

Synthesis and Photoelectric Properties of Coaxial Schottky Junctions of ZnS and Carbon Nanotubes

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One-dimensional (1D) nanostructures of the wide band gap semiconductors are promising building blocks for photoelectric nanodevices. However, some problems like strong 1D confinement largely hamper their applications. To avoid these problems, here, we provide another 1D configuration, in which an inner-wire coaxial Schottky junction exists, thus effectively avoiding the recombination of the photoexcited carriers. As an example, we produce ZnS/carbon nanotube nanocables with uniform morphologies by a two-step vapor deposition method and find that they have good conductance, obvious light response, and ohmic contacts with electrodes, avoiding the limitations of both the pristine nanomaterials. We believe that this configuration would be valuable for applying the 1D nanomaterials in photoelectronics.

1. Introduction

One-dimensional (1D) nanostructures of the wide band gap semiconductors are promising building blocks for various types of photoelectric nanodevices.^{1,2} Due to their fascinating applications, a considerable amount of research has been focused here recently;^{1,3} however, there are still some problems. For instance, the wide band gap causes low conductance and poor contacts with electrodes. Importantly, the strong 1D confinement leads to large Coulombic coupling between the photoexcited electrons and holes, which largely suppresses the photoconductivity due to the recombination of the photoexcited carriers.⁴ To avoid these problems and to improve the photoelectric applications of the 1D nanomaterials, here, we provide another configuration of 1D nanomaterials, in which a coaxial Schottky junction exists along its total length. As an example, ZnS/carbon nanotube (CNT) nanocables are researched.

ZnS is an important wide band gap semiconductor, which is widely used in light-emitting diodes,⁵ photodetectors,⁶ photochemistry,⁷ lasers,⁸ etc., while CNTs are one promising nanomaterial for nanoelectronics.⁹ According to the layer number of the tube walls, CNTs are either single-walled CNTs (SWNTs) or multiwalled CNTs (MWNTs). SWNTs have good photoelectric properties; thus, various types of photoelectric devices have been fabricated by using SWNTs.¹⁰ However, SWNTs are either metallic or semiconducting, and their electronic and photoelectric properties would be different according to their chiralities. In contrast, almost all MWNTs are metallic with a several tens of millielectronvolts band gap;¹¹ thus, a reliable coaxial Schottky junction can be constructed between ZnS and the MWNTs. Moreover, MWNTs favor an ohmic contact and show excellent electronic properties like ballistic transport¹² and large current carrying.¹³

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- (1) Huang, M. H.; Mao, S.; Feick, H.; Yan, H. Q.; Wu, Y. Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. D. *Science* **2001**, 292, 1897–1899. (b) Xia, Y. N.; Yang, P. D.; Sun, Y. G.; Wu, Y. Y.; Mayers, B.; Gates, B.; Yin, Y. D.; Kim, F.; Yan, H. Q. *Adv. Mater.* **2003**, 15, 353–389. (c) Li, Y.; Qian, F.; Xiang, J.; Lieber, C. M. *Mater. Today* **2006**, 9, 18–27.
- (2) Wang, J. F.; Gudiksen, M. S.; Duan, X. F.; Cui, Y.; Lieber, C. M. *Science* **2001**, 293, 1455–1457.
- (3) Jie, J. S.; Zhang, W. J.; Meng, X. M.; Li, Y. Q.; Lee, S. T. *Nano Lett.* **2006**, 6, 1887–1892.
- (4) (a) Freitag, M.; Martin, Y.; Misewich, J. A.; Martel, R.; Avouris, P. *Nano Lett.* **2003**, 3, 1067–1071. (b) Ando, J. *J. Phys. Soc. Jpn.* **1997**, 66, 1066–1073. (c) Pedersen, T. G. *Phys. Rev. B* **2003**, 67, 073401. (d) Kane, C. L.; Mele, E. J. *Phys. Rev. Lett.* **2003**, 90, 207401. (e) Yang, L.; Spataru, C. D.; Louie, S. G.; Chou, M. Y. *Phys. Rev. B* **2007**, 75, 201304.

