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TiO$_2$/Bi$_2$S$_3$ core/shell nanowire arrays for photoelectrochemical hydrogen generation

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TOC Graph

This paper demonstrates the way for construction of nontoxic TiO$_2$/Bi$_2$S$_3$ core/shell NWAs photoanode for PEC hydrogen generation.

**ABSTRACT:** A facile and effective procedure for the synthesis of quasi-vertically aligned TiO$_2$/Bi$_2$S$_3$ core/shell nanowire arrays (NWAs) is reported. The nontoxic and earth abundant Bi$_2$S$_3$ was assembled onto the hydrothermal pre-grown TiO$_2$ NWAs via successive ionic layer adsorption and reaction (SILAR) method. The morphologies, microstructures, and optical properties of the pristine TiO$_2$ and composite TiO$_2$/Bi$_2$S$_3$ with different SILAR circles were characterized in detail. For photoelectrochemical (PEC) measurements, the TiO$_2$/Bi$_2$S$_3$ core/shell NWAs exhibited not only an enhanced photocurrent density (2.8 times higher than that of pristine TiO$_2$), but also a negatively shifted onset potential from 0.067 to -0.072V vs. RHE, as compared to the TiO$_2$. This better PEC performance results from the broadened light absorption and the improved charge carrier separation efficiency. Our results provide a green photoelectrode for PEC hydrogen generation.
Introduction

Since the seminal work of Fujishima and Honda,\textsuperscript{1} Titanium dioxide (TiO$_2$) has been widely investigated as the photoanode material for photoelectrochemical (PEC) hydrogen production owing to its excellent chemical stability, low cost, nontoxicity and environment-friendly feature.\textsuperscript{2-7} Among various nanostructured TiO$_2$, the one dimensional TiO$_2$ nanowire arrays (NWAs) on transparent FTO substrate has attracted considerable interest due to its facile fabrication, good oriented charge-transport property, and the large specific surfaces for light trapping.\textsuperscript{8-14} Despite these advantages, the photoconversion efficiencies of TiO$_2$ NWAs photoanodes are extremely depressed due to the large energy band gap (3.0 eV for rutile TiO$_2$).\textsuperscript{15, 16} This large energy band gap restricts its solar energy utilization only in the ultraviolet region. Therefore, considerable efforts have been made to enhance their visible light harvesting ability.\textsuperscript{17-23} For example, Wang et al. reported that the transition-metal doped TiO$_2$ NWAs exhibited dramatically improved visible light absorptions and photocatalytic properties in comparison to the pristine TiO$_2$ samples.\textsuperscript{24} Moreover, using morphology controlling strategies to design novel architectures also is explored to the enhanced the light utilization ability of TiO$_2$, such as the branched TiO$_2$ nanorod arrays electrode reported by Cho et al. and co-workers.\textsuperscript{25}

Sensitizing TiO$_2$ NWAs with short band gap semiconductors is another approach to extend the working spectrum into the visible range. In this case, the type-II heterostructure NWAs is integrated, and the light absorption can be extended by the narrower band gap sensitizers. In addition, the charge separation efficiency can also be largely improved due to the build-in space electric field. The conventional II-VI semiconductors such as CdS and CdSe, have exhibited considerable PEC performance improvement as sensitizers for TiO$_2$ NWAs. However, their fatal toxicity is a worrying issue when used for practical applications. Recently, Bi$_2$S$_3$ has been emerging to be an effective, inexpensive and environmentally friendly light absorber material for wide band gap semiconductors.\textsuperscript{26} For example, Gao et al. reported the Bi$_2$S$_3$-coated BiVO$_4$ discoids by in situ transform the surface BiVO$_4$ into Bi$_2$S$_3$.\textsuperscript{27} The
heterostructured BiVO$_4$/Bi$_2$S$_3$ exhibited superior photocurrent response and photocatalytic activity for the reduction of Cr$^{VI}$ under visible light illumination. Besides, Lin et al. demonstrated that the Bi$_2$S$_3$ quantum dots sensitized SnO$_2$ porous film photoelectrode achieved a high photocurrent density of 0.9 mA cm$^{-2}$ under 0.109 sun illumination.$^{28}$ Also, there has been several reports on the hybridization of TiO$_2$ with Bi$_2$S$_3$ for PEC application.$^{29-31}$ For example, Zumeta-Dube et al. reported the Bi$_2$S$_3$ quantum dots (QDs) sensitized TiO$_2$-P25 with PEC conversion efficiency of 0.84%.$^{32}$

