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Seed-Mediated Growth of ZnO Nanorods on Multiwalled Carbon Nanotubes

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The heterostructures of ZnO nanorods on multiwalled carbon nanotubes (MWNTs) were fabricated by a seed-mediated growth method. First, the surfaces of the carbon nanotubes (CNTs) were coated *in situ* with mono-dispersed ZnO nanocrystals of about 7 nm by the reaction of zinc acetate and sodium hydroxide. These nanocrystals were then served as the seeds for further growth of ZnO nanorods. In the second step, ZnO nanorods were grown on MWNTs coated with ZnO nanocrystals in an aqueous solution of zinc nitrate and equimolar hexamethylenetetramine at 85 °C. Typically, the ZnO nanorods had the length of 300–600 nm and the diameter of 40–140 nm and took a random direction on the outside walls of MWNTs. The morphology of the ZnO nanorods was dependent on pH, reactant concentration, and growing time.

Keywords: Carbon Nanotubes, ZnO Nanorods, Seed-Mediated Growth.

1. INTRODUCTION

Nanoscale architectures composed of various one-dimensional (1D) building blocks such as nanorods, nanowires, nanobelts and nanotubes have attracted extensive attention due to their promising prospects in future electronics and optoelectronics.[1–5] During the past few years, various heterostructures incorporated with various 1D nanomaterials have been synthesized, such as CNT/Si,[6] NiSi/Si,[7] InN/GaN,[8] Au/CNT,[9] SiC/CNT,[10] TiC/CNT,[10] Si/SiGe,[11] Ag/CNT,[12] GaN/CNT,[13] ZnO/CNT.[13–15] The development of various nanometer-scaled heterostructures not only enables ohmic contacts but also tailors physical properties of 1D nanostructures.

Carbon nanotubes have been recognized as good candidates for building next-generation optical and electronic devices due to their unique mechanical, electronic and optical properties.[16–23] For example, novel CNT-based nanodevices such as transistors,[16,17] field emitters,[18,19] sensors,[20,21] and probes[22,23] have been designed. Obviously, the fabrication of 1D nanoscale heterostructures based on CNTs will open a new way to versatile nanodevices with good performance. Therefore, the combination of various 1D semiconducting or metallic nanostructures with CNTs has attracted much interest.[6,10,12–14] However, most of these heterostructures were produced via chemical vapor deposition process at high temperature. In comparison with the high-temperature strategy, a wet chemical method is considered an economic and reasonable choice for its mild, productive and flexible reaction route.

1D ZnO nanostructures which have important applications in solar cells,[24] gas sensors,[25] lasers,[26] piezoelectric generators[27] and logic circuits[28] have been successfully produced using solution chemical approaches under low-temperature hydrothermal conditions (<100 °C) on various subtrates.[29,30] In this regard, the substrate was generally precoated with a thin layer of seeds prior to the growth of arrays of ZnO nanorods or nanowires. The existence of the seed layer makes heterogeneous nucleation on a substrate possess lower free energy of activation compared with homogeneous nucleation in solution by providing a good structural match, so the ZnO crystalline nanostructures can preferentially be formed on the substrate.[30] Since the growth of ZnO nanorods or nanowires in the seed-mediated growth process is dependent on the seed film, it is possible to realize the selective growth of 1D ZnO nanostructures by precoating different regions on a substrate or any assigned surface with seeds.[15,31–32]

In the present paper, we grew ZnO nanorods on MWNTs via a two-step wet chemical approach. First, ZnO nanocrystals formed via the reaction between NaOH and zinc acetate ($Zn(Ac)_2$) in 2-propanol were *in situ* self-assembled on the surface of oxidized MWNTs. Then, the ZnO nanocrystals were grown into ZnO nanorods on

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the outer shells of MWNTs in an aqueous solution of $Zn(NO_3)_2$ and hexamethylenetetramine (HMT,$C_6H_{12}N_4$). Since any catalyst or surfactant was not involved in the process, relatively clean ZnO nanorod/MWNT heterostructures were obtained. Such composite nanostructures of CNTs anchored with ZnO nanorods might be used as electrode materials for photoelectrochemical cells. Owing to the high electrical conductivity of CNTs, the good electron transportation channel provided by single crystalline ZnO nanorods and clean heterojunction between ZnO nanorods and CNTs, the application of such composites may be able to enhance the photocurrent by overcoming the charge recombination problem.

