JOURNAL OF Materials CHEMISTRY

Catalytic growth of very long composite nanofibres containing Co (or Fe, Ni), SrO and trace carbon

Z. Y. Zhong,[a] K. Y. Lim,[a] H. C. Soon,[a] B. H. Liu,[b] H. Xu,[a] J. Ding,[b] J. Lin*[a] and K. L. Tan[a]

[a]*Department of Physics, Surface Science Laboratory, National University of Singapore, 10 Kent Ridge Crescent, Singapore 117542. E-mail: phylinjy@nus.edu.sg*
[b]*Department of Materials Science, Faculty of Science, National University of Singapore, Singapore 119260*

Received 26th November 2001, Accepted 16th April 2002
First published as an Advance Article on the web 27th May 2002

We demonstrate in this study that nanofibres containing Co (or Fe, Ni), SrO and trace carbon can be synthesized *via* a catalytic process using CH_4 or C_2H_4 as the reaction gas. The synthesized nanofibres are 50–200 nm in diameter and 1–15 μm in length. The length of the fibres can be controlled *via* a change of the reaction temperature. The formation mechanism is likely to be a two-step process combining catalytic decomposition of a carbon-containing gas and a sequential self-assembly process of growth into nanofibres.

Introduction

In recent years, intensive research efforts have been focused on one-dimensional nanostructures that may have extensive applications in industry and fundamental research due to their unique optical, electronic, and mechanical properties.[1] A variety of techniques and methods have been applied to the synthesis of these one-dimensional micro- or nanostructures, including laser ablation,[2,3] sol–gel method,[4] arc-discharge,[5,6] chemical vapor-phase transport and/or reaction,[7–10] soft lithography,[11,12] template[13–16] and solution-phase reaction and crystallization.[17] The synthesized materials range from III-V semiconductors,[17,11,12] nanotubes of carbon,[18] anatase TiO_2,[16] WS_2,[10] and metals,[13,14] oxides,[4] carbides[19] and nitrides.[20,21] Three geometrical morphologies have been observed for these one-dimensional structures, namely hollow nanotubes, solid nanofibres with a cylindrical symmetric cross section, or nanobelts with a rectangular cross section.[8]

It is expected that the properties of the synthesized one-dimensional structures can be improved through doping,[22] coating[23,24] other elements in/on the nanostructures, or formation of the composite materials during their synthesis.[5] One of the challenges lies in adjusting the composition of the synthesized materials while keeping its one-dimensional structure.

Recently in several reports,[7–9] the controlled thermal evaporation process with the assistance of the metal catalysts has proved to be an efficient approach in the synthesis of one-dimensional semiconducting oxides. Since the thermal evaporation processes are usually conducted at very high temperatures and in the presence of an inert gas (Ar gas), it is suggested that the processes follow the Vapor–Liquid–Solid (VLS)[7,9] or Vapor–Solid[8] mechanism. Here we report our new finding that nanofibres containing Co (or Fe, Ni), SrO and trace carbon can be formed by catalytic decomposition of CH_4 or C_2H_4 gas. The main difference between the present work and previous studies is the formation of a composite one-dimensional structure that could not be yielded directly in previous studies. In addition, the catalytic growth method can be easily scaled up for the large-scale production of such nanofibres. We believe this study is just a beginning and the method could be extended to other systems for the production of one-dimensional structure with various compositions.

On the other hand, it seems unlikely that the formation of the nanofibres follows the reported VLS mechanism because the formation process proceeded at relatively low temperatures. We suggest the decomposition of the reaction gases and the sequential deposition of carbon induced the formation of the nanofibres with the assistance of the catalytic action of the metals.

Experimental section

Materials

$Sr(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and citric acid were obtained from Aldrich and were used as received.