In this paper, we report the heterostructured TiO$_2$/Bi$_2$S$_3$ core/shell NWAs synthesized by successive ionic layer adsorption and reaction of Bi$_2$S$_3$ onto the pre-grown TiO$_2$ NWAs for solar-light-driven PEC hydrogen generation. This hybrid TiO$_2$/Bi$_2$S$_3$ outstands itself from the early reported TiO$_2$/Bi$_2$S$_3$ composites by its one dimensional morphology. Comparing to the conventional II-VI semiconductors (such as CdS and CdSe) sensitized TiO$_2$, this composite TiO$_2$/Bi$_2$S$_3$ is environment-friendly and low-cost. The as-obtained photoanode exhibits strong absorption in the visible spectrum up to 800 nm. With light illumination, the optimized photoanode yields a photocurrent of ~0.97 mA/cm$^2$ at 0.2671 V vs. RHE, which is 2.8 times of that of pure TiO$_2$ samples. Moreover, the TiO$_2$/Bi$_2$S$_3$ composite photoanodes induce a cathodic shift of the onset potential. The excellent PEC properties of our photoanodes show that the hybridization of Bi$_2$S$_3$ on the TiO$_2$ NWAs has potential applications in QDs sensitized solar cells, PEC hydrogen generation and photocatalysis.

**Experimental details**

**Preparation of TiO$_2$ NWAs by hydrothermal method**

TiO$_2$ NWAs were grown onto fluorine-doped tin oxide (FTO) substrates using a hydrothermal method reported previously.$^{33}$ Briefly, 0.45 ml titanium n-butoxide and 0.6 g NaCl were added into the 30 ml diluted hydrochloric acid (mass fraction 18.25-19%) and stirred until the mixture became clear. After that, the above precursor was transferred into a 100 ml Teflon-lined stainless steel autoclave in which the FTO substrates were placed with an angle against the in-wall with the conductive side
facing down. The hydrothermal process was conducted in an electric oven at 150 °C for 8 h. After cooling, the resultant samples were removed and rinsed with water to get rid of any residual reactants and dried in air at 80 °C.

**Preparation of Bi$_2$S$_3$-sensitized TiO$_2$ NWAs by SILAR**

For Bi$_2$S$_3$ sensitization, the as-synthesized TiO$_2$ NWAs were successively immersed into two different solutions for 1 min each, first in 0.05 M Bi(NO$_3$)$_3$ solution and then in 0.1 M Na$_2$S in aqueous solution. The Bi(NO$_3$)$_3$ solution was ultrasonic dissolved with the pH adjusted to 1~2 by concentrated nitric acid. Following each immersion, the electrodes were rinsed with deionized water and dried with a nitrogen stream to remove excess precursors before the next dipping. The two-step dipping procedure was called one SILAR cycle. Sample that went through $n$ SILAR cycles is referred to as TiO$_2$/ Bi$_2$S$_3$($n$). Finally, the as-prepared TiO$_2$/ Bi$_2$S$_3$ hybrid electrodes and the bare TiO$_2$ electrode were annealed at 250 °C in Ar atmosphere for 1 hour.

