Cu nanostructures formed via redox reaction of Zn nanowire and Cu^{2+} containing solutions

Quan Li [*], Chunrui Wang

Department of Physics, The Chinese University of Hong Kong, Shatin, New Territory, Hong Kong, China

Received 27 March 2003; in final form 12 May 2003

Abstract

A series of redox reactions were performed using Zn nanowire and Cu^{2+} containing solutions with different concentration. Various Cu containing nanostructures resulted from the solution reaction, including Cu particle decorated ZnO nanotube, Cu particle chain and uniform single crystalline Cu nanorods. Transmission electron microscope equipped with energy dispersive X-ray spectrometer and energy filtering system was used to investigate the morphology and the chemical composition of the resulting nanostructures. The experimental data strongly suggested that the redox reaction occurred both at the Zn nanowire broken surface and its oxide sheath surface. Possible formation mechanisms of these nanostructures were discussed.
© 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years, great attention has been focused on the synthesis of low-dimensional nanostructures because their size and geometrical configuration lead to intriguing electronic, optical, and catalytical properties [1–3]. Various types nanostructures have been successfully fabricated using chemical and physical methods. Among them, template [4–15] is one of the most popularly employed techniques due to its simplicity and easy control in achieving different nanostructures. Commonly used template materials include carbon nanotubes [4–6], porous silica and alumina [7–10], block copolymer [11,12], DNA [13], and various membranes [14,15]. Nanowires [16], mesoporous structures [17] and other nanostructured networks [18] can be obtained by choosing different template material types or geometrical configurations. It was recently discovered that the surface of certain synthesized nanowires/tubes might induce chemical redox reaction. Sun et al. [19,20] found out that silver and copper ions could be reduced from the solution by hydrogen-passivated silicon nanowire surface; Choi et al. [21] reported the spontaneous reduction of metal ions on the sidewalls of carbon nanotubes. Other than serving as the reducing agent in the chemical reaction, these nanowires/tubes may act as template materials at the same time, which control the final morphology of the

---

* Corresponding author. Fax: +852-2603-5204.
  E-mail address: liquan@phy.cuhk.edu.hk (Q. Li).

reduced materials and lead to interesting nano-structures [19,20].

In this Letter, we demonstrate that various Cu nanostructures including particle, particle chain, and nanorod can be achieved via a solution redox reaction using Zn nanowire as the reducing agent. The morphologies of the Cu nanostructures are sensitive to the concentration of the Cu^{2+} containing solutions and copper ion stability. The reduction process of Cu^{2+} by the Zn nanowire is discussed based on the morphology of the reduced Cu and ZnO sheath (originally covered Zn nanowire) left in the solution.

2. Experimental

Zn nanowires were fabricated via a thermal reduction route using ZnS as the starting materials and hydrogen as the reducing agent. The resulting Zn nanowire has a coaxial Zn/ZnO nanocable configuration, i.e., with a metallic Zn core and a thin epitaxial ZnO sheath [22]. Two different Cu^{2+} containing solution: $CuSO_4$ and $[Cu(NH_3)_4]^{2+}$ with different concentrations were chosen as the copper providing material. Zn nanowires were first dispersed into methanol (0.05 g in 10 ml methanol) by ultrasonic method. The Zn nanowire containing solution was then dropped into the Cu^{2+} solution, which was vigorously stirred at room temperature. Detailed experimental conditions are listed in Table 1. A control experiment was performed using commercial Zn powder (Goodfellow +99%) and the $[Cu(NH_3)_4]^{2+}$ solution. The products from the solution reaction were then collected using carbon film on gold grid (Ted Pella, Inc.). A Philips CM 120 (operated at 120 kV) equipped with energy dispersive X-ray spectrometer (Oxford

Instrument) and a Tecnai 20ST (FEG, 200 kV) equipped with image filtering system (Gatan GIF) were used to investigate the chemical composition and the morphology of the solution reaction products.