The preparation of catalysts and synthesis of the nanofibres followed closely the procedures that have been described in our previous report.[25] Typically a molar ratio of Co (or Fe, Ni) : Sr = 3 : 1 was selected. The mixture of the Co (or Fe, Ni) and Sr nitrates and citric acid was dissolved in distilled water and the aqueous solution was heated at 60–70 °C to get a viscous fluid through a sol–gel process. The gelled fluid was further treated at 200 °C for 1 h, 400 °C for 1 h, and 700 °C for 5 h, respectively, in air. The reduction of the catalyst in hydrogen gas and the sequential catalytic decomposition of CH_4 or C_2H_4 were carried out in a horizontal quartz tubular reactor at defined temperatures. For comparison, three reaction temperatures of 600, 700 and 800 °C were selected. The flow rate of the reaction gas was 30 ml min^{-1}.

The microstructure and morphology of the catalysts as well as the carbon-deposited catalysts were observed employing a JEM-100CX transmission electron microscope (TEM) at a high voltage of 100 KV, and a XL-FEG scanning electron microscope (SEM). The composition of the deposited samples in a micro-region was obtained using energy-dispersive X-ray spectroscopy (EDX) on the SEM. The X-ray diffraction (XRD) measurements were conducted on a Bruker D8 Advance diffractometer with Cu radiation. The magnetic measurements were carried out on a superconducting vibration sample magnetometer (Oxford Instruments) where the samples were shaped into small pellets before the measurement.

Results and discussion

It is found that the formation of the nanofibres with carbon deposition depends on the reaction temperature. Fig. 1A shows

DOI: 10.1039/b110816f

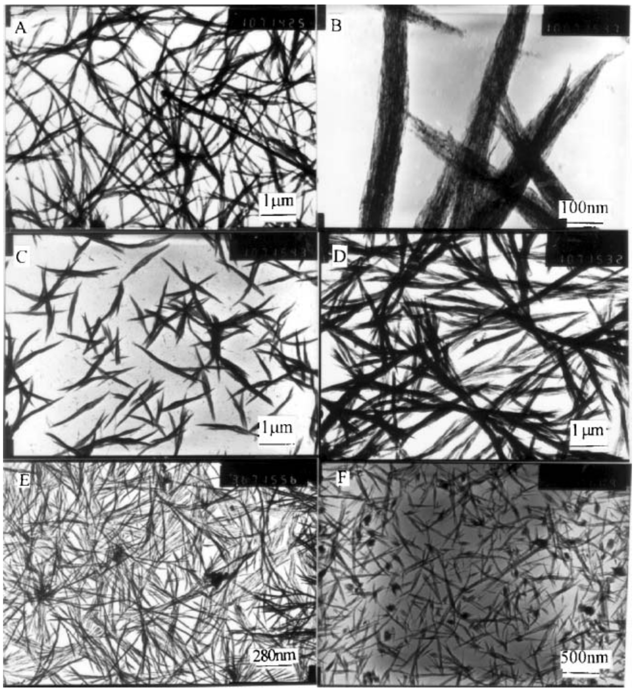

Fig. 1 Typical TEM images of the synthesized nanofibres from the decomposition of CH_4 (A) over catalyst Co/SrO (molar ratio Co : Sr = 3 : 1) at 700 °C for 1 h and imaged at low magnification; (B) at medium magnification of (A); (C) at 600 °C for 1 h and (D) 800 °C for 1 h; (E) Ni/SrO (3 : 1) and (F) Fe/SrO (3 : 1), both exposed to methane at 700 °C for 1 h.

a typical TEM image of the synthesized nanofibres using the 3 : 1 Co/SrO catalyst that has been exposed to CH_4gas at 700 °C for 1 h. All of the fibres have diameters between 50–100 nm and lengths between 3–10 µm. In this sample, few particles with diameter *ca.* 100 nm were observed, and almost all of the reaction products under TEM observation were nanofibres. It is evaluated that the fibre content in the as-deposited sample is higher than 90 vol%. From Fig. 1A we can see some dendritic structures indicating that the nanofibres are grown out from the catalyst particles.