- (5) Tang, W.; Cameron, D. C. *Thin Solid Films* **1996**, 280, 221–226.
- (6) Monroy, E.; Omnes, F.; Calle, F. *Semicond. Sci. Technol.* **2003**, 18, R33–R51.
- (7) Wada, Y.; Yin, H.; Kitamura, T.; Yanagida, S. *Chem. Commun.* **1998**, 24, 2683–2685.
- (8) Falcony, C.; Garcia, M.; Ortiz, A.; Alonso, J. C. *J. Appl. Phys.* **1992**, 72, 1525–1527.
- (9) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, 297, 787–792.
- (10) (a) Freitag, M.; Martin, Y.; Misewich, J. A.; Martel, R.; Avouris, P. *Nano Lett.* **2003**, 3, 1067–1071. (b) Chen, J.; Perebeinos, V.; Freitag, M.; Tsang, J.; Fu, Q.; Liu, J.; Avouris, P. *Science* **2005**, 310, 1171–1174.
- (11) Forro, L.; Schonenberger, C. In *Carbon Nanotubes, Topics of Applied Physics*; Dresselhaus, M. S., Dresselhaus, G., Avouris, P., Eds.; Springer-Verlag: Berlin, Germany, 2001; Chapter 13.
- (12) Frank, S.; Poncharal, P.; Wang, Z. L.; de Heer, W. A. *Science* **1998**, 280, 1744–1746.
- (13) Li, H. J.; Lu, W. G.; Li, J. J.; Bai, X. D.; Gu, C. Z. *Phys. Rev. Lett.* **2005**, 95, 086601.

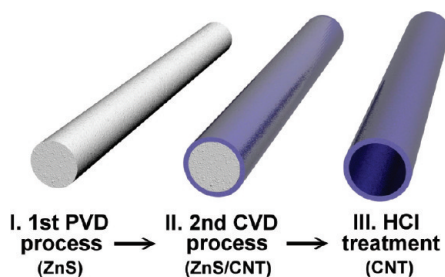


Figure 1. Schematic diagram of the preparation of the ZnS/CNT nanocables and the MWNTs with a straight, continuous cavity and open ends.

1D heterojunctions are of significance to both scientific fundamentals and potential applications in nanoscience.¹⁴ Although MWNTs have poor photoelectric properties, the formation of 1D heterojunction nanostructures can largely expand, improve, or alter the properties and the applications of the pristine MWNTs.¹⁵ Cablelike coaxial heterojunction is one basic configuration of such structure. Recently, intensive research shows that the nanocables have a wide range of applications in high performance field effect transistors,¹⁶ light-emitting diodes,¹⁷ solar cells,¹⁸ etc. In this article, we use the ZnS/CNT nanocables in photoelectric applications. In fact, some groups have successfully produced the coaxial ZnS/CNT nanostructures;^{19,20} however, for the device application, the ZnS/CNT nanocables with uniform morphologies are required, which are still hard to produce by the present synthetic method. Thus, we develop a two-step vapor deposition technique, as illustrated in Figure 1, to synthesize uniform ZnS/CNT nanocables. After coating the ZnS nanowires with a uniform layer of metallic MWNT sidewalls, the nanocables show good conductance, obvious light response, and ideal ohmic contacts with electrodes. A built-in electric field across the coaxial Schottky junction separates the photoexcited carriers; thus, their recombination is avoided. Moreover, after removing the ZnS cores, MWNTs with a straight, continuous cavity and open ends are obtained.

2. Experimental Section

Synthesis. The experimental setups were shown in Figure S1 (Supporting Information). The ZnS/CNT nanocables were produced by a two-step vapor deposition method. Both steps were performed in a horizontal quartz tube (outer diameter ca. 2.2 cm; length ca. 120 cm) mounted inside a high-temperature furnace. In the first step, the ZnS nanowires were synthesized by

a physical vapor deposition (PVD) method by using 100 sccm high pure Ar mixed with 3–8% H₂ as the carrier gas. An alumina boat, which was contained with 0.1 g of ZnS powder (Sigma-Aldrich, purity > 99.99%) and 0.5 g graphite powder, was placed at the high temperature region (1000 °C), and then, the ZnS nanowires were grown on a Si wafer with a 20 nm thick Au film, which was located at the region 25 cm downstream with lower temperature. In the second step, the ZnS nanowires were placed at the region of 650 °C, then 100 sccm CH₄ was introduced as the carbon source, and 50 sccm Ar and 50 sccm H₂ were introduced as the carrier gas. This chemical vapor deposition (CVD) process was performed for 15 min. After both steps, the reactor was cooled to room temperature under ambient H₂. To prepare CNTs, the ZnS cores were removed by dispersing the ZnS/CNT nanocables in 0.1 M HCl for 30 min, and then, the samples were filtrated and washed by distilled water. Finally, the samples were dried at 120 °C for 2 h.