2. EXPERIMENTAL DETAILS

2.1. Synthesis

MWNTs were purchased from Shenzhen Nanotech Port Co. Ltd, China. All other chemicals are of analytical grade and used as received. The as-received purified MWNTs were first oxidized by refluxing at 130 °C in concentrated nitric acid for 12 h. ZnO nanocrystals were synthesized according to the reported methods[33, 34] and self-assembled on the MWNT walls.

For a typical synthesis, 0.5 mmol of zinc acetate was dissolved in 40 ml 2-propanol under vigorous stirring at 45 °C. 5 mg oxidized MWNTs were dispersed in 64 ml 2-propanol by sonication for 20 min and subsequently 8 ml $Zn(Ac)_2$ solution was added to the black MWNT suspension. 8 ml of 0.02 M NaOH 2-propanol solution was rapidly added to the mixture of $Zn(Ac)_2$ and MWNTs at ~0 °C under constant stirring. The reaction flask was then immersed in a preheated water bath at 65 °C for 2 h. Aged overnight, the suspension was centrifuged at 7500 rpm for 15 min. The composites were then re-dispersed in 2-propanol for the seed-mediated growth of ZnO nanorods on the sidewalls of MWNTs.

ZnO nanorods were grown on MWNTs using a two-step process similar to that used to grow oriented ZnO nanowire arrays on various substrates reported by Greene et al.[29] The suspension of ZnO nanocrystals/MWNTs composites in 2-propanol was spin-coated onto a clean Si/SiO_x wafer which had been treated with Piranha solution at 90 °C for 30 min and rinsed with deionized water. Then the wafer scattered with composites of ZnO nanocrystals/MWNTs was annealed at 150 °C to achieve a good adhesion between the coating and the substrate. Subsequently, a flask with a sealing lid was infused with growth solution of equimolar $Zn(NO_3)_2$ and HMT and placed in a water bath at 85 °C. Dilute HNO_3 or NaOH solution was used to adjust the pH value of the solution. The annealed wafer coated with ZnO nanocrystals/MWNTs composites was floated upside-down in the growth solution under a mild electromagnetic stirring for 0.5–4 h. Typically, heterostructures of ZnO nanorods and MWNTs could be formed at 85 °C for 1 h in the solution of 0.01 M $Zn(NO_3)_2$ and equimolar HMT with initial pH of 5.6.

2.2. Characterization

A JEOL-200 CX transmission electron microscope and a Tecnai F30 field emission transmission electron microscope were used to obtain the TEM and HRTEM images of the products. The morphology and size of ZnO nanorods grown on MWNTs were observed through Quanta 200FEG scanning electron microscope with an accelerating voltage of 15 kV. The X-ray diffraction (XRD) measurements were performed on a Rigaku Dmax-2000 X-ray diffractometer by Cu kα radiation ($\lambda = 1.5406$ Å) with an accelerating voltage of 40 kV. From the XRD patterns, the crystallite size of the ZnO nanocrystals assembled on MWNTs was calculated according to Scherrer equation:

$$d = \frac{0.9\lambda}{\sigma \cos\theta}$$

where λ is the X-ray wavelength, σ is the full-width half-maximum of the characteristic (100) peak, and θ is the diffraction angle for the (100) planes.

3. RESULTS AND DISCUSSION

3.1. Self-Assembling of ZnO Nanocrystals on Surfaces of MWNTs

Figure 1 shows the XRD and TEM characterizations of ZnO nanocrystals coated MWNTs. The diffraction peaks were all assigned to MWNTs and hexagonal ZnO. The peaks at $2\theta = 25.78°$ and $42.90°$ were attributed to (002) and (101) of MWNTs, respectively. The peaks at $2\theta = 31.56°, 34.28°, 36.02°, 47.42°, 56.41°, 62.71°, 68.08°$ were assigned to (100), (002), (101), (102), (110), (103) and (112) planes of wurtzite structured ZnO (JCPDS 36-1451). The average grain size of ZnO nanocrystals calculated by the Sherrer formula was 9.0 nm. It is noted from the TEM image that the outer shells of MWNTs were densely coated with uniform small ZnO particles. HRTEM image of Figure 1(c) reveals these ZnO nanoparticles attached to MWNTs were nearly spherical with clear lattice fringes. The amplified image in Figure 1(d) shows the fringe distance was 0.28 nm, which fits exactly to that of (100) in wurtzite ZnO. The size of the nanocrystals measured from HRTEM image was ~7 nm, which is similar to the result from XRD.