Fig. 1B is a magnified image of Fig. 1A. It seems that the big fibres are composed of finer fibres with some black particles distributed among them. At lower reaction temperatures, such as 600 °C, shorter fibres with lengths of 1–3 µm and diameters of 80–150 nm (Fig. 1C) were obtained. In this sample, we observed more rounded particles (which were attributed to the catalyst particles) than those prepared at 700 °C (Fig. 1A). It can be deduced that the reaction at 600 °C is not sufficient to complete the growth process of the fibres from the catalyst particles. Hence, the low-temperature product contains more rounded catalyst particles and shorter fibres. In the sample prepared at 700 °C, the content of the fibres increased remarkably compared to the sample reacted at 600 °C. Further increase of the reaction temperature to 800 °C resulted in the fibres growing to 7–15 µm in length (Fig. 1D). Hence, the growth of the fibres is a temperature-dependent process. The higher the temperature is, the longer the fibres are. When the temperature is lower than 600 °C, almost no fibres can be formed. This temperature is close to the limitation temperature at which methane can be decomposed. As will be discussed later, the presence of carbon in the sample is important to the self-assembled growth of the fibres.

The influence of the molar ratio between Co and Sr on the formation of the fibres has also been studied. When the molar ratio between Co and Sr is less than 1 : 2, the reaction products consist of round catalyst particles with some fibres but no carbon nanotubes. This is different from the case using MgO as the catalyst support where carbon nanotubes were obtained.[25,26] With an increase of Co loading, more and more fibres were observed. As the molar ratio of Co : Sr increased up to 3 : 1, almost only nanofibres were observed in the reaction product. It is reasonable to deduce that the fibres contain metallic Co, especially those fibres produced from the catalysts with higher Co loadings.

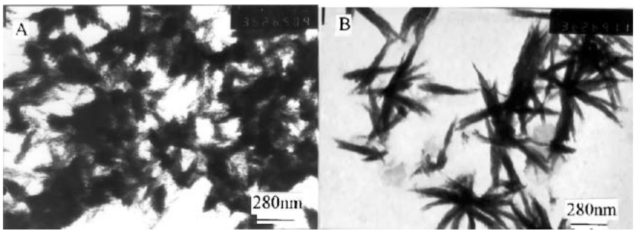

Fig. 2 TEM images of the Co/SrO 3 : 1 catalyst exposed to (A) CO and (B) C_2H_4 at 700 °C for 1 h.

Similar results were observed when Fe or Ni substituted Co in the catalysts. In the products of methane decomposition on these catalysts at 700 °C some nanofibres of thinner diameter (Fig. 1E) and shorter in length can be obtained (Fig. 1F), respectively.

It should also be noted that the presence of citric acid is essential for the growth of nanofibres. Experiments done without citric acid were unable to yield the nanofibres as upon drying during the sol–gel process, recrystallization of the initial reactants, instead of the formation of a gelled liquid, took place.

Reaction gases also play an important role in the formation of the nanofibres. Employing CO as the reaction gas at 700 °C failed to produce any long nanofibres. As shown in Fig. 2A only fine particles are observed. When C_2H_4 was decomposed over the 3 : 1 Co/Sr catalyst at 700 °C, short fibres were also found in the product (Fig. 2B), though the content of the fibres was much lower than that using CH_4 gas.

To determine what the active component in the catalysts for the formation of the fibres is, several samples derived from various catalysts were studied by TEM measurements. The first sample was pure strontium oxide that had been subjected to heating in air, reduction in H_2 and treatment with methane gas at 700 °C; the second and the third samples were the 3 : 1 Co/Sr catalyst heated in air at 700 °C for 5 h then followed with/without a reduction treatment at 700 °C in hydrogen, respectively, but without CH_4/CO decomposition. TEM observation indicated that there are no long nanofibres in these samples and their morphologies are very similar to the sample shown in Fig. 2A, indicating that the formation of nanofibres is a synergetic behavior of the metal active components and the decomposition of carbon-containing gases.

Fig. 3 shows the SEM image of the same sample depicted in Fig. 1A. A large quantity of wirelike nanostructures is revealed. Each nanostructure has a sharp tip, as observed in TEM measurements. Moreover, almost no big round particles can be found, indicating the effectiveness of the synthesis method in the production of one-dimensional structures.