3. Results and discussion

All the reactions complete within minutes. The reaction of Zn nanowire and 0.5 M $CuSO_4$ solution (Sample C001) results in large dark brown-reddish particles (dissipates visible to the eye), which are proved to be Cu by energy dispersive X-ray (EDX) performed by focusing the electron beam on the Cu particle (Fig. 1). The Au peak comes from the gold grid supporting the carbon film. These particles are in the order of hundreds of nanometers or larger in size. ZnO nanotubes are also found in the solution. Fig. 2a shows a low-magnification bright field TEM image of such nanotubes, compared to that of the unreacted Zn nanowire with a thin oxide layer (Fig. 2b) [22]. The dark/light/dark contrast along the tube redial direction is due to the mass-thickness contrast of the tubular configuration [22]. A selected area diffraction (SAD) pattern in the inset of Fig. 2a shows that the smeared diffraction spots form ring-like patterns, which can be indexed to ZnO (0 0 2), $(\bar{2}\,1\,0)$, $(\bar{2}\,1\,2)$ diffractions, respectively. Although most of the ZnO nanotube left in the solution are usually shorter and with two ends broken compared to the original Zn nanowire, its tubular structure appears to be intact. The surface of ZnO nanotube is relatively clean, only small amount of Cu particles are found to stick on it.

The result of sample (C002) is similar to that of sample (C001). Cu particles result from the solu-

Table 1
Parameters of the solution reaction using Zn nanowire and Cu^{2+}

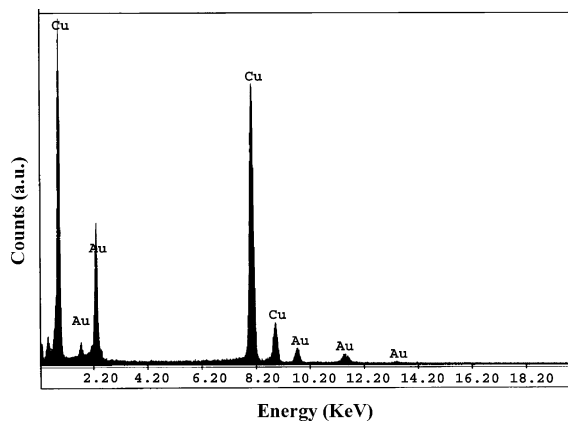|	Zn nanowires	Cu^{2+} containing solution	
C001	Zn nanowires dispersed in methanol (0.05 g in 10 ml)	$CuSO_4$	0.5 M
C002		$CuSO_4$	0.1 M
C003		$CuSO_4$	0.01 M
C004		$[Cu(NH_3)_4]^{2+}$	0.1 M
C005	Zn powder dispersed in methanol (0.05 g in 10 ml)	$[Cu(NH_3)_4]^{2+}$	0.1 M

Fig. 1. EDX spectrum of the Cu nanostructures obtained from the solution redox reaction.

tion reaction. Nevertheless, the size of the Cu particle is much smaller, usually in the range of several tens of nanometers (Fig. 3a). These Cu particles are found to either stick to the surface of ZnO nanotube or agglomerate into small groups in the solution (detached from the ZnO nanotube), which are marked by arrows in Fig. 3a. A SAD pattern taken from the same nanotube is shown in Fig. 3b. The ring-like pattern can be indexed to ZnO (0 0 2) and Cu (1 1 1), (2 0 0), (2 2 0) diffractions, respectively. A high-resolution TEM image of a typical Cu particle is shown in Fig. 3c, confirming the crystalline nature of these Cu particles. Figs. 3d–f show a bright field TEM image of another particle-wrapped nanotube and its corresponding energy loss maps [using Cu L edge at 931 eV (Fig. 3e), and Zn L edge at 1020 eV (Fig. 3f)], which further confirm its chemical composition and give a clear picture of the spatial distribution of the Cu particles on such nanotube.

Another interesting feature found in sample C002 is Cu particle chain (Fig. 4). The particle chain consists of several large Cu particles (in the range of 150 nm). The size of these particles is not uniform. The chemical composition of them are confirmed by EDX.