Characterization. The samples were characterized by scanning electron microscopy (SEM, Hitachi S-4300, operated at 15 kV) and transmission electron microscopy (TEM, JEOL-2010, operated at 200 kV) equipped with an X-ray energy dispersive spectrometer (EDS), X-ray photoelectron spectroscopy (XPS, ESCA Lab220I-XL), and Raman spectroscopy (LabRam HR800 with laser excitation at 633 nm).

Device and Electrical Measurement. The ZnS/CNT nanocables were dispersed in ethanol by mild sonication, and then, the solution was spin-coated onto a 500 nm thick thermally oxidized-silicon surface with Au/Ti contact pads. Using a focused-ion-beam (FIB) etching and deposition system (Strata DB235, FEI Co.), the surface was visualized at a low beam current (1 pA) in order to search the ZnS/CNT nanocables. Once found, Pt leads were patterned between each end of the nanocable and the Au/Ti pads. A 30 kV Ga⁺ beam at 10 pA was used to decompose trimethylcyclopentadienylplatinum [CH₃C₅H₄Pt(CH₃)₃] into a predetermined lead. The patterning was performed under computer control without further visualization of the sample before electrical measurement. In general, the ion-beam deposition conditions must be carefully chosen to avoid significant damage or complete destruction of the sample by the massive Ga ions.²¹ We found no evidence for such damage, and no device shorting was seen. Furthermore, to avoid possible shorting by the Pt spreading, we kept the device length at 3.0 μm or greater, and the Pt deposition time around the predetermined regions of the sample was less than 30 s. All of the samples were prepared with exactly the same procedure and doses. To obtain better contact between the nanocable and the Pt leads, thermal annealing was performed in Ar atmosphere at 350 °C for 20 min in a tube furnace. The electrical properties were measured by using a probe station (Wentworth Company MP1008) and a semiconductor parameter analyzer (Hewlett-Packard 4140B) at room temperature in air, and a high-pressure Hg lamp (200 W) was used as the white light source for the photoelectric testing.

3. Results and Discussion

SEM and TEM images (Figure 2a) show that the products of the first step have a filamentous morphology with a length about several tens of micrometers and a diameter, ranging from 20 to 200 nm, which is uniform along the total length of the nanowires. A few nanowires have a larger diameter, ranging from 200 to 500 nm. In the

- (14) (a) Wei, D. C.; Liu, Y. Q. *Adv. Mater.* **2008**, *20*, 2815–2841. (b) Mieszawska, A. J.; Jalilian, R.; Sumanasekera, G. U.; Zamborini, F. P. *Small* **2007**, *3*, 722–756.
- (15) Mieszawska, A. J.; Jalilian, R.; Sumanasekera, G. U.; Zamborini, F. P. *Small* **2007**, *3*, 722–756.
- (16) Xiang, J.; Lu, W.; Hu, Y. J.; Wu, Y.; Yan, H.; Lieber, C. M. *Nature* **2006**, *441*, 489–493.
- (17) (a) Hayden, O.; Greytak, A. B.; Bell, D. C. *Adv. Mater.* **2005**, *17*, 701–704. (b) Qian, F.; Gradecak, S.; Li, Y.; Wen, C. Y.; Lieber, C. M. *Nano Lett.* **2005**, *5*, 2287–2291.
- (18) Tian, B.; Zheng, X. L.; Kempa, T. J.; Fang, Y.; Yu, N. F.; Yu, G. H.; Huang, J. L.; Lieber, C. M. *Nature* **2007**, *449*, 885–890.
- (19) Shen, G. Z.; Bando, Y.; Golberg, D. *J. Phys. Chem. B* **2006**, *110*, 20777–20780.
- (20) Du, J. M.; Fu, L.; Liu, Z. M.; Han, B. X.; Li, Z. H.; Liu, Y. Q.; Sun, Z. Y.; Zhu, D. B. *J. Phys. Chem. B* **2005**, *109*, 12772–12776.