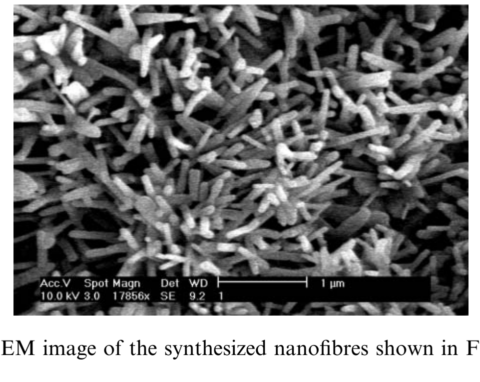

Fig. 3 SEM image of the synthesized nanofibres shown in Fig. 1(A).

However, all the synthesized nanostructures are not stable in air. After being exposed to air for two months, almost 90% of the fibres collapsed into big pieces as a result of the TEM observation. In addition, all these nanofibres can be dissolved in nitric acid solution.

The composition of the nanofibres was determined by EDX microanalysis. Interestingly, it was found that the carbon deposit is only *ca.* 5.0 wt% in the sample prepared by exposing the 3 : 1 Co/Sr catalyst to methane at 700 °C for 1 h. This result is coincident with the carbon content calculated from the weight change of the above catalyst before and after the reaction, in which a weight loss of about 30 mg after reaction was obtained when an initial weight of 200 mg catalyst was used. The calculated carbon deposit was about 4.3 wt% presuming all Co_3O_4 in the initial catalyst was reduced to Co after the reaction and the weight increase was due to the carbon deposition. Fig. 4 shows the XRD patterns for the 3 : 1 Co/Sr catalysts before and after the reaction. It is seen that the catalyst heated in air at 700 °C is composed of Co_3O_4 (as labeled by open circles) and strontium oxide (no label), and no binary oxide of Co and Sr is formed. The H_2-reduced and the CH_4-treated samples exhibit strong metallic cobalt diffractions (as labeled by *). The carbon diffraction peak is very weak ($2\theta = 26°$) and can almost go unnoticed. Therefore, it can be concluded that the synthesized nanofibres are mainly composed of metal Co, SrO and trace carbon.

The formation of the nanofibres is a complicated process. Since the reaction temperature in our study is far below the melting points of the strontium oxide[27] and the metals Co, Fe and Ni, it is unlikely that the above substances will undergo an evaporation and condensation process if a VLS[7,9] or a vapor–solid[8] mechanism is followed. It has been reported that Ni or its alloy can form a quasi-liquid state near 1000 K due to the size effect of the metal at the nanometer scale and the interfacial effect between nanocarbon and nanometal.[28] However, in our case, as the metal loading is very high, the metal particles are big in size, ranging in the order of a few hundred nanometers, as confirmed by TEM observations. This can be evidenced from the low carbon deposit after being exposed to methane. Recently Remskar *et al* reported that C_{60} could promote a powder of WS_2 to self-assemble into WS_2 nanotubes.[29] It is likely that the decomposition of carbon-containing gases such as CH_4 and C_2H_4 and the deposition of the carbon occur on the active metals and, successively, the deposited carbon can promote the growth of the nanofibres. The metal active components and the deposited carbon play their own roles in two sequential catalytic steps, namely the carbon deposition and the fibre growth. The self-assembled nanofibres should thus be a stable state under the reaction conditions.

