SiC nanowires: A photocatalytic nanomaterial

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Single-crystal β-SiC nanowires coated with amorphous SiO2 were synthesized by a simple thermal evaporation technique. The photocatalytic activity of the SiC nanowires was characterized by measuring the photodegradation rate of acetaldehyde catalyzed by SiC as a function of UV irradiation time. It exhibited excellent photocatalytic activity, leading to the efficient decomposition of acetaldehyde by irradiation with UV light. The progress of the photocatalytic reaction can be monitored by the evolution of one of the products, CO2. It has been observed that the as-synthesized SiC nanowires (with the SiO2 coating) have higher catalytic activity than the HF-etched, oxide-free SiC nanowires. © 2006 American Institute of Physics. [DOI: 10.1063/1.2219139]

Since Fujishima and Honda’s finding of photoinduced decomposition of water on titanium dioxide (TiO2) electrodes in 1972, the huge potential of photocatalysts has been recognized and a variety of materials have been studied for their photocatalytic properties. These materials include various oxides and sulfides with structure similar to TiO2, such as WO3, ZrO2, V2O3, ZnO, CdS, and SeO2.1–5 Among these photocatalysts, most of them are wide-band-gap semiconductors. The fact that many photocatalysts are wide-band-gap semiconductors leads many scientists to seek for new photocatalysts in semiconductors intensively. Bulk silicon carbide (SiC), one of the third-generation wide-band-gap semiconductor materials, has been extensively researched on its electrical, physical, and chemical properties. Also, a great deal of effort has been ongoing to the research on fabrication, characterization, and properties of SiC in the form of nanowires, due to its usage as the reinforcement in composites and the components in constructing nanodevices.19–28 In contrast to the extensive research in the above fields, very few studies have involved in the photocatalytic activity of SiC nanowires. In this letter, we report the photocatalytic activity of the β-SiC nanowires fabricated by high-frequency induction heating method.

The β-SiC nanowire was prepared in a vertical high-frequency induction-heating furnace. The furnace is comprised of a cylindrical quartz tube and a cylinder graphite crucible coated by a layer of activated carbon fiber (ACF). The detailed experiment was described elsewhere.29

The x-ray diffraction (XRD) pattern of the obtained product is shown in Fig. 1(a) and it was indexed to a β-SiC structure. Figure 1(b) is a field-emission scanning electron microscopy (FESEM) image of SiC sample and it shows that the SiC exhibits a wirelike nanostructure with an average diameter of 8–20 nm and a maximum length of up to tens of microns. In addition, a low-magnification transmission electron microscopy (TEM) image [Fig. 1(c)] indicates that SiC nanowires are coated by a trace of amorphous layer that is identified as silicon oxide.29

It is well known that the photocatalytic activity of a semiconductor material strongly depends on the specific surface area of the material, and the large surface area of the nanosized material can yield higher efficiency photocatalytic reactions. In our research, the specific surface area of the samples was analyzed by Brunau-Emmet-Teller (BET) method using an Autosorb-1 (NOVA1000 Series) with nitrogen adsorption at 77 K. Prior to adsorption, the samples were purged in helium gas atmosphere at 473 K for 1 h. As a result, the as-synthesized SiC nanowires have a BET specific surface area as large as 62.3432 m2 g−1, implicating a strong...
ability of absorbing gaseous acetaldehyde, which is selected as target pollutant during the following measurement of photocatalytic activity of SiC.

The optics transmittance of the samples was measured by double light beam ultraviolet visible light spectrophotometer (TU-1901). Figure 2 shows the optical transmittance as a function of wavelength for SiC de-ionized (DI) water solutions with different concentrations. Despite their different concentrations, the transmittances of three SiC solution samples increase monotonically with the wavelength. Moreover, at a certain wavelength, the higher the SiC nanowire concentration in the solution, the lower transmittance of the solution is. As can be seen from Fig. 2, when the wavelength is smaller than 450 nm, the transmittances of all the three SiC solutions decrease rapidly. Moreover, the absorption edge of the solution is shown to shift with the variation of concentration of SiC nanowires in the solution.

According to Ref. 30, the transmittance $T$ can be expressed as follows:

$$T = e^{-\alpha x},$$

where $T$ is transmittance, $\chi$ is the effective thickness of the sample, and $\alpha$ is the absorption coefficient. It is known that the relationship between the absorption coefficient $\alpha$ near the absorption edge and the optical band gap $E_g$ for indirect intraband transitions follows

$$\alpha^{1/2} = A^* (h\nu - E_g),$$

where $A^*$ is constant, $h\nu$ is the photoenergy, $h$ is the Planck constant ($6.63 \times 10^{-34}$ J s), $v$ is the frequency of the incident light, and $E_g$ is the optics band gap of the semiconductor. The absorption coefficient $\alpha^{1/2}$ of SiC nanowire solution as a function of the photon energy $h\nu$ was plotted in Fig. 3. The band gap energies were determined by extrapolating of the linear part of curves to $\alpha$=0. It can be clearly seen that the band-gap energy of SiC nanowires is $2.5$ eV with a slight blueshift with respect to that of bulk $\beta$-SiC ($2.3$ eV), as is probably caused by the quantum-size effect of nanomaterials. So, the SiC nanowires have stronger UV absorption ability. As the result of the confinement, the band gap of SiC nanowire increases and the band edge shifts.31

The photocatalytic activity of the SiC nanowires was evaluated by measuring the photodegradation rates of CH$_3$CHO for SiC in a quartz vessel as a function of UV irradiation time under UV light. The photodegradation rate is calculated by the following equation:

$$\text{photodegradation rate} = (C_0 - C)/C_0 \times 100\%,$$

where $C_0$ is initial concentration of gaseous acetaldehyde (CH$_3$CHO) and $C$ is the CH$_3$CHO concentration at time $t$. From Fig. 4(a), we observed that the photodegradation rate of CH$_3$CHO increases monotonically with the extension of irradiation time $t$. Plots of ln$(C_0 - C)/C$ vs. $t$ for each run fit on a straight line, which indicates that CH$_3$CHO decomposition is a first order reaction.