**Structural and optical characterizations**

The morphology and microstructure of the samples were characterized using the field emission scanning electron microscope (NOVA NANOSEM 450, FEI, USA) equipped with an energy-dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM, JEM2010-HR, 200 KV). Raman spectra of the as-obtained samples were recorded on a Renishaw InVia system with a laser operating at $\lambda$=532 nm as the excitation source. The crystal structure was characterized by a Rigaku Dmax 2500 X-ray diffractometer with Cu K$_\alpha$ radiation. The light absorption was recorded by UV-vis spectrophotometer (UV-2500, Shimadzu, Japan).

**PEC measurements**

The PEC properties of the photoelectrodes were studied on an electrochemical workstation (CH Instruments, model CHI660E). The three-electrode system was used with the TiO$_2$ or TiO$_2$/Bi$_2$S$_3$ NWAs on FTO substrates as the working electrodes, a Pt foil as counter electrode and Ag/AgCl as reference electrode. A mixture aqueous solution of 0.24 M Na$_2$S and 0.35 M Na$_2$SO$_3$ (pH=11.5) was used as the electrolyte and sacrificial reagent for all PEC measurements. A 150 W Xe lamp was used as the light source. Before test, the incident light intensity was calibrated to 100 mW cm$^{-2}$. 
with a digital power meter. The photocurrent densities vs. measured potential ($i$–$v$ curves) measurements were carried out at a scan rate of 25 mV s$^{-1}$. The $i$–$t$ curves were measured with a chopped light illumination at -0.6 V bias vs. Ag/AgCl. Electrochemical impedance spectroscopy (EIS) was measured under light at the open-circuit potential, with frequency range from 0.01 Hz to 100 kHz and the modulation amplitude of 5 mV. Mott–Schottky plots were measured in the dark at an AC frequency of 1.0 kHz. For all PEC measurements, the active area of the working electrodes was strictly kept within 1 cm$^2$. Hereafter, the electrode potential versus the Ag/AgCl is converted to the reversible hydrogen electrode (RHE) potential according to the Nernst equation$^{34}$

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \, pH + E_{\text{Ag/AgCl}}^\theta$$

where $E_{\text{RHE}}$ is the converted potential vs. RHE, $E_{\text{Ag/AgCl}}^\theta = 0.1976$ V at 25 °C, and $E_{\text{Ag/AgCl}}$ is the experimental potential measured against the Ag/AgCl reference electrode.
Fig. 1 SEM images of bare TiO$_2$ (a) and TiO$_2$/Bi$_2$S$_3$(20) (b) NWAs, respectively. (c) Magnified SEM image of TiO$_2$/Bi$_2$S$_3$(20) NWAs. (d) EDS of TiO$_2$/Bi$_2$S$_3$(20) NWAs. TEM (e) and HRTEM (f) images of TiO$_2$/Bi$_2$S$_3$(20) NWAs, respectively.