As described above, the ZnO nanocrystals obtained were very uniform in size and coated evenly onto the outer walls of MWNTs. We attributed this much to the *in situ* assembling process. Assemblies of ZnO nanocrystals and MWNTs can also be obtained by mixing preformed ZnO nanoparticles and CNTs in aqueous phase via electrostatic and coordinate interactions between Zn(II) and O atoms from the functional groups of oxidized carbon nanotubes.[35]

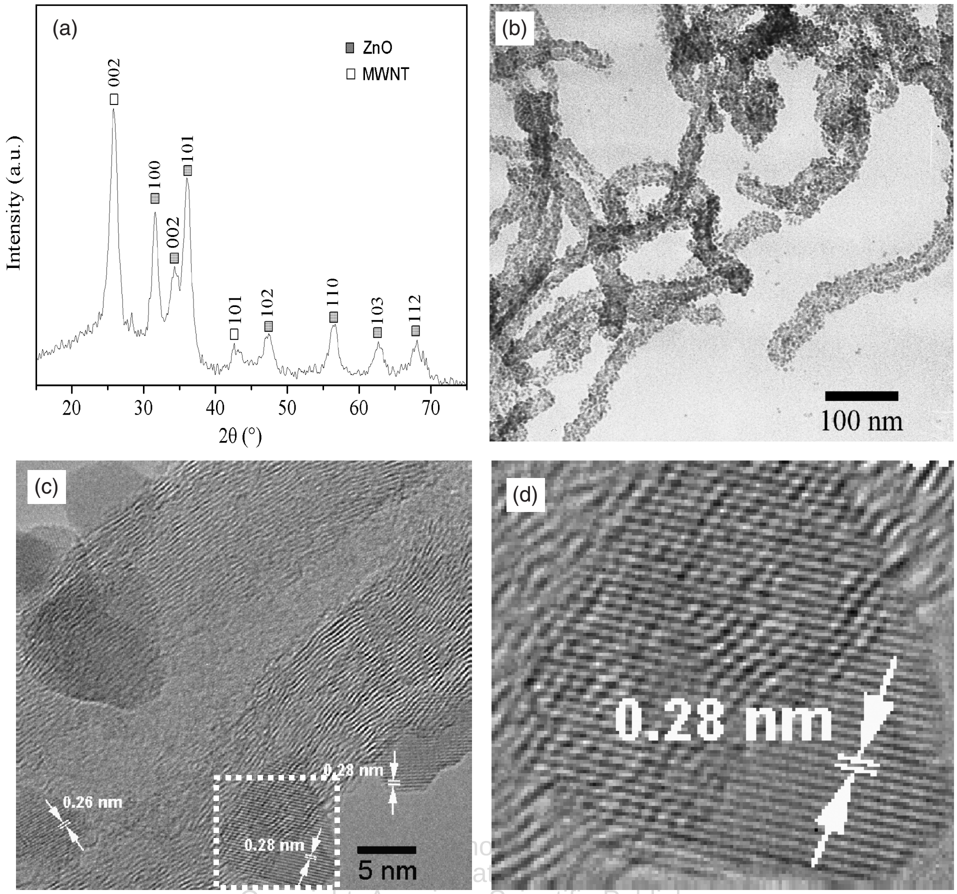

Fig. 1. XRD pattern (a), TEM (b) and HRTEM (c and d) images of self-assembled ZnO nanocrystals on MWNT surfaces.

