TiO₂–CdSe nanowire arrays showing visible-range light absorption

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High-density single crystalline TiO₂ nanowires (~50 nm diameter) were grown on Ti substrates by chemical vapor deposition, and they were overcoated with the solution containing CdSe nanocrystals (~5 nm diameter) and heat treated at 600 °C to form TiO₂ heterostructured nanowire arrays. The TiO₂ nanowire arrays showed uniformly distributed CdSe nanocrystals and high crystallinity of rutile and wurtzite from the TiO₂ and the CdSe, respectively. Owing to the heterostructure of TiO₂, they demonstrate almost full visible-range light absorption, and thus enhanced photocatalytic activity by the charge separation via electron and hole transfers between the CdSe and the TiO₂.

TiO₂ is one of the most important oxide semiconductors showing distinct photochemical activities due to its unique energy band gap characteristics. Thus, for many years, it has been intensively exploited for the purification of contaminated water and air1–4 and for the generation of renewable energy.5–8 Recently, TiO₂ nanostructures have attracted a great deal of interest due to the large surface-to-volume ratio that is beneficial to most of the TiO₂-based devices. As the surface absorbing the light and reacting with surrounding substances increases, the photochemical activity can be considerably enhanced.9 However, the poor natural light absorption capability due to its intrinsically large energy band gap (~3.2 eV) has been significantly limiting the broad applications of the TiO₂ nanostructure for photocatalysts and photoelectrodes. To overcome this drawback, organic or inorganic dye-sensitized TiO₂ heterostructures have been developed, and the improvement of their natural light absorption capability has been reported.10,11 Also, the dyesensitized TiO₂ can show active photochemical reactions by charge separation.12 The free electrons generated in the dye by the visible light excitation can be injected to the TiO₂, and the holes from the TiO₂ can transfer to the dye, which can prevent the electron-hole recombination effectively, and provide high photovoltaic and photocatalytic efficiencies. Semiconductors such as CdSe, CdS, PbS, etc., have energy band gap corresponding to the energy of visible-range light and can serve as the inorganic dye for the TiO₂.13–15 These inorganic dyes show the superior thermal stability, photostability, and chemical stability compared to the organic dyes. It has been well known that due to the intrinsic energy band gap structure, the CdSe–TiO₂ is a good combination to obtain high photoconversion and high photodecomposition efficiencies. In the TiO₂–CdSe heterostructure, prior to the electron-hole recombination, photogenerated electrons from the CdSe transfer to the TiO₂, while the holes from the TiO₂ transfer to the CdSe.

TiO₂ nanowire is a desirable structure for both the photovoltaic and photocatalyst applications due to its array structure on a substrate compared to the common particle form.16–18 Each individual nanowire can supply plenty of surface area, while the nanoparticles are apt to agglomerate and lose the surface area. Also, the nanowire can provide the free electrons with the fast diffusion path between the two electrodes in dye-sensitized solar cells. Recently, we developed single-crystalline TiO₂ nanowire arrays on sapphire and silica, and Ti substrates, respectively, by chemical vapor deposition.16 Especially, we could grow the nanowires of ~50 nm diameter and ~10 μm length on Ti substrates at a very low temperature (~700 °C) within a very short period of time (~10 min) due to the seeding effect of the TiO₂ (rutile) layer formed at the surface of Ti substrates. In this letter, we report the synthesis of TiO₂–CdSe nanowire arrays through the overcoating of the surface of TiO₂ nanowires, grown on Ti substrates, with CdSe nanocrystals. The light absorption and photocatalytic characteristics of the heterostructure were investigated and compared with those of the bare TiO₂ nanowire arrays.

