Growth of Ultralong ZnO Nanowires on Silicon Substrates by Vapor Transport and Their Use as Recyclable Photocatalysts

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We report the growth of ultralong ZnO nanowires on silicon (100) substrates via the gold-catalyzed vapor transport approach. An ample supply of zinc vapor generated through carbothermal reduction of ZnO powder at 917 °C and a suitable amount of oxygen facilitate the rapid growth of nanowires. These ZnO nanowires are extremely long with lengths of 85−100 μm, and exhibit an overall vertical orientation. The nanowires have largely diameters of 250−400 nm. Crystal structure analysis indicates typical ZnO nanowire growth along the [0001] direction. The band gap of these nanowires was determined to be 3.22 eV. These nanowires show a relatively weak near-band-edge emission peak at 390 nm, and a significant oxygen vacancy-related emission band at 495 nm. Good photocatalytic activity of these nanowires on substrates toward the photodegradation of rhodamine B and 4-chlorophenol was demonstrated. Furthermore, we showed that these nanowires on substrates can serve as effective and convenient recyclable photocatalysts. Only a slight decrease in the photodecomposition rate was observed after 10 cycles of the photocatalysis experiment. The photocatalysts also work well under natural sunlight.

Introduction

The interest in the preparation of one-dimensional (1D) ZnO nanostructures such as nanowires, nanobelts, and nanorods continued in the past few years partly because of their potential uses as active components in the fabrication of UV nanolasers,[1] field emission devices,[2] dye-sensitized solar cells,[3] photodetectors,[4] and electroluminescent devices.[5] In addition, the photocatalytic activity of 1D ZnO nanostructures has also been examined, although to a lesser extent.[6] For many of these applications, it is interesting to investigate the device characteristics using long and highly oriented nanowires and to see if nanowire length control can improve the device performance and design. Despite the large number of reports on the synthesis of 1D ZnO nanostructures, procedures describing the vapor or solution-phase growth of ultralong ZnO nanowires and nanobelts with lengths over tens of microns are rare.[2b,7−9] Furthermore, a report discussing the growth of ultralong (that is, around 100 μm) and highly vertically aligned ZnO nanowires on silicon substrates without catalyst particles at the tips that might hinder certain applications does not seem to be available yet. In this study, we present the growth of ultralong and largely vertically oriented ZnO nanowires by the chemical vapor transport method on silicon substrates coated with a very thin gold catalyst film. The nanowires can reach lengths of close to 100 μm and do not show catalyst particles at the tips. We have also characterized their crystal structure and optical properties. Another interesting property one can examine with these ultralong ZnO nanowires on substrates is their use as recyclable photocatalysts. Although the photocatalytic activities of various solution-dispersed ZnO nanostructures toward organic molecules have been widely documented, studies on their renewable photocatalytic properties are rarely performed, presumably because nanoparticle photocatalysts are less readily recovered for multiple use.[10−12] Here we also present our work on the use of these ultralong ZnO nanowires as recyclable photocatalysts. The photocatalytic activity of these nanowires under natural bright sunlight was also examined.

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(1) (a) Huang, M. H.; Mao, S.; Feick, H.; Yang, H.; Wu, Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. *Science* **2001**, *292*, 1897. (b) Zou, B.; Liu, R.; Wang, F.; Pan, A.; Cao, L.; Wang, Z. L. *J. Phys. Chem. B* **2006**, *110*, 12865.

(2) (a) Tseng, Y.-K.; Huang, C.-J.; Cheng, H.-M.; Lin, I.-N.; Liu, K.-S.; Chen, I.-C. *Adv. Funct. Mater.* **2003**, *13*, 811. (b) Wang, W.; Zeng, B.; Yang, J.; Poudel, B.; Huang, J.; Naughton, M. J.; Ren, Z. *Adv. Mater.* **2006**, *18*, 3275. (c) Park, C. J.; Choi, D.-K.; Yoo, J.; Yi, G.-C.; Lee, C. J. *Appl. Phys. Lett.* **2007**, *90*, 083107.

(3) (a) Law, M.; Greene, L. E.; Johnson, J. C.; Saykally, R.; Yang, P. *Nat. Mater.* **2005**, *4*, 455. (b) Law, M.; Greene, L. E.; Radenovic, A.; Kuykendall, T.; Liphardt, J. Yang, P. *J. Phys. Chem. B* **2006**, *110*, 22652. (c) Galoppini, E.; Rochford, J.; Chen, H.; Saraf, G.; Lu, Y.; Hagfeldt, A.; Boschloo, G. *J. Phys. Chem. B* **2006**, *110*, 16159.

