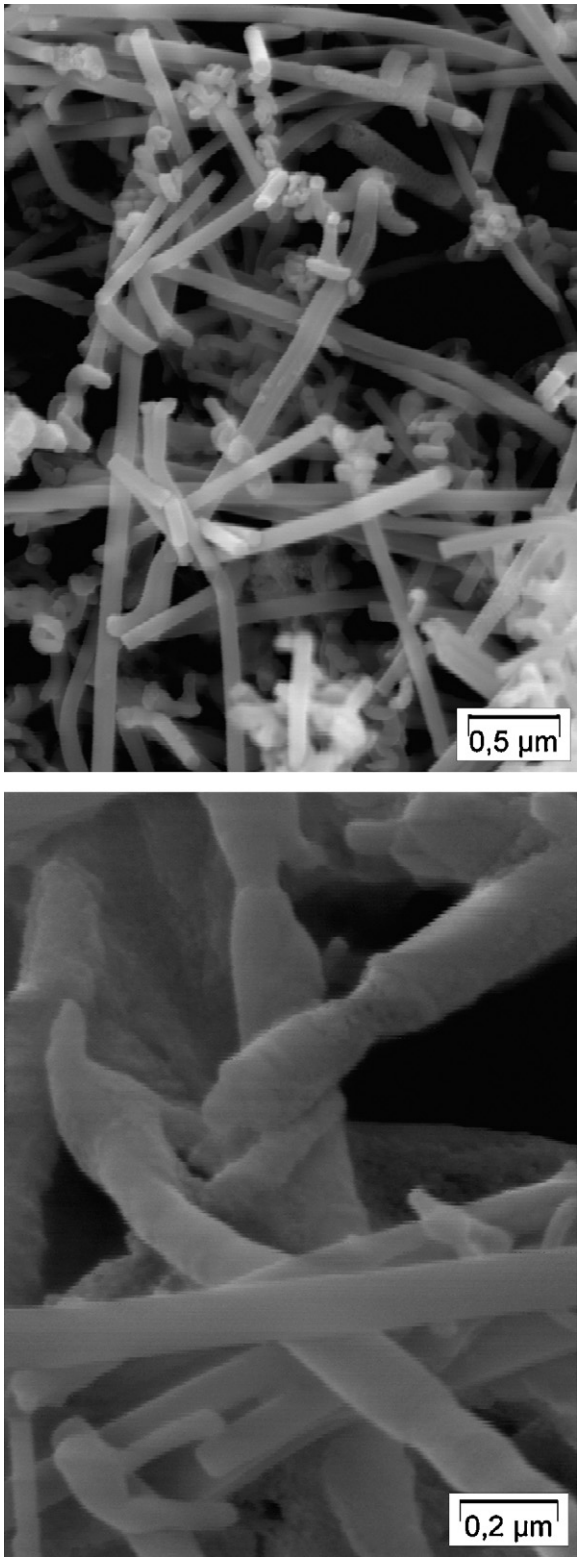

Fig. 7. SEM images at different magnification of the sample derived from $SiC@SiO_2$ nanocables after heating up to 600 °C.

sample was analyzed by XRD and SEM. XRD analysis showed only the peaks featuring cubic silicon carbide, indicating that any ZnO locating in the sample would be amorphous. Fig. 5 shows the SEM image of the crude sample.

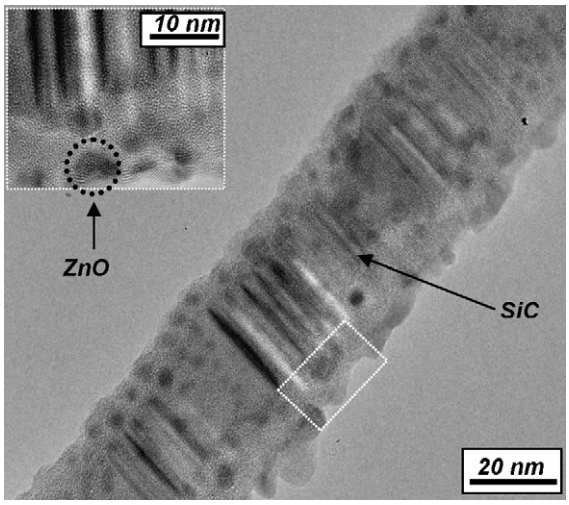

Fig. 8. HRTEM images of the $SiC@SiO_2@ZnO$ nanostructures after heating up to 600 °C.

It appears from Fig. 5 that the crude product still consists in interlaced nanostructures, but it was not possible to establish from this observation if a ZnO-based coating has been synthesized on the starting nanocables. In order to perform (HR)TEM analysis and therefore to investigate the presence or not of ZnO at the surface of the nanostructures, thermal treatment was performed up to 600 °C. This thermal treatment is expected first to crystallize ZnO and second to allow a differentiation of ZnO and amorphous silica during TEM analysis. The thermal treatment has been conducted under argon in order to preclude any further oxidation of SiC. Fig. 6 shows the XRD patterns of the crude product at rt and after heating up to 200 °C, 400 °C and 600 °C.