First, high-density TiO₂ nanowire array was prepared on the Ti substrates by chemical vapor transport of TiCl₄ via the vapor-liquid-solid growth. Au layer was used as a catalyst, and O₂ [0.5 SCCM (SCCM denotes cubic centimeter per minute at STP)] and H₂ (20 SCCM)/Ar (100 SCCM) was used as a reactive and a carrier gas, respectively. The substrate temperature was 700 °C, and the time period for the growth of TiO₂ nanowires was 10 min. Next, the CdSe nanocrystals were synthesized using inverse micelles of paraffin oil and oleic acid. CdO and Se shots were used as precursors for the CdSe nanocrystals. Rapid injection of Cd–oleic acid solution at 160 °C into the Se–paraffin oil solution at 220 °C induces the fast nucleation and slow growth of the CdSe nanocrystals. The TiO₂ nanowires were overcoated by the CdSe nanocrystal-bearing solution and heat treated at 600 °C for 30 min in Ar gas for strong attachment of the nanocrystals and removal of organic remaining.

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Figure 1 shows field-emission scanning electron microscopy (FESEM) images of the (a) bare single-crystalline TiO\textsubscript{2} and (b) heterostructured TiO\textsubscript{2}–CdSe nanowire arrays annealed at 600 °C for 30 min, respectively. The FESEM image shows that uniform TiO\textsubscript{2} nanowires with a diameter of 50–70 nm and a length of 5–10 μm were formed at 700 °C within 5 min. This is a noticeable progress in the vapor-phase TiO\textsubscript{2} nanowire synthesis compared to the previous processes conducted at ~1000 °C for ~90 min.\textsuperscript{16-18} These enhanced kinetics of the nanowire growth can originate from the seeding effect of the rutile TiO\textsubscript{2} layer formed at the surface of the Ti substrates as well as the supplementary Ti vapor supply from the Ti substrates to the Au catalyst. The rutile seed layer can decrease the activation energy barrier for the nucleation of the rutile crystals due to the epitaxy and in turn significantly enhance the nucleation and growth kinetics of the rutile TiO\textsubscript{2} nanowires. The TiO\textsubscript{2}–CdSe nanowires showed very rough surface due to the attachment of the CdSe nanocrystals.

The TiO\textsubscript{2}–CdSe nanowires were uniformly attached to the surface of the TiO\textsubscript{2} nanowire. The SAED on the TiO\textsubscript{2}–CdSe nanostructure shows the apparent ring diffraction patterns from the crystallinity of the wurtzite CdSe nanocrystals as well as spot diffraction patterns from the rutile TiO\textsubscript{2} nanowires.

Figure 3 shows the comparison in the UV-visible light absorption spectroscopy results of the bare TiO\textsubscript{2} and TiO\textsubscript{2}–CdSe heterostructured nanowires. The TiO\textsubscript{2} nanowires arrays were grown on a large Ti substrate and it was cut into two pieces, respectively, for the preparation of the TiO\textsubscript{2} and TiO\textsubscript{2}–CdSe nanowire samples. Thus, we can safely consider that the density of TiO\textsubscript{2} nanowires is almost identical both in the bare TiO\textsubscript{2} and TiO\textsubscript{2}–CdSe nanowire samples. The TiO\textsubscript{2}–CdSe nanowires show apparent increase in the light absorbance of the visible light ranging from ~400 to 700 nm. This much enhanced visible-range light absorption in the TiO\textsubscript{2}–CdSe nanowires is attributed to the excitation of electrons in the CdSe. Since the size distribution of the CdSe nanocrystals attached to the surface of the TiO\textsubscript{2} nanowires was ~5–10 nm, the energy band gap of them ranges from 2.48 to 1.74 eV, according to the following quantum confinement effect,\textsuperscript{19} and the corresponding light absorption wavelength ranges from 500 to 714 nm.