(4) (a) Kind, H.; Yang, H.; Messer, B.; Law, M.; Yang, P. *Adv. Mater.* **2002**, *14*, 158. (b) Law, J. B. K.; Thong, J. T. L. *Appl. Phys. Lett.* **2006**, *88*, 133114.

(5) (a) Park, W. I.; Yi, G.-C. *Adv. Mater.* **2004**, *16*, 87. (b) Könenkamp, R.; Word, R. C.; Godinez, M. *Nano Lett.* **2005**, *5*, 2005.

(6) (a) Yang, J. L.; An, S. J.; Park, W. I.; Yi, G.-C.; Choi, W. *Adv. Mater.* **2004**, *16*, 1661. (b) Tian, Z. R.; Voigt, J. A.; Liu, J.; McKenzie, B.; McDermott, M. J.; Rodriguez, M. A.; Konishi, H.; Xu, H. *Nat. Mater.* **2003**, *2*, 821.

(7) Pan, Z. W.; Dai, S.; Rouleau, C. M.; Lowndes, D. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 274.

(8) Chang, P.-C.; Fan, Z.; Wang, D.; Tseng, W-Y.; Chiou, W.-A.; Hong, J.; Lu, J. G. *Chem. Mater.* **2004**, *16*, 5133.

(9) Lu, C.; Qi, L.; Yang, J.; Tang, L.; Zhang, D.; Ma, J. *Chem. Commun.* **2006**, 3551.

(10) Ye, C.; Bando, Y.; Shen, G.; Golberg, D. *J. Phys. Chem. B* **2006**, *110*, 15146.

(11) Wan, Q.; Wang, T. H.; Zhao, J. C. *Appl. Phys. Lett.* **2005**, *87*, 083105.

(12) Kuo, C.-L.; Kuo, T.-J.; Huang, M. H. *J. Phys. Chem. B* **2005**, *109*, 20115.

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Experimental Section

For the growth of ZnO nanowires on silicon substrates, 0.8 g of zinc oxide powder (J. T. Baker, 99.7%) and 0.8 g of fine graphite powder (Riedel-de Haën) were first well mixed by grinding. The powder mixture was transferred to a ceramic boat. Silicon (100) wafers cut to 1.5 cm × 1.5 cm were boiled with piranha acid (H_2SO_4:H_2O in 4:1 volume ratio) for 45 min, in deionized water for another 45 min, and then sonicated in acetone and 2-propanol for 5 min, respectively. After being dried with a nitrogen stream, these substrates were sputtered with a 1-nm gold thin film as the catalyst for nanowire growth. Four substrates were mounted on the ceramic boat with the gold film facing the powder mixture for enhanced nanowire growth. The distance between the substrates and the reagent powder was about 2−3 mm. The ceramic boat was placed in the middle of a tube furnace with a 2-in. quartz tube (Thermolyne 79300). The quartz tube was purged with 50 sccm of argon and 15 sccm of oxygen. Then the furnace temperature was raised to 917 °C at a rate of ∼50 °C/min and under the same carrier gas flow. After reaction for 15 min, the furnace was allowed to cool to collect the nanowire product.

To examine the photocatalytic activity of the synthesized ultralong ZnO nanowires on silicon substrates, rhodamine B (Aldrich) and 4-chlorophenol (Sigma) were chosen for the photodecomposition study. First, 3 mL of 1.0×10^{-5} M rhodamine B solution was added to a typical quartz cell, and 3 mL of 1.0×10^{-4} M 4-chlorophenol solution was added to another. Two substrates with the ultralong ZnO nanowires cut to 1.5 cm × 1 cm were vertically immersed into the two solutions separately. The two quartz cells were placed side-by-side and irradiated with light produced from a 100-W mercury lamp. The cells were placed about 25 cm from the light source to minimize the heat effect. The light intensity reaching the cells was 200 mW, as measured by a power meter. The UV−vis absorption spectra of the solutions as a function of time were recorded by removing the substrates. The spectra were obtained using a JASCO V-570 spectrophotometer. After the spectral measurements, the substrates were placed back into the solutions for further irradiation at intervals of 30 min for up to 300 min. For the examination of the ZnO nanowires on the silicon substrates as recyclable photocatalysts, UV−vis absorption spectra were taken before and after irradiation for 60 and 120 min. After that, the substrates were rinsed with deionized water to fully remove the residual organic species on the substrates. The same substrates were subsequently immersed into fresh rhodamine B and 4-chlorophenol solutions at the same concentrations for another run of experiment. The procedure was performed for 10 cycles to evaluate the suitability of the ZnO nanowires for multiple uses in the photodecomposition of common organic dye molecules and environmental contaminants. In addition, photodecomposition of rhodamine B under direct sunlight was tested. The same concentration of rhodamine B solution was used. UV−vis absorption spectra of the samples with and without placing a substrate with ZnO nanowires were taken after 6 h of bright sunlight irradiation.