The Cu particles obtained from sample C003 are even smaller (in the range of 20 nm or less) than those from C002. Again, they were found to attach to the ZnO nanotube surface as well as in the solution.
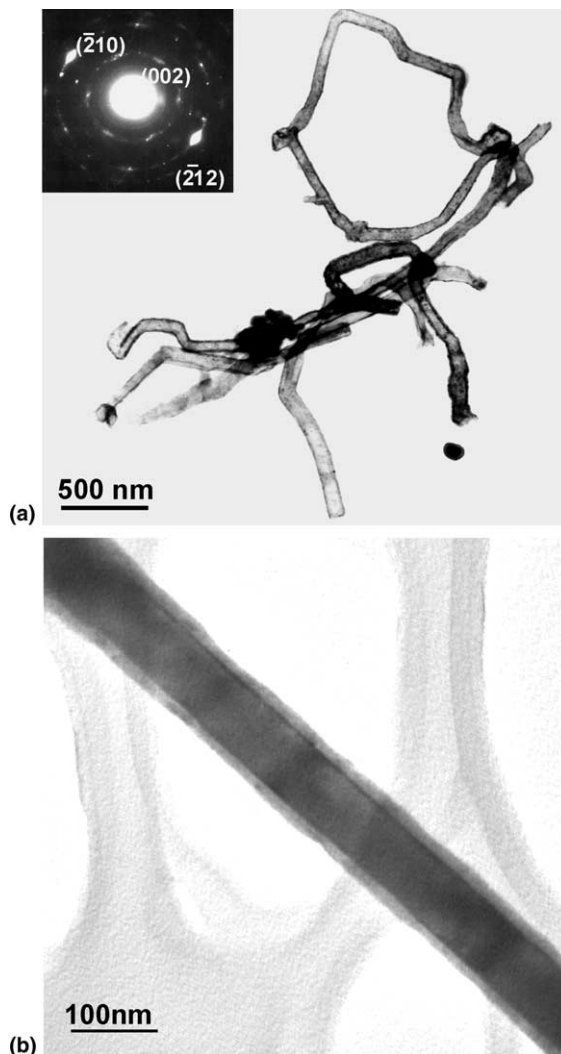

Fig. 2. (a) TEM image of the Zn nanowires after the redox reaction, showing hollow nanotube configuration. The SAD pattern in the inset corresponds to the ZnO (0 0 2), ($\bar{2}$ 1 0), ($\bar{2}$ 1 2) diffractions, respectively; (b) TEM image of unreacted Zn nanowire.

The products from sample C004 (Zn nanowire reaction with $[Cu(NH_3)_4]^{2+}$) appear to be quite different from the previous three samples. There is no obvious precipitate resulting from the solution reaction. Although the observation of the ZnO nanotube is consistent with the three previous samples, the surface of these ZnO nanotube appears to be clean, very small amount of Cu
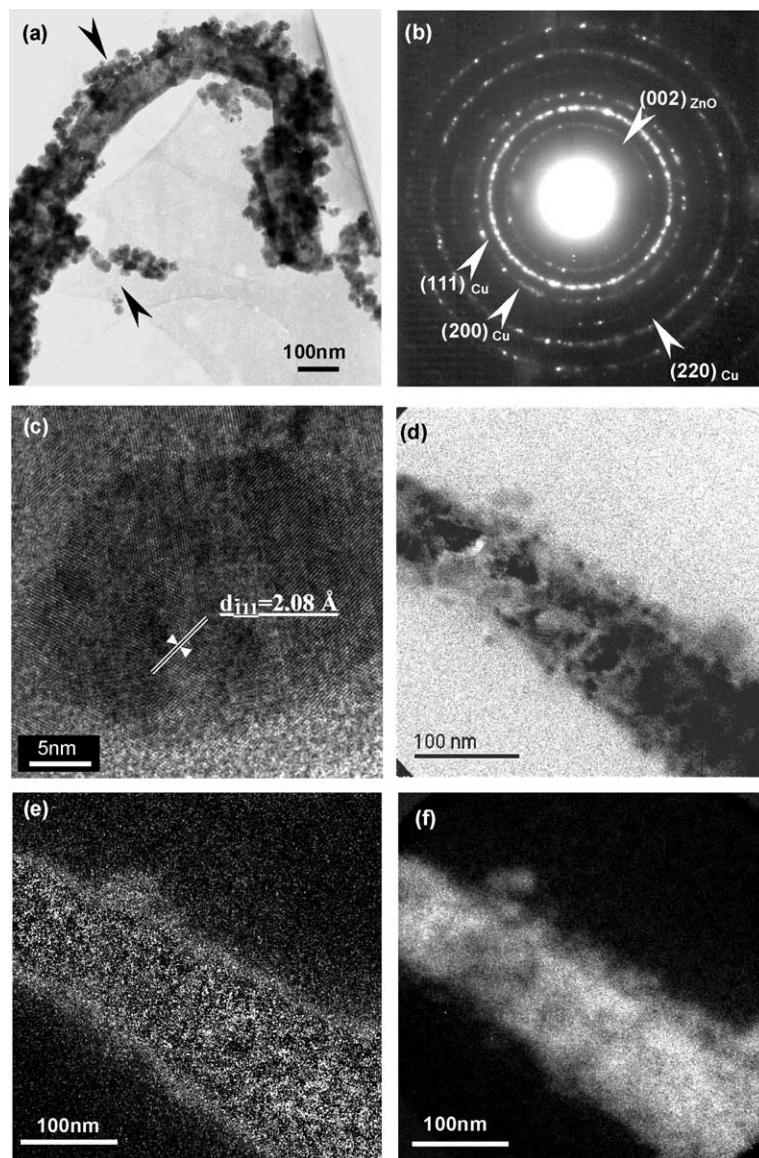
Fig. 3. (a) TEM image of Cu nanoparticles either sticking to a ZnO nanotube, or dispersed on the carbon film (detached from the ZnO tube); (b) SAD pattern taken from the Cu particle decorated ZnO nanotube in (a); (c) high-resolution image of a typical Cu particle reduced from the solution reaction, revealing its crystalline nature; (d) bright field TEM image of another Cu particle decorated ZnO nanotube; (e) the corresponding energy loss map of (d) using the Zn L edge at 1020 eV; (f) the corresponding energy loss map of (d) using the Cu L edge at 931 eV.