It appears from Fig. 6 that (i) the crude sample contained a ZnO phase and (ii) the thermal treatment induced a progressive crystallization of that ZnO phase. Indeed besides peaks featuring the reflections of cubic SiC (labeled (*)), Fig. 6 shows the peaks corresponding to the hexagonal phase of ZnO (indexed in Fig. 6). Fig. 7 shows the SEM image of the product after heating up to 600 °C.

SEM investigation indicates that the product is made of interlaced nanostructures. However, the presence of traces of agglomerated nanoparticles embedded into the 3D network indicates that the process has to be optimized. Residual gel may have been trapped into the network and gave free agglomerated nanoparticles upon heating.

The 1D nanostructures obtained at 600 °C were analyzed by (HR)TEM (Fig. 8).

These HRTEM images clearly show two main components in the resulting nanostructure: a SiC core and ZnO nanocrystals. The latter are randomly stick around the nanowires. The average size of the well-crystallized ZnO nanoparticles has been estimated as less than 5 nm. These nanocrystals seem to be embedded into an amorphous phase. The SiO_2 layer, originally observed around the SiC nanowires (Fig. 4) before the impregnation, cannot be clearly distinguished from this amorphous phase.

4. Conclusion

As we found, impregnation of cotton-like solid made of interlaced SiC@SiO_2 nanocables into a ZnO sol yielded, after thermal treatment up to 600 °C under argon, SiC@SiO_2@ZnO nanostructures. These novel nanostructures consist in SiC@SiO_2 nanocables decorated by numerous agglomerated ZnO nanoparticles. The latter are less than 5 nm in diameter. This result is to our knowledge the first example of a physical templating technique involving SiC-based nanowires. Moreover, we have obtained localized ZnO nanoparticles. This localization can be of interests for a further study of their physical properties. When a similar experiment was conducted with pure SiC nanowires, there was no interaction between the NWs and the solution, resulting in the formation of agglomerated ZnO NPs embedded into the 3D NWs network. Further works will be devoted to the investigations of the optical properties of the SiC@SiO_2@ZnO nanostructures, and to the development of the physical templating method for preparation of other innovative 1D nanostructures.

References

1. Yang, P., Yan, H., Mao, S., Russo, R., Johnson, J., Saykally, R. *et al.*, Controlled growth of ZnO nanowires and their optical properties. *Adv. Funct. Mater.*, 2002, **12**(5), 323–331.
2. Yi, G.-C., Wang, C. and Park, W. I. I., ZnO nanorods: synthesis, characterization and applications. *Semicond. Sci. Technol.*, 2005, **20**, S22–S34.
3. Cao, H., Xu, J. Y., Zhang, D. Z., Chang, S. H., Ho, S. T., Seelig, E. W. *et al.*, Spatial confinement of laser light in active random media. *Phys. Rev. Lett.*, 2000, **84**(24), 5584–5587.
4. Fujitani, T. and Nakamura, J., The effect of ZnO in methanol synthesis catalysts on Cu dispersion and the specific activity. *Catal. Lett.*, 1998, **56**, 119–124.
5. Tien, L. C., Sadik, P. W., Norton, D. P., Voss, L. F., Pearton, S. J., Wang, H. T. *et al.*, Hydrogen sensing at room temperature with Pt-coated ZnO thin films and nanorods. *Appl. Phys. Lett.*, 2005, **87**, 222106–222109.
6. Xiao, Y., Li, L., Li, Y., Fang, M. and Zhang, L., Synthesis of mesoporous ZnO nanowires through a simple in situ precipitation method. *Nanotechnology*, 2005, **16**, 671–674.
7. Leprince-Wanga, Y., Wangb, G. Y., Zhang, X. Z. and Yu, D. P., Study on the microstructure and growth mechanism of electrochemical deposited ZnO nanowires. *J. Cryst. Growth*, 2006, **287**, 89–93.
8. Meulenkamp, E. A., Synthesis and Growth of ZnO Nanoparticles. *J. Phys. Chem. B*, 1998, **102**, 5566–5572.
9. Wu, G. S., Xie, T., Yuan, X. Y., Li, Y., Yang, L., Xia, Y. H. *et al.*, Controlled synthesis of ZnO nanowires or nanotubes via sol–gel template process. *Solid State Commun.*, 2005, **134**, 485–489.
10. Koch, U., Fojtik, A., Weller, H. and Henglein, A., Photochemistry of semiconductor colloids: preparation of extremely small ZnO particles, fluorescence phenomena and size quantization effects. *Chem. Phys. Lett.*, 1985, **122**(5), 507–510.
11. Bechelany, M., Cornu, D., and Miele, P., Procédé de croissance de nanofils β-SiC ou de α-Si_3N_4, éventuellement enrobés. International Patent No. PCT/FR 2005003145, December 21, 2004.
12. Bechelany, M., Cornu, D., Chassagneux, F., Bernard, S. and Miele, P., Chemical surface transformation of SiC-based nanocables. *J. Optoelectron. Adv. M.*, 2006, **8**, 638–642.
13. Xiong, Y., Mayers, B. T. and Xia, Y., Some Recent development ion the chemical synthesis of inorganic nanotubes. *Chem. Commun.*, 2005, 5013–5022.
14. Spanhel, L. and Anderson, M. A., Semiconductor clusters in the sol–gel process: quantized aggregation, gelation, and crystal growth in concentrated ZnO colloids. *J. Am. Chem. Soc.*, 1991, **113**, 2826–2833.