The morphology of the as-synthesized ZnO nanowire samples was examined with the use of field emission scanning electron microscopes (FE-SEM) (Hitachi S4700 and JEOL JSM-6360F). The substrates were purposely cut and placed vertically to examine the nanowire growth condition on the substrate surface. A JEOL JEM-3000F field emission transmission electron microscope (TEM) operated at 300 kV was used for the detailed structural characterization of the nanowires. Powder X-ray diffraction (XRD) patterns of the nanowire samples were obtained with a Shimadzu XRD-6000 diffractometer with Cu Kα radiation. UV−vis diffuse reflectance spectra of the samples were recorded on a Hitachi U-3310 spectrophotometer equipped with an integrating sphere. A Hitachi F-4500 fluorescence spectrophotometer with a solid sample holder was used for the photoluminescence spectra of the nanowire samples.

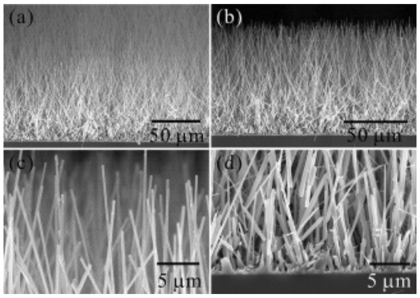

Figure 1. FE-SEM images of the as-synthesized ZnO nanowires on silicon substrates. (a) Tilted view of the nanowires over a large area. The underlying silicon substrate was also imaged. (b) Cross sectional view of the nanowires. (c) Close view of the tip region of the nanowires. (d) Close view of the base region of the nanowires. Some nanowires appear to be suspended above the substrate due to breakage of the substrate to reveal the cross section.

Results and Discussion

The ultralong ZnO nanowires were synthesized by transporting zinc vapor, generated through the carbothermal reduction of ZnO powder at 917 °C (1:1 weight ratio of ZnO and graphite powder), onto gold-catalyzed silicon substrates in a mixed argon−oxygen carrier gas flow. The substrates were placed just millimeters away from the zinc vapor source. The reaction conditions were optimized to grow the longest ZnO nanowires possible. Figure 1 shows the large-area and close FE-SEM views of the as-synthesized ZnO nanowires on silicon (100) substrates. The nanowires are extremely long with typical lengths of 85−100 μm. They are largely vertically oriented, although a portion of them are tilted at some angles, presumably due to the crowding effect and crystal growth condition at the base of the nanowires (see Figure 1d). These nanowires can grow to such ultralong lengths possibly because of the ample supply of zinc vapor and oxygen near the substrate surface that enhances rapid nanowire growth. The nanowire diameters are largely in the range of 250−400 nm (see Figure 1c). No catalyst particles were observed at the flat wire tips. The relatively large diameters give the nanowires a straight and rigid appearance. A smaller portion of thinner nanowires in the range of 100−200 nm are also present and can be as thin as less than 100 nm. In many cases, the nanowire diameters were found to be larger near the base region as a result of side crystal growth. This side growth is related to the fast and dense growth of ZnO nanowires on the substrate such that a thin ZnO crystal film appears to cover the substrate surface (see Figure 1d). The initial nanowire growth may be gold-catalyzed, but the large and continuous arrival of reagent vapor can then deposit on the substrate surface, leading to the elongation of the nanowires and the side growth of crystals near the substrate surface. Without the thin gold film, nanowire growth was not observed. This firm nanowire base and the rigid wire structure enable the growth of ultralong nanowires with highly vertical orientation. Alternatively, the nanowire growth may start from a thicker base and then reduce the wire diameter as the growth front