particles are found to stick to the ZnO tube surface. The morphology of the reduced Cu is shown in Fig. 5. Cu nanorods are normally ~50 nm in diameter and ~500 nm in length. The nanorods are uniform in size. Very small amount of Cu particles are also found in the solution (marked by arrows in the Fig. 5). A SAD pattern taken from single nanorod is shown in the inset of Fig. 5, which can be indexed to the Cu $\langle 100 \rangle$ zone axis. This indicates the single crystallinity of the nanorods.
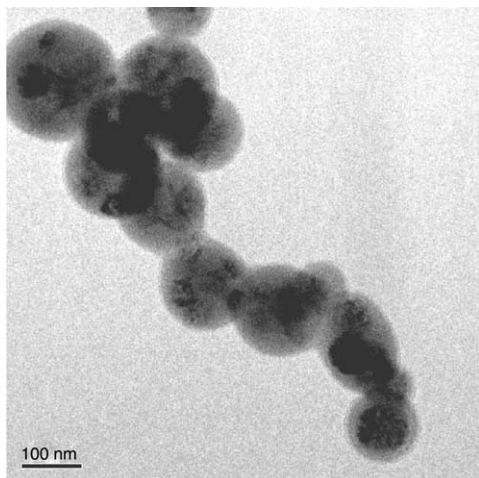
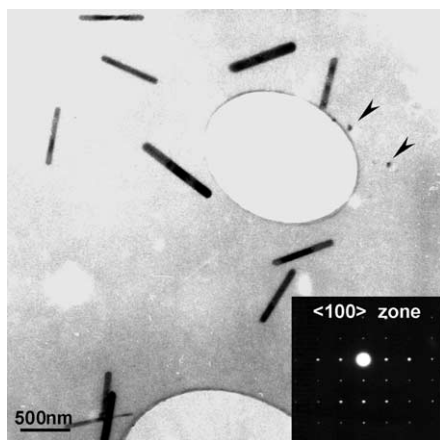Fig. 4. TEM image of Cu particle chain.

Fig. 5. TEM image of uniform Cu nanorods dispersed on carbon film (from sample C004). The diffraction pattern in the inset can be indexed to the Cu (1 0 0) zone axis.

Only non-uniform (in the range of tens of nanometers) Cu particles are observed in sample C005, where commercial Zn powder is used as the reducing agent.