- (21) Gopal, V.; Radmilovic, V. R.; Daraio, C.; Jin, S.; Yang, P.; Stach, E. A. *Nano. Lett.* **2004**, *4*, 2059–2063.

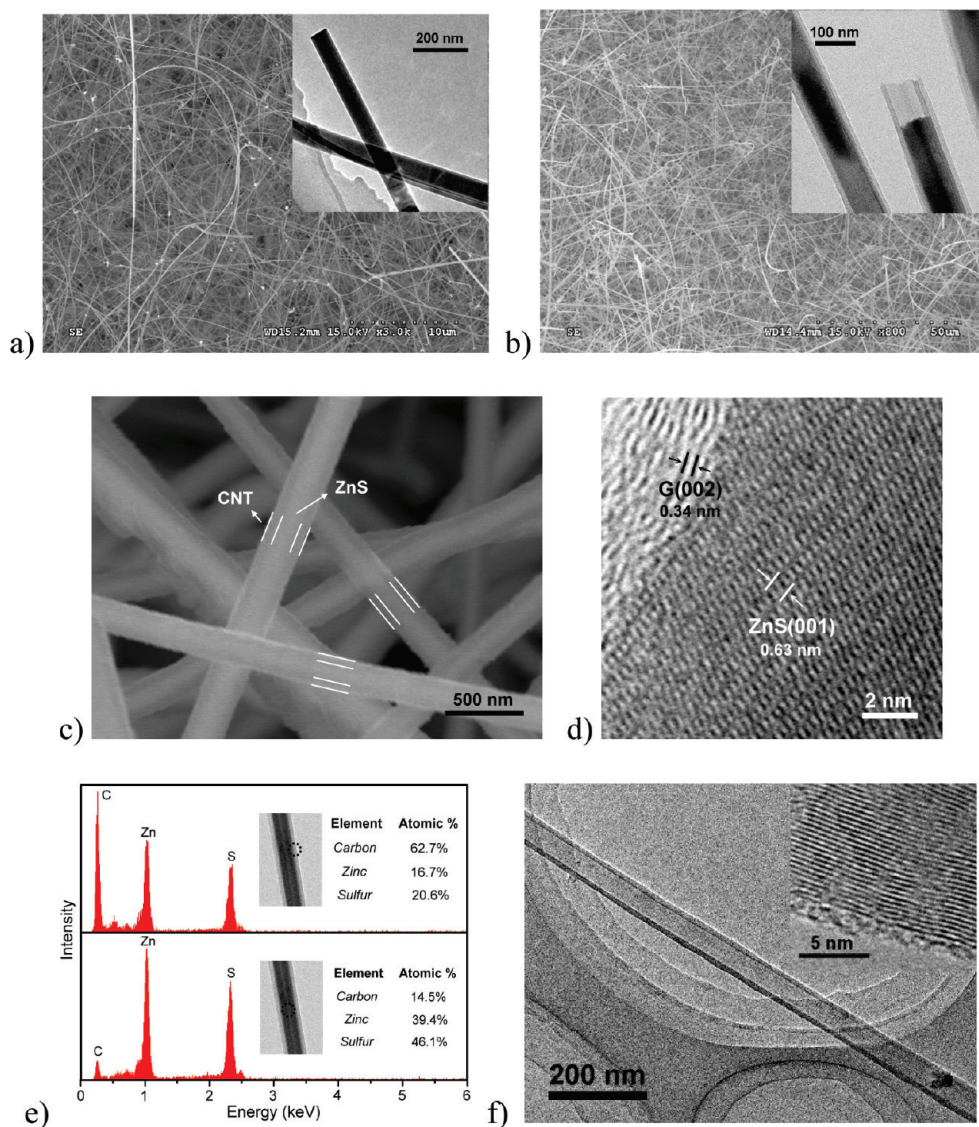


Figure 2. (a) SEM and TEM (inset) images of the ZnS nanowires. (b) SEM and TEM (inset) images of the ZnS/CNT nanocables. (c) Magnified SEM image of the ZnS/CNT nanocables. (d) HRTEM image of the interface between the ZnS core and the sidewalls of the CNT. (e) EDS spectra taken from the areas marked by the dashed circles in the insets, which are TEM images of a ZnS/CNT nanocable. (f) TEM and HRTEM (inset) images of the CNTs produced by removing the ZnS cores.