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E_g(\text{dot}) = E_g(\text{bulk}) + \frac{\hbar^2}{2m^*d^2} - \frac{1.8e^2}{2\pi\varepsilon_0d}.
\]

Here, \(E_g(\text{dot})\) is the energy band gap of a nanocrystal quantum dot, \(E_g(\text{bulk})\) is the energy band gap of a bulk semiconductor, \(\hbar\) is the Planck constant, \(m^*\) is the reduced mass of exciton, \(d\) is the diameter of a nanocrystal, \(e\) is the electron charge, \(\varepsilon_0\) is the relative dielectric constant, and \(\varepsilon_0\) is the space dielectric constant. Therefore, almost full visible-range light can be absorbed by the CdSe nanocrystals, and the exited electrons can be injected into the TiO\textsubscript{2}. The bare TiO\textsubscript{2} and the TiO\textsubscript{2}–CdSe nanowires show the light absorption peaks at 335 and 353 nm, respectively, which corresponds to the energy band gaps of 3.70 and 3.52 eV. Both of the nanostructures show quantum confinement effect, since the pure rutile possesses the energy band gap of 3.2 eV. The redshift in the UV-visible light absorption of the TiO\textsubscript{2}–CdSe nanowires can come from the extension of the electron wave function of TiO\textsubscript{2} into CdSe.\textsuperscript{20} The TiO\textsubscript{2}–CdSe nanowires...
show the second light absorption peak around 664 nm, which corresponds to the energy band gap of 1.86 eV and the average particle size of 8.2 nm of the CdSe nanocrystals.

Photocatalytic efficiency of the TiO$_2$–CdSe nanowires was evaluated using the degradation of a methylene blue (MB) solution, and it was compared with that of the bare TiO$_2$. The MB solution containing the nanostructures was irradiated by ultraviolet (UV) light for photocatalytic reactions. The decrease in the intensity of visible light absorption peaks at 664 nm, corresponding to the decomposition of the MB, was monitored according to the UV-light exposure time period. Figure 4 shows the normalized variation in the absorbance of the MB solutions containing the bare TiO$_2$ and TiO$_2$–CdSe nanowires. The TiO$_2$–CdSe nanowires almost completely decomposed the MB solution within 80 min, while the bare TiO$_2$ nanowires decomposed it within 110 min. It is certain that the visible-light absorption could contribute to the photodecomposition reaction in the heterostructured TiO$_2$–CdSe nanowires. The possible mechanism for the enhanced photocatalytic activity even under the visible-range light irradiation was considered using the energy band diagram for the heterostructured TiO$_2$–CdSe nanowires, as indicated in the inset of Fig. 4. Absorption of a unit of the visible-range light, associated with the formation of a conduction band free electron and a valence band hole, occurs in the CdSe nanocrystals during the visible-light irradiation, and the migration of the photogenerated electron to the surface and the transfer to the TiO$_2$ nanowire occurs subsequently. Since there is very low concentration of holes to recombine with, therefore the electron has high opportunity to participate in the reduction reaction to form oxygen radicals, which is a very strong oxidant and can decompose organic substances effectively. Also, the photogenerated holes in the CdSe nanocrystals theoretically migrate to the surface and participate in the oxidation reaction to form hydroxyl radicals, which is more effective to decompose the organic substances. The TiO$_2$ nanowire itself can show photodecomposition activity only under the UV-light irradiation due to the high energy band gap. The holes created by the UV light irradiation to the TiO$_2$ can transfer to the CdSe, and the opportunities of the electron-hole recombination can be substantially reduced.

In this study, the heterostructured TiO$_2$–CdSe nanostructure arrays were achieved through overcoating the surface of the single-crystalline TiO$_2$ nanowires with the CdSe nanocrystal-containing solution. The TiO$_2$–CdSe nanowires show the absorption of UV-visible light ranging from 355 to 614 nm. The enhanced visible light absorption in the TiO$_2$–CdSe is due to the charge separation between the CdSe and TiO$_2$. Due to the visible-light absorbing capability, the TiO$_2$–CdSe nanowires show enhanced photocatalytic efficiency compared to the bare TiO$_2$ nanowires. This TiO$_2$–CdSe heterostructure can also be a strong candidate for the dye-sensitized solar cells due to the high quantum yield from the charge separation under the visible-light irradiation.

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FIG. 4. (Color online) Comparison in the photodecomposition efficiency of the bare TiO$_2$ and the TiO$_2$–CdSe nanowires.