**Results and discussion**

Fig. 1a shows the typical top view SEM image of the bare TiO$_2$ NWAs. As seen, the TiO$_2$ NWAs are uniformly grown on the entire substrate with diameter around 75 nm, and the rod exhibits a regular tetragonal growth. For composite photoanodes, we synthesized three TiO$_2$/Bi$_2$S$_3$ core/shell NWAs samples with 10, 20 and 30 SILAR circles, and referred to them as TiO$_2$/Bi$_2$S$_3$(10), TiO$_2$/Bi$_2$S$_3$(20) and TiO$_2$/Bi$_2$S$_3$(30), respectively. After the deposition of Bi$_2$S$_3$ layer, the surfaces of the TiO$_2$ NW become rough. Fig. 1b shows the low magnification SEM image of the TiO$_2$/Bi$_2$S$_3$ NWAs
with 20 SILAR deposition circles. Compare to Fig. 1a, Bi$_2$S$_3$ modified TiO$_2$ shows similar NWA feature but the image is slightly bright, suggest that the Bi$_2$S$_3$ sensitizers make the surfaces more conductive. Fig. 1c shows the morphology of the TiO$_2$/Bi$_2$S$_3$(20) sample under higher magnification. As can be seen from Fig. 1c, Bi$_2$S$_3$ is uniformly deposited onto the TiO$_2$ NW surfaces and the diameter TiO$_2$/Bi$_2$S$_3$(20) is increased to approximately 100 nm. Hence, the Bi$_2$S$_3$ deposition thickness is approximately 13 nm. These observations indicate the successful synthesis of core-shell TiO$_2$/Bi$_2$S$_3$ NWA heterostructures. The morphologies of the composite TiO$_2$/Bi$_2$S$_3$ NWAs with different SILAR circles are also exhibited in Fig. S1(a-c) (see supporting information). With increasing of SILAR circles, a larger diameter and rougher surface of TiO$_2$/Bi$_2$S$_3$ composite NWAs are displayed. In addition, some overdosed Bi$_2$S$_3$ nanoparticles are blocked at the interspaces of NWAs when the SILAR circles increased up to 30. This overloading of Bi$_2$S$_3$ is detrimental for PEC performance of TiO$_2$/Bi$_2$S$_3$ photoelectrode which will be discussed later. The TEM images of the Fig. S1(e-f) gives a more straight-forward observation of the thickness of the Bi$_2$S$_3$ layer with different SILAR circles, from which we can also reckon the particle-initiated growth behavior of the Bi$_2$S$_3$ layer. When the SILAR circle is 10, only a few separated Bi$_2$S$_3$ particles are decorated on the TiO$_2$ NW, the average diameter of the Bi$_2$S$_3$ particles is 20 nm. Increasing the SILAR circle up to 20, more Bi$_2$S$_3$ particles are loaded on the TiO$_2$ NW (dark dot in Fig. S1e), and the particles tend to interlink to each other resulting in an overall covering of the TiO$_2$ NW surface. The 30 SILAR circles make a ~25 nm thickness shell on the TiO$_2$ NW (inset in Fig. S1f), and the particle-stacked Bi$_2$S$_3$ shell can be directly seen. Fig. 1d displays the EDS spectrum of the TiO$_2$/Bi$_2$S$_3$ NWAs, the atomic ratio of Bi:S is found to be ~2:3, showing that the samples are in even stoichiometric. The other peaks of Ti, Si, Sn, Ca, and O are attributed to the chemical components of TiO$_2$ NWAs and the FTO glass substrate. Fig. 1e shows the TEM image of TiO$_2$/Bi$_2$S$_3$(20) core/shell NWs, it can be observed that the 1D TiO$_2$ NW is sheathed by the Bi$_2$S$_3$ nanoparticles throughout the length. Fig. 1f is the HRTEM image taken from the red square in Fig. 1e. The observed interplanar spacing of 0.397 nm corresponds to the (220) plane of
orthorhombic Bi$_2$S$_3$, which is agree with the result observed by XRD below.

![XRD and Raman spectra](image)

**Fig. 2** (a) XRD patterns and (b) Raman scattering spectra of the pristine TiO$_2$ and composite TiO$_2$/Bi$_2$S$_3$ NWAs on FTO substrates.