TEM images (Figure 2a, S2), inhomogeneous contrast can be observed along the surface of the nanowires. This phenomenon is due to the bending of the nanowires.^{22,23} The high resolution TEM (HRTEM) image (Figure S2 of the Supporting Information) shows that the nanowires have a perfect wurtzite structure of ZnS, and the selected-area electron diffraction (SAED) pattern (Figure S2) also confirms the single crystalline structure. After the second step, C is deposited as the sidewalls of CNTs on the surface of the ZnS nanowires; thus, nanocables with ZnS cores and MWNT sheaths are obtained. SEM images (Figure 2b, S3) show that the products have a filamentous morphology similar to the ZnS nanowires, and according to the SEM characterization, the diameter distributions of the ZnS nanowires and the ZnS/CNT

nanocables are shown in Figure S4. The magnified SEM image (Figure 2c) reveals that all of the nanowires are completely and uniformly sheathed by a layer with light contrast. TEM images (Figure S5, inset of Figure 2b) confirm the coaxial heterostructure, and both the diameter of the cores and the thickness of the sheaths are uniform along the total length of the nanocables. A typical HRTEM image (Figure 2d) reveals the crystal-line structure of the nanocables. The (001) crystal plane (0.63 nm) of the wurtzite ZnS and the graphite (002) of the CNT sidewalls (0.34 nm) can be clearly resolved, indicating the good crystallization of the nanocables. The elemental compositions of the nanocable in each area can be detected by EDS equipped on TEM. The EDS spectra (Figure 2e, Figure S6) reveal that the nanocables are composed of Zn, S, and C elements. The EDS spectrum taken from the shell area shows a high content of the C element; while the EDS spectrum taken from the core area shows the domination of Zn and S elements, thus the

(22) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, *291*, 1947–1949.
 (23) Williams, D. B.; Carter C. B. *Transmission Electron Microscopy: A Textbook For Materials Science*; Plenum Press: New York, 1996.

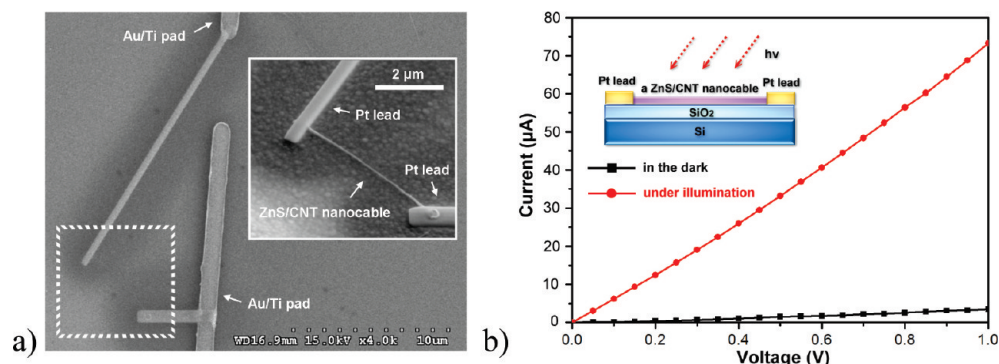


Figure 3. (a) SEM image of a ZnS/CNT nanocable device fabricated by FIB. The inset is the enlarged SEM image of the device. (b) I – V curves of the ZnS/CNT nanocable device in the dark and under illumination. The inset shows the configuration of the device.

nanocable consists of a ZnS core and a C sheath. Moreover, we note that the ZnS cores are not very uniform, as the atomic ratio of Zn:S measured by EDS would be different from one part to another (Figure 2e, Figure S6). The nonuniformity would come from the growth process.²⁴ Compared with EDS, XPS spectra provide an average elemental composition of the samples. As measured by XPS (Figure S7), the average atomic content of Zn is higher than S.