The solution reaction in achieving the above Cu nanostructures utilizes simple redox chemistry

$$Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$$
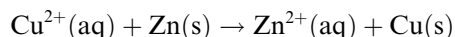
The reaction associates with an electrochemical potential E^0 of 1.0068 V [23], which indicates that

such reaction will take place in the positive direction. Reactions of regular copper salts (CuSO$_4$ in the current study, reaction with CuCl$_2$ was also investigated and similar results were obtained) with the Zn nanowires lead to mostly large sized Cu structures without much control over the copper morphology (nanoparticles, particle chains, and nanowires are obtained within the same solution reaction). Decreasing the concentration of the Cu^{2+} solution leads to smaller size of the Cu nanostructures. This observation may be explained by facts that metal ion concentration affects the redox reaction kinetics and small metal clusters diffuse and aggregate to form larger structure networks upon reduction from metal ions [24–27]. Changing the Cu ion to a more stable form, i.e., $[Cu(NH_3)_4]^{2+}$ ligand leads a completely different Cu nanostructure – uniform Cu nanorod with fine size. The stability difference in Cu^{2+} may result in different solution reaction kinetics, and thus a different Cu nanostructure [28]. The $[Cu(NH_3)_4]^{2+}$ ligand configuration may be important in achieving the specific Cu nanostructure. Nevertheless, it is not clear whether such a configuration acts as the template/stabilizer for the Cu nanorods during the redox reaction.

The Zn core/ZnO sheath configuration is an important factor in achieving various Cu nanostructures, as the control experiment (using commercial Zn powder and $[Cu(NH_3)_4]^{2+}$) only result in Cu particles with a random size distribution. In the study of Cu^{2+} reacting with Zn nanowires, it was observed that most ZnO nanotubes left in the solution after the redox reaction are intact but usually shorter than the original Zn nanowire (with Zn core/ZnO sheath configuration), which suggests the reducing agent Zn is released to the Cu^{2+} solution from the broken surface of the Zn nanowire. On the other hand, large amount of Cu particles are observed to stick to the surface of the ZnO nanotube in sample C002 and C003, suggesting another possible Zn-releasing location, i.e., the surface of the ZnO sheath. The ZnO layer is normally formed by the oxidation of the metallic Zn surface [29]. Such ZnO layer is oxygen deficient, especially for area close to the Zn/ZnO interface. Zn^{2+} and electrons exist in the interstitial site of the oxide layer and a concentration gradient

(Zn_i^{2+} with 2e) is established from the Zn/ZnO interface to the outer ZnO surface [29], which acts as the driving force for the continuous redox process with Cu^{2+}. This process is analogy to the oxidation process of Zn [29].

$$[Zn_i^{2+} + 2e] + Cu^{2+}(aq) = Zn^{2+}(aq) + Cu(s)$$
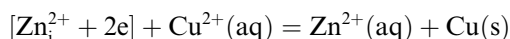
Unlike oxygen, which accepts electron at the ZnO surface and become O^{2-}, diffuses into the ZnO lattice, and forms ZnO with Zn^{2+} [28], the reduced Cu sticks to the ZnO surface. The Zn^{2+} has to leave the ZnO layer to the solution in order to keep the ZnO electrical neutral. Nevertheless, it is not possible to tell whether the Cu^{2+} can also diffuse through the ZnO and form Cu inside the ZnO tube. Larger particles may detach from the ZnO surface [19,20], which explains that little Cu particle is observed sticking to the ZnO surface in sample C001. It is observed that the surface ZnO nanotube from sample C004 is also almost free of Cu. However, it is not clear whether the nanorods naturally detach from the ZnO surface or it is due to some protective effect of the $[Cu(NH_3)_4]^{2+}$ configuration.

When large amount of Cu nanoparticles stick to the ZnO surface, they may rotate, migrate and aggregate to form large particles, which processes eventually lead to the reduction of the total surface energy [30]. This provides reasonable explanation for the formation of Cu particle chain in sample C002 (Fig. 4a), in which the ZnO nanotube may also work as a template material.

4. Conclusions

In conclusion, various Cu containing nano-structures are observed resulting from simple redox reaction using Zn nanowires and Cu^{2+} solution. The concentration and the stability of Cu^{2+} affect the reaction kinetics, which may contribute to the size distribution and the morphology of the Cu nanostructures. The experimental results suggest that the reducing agent Zn may be released from two locations, i.e., the broken cross-section of the Zn wire and the surface of the ZnO.