However, the ZnO nanocrystals tend to form aggregates on the local areas of CNTs due to the conglomeration behavior of the ZnO nanoparticles. In our process, ZnO nanocrystals were formed by the reaction of $Zn(Ac)_2$ and NaOH in 2-propanol.[33] 2-propanol is a relative hydrophilic solvent which contains a certain amount of water used to dissolve and ionize electrolytes as well as to promote hydrolysis and condensation/nucleation.[37–39] In the presence of water, the nucleation and growth of ZnO nanocrystals were preceded by the formation of polycations such as $[ZnL_h(OH_2)_{N-h}]^{(2-h)+}$, where L is an anionic ligand such as OH^- or CH_3COO^-.[37,38] For nitric acid-treated CNTs, surface-bound carboxyl acid groups can be negatively charged by dissociation over a wide pH value range of 2∼10.[40] Therefore, the Zn(II)-centered polycations are likely to be trapped by these negative-charged active groups through electrostatic interaction and form specific nucleation sites for the growth of ZnO nanocrystals on the surface of MWNTs.

3.2. Seed-Mediated Growth of ZnO Nanorods on Surfaces of MWNTs

Using the ZnO nanocrystals-MWNT assemblies dispersed on silicon wafers as the starting materials, we successfully obtained the heterostructures of ZnO nanorods-coated MWNTs. The SEM images at low and high magnifications of typical heterostructures of ZnO nanorods-coated MWNTs were shown in Figures 2(a) and (b), respectively. The images clearly indicate that almost the entire surface of MWNTs was covered with ZnO nanorods. The high magnification micrograph revealed that the width and the length of these ZnO nanorods were in the range of 40–140 and 300–600 nm, respectively. Furthermore, the diameters of some nanorods were reduced at the top regions which were resulted from the decreasing precursor concentration in the solution during the seeded-growth process.[41] The ZnO nanorods were grown in a random direction ascribed to the uncontrollable orientation of ZnO nanocrystal seeds on MWNTs.[42] The XRD pattern (Fig. 2(c)) only shows the sharp (100), (002) and (101) peaks indexed to crystalline ZnO nanorods. The diffraction of MWNTs was not detectable due to the densely coated ZnO nanorods as well as the strong signal of the Si/SiO_x substrate. HRTEM characterization (Fig. 2(d)) of individual nanorods grown from ZnO nanocrystals-coated MWNTs on a copper grid indicated that it is single-crystalline and grown along the [0001] direction.

It was found that the precoating of ZnO seeds is essential. When we applied the same growth operation to