There have been many reports on the encapsulation of CNTs.^{25–27} In normal cases, the encapsulation includes opening and filling of CNTs by capillarity;²⁶ however, ZnS has a very high melting point (1820 °C). In other cases, the 1D core and the CNT sheath come into being synchronously in a CVD process.^{19,27} In our case, the ZnS/CNT nanocables form via another strategy, that the CNT sidewalls deposit on and then coat the ZnS nanowires in a two-step vapor deposition process. In the process, the ZnS nanowires serve as both the template and the catalyst for growth of the CNTs. The surface of the ZnS nanowires is reduced to Zn by H_2 at high temperature. As Zn can catalyze the growth of the CNTs,²⁸ CH_4 decomposes and dissolves in Zn, and then graphitic carbon layers grow from the saturated Zn by means of precipitation, leading to the formation of the coaxial ZnS/CNT structure.

Furthermore, ZnS can be dissolved by HCl. After HCl treatment, CNTs are obtained. We measured the CNTs by Raman and obtained a typical Raman spectrum of MWNTs with a D-band centered at 1332 cm^{-1} and a G-band centered at 1590 cm^{-1} (Figure S8 of the Supporting Information). In normal cases, MWNTs, produced by other methods, usually have closed ends and some partitions in the inner cavity. TEM images (Figure 2f) show that the MWNTs have not only a good crystalline

structure but also a straight and continuous cavity with open ends.

As an application, we fabricated photoelectric devices by FIB using individual ZnS/CNT nanocables, MWNTs, or ZnS nanowires. An example of the device is shown in Figure 3a. We measured the devices made of an individual MWNTs or ZnS nanowire in the dark and under white light illumination of a 200 W high-pressure Hg lamp, and the current–voltage (I – V) curves are shown in Figure S9 and Figure S10 (Supporting Information), respectively. The MWNTs exhibit good conductance and ideal ohmic contacts with electrodes but poor light response. Almost no obvious response can be detected under illumination. The ZnS nanowires show large light response, so that the conductance increases by more than 2 orders of magnitude under illumination. However, compared with the MWNTs, they have low conductance and poor contacts with electrodes. Typical I – V characteristics of a device made of a ZnS/CNT nanocable, which were measured in the dark and under illumination, are shown in Figure 3b. Good conductance and obvious light response are observed. Under illumination, the conductance increases by 1 order of magnitude from 0.7 to $14.7\text{ }\mu\text{S}$. The approximately linear shape of the I – V curves reveals ideal ohmic contacts between the nanocable and the electrodes. Therefore, compared with the bare ZnS nanowires and the MWNTs, the ZnS/CNT nanocables avoid the shortcomings of both of the pristine materials and show potential applications in photoelectronics.

Charge transfer in the hybrid nanostructures is usually considered to be responsible for many of their novel properties and applications. For instance, Li et al. fabricated bistable memories by using MWNTs with CdSe/ZnSe quantum dots covalently attached on the outer surface.²⁹ A bias-dependent charge transfer between the CdSe/ZnSe dots and the MWNTs occurred and gave rise to an internal electric field along the direction of the applied voltage, which resulted in a high-conductivity ON state of the MWNTs. In our case, MWNTs are encapsulated with ZnS cores, and along them, a coaxial Schottky junction exists. Under illumination, a built-in electric field across the junction separates the photoexcited electrons and holes. On

(24) Kim, Y.; Joyce, H. J.; Gao, Q.; Tan, H. H.; Jagadish, C.; Paladugu, M.; Zou, J.; Suvorova, A. A. *Nano Lett.* **2006**, *6*, 599–604.

(25) (a) Wei, D. C.; Cao, L. C.; Fu, L.; Li, X. L.; Wang, Y.; Yu, G.; Liu, Y. Q. *Adv. Mater.* **2007**, *19*, 386–390. (b) Wei, D. C.; Liu, Y. Q.; Cao, L. C.; Fu, L.; Li, X. L.; Wang, Y.; Yu, G. *J. Am. Chem. Soc.* **2007**, *129*, 7364–7368.

(26) (a) Dujardin, E.; Ebbesen, T. W.; Hiura, H.; Tanigaki, K. *Science* **1994**, *265*, 1850–1852. (b) Ajayan, P. M.; Iijima, S. *Nature* **1993**, *361*, 333–334.

(27) Hu, J. Q.; Bando, Y.; Zhan, J. H.; Zhi, C. Y.; Golberg, D. *Nano Lett.* **2006**, *6*, 1136–1140.