The XRD patterns of the as-obtained samples were collected to characterize their crystallographic phases (Fig. 2a). The pattern of the pristine TiO$_2$ NWAs (black line in Fig. 2a) reveal that the TiO$_2$ have a rutile structure (JPCDS 21-1276). Apart from the peaks of TiO$_2$ and FTO substrate (JPCDS 77-0448), the additional diffraction peaks (red line in Fig. 2a) can be readily indexed to the orthorhombic phase of Bi$_2$S$_3$ (JCPDS 17-0320) for TiO$_2$/Bi$_2$S$_3$ composite electrode. The main peaks at $2\theta$ of 23.7, 24.9, 25.2, 28.6, and 31.76 are corresponding to the (101), (130), (310), (211) and (221) planes of orthorhombic Bi$_2$S$_3$, respectively. Fig. 2b shows the Raman spectra of the TiO$_2$ and TiO$_2$/Bi$_2$S$_3$ NWAs photoanodes. The pristine TiO$_2$ exhibits two sharp peaks at 447 and 608 cm$^{-1}$, which can be attributed to the $E_g$ and $A_{1g}$ mode in rutile
TiO$_2$ as reported by Porto et al.$^{35}$ The broad peak at 239 cm$^{-1}$ is of a complex nature, which is relevant to the second-order scattering and disorder effects. The coating of Bi$_2$S$_3$ layer weakens characteristic peaks of the TiO$_2$ and three new peaks at 237 and 261 cm$^{-1}$ and 187 cm$^{-1}$ are emerged. The added peaks can be attributed to the $A_g$, $B_{g1}$ and $A_g$ mode of the Bi$_2$S$_3$, which indicates the crystalline character of Bi$_2$S$_3$ layer in the TiO$_2$/Bi$_2$S$_3$ composite NWAs.

![Normalized UV-vis absorption spectra of TiO$_2$ and TiO$_2$/Bi$_2$S$_3$ core/shell NWAs on FTO substrates.](image)

**Fig. 3** Normalized UV-vis absorption spectra of TiO$_2$ and TiO$_2$/Bi$_2$S$_3$ core/shell NWAs on FTO substrates.

The optical absorption properties of the TiO$_2$ and TiO$_2$/Bi$_2$S$_3$ were characterized by absorption spectra, as shown in Fig. 3. We can see that the absorption wavelength of TiO$_2$ NWAs is less than 410 nm. In the case of the composite TiO$_2$/Bi$_2$S$_3$ NWAs, its absorption extends to cover the whole visible light range and even beyond 800 nm. In addition, UV-vis absorption spectra show that as the SILAR deposition circle increases the light absorption ability also increases. The relationship between the incident photon energy and the absorption coefficient is given by the following equation: $(a\nu)^2 = A(\nu - E_g)$, where $a$, $\nu$ and $E_g$ are the optical absorption coefficient, Planck constant, the photon frequency and band gap of semiconductor, respectively. $A$ is a constant. The band-gap values of TiO$_2$ and TiO$_2$/Bi$_2$S$_3$(20) are derived to be 3.02 and 1.6 eV, respectively. This enhancement of light trapping effect for TiO$_2$/Bi$_2$S$_3$(20) is beneficial for the PEC hydrogen generation application.
Fig. 4 (a) $i$-$v$ curves under AM 1.5G in the dark and at 100 mW cm$^{-2}$ illumination for pristine TiO$_2$ NWAs and TiO$_2$/Bi$_2$S$_3$ core/shell NWAs with different circles SILAR. (b) Amperometric $i$-$t$ curves of the TiO$_2$/Bi$_2$S$_3$ (10, 20, 30) core/shell NWAs at 0.2761 V versus RHE with light on/off cycles.