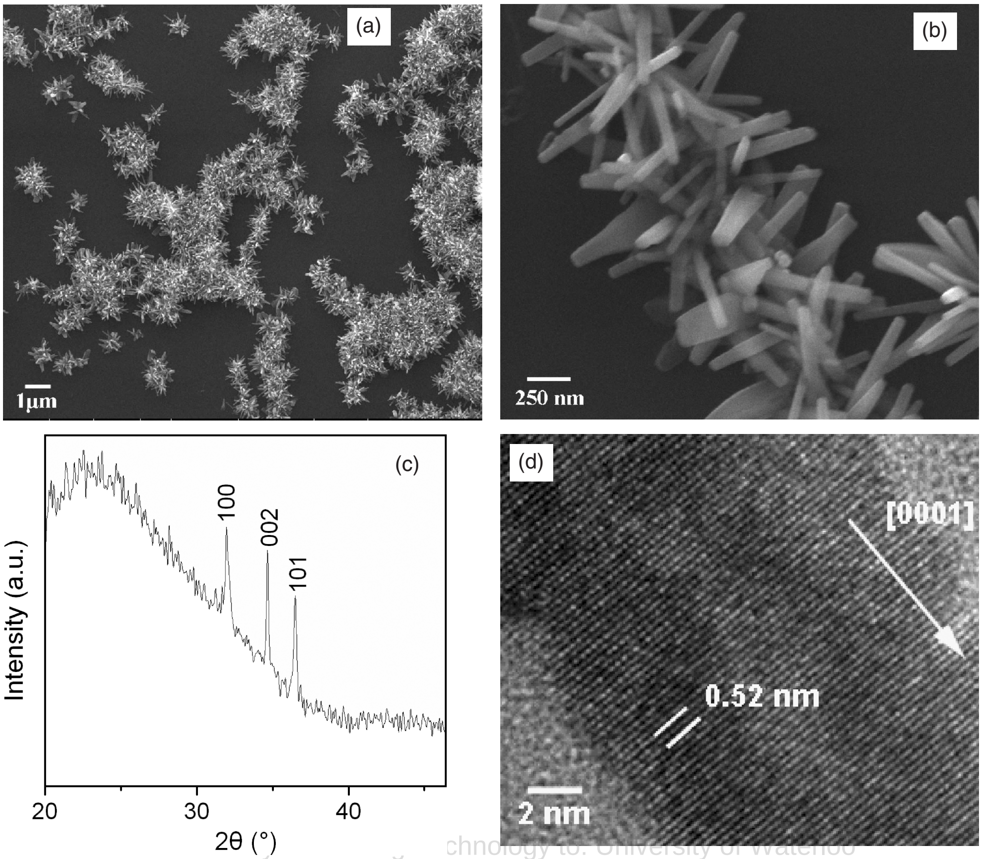

Fig. 2. Low (a) and high (b) magnification SEM images, (c) XRD pattern and (d) HRTEM image of the ZnO nanorods-coated MWNTs.

oxidized MWNTs with no ZnO seeds, none ZnO nanorods were found on the MWNT surface. Here the ZnO nanocrystals self-assembled on MWNTs might play a role of decreasing nucleation energy barrier, which makes it easier to grow ZnO nanorods on seeds-covered MWNT walls than on seed-lacking surface or in growth solution.[30]

Effect of pH value on the size and morphology of ZnO nanorods on MWNT surface was studied (Fig. 3). At pH = 7.0, thin nanorods with diameters of 20–40 nm sparely attached to MWNTs. However, as the pH value was lowered to 6.4, dense ZnO nanorods with 20–90 nm in diameter and 150–250 nm in length were found. The ZnO nanorods were still kept very close to each other but remarkably reduced in diameter with the further reduction of pH value to 5.6. Once the pH was decreased to 4.4, a few micro-rods were linked with MWNTs, and most surface areas were kept bare.

The formation of ZnO nanorods in the solution of zinc salts and HMT is based on the following chemical reactions:[43]

$$(CH_2)_6N_4 + 6H_2O \xrightarrow{\triangle} 6HCHO + 4NH_3$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$2OH^- + Zn^{2+} \rightarrow Zn(OH)_2 \rightarrow ZnO_{(s)} + H_2O$$

ZnO crystals may be formed both in solution and on surface via heterogeneous and homogeneous nucleation, respectively. At high pH value (~7.0), the homogeneous nucleation process is dominant by virtue of the higher concentration of OH^- ions. In fact, when pH reached 7.1,

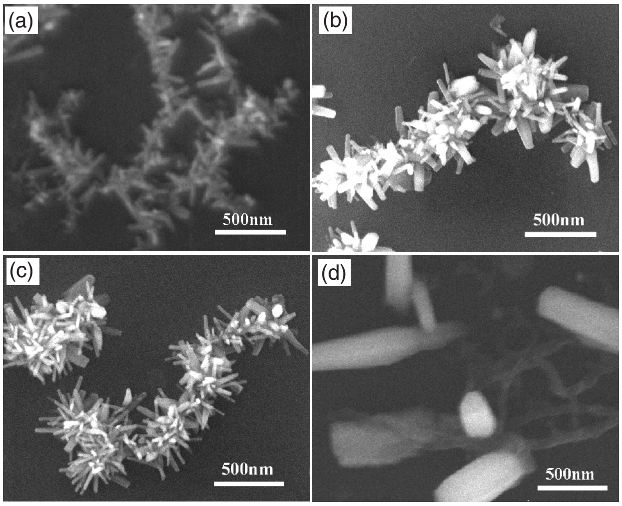

Fig. 3. SEM images showing the pH dependence of ZnO nanorods attached to MWNTs. (a) pH = 7.0, (b) pH = 6.4, (c) pH = 5.6 and (d) pH = 4.4.

