Bi$_2$Se$_3$, Bi$_2$Te$_3$ quantum dots-sensitized rutile TiO$_2$ nanorod arrays for enhanced solar photoelectrocatalysis in azo dye degradation

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Abstract

Rutile TiO$_2$ nanorod arrays vertically aligned on conductive fluorine-doped tin oxide glass are optimized for photocatalysis in terms of the density and diameter of nanorods by tuning the concentration of Ti precursor and reaction time during the hydrothermal process. Quantum dots (QDs) of V$_2$V$_3$ (V = Bi, VI = Se, Te) topographic insulators are then employed as sensitizers to enhance the visible-light response of TiO$_2$. Electrochemical measurements show that the decoration of Bi$_2$Se$_3$ or Bi$_2$Te$_3$ significantly increases the photocurrent due to the enhanced light harvesting properties and the charge carrier separation capability mediated by the topographic isolation effect of V$_2$V$_3$ QDs. Photoelectrocatalytic (PEC) activity evaluation is conducted towards the decoloration of azo dyes, including methyl orange and methylene blue under the sunlight irradiation. The elaborated Bi$_2$Se$_3$/TiO$_2$ nanorod array exhibits the superior PEC performances, presenting shows great potentials in environmental remediation.

1. Introduction

The sun supplies the currently known largest renewable energy resource to the Earth. Efficient capture, conversion and storage of solar energy have attracted continuous research interest. Since the discovery of the Honda–Fujishima effect in the 1970s [1], semiconductor-mediated photoelectrocatalysis (PEC) has been a highly researched field. Group III/V semiconductors (e.g. GaAs [2, 3], InP [4, 5], etc) exhibit the superior PEC activity under the solar irradiation. However, determined by their band positions, these narrow-bandgap materials suffer from the photocorrosion effect [6]. The redox reactions, induced by the photoexcited charge carriers, occur on the semiconductor itself favorably instead of the targeted water/organics/ions, leading to the decomposition of semiconductor and the dramatical decrease in PEC performance [7]. Alternatively, metal oxides (e.g. TiO$_2$ [8–11], WO$_3$ [12, 13], Cu$_2$O [14, 15], etc) with excellent durability and low cost have attracted enormous research interest. TiO$_2$ is the by far most frequently studied photocatalysts owing to its outstanding photoelectrochemical properties (low toxicity, abundancy, easy processability, chemical inertness, photostability, etc). Unfortunately, the bandgap of TiO$_2$ is relatively wide, i.e. ~3.0 eV for rutile TiO$_2$ and 3.2 eV for anatase TiO$_2$) [16], and thus only the UV radiation, accounting for only ~3% of the solar spectrum at ground level, can be captured for the subsequent photochemical processes.

Various design strategies have been developed to extend the light absorption of TiO$_2$ to the visible range by, for example, tuning the band structure via doping or ion implant [17], coupling with secondary semiconductor with a narrower bandgap to form heterojunction [18, 19], employing metal nanoparticles...
with the localized surface plasmon resonance effect [20], and sensitizing with dye or quantum dots (QDs) [21–24]. Moreover, construction of appropriate nanostructured TiO₂ photoanodes is crucial to enhance their PEC properties. Recently, TiO₂ nanorod arrays vertically standing on the conductive substrates have been developed as an ideal photoanode for the environmental and energy PEC [25, 26]. Compared with the conventional nanoparticulate films randomly coated on substrate, the 1D nanostructure has been demonstrated to deliver an excellent electron collection efficiency [27]. Moreover, due to their open, perpendicular, and accessible alignment, these 1D TiO₂ nanorod arrays offer versatile scaffolds for the facile loading of metals, semiconductors for various PEC applications [28].

Increasing research efforts have been devoted to V₂V₁₃ chalcogenides as potential photo(electro)catalysts in the light of the significant progress in wet-chemical synthesis [29]. Coupling of V₂V₁₃ chalcogenides with TiO₂ has been also reported recently [30–32], and most of the studied V₂V₁₃ materials have concentrated on sulfides. For example, Sun et al reported that coupling Sb₂S₃ with TiO₂ nanoparticles lead to a red shift in absorption spectra, and the resultant heterojunction photocatalysts showed a high photocatalytic activity in decoloration of azo dyes upon the visible light irradiation [30]. Yang et al synthesized Bi₂S₃/TiO₂ photocatalysts by electrochemical deposition [31]. The prepared composites represented increased Cr (VI) and 2,4-dichlorophenoxyacetic acid decomposition activity [31]. Similarly, Bi₂S₃/TiO₂ nanocomposites fabricated by Dhouadi et al exhibited enhanced photocurrent and smaller bandgap for the decomposition of aqueous ketoprofen [32]. Although V₂V₁₃ sulfides have demonstrated high efficiency in assisting the photo(electro)catalysis of TiO₂, Bi₂Se₃ and Bi₂Te₃, to the best of our knowledges, are seldom used to couple with TiO₂ [33].