It was found from Fig. 4(a) that the increase of the initial gaseous acetaldehyde concentration leads to a strengthened conversion of gaseous acetaldehyde. This is attributed to the larger amount of those gaseous acetaldehyde molecules attached to the surface of the SiC nanowire powders. After 6 h,
the photodegradation of SiC to initial 100 ppm of gaseous acetaldehyde is 54.99%, increased by 12% for the initial 50 ppm of gaseous acetaldehyde. These results shown in Fig. 4(b) are also corroborated by the concentration variation of produced CO2, evolved as result of photodecomposition of acetaldehyde, as a function of irradiation time. The CO2 concentration increases with the photodegradation rate of gaseous acetaldehyde. That is to say, the acetaldehyde is converted into CO2. However, the CO2 concentration increase is not linear because of the appearance of intermediate compound during the conversion process. In the subsequent reactions, it is generally agreed that the formed acetic acid is the intermediate compound from the conversion of acetaldehyde by photocatalysis in gaseous phase. Moreover, the enhanced photocatalytic activity of SiC nanowires is attributed to the generation of the strong oxidant OH radical.

\[
\text{SiC} + h\nu \rightarrow e^- (\text{electron}) + h^+ (\text{hole}),
\]

\[
\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-,
\]

\[
h^+ + \text{OH}^- \rightarrow \text{OH},
\]

\[
\text{H}_2\text{O} + h^+ \rightarrow \text{H}^+ + \text{OH}^-,
\]

\[
\text{CH}_3\text{CO} + \text{H}_2\text{O} + 2h^+ \rightarrow \text{CH}_3\text{COOH} + \text{H}^+ + 2\text{OH}^-,
\]

\[
\text{CH}_3\text{COOH} + 2h^+ + 2\text{OH}^- \rightarrow 2\text{CO}_2 + 2\text{H}^+. 
\]

To investigate the effect of the SiO2 coating on SiC nanowires on photodegradation activity of SiC nanowires, the 5% HF etched SiC nanowires (remove off the coated SiO2 layer completely) were also studied under the same conditions. As can be seen from Fig. 4, the synthesized SiC nanowires have higher photocatalytic activity than the HF-treated SiC nanowires. The enhanced photocatalytic activity of synthesized SiC nanowires can be explained by the enhanced absorption of gaseous acetaldehyde on the SiC nanowires over the HF-treated SiC nanowires, or by the high probability of trapping of an excited electron in the conductive band of SiC coated by SiO2 and holes remain in the valence band of SiC. The process leads to more efficient and longer charge separation by minimizing the electron-hole recombination. Nanosized SiO2 was rich in massive superficial hydroxyl radicals (−OH), which can form activate hydroxyl radicals (OH) according to a reaction with excited electronic and hole. In addition, based on the consumption of lattice oxygen atoms for the “related” TiO2 system proposed by Thompson et al., the SiO2 layer is probably responsible for the enhanced catalytic activity for acetaldehyde because it may be a significant source of oxygen for the oxidation of acetaldehyde.

In conclusion, large-scale β-SiC nanowires coated with a trace of amorphous silicon oxide layer were synthesized by high-frequency induction heating of SiO powders. Particularly a single nanowire has an average core of 8–20 nm in diameter. The optical band gap was evaluated to be about 2.5 eV, which indicates a slight blueshift from the bulk SiC. The photocatalytic activity of the obtained β-SiC nanowires was evaluated by the photocatalytic decomposition of gaseous acetaldehyde accompanied by the generation of CO2. The result shows that the β-SiC nanowire exhibits the characteristic of an excellent photocatalyst. Furthermore, it is found that the as-synthesized amorphous SiO2 coated SiC mani-

fests higher photocatalytic activity than the bare SiC nanowires, resulting from their stronger absorption of gaseous acetaldehyde and higher probability of trapping of an excited electron in the conductive band of SiC covered by SiO2 and holes remaining in the valence band of SiC.

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\[\text{SiO}_2 + 2\text{H}_2\text{O} + 2h^+ \rightarrow 2\text{H}_2\text{O} + 2\text{OH}^- + 2\text{O}^- + 2\text{H}^+\]

\[\text{H}_2\text{O} + h^+ \rightarrow \text{H}^+ + \text{OH}^-\]

\[\text{CH}_3\text{CO} + \text{H}_2\text{O} + 2h^+ \rightarrow \text{CH}_3\text{COOH} + \text{H}^+ + 2\text{OH}^-\]

\[\text{CH}_3\text{COOH} + 2h^+ + 2\text{OH}^- \rightarrow 2\text{CO}_2 + 2\text{H}^+\]