(28) Liu, J. W.; Li, X. J.; Dai, L. M. *Adv. Mater.* **2006**, *18*, 1740–1744.

(29) Li, F.; Son, D. I.; Kim, T. W.; Ryu, E.; Kim, S. W. *Nanotech.* **2009**, *20*, 085202.

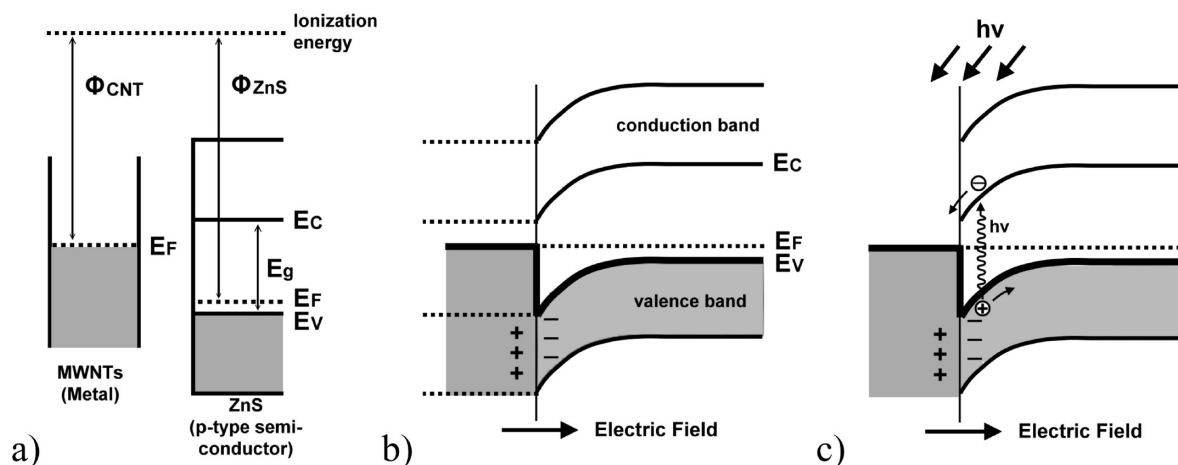


Figure 4. Schematic band diagrams for (a) a MWNT and ZnS, (b) a ZnS/CNT heterojunction, and (c) a ZnS/CNT heterojunction under illumination.

the basis of this photoexcited charge transfer, various types of photovoltaic devices have been built by using the coaxial nanostructures.^{30,31} In these devices, the electrodes contacted both the core and the shell of the coaxial junctions, and then the photoexcited charge transfer gave rise to a photogenerated current between the electrodes. In our case, both electrodes contact only the shell, thus the outmost shells of the MWNTs serve as the conducting channel, so it is not a photovoltaic device but a photoconductive device. In case of the normal photoconductive devices, light illumination excites electrons from the valence band into the conduction band, giving rise to an increased conductance and an obvious light response.³² MWNTs are usually regarded as a metallic material with a very small band gap (tens of millielectronvolts),¹¹ thus they show poor light response. However, the light response of the MWNTs is obviously improved in the case of the coaxial ZnS/CNT structure. The photoexcited charge transfer across the ZnS/CNT junction should be responsible for the improved light response. The band structures of the MWNTs and the ZnS are shown in Figure 4a. The MWNTs are metallic with good conductance,^{12,13,33} while the ZnS is a typical semiconductor with a wide band gap (ca. 3.7 eV). Due to its wide band gap, the ZnS shows perfect light response but very low conductance and poor contacts with electrodes. When ZnS is in contact with MWNTs, a Schottky junction forms at the interface, and this can be confirmed by the rectifying behavior across the ZnS/CNT junction measured by Du et al.²⁰ Figure 4b schematically depicts the band structure of the open-circuit ZnS/CNT junction. The work function of the p-type semiconductor ZnS (Φ_{ZnS}) amounts to about 7.0 eV,³⁴ while the MWNTs have a lower work