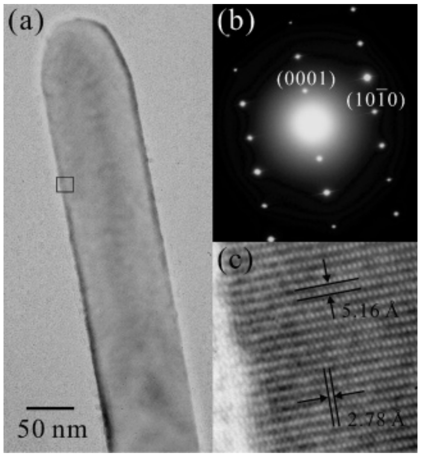

Figure 2. (a) TEM image of a single ZnO nanowire. This thin nanowire was used for the structural characterization. (b) SAED pattern of this nanowire. (c) High-resolution TEM image of the square region in panel a.

condition changes to favor thinner wire formation. If the reaction temperature was raised to 925 °C, the nanowires became thicker, because of the enhanced lateral growth. At a reaction temperature of 900 °C, the zinc vapor pressure was decreased, and the resulting nanowires were thinner with lengths of just about 20 μm. The flow rate of oxygen was also optimized. Upon increasing the oxygen flow rate to 25 sccm, shorter and thinner nanowires were obtained, due to the faster reaction of oxygen with graphite powder and the reduction of zinc vapor generation. On the other hand, low oxygen levels (or without oxygen flow) can lead to a fast lateral growth at such high temperatures and thus do not favor the formation of ultralong nanowires (see the Supporting Information).

The crystal structure of these nanowires was characterized using XRD patterns and TEM images. The XRD pattern of these nanowires reveals a typical diffraction pattern of pure ZnO with an exceptionally strong (002) peak, indicating preferential growth of these nanowires along the *c*-axis of ZnO (see the Supporting Information). The TEM image of a thin ZnO nanowire is provided in Figure 2. Again no catalyst particle can be seen. The selected-area electron diffraction (SAED) pattern of this nanowire indicates wire growth along the [0001] direction. The high-resolution TEM image of this nanowire, shown in Figure 2c, reveals clear lattice fringes. Two sets of lattices with distances of 5.16 and 2.78 Å were measured and should correspond to the (0001) and (10$\bar{1}$0) planes of wurtzite ZnO, respectively.

Measurements of the optical properties of these ZnO nanowires were also performed. UV−vis diffuse reflectance spectrum of the nanowires on a silicon substrate was used to determine the band gap of these nanowires (see Figure 3). A band gap of 3.22 eV was obtained. This band gap is slightly smaller than the well-known band gap of 3.37 eV for bulk ZnO. We have taken the same diffuse reflectance spectrum using ZnO powder purchased from J. T. Baker Inc. with irregularly shaped particles several hundred nanometers to 1 μm in length and got the same band gap energy. The same band gap energy of 3.22 eV for vertically grown

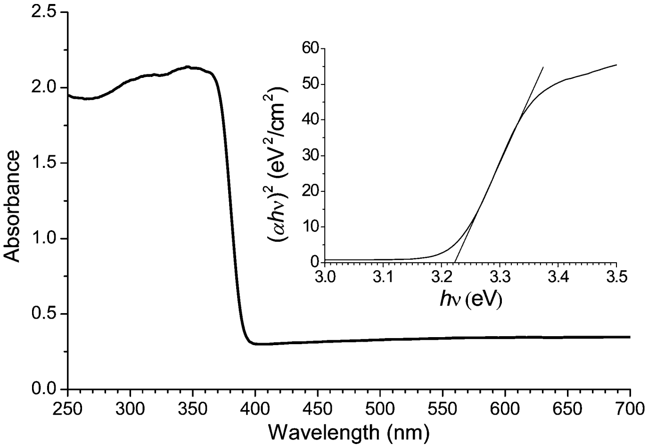

Figure 3. UV−vis diffuse reflectance spectrum of the as-synthesized ZnO nanowires on a silicon substrate. The inset shows a plot of $(\alpha h\nu)^2$ vs $h\nu$ for the determination of the direct band gap of the nanowires. The numerical values of $(\alpha h\nu)^2$ may not be right due to a lack of information on the sample thickness or path length.