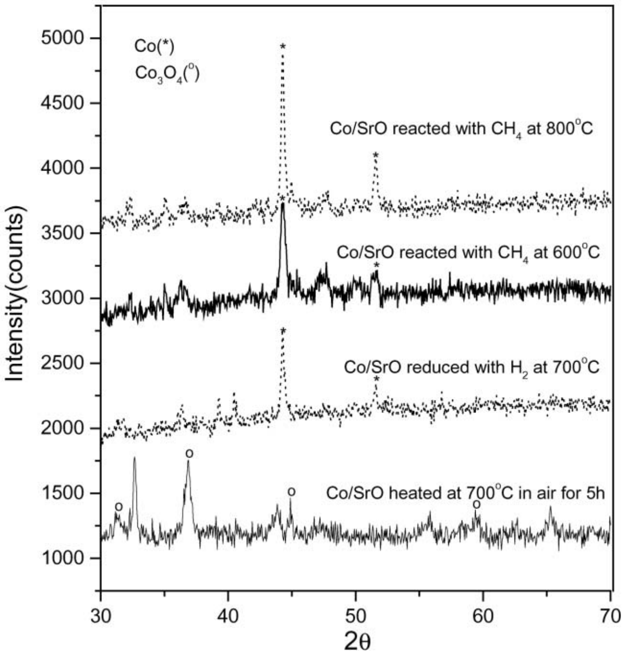

Fig. 4 XRD patterns for the catalyst Co/SrO (molar ratio Co : Sr = 3 : 1) (A) heated at 750 °C for 5 h in air and (B) reduced at 700 °C for 1 h in H_2, and for the composite fibres formed from the following reaction with CH_4 at 600 °C (C) and 800 °C (D), respectively, for 1 h.

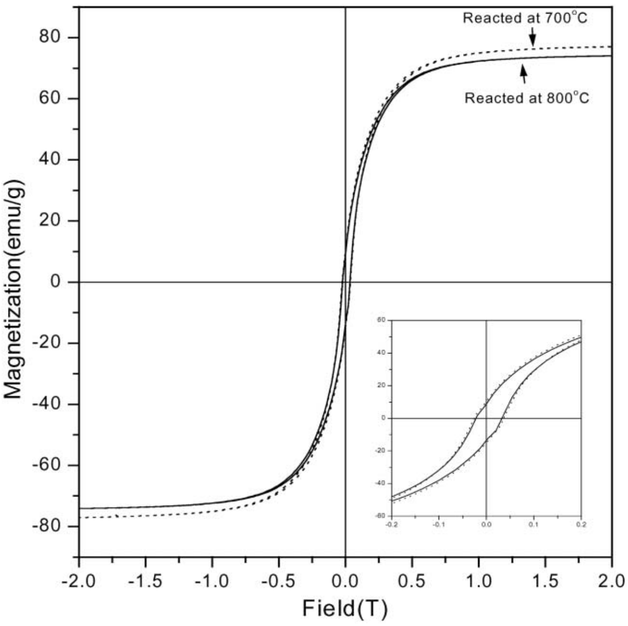

Fig. 5 Magnetic curves for the composite fibres formed by exposing the 3 : 1 Co/SrO catalyst to CH_4 gas at 700 and 800 °C, respectively. With CH_4 at 700 °C and 800 °C respectively.

The Co (or Fe, Ni)-containing nanofibres should be good magnetic materials. In fact magnetic measurements show that the formed nanofibres are paramagnetic materials with a low coercive force (Fig. 5). The magnetic curves of the two samples obtained from the methane treated 3 : 1 Co/Sr catalysts at 700 and 800 °C, respectively, are very similar, indicating that differences in size and distribution of the Co particles between the two nanofibres samples are very small. We believe these Co (or Fe, Ni)-containing nanofibres will have potential applications in magnetic and/or electronic industry. The above process can also be extended to the fabrication of one-dimensional nanostructures for other systems with various compositions.

Conclusions

A novel approach to the synthesis of nanofibres containing Co (or Fe, Ni) and trace carbon has been reported. The catalysts are Co or Fe, or Ni supported on SrO, and the reaction gases are CH_4 or C_2H_4. Increasing the loadings of Co or the reaction temperatures can lead to an increase in the content of the nanofibres in the products. Also, the length of the nanofibres increases with the reaction temperature. If the reaction temperature is lower than 600 °C or the loading of Co is less than 30 mol%, no nanofibres can be formed. The formation mechanism of the nanofibres is likely to be a self-assembly process promoted by the deposited carbon.

Acknowledgement

The financial support (GR6773) from National Science and Technology Board of Singapore is gratefully acknowledged.