This work therefore aims at studying the role and of narrow-bandgap metal chalcogens of Bi₂Se₃ and Bi₂Te₃ deposited onto the TiO₂ nanorod array for the PEC decoloration of azo dyes, including methyl orange (MO) and methylene blue (MB). We firstly optimize the hydrothermal condition for the reproducible growth of rutile TiO₂ nanorod arrays on fluorine-doped tin oxide (FTO) glass. Tuning the concentration of Ti precursor allows to control the surface morphology of rutile TiO₂ nanorod array. Bi₂Se₃ and Bi₂Te₃ nanoparticles are then deposited onto the surface of TiO₂ nanorods through solution processing. The physicochemical properties of the formed nanocomposite arrays are characterized, and the constructed photoanodes. The PEC properties of the nanocomposite arrays are assessed via linear sweep voltammetry (LSV), transient current and electrochemical impedance spectroscopy (EIS). Further, the photoanodes were utilized to degrade MO and MB for the evaluation of PEC water treatment performances.

2. Experimental

2.1. Fabrication of rutile TiO₂ nanorod arrays

TiO₂ nanorod arrays were grown on FTO glass (Pilkington TEC 7; sheet resistance: ∼7 Ω sq⁻¹; thickness: 2.2 mm) by hydrothermal method [25]. In a typical synthesis, the nutrient solution was prepared by dropping titanium isopropoxide (TTIP, >97 wt%, Sigma-Aldrich) into 30 ml of 5 mol l⁻¹ HCl aqueous solution with continuous stirring. After stirring for 20 min, the formed homogeneous solution (20.0 mmol l⁻¹) was transferred into a 50 ml Teflon lined autoclave. Then, a cleaned FTO glass with a size of 2 × 4 cm² was positioned against the wall of liner with conducting face down. Hydrothermal reaction was conducted at 160 °C for 12 h. After cooling to room temperature, the as-obtained rutile TiO₂ photoelectrodes were washed by deionized water for three times and calcined at 450 °C for 1 h with a heating ramp of 5 °C min⁻¹. For experimental parameter optimization, the concentration of TTIP (C₉) was tuned to 10, 20 (optimal), 30 mmol l⁻¹, the resultant rutile TiO₂ nanorod arrays were assigned as T₁, T₂, T₃, respectively. Also, the hydrothermal reaction time (t) were adjusted from 2 to 14 h for the comparison of the morphological evolution of the as-synthesized rutile TiO₂ nanorod array.

2.2. Decoration of V₂V₁₃ quantum dots

A spin-coating technology was developed to decorate V₂V₁₃ (Bi₂Te₃, Bi₂Se₃) QDs onto T2. The precursor solution was prepared according to the method newly developed by Webber et al [29]. Briefly, 0.50 g of V₂V₁₃ powders (Aladdin) were dissolved in a mixed solution containing 10.0 ml of ethylenediamine (Alfa) and 1.0 ml of 1,2-ethanediithiol (Alfa) under argon atmosphere. To increase the uniformity of QD sizes, PTFE filters (pore size: ∼0.2 µm, jinteng, China) were used to filter the undissolved large-size V₂V₁₃ particles. The obtained orange Bi₂Se₃ and dark red Bi₂Te₃ solution was spin-coated on T2. The spin speed was raised to 1000 rpm with an acceleration of 250 rpm s⁻¹ and the dwell time was set to 20 s. Eventually, the as-formed Bi₂Te₃/T2 and Bi₂Te₃/T2 nanorod arrays were obtained by annealing in N₂ flow at 350 °C for 30 min.
2.3. Materials characterization

The morphology of the rutile TiO$_2$-based arrays was observed by a JEOL JSM-7800F Schottky Field Emission scanning electron microscope (SEM) at 10 kV. To observe the single nanorod, a Philips Tecnai F20 high-resolution field emission transmission electron microscope (TEM) was used with an energy-dispersive x-ray spectroscopy (EDS) module for elemental analysis. X-ray diffraction (XRD) measurement was performed on a Bruker D8 Advance x-ray diffractometer with CuK$\alpha$ radiation ($\lambda = 1.5418$ Å) in the $2\theta$ range of 20–60°. UV–Vis spectra were recorded on a Metash UV-8000A spectrophotometer with a bare FTO glass as the reference.