function (Φ_{CNT}) of about 4.8 eV,³⁵ thus electron transfer occurs across the interface from the MWNTs to the ZnS to provide equilibrium between the Fermi level of the MWNTs and the ZnS. As a consequence, the MWNTs are charged positively, while the ZnS is charged negatively. At the interface, an electrically charged layer and a built-in electric field form, producing a band bending close to the interface. Under illumination, electrons are excited from the valence band to the conduction band, thus the photoexcited electrons and holes, which act as free carriers for conduction, form. However, in normal cases, the strong 1D confinement leads to large Coulombic coupling between the photoexcited electrons and holes to create strongly bound excitons,⁴ thus the recombination of the photoexcited carriers largely decreases the photoconductivity. In our case, an inner-wire Schottky junction, which has a large built-in voltage (2.2 V), exists in the nanocables, thus the built-in electric field across the junction results in the separation of the photoexcited electrons and holes (Figure 4c), avoiding their recombination. Importantly, because of the cablelike configuration, the Schottky junction distributes along the total length of the nanocables, thus it results in a high efficiency of the electron–hole separation. In the ZnS/CNT nanocables, the MWNTs serve as the current-transport channel and the photoexcited electrons transfer to and concentrate into the MWNTs, causing an obvious increase of the conductance. At the same time, the photoexcited holes, which will be released in the dark, are trapped in the ZnS cores. Therefore, due to the photoexcited charge transfer, improved photoelectric properties are observed in the case of the coaxial ZnS/CNT nanocables. Furthermore, compared with the bare ZnS nanowires, the coaxial ZnS/CNT nanostructure also shows some other advantages. For example, the MWNTs favor ohmic contact,¹¹ thus the contact between the nanocables and the electrodes is improved, compared with the bare ZnS nanowires. In addition, the sheathing of inert sidewalls of the MWNTs can effectively prevent the inner ZnS,³⁶ thus ensuring a long-term stability of the ZnS cores.

- (30) Dong, Y. J.; Tian, B. Z.; Kempa, T. J.; Lieber, C. M. *Nano Lett.* **2009**, *9*, 2183–2187.
 (31) Tian, B. Z.; Zheng, X. L.; Kempa, T. J.; Fang, Y.; Yu, N. F.; Yu, G. H.; Huang, J. L.; Lieber, C. M. *Nature* **2007**, *449*, 885–890.
 (32) Jie, J. S.; Zhang, W. J.; Jiang, Y.; Meng, X. M.; Li, Y. Q.; Lee, S. T. *Nano Lett.* **2006**, *6*, 1887–1892.
 (33) (a) Frank, S.; Poncharal, P.; Wang, Z. L.; Heer, W. A. D. *Science* **1998**, *280*, 1744–1746. (b) Li, H. J.; Lu, W. G.; Li, J. J.; Bai, X. D.; Gu, C. Z. *Phys. Rev. Lett.* **2005**, *95*, 086601.
 (34) Fang, X. S.; Bando, Y.; Gautam, U. K.; Ye, C. H.; Golberg, D. *J. Mater. Chem.* **2008**, *18*, 509–522.
 (35) Suzuki, S.; Bower, C.; Watanabe, Y.; Zhou, O. *Appl. Phys. Lett.* **2000**, *76*, 4007–4009.

- (36) Wei, D. P.; Ma, Y.; Pan, H. Y.; Chen, Q. *J. Phys. Chem. C* **2008**, *112*, 8594–8599.

4. Conclusion

In summary, we produce the ZnS/CNT nanocables with uniform morphologies by a two-step vapor deposition method. After removing the ZnS cores, MWNTs with a straight, continuous cavity and open ends are obtained. These MWNTs can be used as nanocontainers or nanopipes and have potential applications as mass carriers, mass transportation devices, fluid field transistors, etc. The ZnS/CNT nanocables avoid the limitations of the ZnS nanowires and the CNTs, showing good conductance, obvious light response, and ohmic contacts with electrodes. A coaxial Schottky junction exists along the total length of the nanocables. The built-in electric field across the junction effectively separates the photoexcited carriers and avoids their recombination. Although current results are based on the ZnS/CNT nanocables, other 1D

nanomaterials with the coaxial Schottky junctions would also hold promise for high performance photoelectric devices. We believe that the present finding would be valuable for the current efforts to apply the 1D nanomaterials in photoelectronics.

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Supporting Information Available: Figure S1–S10. This material is available free of charge via the Internet at <http://pubs.acs.org>.