References

1 Y. Huang, X. Duan, Q. Wei and C. M. Lieber, *Science*, 2001, **291**, 630.
2 A. M. Morales and C. M. Lieber, *Science*, 1998, **279**, 208.
3 X. Duan and C. M. Lieber, *Adv. Mater.*, 2000, **12**, 298.
4 G. Kordas, *J. Mater. Chem.*, 2000, **10**, 1157.
5 F. Okuyama and I. Ogasawara, *Appl. Phys. Lett.*, 1997, **71**, 623.
6 Y. C. Choi, W. S. Kim, Y. S. Park, S. M. Lee, D. J. Bae, Y. H. Lee, G. S. Park, W. B. Choi, N. S. Lee and J. M. Kim, *Adv. Mater.*, 2000, **12**, 746.
7 C. Liang, G. Meng, Y. Lei, F. Philipp and L. Zhang, *Adv. Mater.*, 2001, **13**, 1330.
8 Z. W. Pan, Z. R. Dai and Z. L. Wang, *Science*, 2001, **291**, 1947.
9 M. H. Huang, Y. Wu, N. T. Feick, E. Weber and P. Yang, *Adv. Mater.*, 2000, **13**, 113.
10 A. Rothschild, R. Popovitz, O. R. Lourie and R. Tenne, *J. Phys. Chem. B*, 2000, **104**, 8976.
11 Y. Yin, B. Gates and Y. Xia, *Adv. Mater.*, 2000, **12**, 1426.
12 B. Messer, J. H. Song and P. Yang, *J. Am. Chem. Soc.*, 2000, **122**, 10232.
13 J. A. Barnard, H. Fujiwara, V. R. Inturi, J. D. Jarrata and T. W. Scharf, *Appl. Phys. Lett.*, 1996, **69**, 2758.
14 S. Yang, H. Zhu, D. Yu, Z. Jin, S. Tang and Y. Du, *J. Magn. Magn. Mater.*, 2000, **22**, 97.
15 D. Xu, D. Chen, Y. Xu, X. Shi, G. Guo, L. Gui and Y. Tang, *Pure Appl. Chem.*, 2000, **72**, 127.
16 H. Imai, Y. Takei, K. Shimizu, M. Matsuda and H. Hirashima, *J. Mater. Chem.*, 1999, **9**, 2971.
17 T. J. Trentler, K. M. Hickman, S. C. Goel, A. M. Viano, P. C. Gibbons and W. E. Buhro, *Science*, 1995, **270**, 1791.
18 S. Iijima, *Nature*, 1991, **354**, 56.
19 H. Dai, E. W. Wong, Y. L. Lu, S. Fan and C. M. Lieber, *Nature*, 1995, **375**, 769.
20 W. Han, S. Fan, Q. Li and Y. Hu, *Science*, 1997, **277**, 1287.
21 X. Duan and C. M. Lieber, *J. Am. Chem. Soc.*, 2000, **122**, 188.
22 K. Hirahara, K. Suenaga, S. Bandow, H. Kato, T. Okazaki, H. Shinohara and S. Iijima, *Phys. Rev. Lett.*, 2000, **85**, 5384.
23 Y. Zhang, N. W. Franklin, R. J. Chen and H. Dai, *Chem. Phys. Lett.*, 2000, **331**, 35.
24 Z. Y. Zhong, B. Liu, L. F. Sun, J. Ding, P. Chen, J. Lin and K. L. Tan, submitted to *Chem. Phys. Lett.*
25 Z. Y. Zhong, H. Chen, S. Tang, J. Ding, J. Lin and K. L. Tan, *Chem. Phys. Lett.*, 2000, **330**, 41.
26 P. Chen, H. B.Zhang, G. D. Lin, Q. Hong and K. R. Tsai, *Carbon*, 1997, **35**, 1495.
27 S. C. Soryna, *Handbook of Stable Strontium*, Plenum Press, New York, 1981, p. 11.
28 Y. Li, J. Chen, Y. Ma, J. Zhao, Y. Qin and L. Chang, *Chem. Commun.*, 1999, 1141.
29 M. Remskar, A. Mrzel, Z. Skraba, A. Jesih, M. Ceh, J. Demšar, P. Stadelmann, F. Lévy and D. Mihailovic, *Science*, 2001, **292**, 479.