To evaluate the Bi$_2$S$_3$ sensitization effect on PEC performance of TiO$_2$, Fig. 4a shows the $i$-$v$ curves of the bare TiO$_2$ and the TiO$_2$/Bi$_2$S$_3$ core/shell NWAs with 10, 20 and 30 SILAR circles. By analyzing the experimental data in Fig. 4a, three conclusions can be reached. First, for all of the TiO$_2$/Bi$_2$S$_3$ NWAs photoanodes, the saturate photocurrent densities are much higher than that of the pristine TiO$_2$. The TiO$_2$/Bi$_2$S$_3$(20) sample achieved a value of 0.98 mA/cm$^2$ at 0.2671 V vs. RHE (-0.6 V
vs. Ag/AgCl), which is higher than that of the bare TiO₂ (0.35 mA cm⁻²) and other composite photoanodes (0.8 mA cm⁻² for TiO₂/Bi₂S₃(10) and 0.95 mA/cm² for TiO₂/Bi₂S₃(30)). It confirms that the coating of Bi₂S₃ is a simple but effective method for enhancing the PEC performance of TiO₂. Second, as compared to TiO₂, the onset potential of TiO₂/Bi₂S₃ is much negatively shifted and leads to the photocurrent saturation at a more negative potential. Typically, the photocurrent increases from the onset potential around -0.072 V vs. RHE and approaches a plateau at 0.05 V vs. RHE for TiO₂/Bi₂S₃(20) sample, whereas the photocurrent plateau in the bare TiO₂ photoanode is 0.3 V vs. RHE. Achieving the saturated photocurrent level at a more negative potential is significantly important because it reduces the applied external bias, and thus increases the overall efficiency of the PEC cells.²² Third, the TiO₂/Bi₂S₃(20) overmatches the one with 10 or 30 SILAR circles deposition. As the Bi₂S₃ deposition increasing, the light absorption of TiO₂/Bi₂S₃ is also increased (see Fig. 3). However, too much Bi₂S₃ deposition blocks the porous structure of the electrodes (see SEM images of Fig. S1 in supporting information) and lengthens the electron diffusion path from Bi₂S₃ to TiO₂. In this case, a more positive external bias is needed to separate the photo-induced charge efficiently for TiO₂/Bi₂S₃(30), which can explain the smaller photocurrent between 0 and 0.3 V vs. RHE but similar photocurrent when the potential exceeds 0.35 V vs. RHE in comparison with TiO₂/Bi₂S₃(20). Fig. 4b shows the i-t curves of the TiO₂ and the TiO₂/Bi₂S₃ (20) core/shell NWAs photoelectrodes at 0.2671 bias vs. RHE under chopped light irradiation. Upon illumination, the photocurrent of TiO₂/Bi₂S₃ (20) flashily rise to a high level, and decay to a relatively steady-state after a few second, displaying a series of spikes in the photoresponse. This behavior might be attributed to the charge carrier accumulation at the electrode-electrolyte interface due to the slow oxygen evolution kinetics or oxidization of trap states on the surface and in the bulk by charge carriers.⁳⁸ And when the light is cut off, the photocurrent densities drop to nearly zero instantaneously. Such fast rise and fall of the photocurrents indicates that carrier transport in the heterojunction material proceeds very quickly.
Fig. 5 (a) Mott-Schottky plots of pristine TiO\textsubscript{2} and TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3}(20) core/shell NWAs. (b) Schematic of energy band level aliment and carrier transferring mechanism in TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3} core/shell NWAs. (c) Nyquist plots and (d) Bode plots of the impedance spectra measured at open circuit condition under 1 sun illumination.

Fig. 5a shows the Mott-Schottky (M-S) plots, in which the flat band potential at the electrode/electrolyte interface can be estimated by the M-S equation\textsuperscript{19}

\[
1/C^2 = \left( \frac{2}{\varepsilon \varepsilon_0 e N_d A^2} \right) [(V - V_{FB}) - kT/e_0]
\]