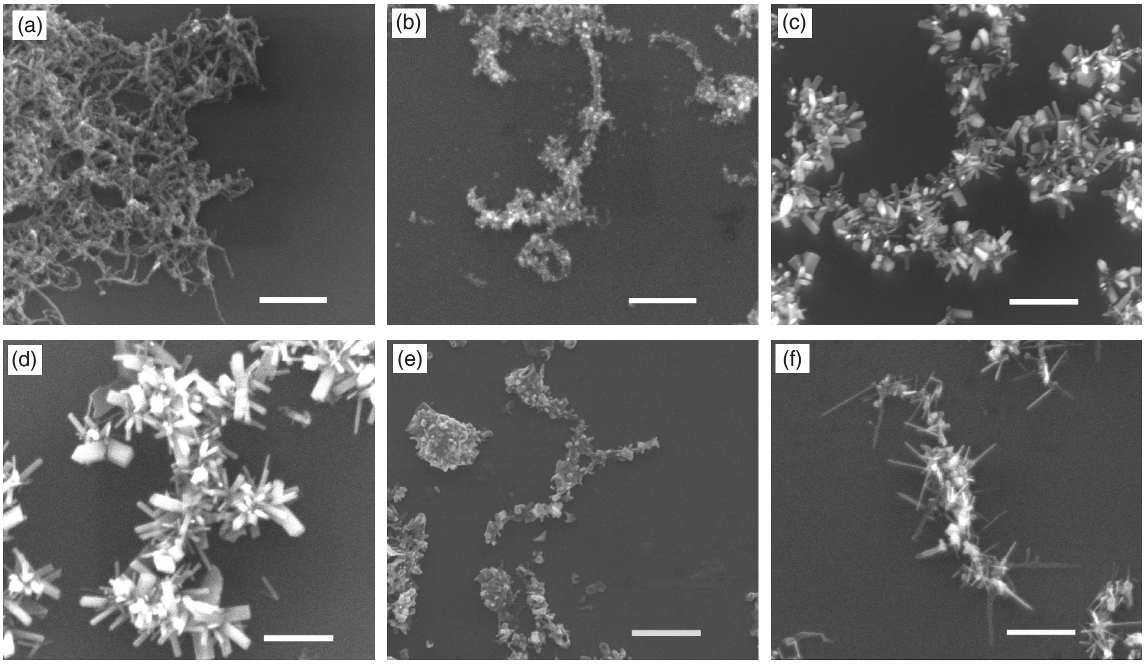

Fig. 4. SEM images of samples obtained at different aging time in 0.01 M or 0.001 M $Zn(NO_3)_2$ and equimolar HMT solution, respectively. (a) the original ZnO seeds coated MWNTs; (b) 0.01 M, 0.5 h; (c) 0.01 M, 1 h; (d) 0.01 M, 4 h; (e) 0.001 M, 1 h; (f) 0.001 M, 2 h. Scale bar = 1 μm.

large $Zn(OH)_2$ flocs appears quickly in the growth solution with 0.01 M reaction species at room temperature. The heterogeneous nucleation associated with the formation of 1D ZnO nanostructures on the substrate was thus inhibited because ZnO precursors were largely consumed in the bulk phase nucleation process, so innutrient rods were formed on MWNT walls in the growth solution of high pH.

On the other hand, due to the amphoteric property of ZnO, ZnO seeds could be etched away partly at higher pH, which causes the ZnO nanorods on MWNTs becoming spare. When pH value varies within the range of 6.8∼5, ZnO precursors mainly feed the energetically preferential heterogeneous nucleation of ZnO nanorods on the seed layer. Hence dense and well-developed ZnO nanorods were found on the MWNT substrate.[44] The formation of thinner ZnO nanorods at pH = 5.6 was ascribed to the decrease of OH^- supply. With the further increase of acidity to pH = 4.4, the ZnO crystal seeds would be etched away by acid, so that no nanorods were formed on the surface of MWNTs. The present micro-rods were actually generated via non-seeded growth process because they were also found on a Si/SiO_x wafer covered with oxidized MWNTs without ZnO seeds.

It was not out of imagination that the ZnO nanorods would grow along with the extending of aging time as shown in Figure 4. As the growth was carried out at the condition near the equilibrium point, and the concentration of OH^- was very low, the growth was not quick at all. The growth behavior of ZnO nanorods was also dependent on reactant concentration. When the concentrations of $Zn(NO_3)_2$ and HMT were both 0.01 M, ZnO nanorods were well formed after 1 h's aging. However, after grown in 0.001 M $Zn(NO_3)_2$ and equimolar HMT for 1 h, ZnO nanocrystals on MWNT walls were developed into bigger particles fused together (Fig. 4(e)). Anyway, when the growth time was increased to 2 h, very thin nanorods with diameters of 30–50 nm appeared at the top of these fused primary particles (Fig. 4(f)).