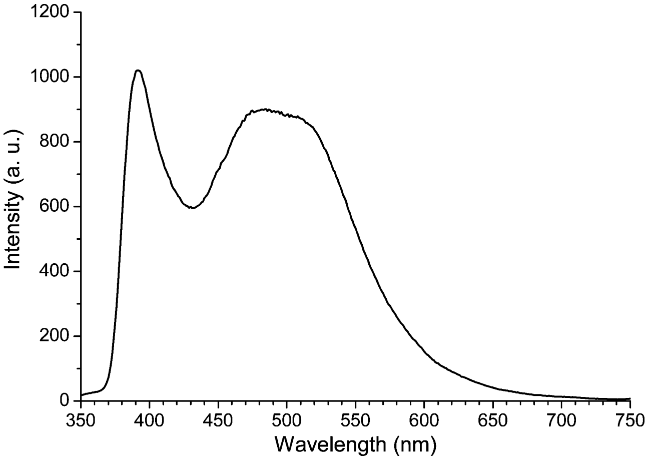

Figure 4. Photoluminescence spectrum of the as-synthesized ZnO nanowires on a silicon substrate.

ZnO nanorods on fused silica has been reported.[13] The photoluminescence spectrum of these nanowires shows a near-band-edge emission peak at 390 nm and a broad oxygen-vacancy-related emission band centered at 495 nm (see Figure 4). This relatively weak near-band-edge emission and significant defect-related emission property of these nanowires may be beneficial to their photocatalytic activity. The surface oxygen deficiencies are electron capture centers, which can reduce the recombination rate of electrons and holes and thus enhance the photocatalytic activity of these nanowires.[11,14]

The photocatalytic activity of these ultralong ZnO nanowires on silicon substrates was investigated using rhodamine B and 4-chlorophenol as test molecules. The substrates were immersed in these solutions and irradiated with light from a mercury lamp. UV−vis absorption spectra of the solutions were recorded before and after irradiation for 30 min over a period of 300 min. Figure 5 shows the changes in the UV−vis absorption spectra of these molecules over this period. The nanowires clearly work as effective photocatalysts. The

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(13) Wu, J.-J.; Liu, S.-C. *J. Phys. Chem. B* **2002**, *106*, 9546.
(14) Lu, G.; Linsebigler, A.; Yates, J. T., Jr. *J. Phys. Chem.* **1995**, *99*, 7626.