References

[1] M. Antonietti, C. Goltner, Angew. Chem. Int. Ed. Engl. 36 (1997) 910.
[2] M. Moffit, A. Eisenberg, Chem. Mater. 7 (1995) 1178.
[3] R.P. Andres, J.D. Bielefeld, J.I. Henderson, D.B. Janes, V.R. Kolagunta, C.P. Kubiak, W.J. Mahoney, R.J. Osifchin, Science 273 (1996) 1690.
[4] J. Sloan, D.M. Wright, H.-G. Woo, S. Bailey, G. Brown, A.P.E. York, K.S. Coleman, J.L. Hutchson, M.L.H. Green, Chem. Commun. (1999) 699.
[5] H.J. Dai, E.W. Wong, Y.Z. Lu, S.S. Fan, C.M. Lieber, Nature 375 (1995) 769.
[6] W.Q. Han, S.S. Fan, Q.Q. Li, Y.D. Hu, Science 277 (1997) 1287.
[7] Y.-J. Han, J.M. Kim, G.D. Stucky, Chem. Mater. 12 (2000) 2068.
[8] C.K. Preston, M. Moskovits, J. Phys. Chem. 97 (1993) 8495.
[9] C.R. Martin, Chem. Mater. 8 (1996) 1739.
[10] G. Che, B.B. Lakshmi, C.R. Martin, E.R. Fisher, R.S. Ruoff, Chem. Mater. 10 (1998) 260.
[11] H.J. Frisch, J.E. Mark, Chem. Mater. 8 (1996) 1735.
[12] K. Shin, K.A. Leach, J.T. Goldbach, D.H. Kim, J.Y. Jho, M. Tuominen, C.J. Hawker, T.P. Russell, Nano Lett. 2 (2002) 933.
[13] E. Braun, Y. Eichen, U. Sivan, G. Ben-Yoseph, Nature 391 (1998) 775.
[14] C.R. Martin, Science 266 (1994) 1961.
[15] R. Schöllhorn, Chem. Mater. 8 (1996) 1747.
[16] G. Sauer, G. Brehm, S. Schneider, K. Nielsch, R.B. Wehrspohn, J. Choi, H. Hofmeister, U. Gösele, J. Appl. Phys. 91 (2002) 3243.
[17] J.S. Yin, Z.L. Wang, Adv. Mater. 11 (1999) 469.
[18] J. Xiao, Y. Xie, R. Tang, M. Chen, X. Tian, Adv. Mater. 13 (2001) 1887.
[19] X.H. Sun, H.Y. Peng, Y.H. Tang, W.S. Shi, N.B. Wong, C.S. Lee, S.T. Lee, T.K. Sham, J. Appl. Phys. 89 (2001) 6396.
[20] X.H. Sun, R. Sammynaiken, S.J. Naftel, Y.H. Tang, P. Zhang, P.S. Kim, T.K. Sham, X.H. Fan, Y.F. Zhang, C.S. Lee, S.T. Lee, N.B. Wong, Y.F. Hu, K.H. Tan, Chem. Mater. 14 (2002) 2519.
[21] H.C. Choi, M. Shim, S. Bangsaruntip, H.J. Dai, J. Am. Chem. Soc. 124 (2002) 9058.
[22] J.Q. Hu, Q. Li, X.M. Meng, C.S. Lee, S.T. Lee, Chem. Mater. 15 (2002) 305.

[23] M.E. Sneed, J.L. Maynard, R.C. Brasted, Comprehensive Inorganic Chemistry, Van Nostrand, New York, 1953.

[24] P. Jena, S.N. Behera, Clusters and Nanostructured Materials, Nova Science Publisers, New York, 1996.

[25] M. Kolb, R. Botet, R. Jullien, Phys. Rev. Lett. 51 (1983) 1123.

[26] P. Meakin, Phys. Rev. Lett. 51 (1983) 1119.

[27] T.A. Witten Jr., L.M. Sander, Phys. Rev. Lett. 47 (1981) 1400.

[28] M.M. Jones, Ligand Reactivity and Catalysis, Academic Press, New York, 1968.

[29] O. Kubaschewski, B.E. Hopkins, Oxidation of Metals and Alloys, Butterworths, London, 1962.

[30] C. Kittel, H. Kroemer, Thermal Physics, W.H. Freeman, New York, 1980.