4. CONCLUSIONS

ZnO nanorods were successfully prepared on the outmost walls of MWNTs by seeded-growth method. By the reaction of $Zn(Ac)_2$ and NaOH in 2-propanol, ZnO nanocrystals were formed and self-assembled on the surface of MWNTs. The resultant nanocrystalline ZnO evenly coated on MWNTs and served as the nucleation sites for the growth of nanorods. Then, in the second growth, ZnO nanorods were grown out from the nanoseeds in the solution of $Zn(NO_3)_2$ and hexamethylenetetramine and heterostructures of ZnO nanorods and MWNTs were obtained. The size and density of the nanorods were controlled by the acidity of the solution, the reactant concentration and the reaction time. Herein, we provided a convenient solution chemical strategy to fabricate heterostructures of ZnO nanorods and functionalized CNTs, which may also be extended to the preparation of heterostructures composed of other nanoscale 1D building blocks. Such composite nanostructures of CNTs anchored with ZnO nanorods might be used as electrode materials to enhance the photocurrent in a photoelectrochemical cell.

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References and Notes

1. J. R. Heath, P. J. Kuekes, G. S. Snider, and R. S. Williams, *Science* 280, 1716 (**1998**).
2. Y. Cui and C. M. Lieber, *Science* 291, 851 (**2001**).
3. Y. Huang, X. F. Duan, Y. Cui, L. J. Lauhon, K. H. Kim, and C. M. Lieber, *Science* 294, 1313 (**2001**).
4. M. S. Gudiksen, L. J. Lauhon, J. F. Wang, D. C. Smith, and C. M. Lieber, *Nature* 415, 617 (**2002**).
5. X. F. Duan, Y. Huang, Y. Cui, J. F. Wang, and C. M. Lieber, *Nature* 409, 66 (**2001**).
6. J. T. Hu, M. Ouyang, P. D. Yang, and C. M. Lieber, *Nature* 399, 48 (**1999**).
7. Y. Wu, J. Xiang, C. Yang, W. Lu, and C. M. Lieber, *Nature* 430, 61 (**2004**).
8. Z. H. Lan, C. H. Liang, C. W. Hsu, C. T. Wu, H. M. Lin, S. Dhara, K. H. Chen, L. C. Chen, and C. C. Chen, *Adv. Funct. Mater.* 14, 233 (**2004**).
9. A. J. Mieszawska, R. Jalilian, G. U. Sumanasekera, and F. P. Zamborini, *J. Am. Chem. Soc.* 127, 10822 (**2005**).
10. Y. Zhang, T. lchihashi, E. Landree, F. Nihey, and S. Lijima, *Science* 285, 1719 (**1999**).
11. Y. Y. Wu, R. Fan, and P. D. Yang, *Nano Lett.* 2, 83 (**2002**).
12. J. Luo, Z. P. Huang, Y. G. Zhao, L. Zhang, and J. Zhu, *Adv. Mater.* 16, 1512 (**2004**).
13. S. Y. Bae, H. W. Seo, H. C. Choi, J. Park, and J. Park, *J. Phys. Chem. B* 108, 12318 (**2004**).
14. H. Kim and W. Sigmund, *Appl. Phys. Lett.* 81, 2085 (**2002**).
15. W. D. Zhang, *Nanotechnology* 17, 1036 (**2006**).
16. A. Bachtold, P. Hadley, T. Nakanishi, and C. Dekker, *Science* 294, 1317 (**2001**).
17. A. Javey, J. Guo, Q. Wang, M. Lundstr, and H. J. Dai, *Nature* 424, 654 (**2003**).
18. J. M. Bonard, J. P. Salvetat, T. Stöckli, L. Forró, and A. Châtelain, *Appl. Phys. A: Mater. Sci. Process* 69, 245 (**1999**).