where \(C\) is the specific capacity, \(\varepsilon\) is the dielectric constant of Bi\textsubscript{2}S\textsubscript{3} or TiO\textsubscript{2}, \(\varepsilon_0\) is the electric permittivity of vacuum, \(N_d\) is the carrier density, \(A\) is the area, \(V\) is the applied potential, \(V_{FB}\) is the flat band potential, \(k\) is the Boltzmann constant, \(T\) is the absolute temperature, and \(e_0\) is the electron charge. The \(V_{FB}\) values of the TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3} and TiO\textsubscript{2} NWAs are determined to be 0.07 V and 0.26 V vs. RHE by extrapolating the X-intercepts of the linear region in the M–S plot, respectively. Such a negative shift of the flat band for the TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3} electrode suggests a higher carrier concentration and lower charge recombination in the TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3} electrode in comparison with the pristine TiO\textsubscript{2}. In addition, the positive slope indicates that the TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3} NWA is an n-type semiconductor. The TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3} shows substantially smaller M-S plot slope compared to the TiO\textsubscript{2}, suggesting an increase of donor density in the TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3}.\textsuperscript{9} Using the resulted \(V_{FB}\) and band gap values of the TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3} and TiO\textsubscript{2}, the energy
band level aliments can be estimated as displayed in Fig. 5b.\textsuperscript{40} The charge transfer and hydrogen production mechanism in the TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3} PEC cell is proposed. When the TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3} heterojunction is irradiated by solar light, electrons are excited to the conduction band (CB) of Bi\textsubscript{2}S\textsubscript{3} and TiO\textsubscript{2}. Subsequently, electrons migrate from Bi\textsubscript{2}S\textsubscript{3} to TiO\textsubscript{2} and finally to the counter electrode to produce H\textsubscript{2}. At the same time, the holes are transported to the valence band (VB) of Bi\textsubscript{2}S\textsubscript{3} and then scavenged by the sacrificial reagents at the electrode/electrolyte interface. Thus, the photogenerated charge separation efficiency is improved because of the formation of type-II heterojunction interface in the TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3} electrode, which is also responsible for its high photocurrent density.

To further examine the intrinsic electronic properties of the TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3} NWAs, the EIS were collected and shown in Fig. 5c. Normally, the smaller the radius in Nyquist plot, the lower the charge transfer impedance at the electrode-electrolyte interface for corresponding electrode.\textsuperscript{41} The TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3} composite electrodes represent much smaller radii than the pristine TiO\textsubscript{2} electrode, implying its more effective charge carrier separations compared to the pristine TiO\textsubscript{2}. The inset in the Nyquist plots is the equivalent circuit model of the PEC cell, where the $R_s$ is the series resistance of the electrochemical device, $R$ and $C$ represent the resistance and capacitance of space charge region, respectively, including charge transfer across the FTO/TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3} interface and the TiO\textsubscript{2}-Bi\textsubscript{2}S\textsubscript{3}/electrolyte interface, $R_{Pt}$ and $C_{Pt}$ are the resistance and capacitance of the Pt cathode, respectively. By fitting the experimental data (dot points) into solid line using the equivalent circuit model, a more quantitative approach to compare the interface charge transfer impedance of TiO\textsubscript{2} and TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3} is reached. As a result, the determined value of $R$ is 3270 and 735 $\Omega$ for pristine TiO\textsubscript{2} and composite TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3} photoelectrodes, respectively. Correspondingly, the TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3} heterojunction shows a lower characteristic peak frequency in the Bode phase plot in Fig. 5d, implying the longer electron lifetime than that of the pristine TiO\textsubscript{2} electrode.\textsuperscript{42} The enhanced charge separation and prolonged electron lifetime in the TiO\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3} composite is also responsible for the improved PEC performance for TiO\textsubscript{2}.
Conclusions

In summary, we have successfully synthesized the TiO$_2$/Bi$_2$S$_3$ core/shell NWAs as photoelectrode for PEC hydrogen generation. The coating of Bi$_2$S$_3$ layer achieves a remarkable enhancement of photocurrent density in the TiO$_2$ NWAs photoanode. Moreover, the onset potential of the composite photoanode is also largely shifted to a negative direction. The broadened light absorption and improved charge carrier separation efficiency in the type-II TiO$_2$/Bi$_2$S$_3$ core/shell NWAs are responsible for the PEC performance enhancement. The present work provides a new photoelectrode with non-toxicity, low cost and easy fabrication, which may have potential application in PEC hydrogen generation and photocatalysis.

Acknowledgements

We thank the financial support of the National Natural Science Foundation of China (Grant no. 51202208, 51172191, and 11274264), The Project Supported by Scientific Research Fund of Hunan Provincial Education Department (Grant no. 12B129), National Basic Research Program of China (no. 2012CB921303) and the Program for Changjiang Scholars and Innovative Research Team in University (IRT13093).

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