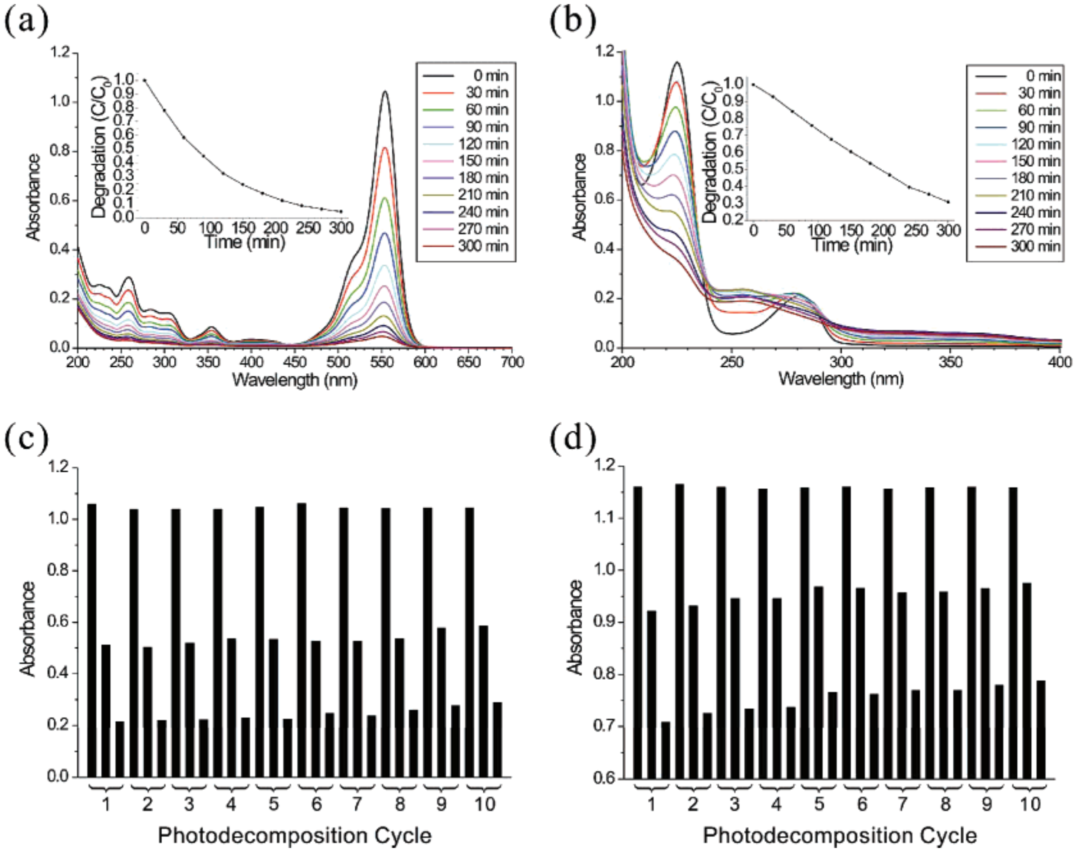

Figure 5. (a and b) UV−vis absorption spectra of rhodamine B and 4-chlorophenol as a function of irradiation time, respectively. The initial solution concentrations were purposely chosen to give an absorbance value above 1.0. Insets show the fraction of remaining molecules with respect to time. (c and d) Tests of absorbance changes as a function of irradiation time over 10 cycles for rhodamine B and 4-chlorophenol, respectively. Absorbance values at 554 nm for rhodamine B and 225 nm for 4-chlorophenol were used. In each cycle, spectra were taken before and after irradiation for 60 and 120 min.

fractions of remaining molecules with respect to time are also given in Figure 5. The exponential decay profiles and plots of ln(C/C_0) versus time suggest that the photodecomposition reactions follow pseudo-first-order rate law. The calculated rate constant for rhodamine B is 0.011 s^{-1} and for 4-chlorophenol is 0.004 s^{-1}. The difference in the rate constants may be related to their different polarity and the degree of adsorption onto the crystal surface. With the successful exhibition of these nanowires as effective photocatalysts, their use as recyclable photocatalysts was further studied. After taking absorption spectra of the solutions before and after 1 and 2 h of irradiation, the substrates were rinsed to remove residual molecules and immersed into fresh solutions of the same concentrations for another cycle of the photodecomposition experiment. The results, given in Figure 5c,d, demonstrate that these nanowires can serve as highly effective and convenient recyclable photocatalysts. After 10 cycles, only a slight decrease in the photodecomposition rate was observed due to a possible loss of some nanowires during the substrate rinse. SEM examination of the substrates after 10 cycles suggested that the nanowire appearance and density did not show noticeable change. Hence, the substrates are expected to be useful for many more cycles. To further extend the photocatalytic applicability of these nanowires in a more practical situation, the photocatalytic activity of these nanowires under natural sunlight was also evaluated. As illustrated in Figure 6, about 65% of rhodamine B was decomposed after exposure to 6 h of bright sunlight. On the other hand, practically no change in the UV−vis absorption spectrum of rhodamine B was recorded in the absence of the ZnO nanowires. The results demonstrate the excellent photocatalytic ability of these ultralong ZnO nanowires without artificial light source.

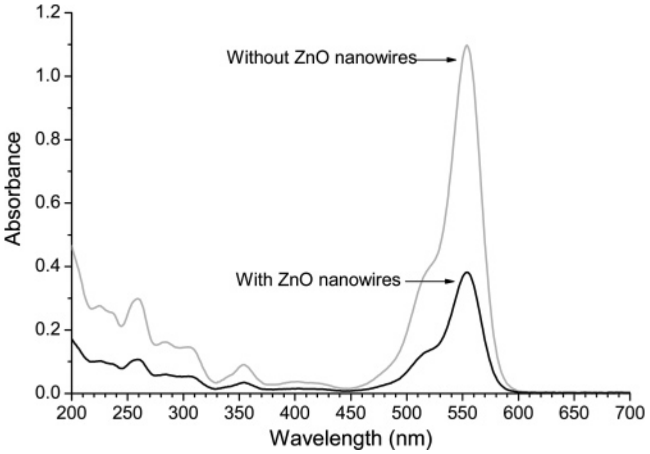

Figure 6. UV−vis absorption spectra of rhodamine B after placing the samples under natural bright sunlight for 6 h in and out of the presence of ZnO nanowire photocatalysts.

Conclusion

In summary, we have successfully grown ZnO nanowires with ultralong lengths of close to 100 μm by the gold-catalyzed vapor transport method. The nanowires are straight and show overall vertical orientation. Their crystal structure and optical properties have been examined. These nanowires have also been demonstrated to work as effective and recyclable photocatalysts and exhibit excellent photocatalytic activity under natural sunlight. It is expected that these ultralong nanowires may possess other interesting properties for optoelectronic applications.

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Supporting Information Available: SEM images of the ZnO nanowires grown under different oxygen flow rates and the XRD pattern of the ZnO nanowires (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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