19. W. I. Milne, K. B. K. Teo, G. A. J. Amaratunga, P. Legagneux, L. Gangloff, J. P. Schnell, V. Semet, V. Thien Binhc, and O. Groening, *J. Mater. Chem.* 14, 933 (**2004**).
20. J. Kong, N. R. Franklin, C. W. Zhou, M. G. Chapline, S. Peng, K. Cho, and H. J. Dai, *Science* 287, 622 (**2000**).
21. J. Li, Y. J. Lu, Q. Ye, M. Cinke, J. Han, and M. Meyyappan, *Nano Lett.* 3, 929 (**2003**).
22. H. J. Dai, J. H. Hafner, A. G. Rinzler, D. T. Colbert, and R. E. Smalley, *Nature* 384, 147 (**1996**).
23. S. S. Wong, E. Joselevich, A. T. Woolley, C. L. Cheung, and C. M. Lieber, *Nature* 394, 52 (**1998**).
24. M. Law, L. E. Greene, J. C. Johnson, R. Saykally, and P. D. Yang, *Nature Mater.* 4, 455 (**2005**).
25. Q. Wan, Q. H. Li, Y. J. Chen, T. H. Wang, X. L. He, J. P. Li, and C. L. Lin, *Appl. Phys. Lett.* 84, 3654 (**2004**).
26. M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, H. Kind, E. Weber, R. Russo, and P. D. Yang, *Science* 292, 1897 (**2001**).
27. Z. L. Wang and J. H. Song, *Science* 312, 242 (**2006**).
28. W. Park, J. S. Kim, G. C. Yi, and H. J. Lee, *Adv. Mater.* 17, 1393 (**2005**).
29. L. E. Greene, M. Law, J. Goldberger, F. Kim, J. C. Johnson, Y. F. Zhang, R. J. Saykally, and P. D. Yang, *Angew. Chem. Int. Ed.* 42, 3031 (**2003**).
30. R. B. Peterson, C. L. Fields, and B. A. Gregg, *Langmuir* 20, 5114 (**2004**).
31. Y. Tak and K. Yong, *J. Phys. Chem. B* 109, 19263 (**2005**).
32. Y. W. Koh, M. Lin, C. K. Tan, Y. L. Foo, and K. P. Loh, *J. Phys. Chem. B* 108, 11419 (**2004**).
33. D. W. Bahnemann, C. Kormann, and M. R. Hoffmann, *J. Phys. Chem.* 91, 3789 (**1987**).
34. E. M. Wong, J. E. Bonevich, and P. C. Searson, *J. phys. Chem. B* 102, 7770 (**1998**).
35. S. Ravindran and C. S. Ozkan, *Nanotechnology* 16, 1130 (**2005**).
36. Z. S. Hu, D. J. E. Ramírez, B. E. H. Cervera, G. Oskam, and P. C. Searson, *J. phys. Chem. B* 109, 11209 (**2005**).
37. C. J. Brinker and G. Scherer, Sol-Gel Science, Acedemic Press, New York (**1989**).
38. M. S. Tokumoto, V. Briois, C. V. Santilli, and S. H. Pulcinelli, *J. Sol-Gel. Sci. Tech.* 26, 547 (**2003**).
39. Z. Hu, J. F. H. Santos, G. Oskam, and P. C. Searson, *J. Coll. and Int. Sci.* 288, 313 (**2005**).
40. H. Hu, A. P. Yu, E. Kim, B. Zhao, M. E. Itkis, E. Bekyarova, and R. C. Haddon, *J. phys. Chem. B* 109, 11520 (**2005**).
41. C. H. Ku and J. J. Wu, *J. Phys. Chem. B* 110, 12981 (**2006**).
42. L. E. Greene, M. Law, D. H. Tan, M. Montano, J. Goldberger, G. Somorjai, and P. D. Yang, *Nano Lett.* 5, 1231 (**2005**).
43. Q. C. Li, V. Kumar, Y. Li, H. T. Zhang, T. J. Marks, and R. P. H. Chang, *Chem. Mater.* 17, 1001 (**2005**).
44. K. Govender, D. S. Boyle, P. B. Kenway, and P. O'Brien, *J. Mater. Chem.* 14, 2575 (**2004**).

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