2.4. PEC activity evaluation

The PEC properties of the obtained V$_2$V$_3$/TiO$_2$ photoelectrodes were analyzed on the CHI-760E electrochemical workstation with a Na$_2$SO$_4$ solution (0.10 mol l$^{-1}$) as the electrolyte. A Xe arc lamp (Perfectlight FX300, light intensity: 100 mW cm$^{-2}$) was used as the light source. A three-electrode electrochemical cell consists a working electrode, a Pt counter electrode and a reference electrode (saturated Ag/AgCl electrode). The measured electrode potentials vs. Ag/AgCl were converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \, \text{pH} + E^0_{\text{Ag/AgCl}}$$

where $E_{\text{RHE}}$ is the converted potential vs. RHE; $E^0_{\text{Ag/AgCl}} = 0.1976$ V at 25 °C; and $E_{\text{Ag/AgCl}}$ is the experimentally measured potential taking the Ag/AgCl electrode as the reference electrode. EIS measurements were carried out in the frequency range of 10–10$^5$ Hz upon solar illumination. Mott–Schottky curves were recorded under the dark condition at a frequency of 1 kHz.

Solar PEC decolorations of MO and MB were conducted at similar conditions with an applied bias potential of 1.0 V. A solar simulator, AULIGHT Xe lamp system (CEL-S500) with a light intensity of one sun (10 mW cm$^{-2}$) was used as the sunlight source. Before irradiation, photoelectrodes were immersed in MO (5.0 mg l$^{-1}$) or MB solution (10.0 mg l$^{-1}$) in the dark for 1 h to reach the adsorption equilibrium. During the PEC reaction, the absorptions of the MO and MB solution were characterized by the UV–Vis spectrometer at given time intervals to indicate the concentration of the solution. The total organic carbon (TOC) contents of the PEC degraded solution were measured with a Analytik Jena Multi N/C 2100S TOC analyzer.

3. Results and discussion

Our rutile TiO$_2$ nanorod arrays were derived from the homogeneous solution of TTIP stabilized by HCl. A hydrothermal process induces the preferential growth of 1D rutile nanorods on FTO substrates. Figure 1 illustrates the XRD patterns of T2 on the FTO glass. The bare FTO substrate exhibits characteristic peaks of bulk tetragonal cassiterite (ICDD #41-1445). After the growth of TiO$_2$ array, three new diffraction peaks at 36.4°, 41.5° and 54.3° appear, which can be assigned to the (101), (111) and (211) plane of rutile TiO$_2$ phase (ICDD #21-1276), respectively. All the observed peaks are sharp and narrow owing to the high crystallinity of TiO$_2$ and SnO$_2$. Excluding the diffraction peaks of FTO glass, the (101) diffraction peak is particularly intensive and much higher than other peaks for the rutile phase. In contrast, the other key diffraction peaks of rutile (110), (200) and (210) planes are almost extinguished, suggesting the preferential growth of 1D rutile nanorods along the [001] direction. As reported by Kim et al [34], the excessive Cl$^-$ ions can complex with TTIP and suppress the growth of (110) facet, guiding the formation of 1D rutile nanorods during the hydrothermal process.

Synthetic parameters of $C_{\text{Ti}}$ and $t$ have great influences on the morphology of array. Figure 2 shows the top and the cross-sectional SEM micrographs of T1, T2 and T3 synthesized with different $C_{\text{Ti}}$. With an increase in $C_{\text{Ti}}$, both averaged diameter and length of TiO$_2$ nanorods dramatically increase, together with the density of nanorods throughout the FTO substrate. At $C_{\text{Ti}} = 10$ mmol l$^{-1}$, T1 only possesses a few tilted and single TiO$_2$ nanorods grown on the FTO substrate. Increasing $C_{\text{Ti}}$ to 20 mmol l$^{-1}$ leads to the formation of vertically aligned nanorods. Individual and bundled nanorods coexist in the resultant T2 array. Each nanorod is of ~1.5 μm in length and 30 ~ 60 nm in diameter. The single nanorods and bundles are almost isolated without significant blocking especially in the bottom (figure 2(c) and (d)). At $C_{\text{Ti}} = 30$ mmol l$^{-1}$, When $C_{\text{Ti}}$ continues to increase to 30 mmol l$^{-1}$, the average diameter (~200 nm) and length (~2 μm) of bundled nanorods increase as well (figures 2(e) and (f)). However, single nanorods cannot be found in T3 during our SEM observation, suggesting that the nanorods with an increased density are prone to aggregation with the formation of the bundles. In addition, in the bottom of nanorods, the nanorods are densely packed, probably due to the crystal fusion between the large sized TiO$_2$ nanorod bundles [25].

We choose the optimal T2 to investigate the influence of $t$ on the microstructure of rutile TiO$_2$ nanorod arrays. At $t < 1$ h, there is no nanorods on the FTO glass. As the reaction time growing, the density of TiO$_2$
rods increases. At $t = 2$ h, the majority of nanorods are $\sim 40$ nm in diameter (figure 3(a)). When the growth time prolongs to 12 h, TiO$_2$ nanorods compact closely with little room between each other with an average diameter of $\sim 150$ nm (figure 3). With the time of hydrothermal process over 14 h, arrays peel off from FTO substrates, indicating the termination of growth.

TEM was used to record the nanostructure of single nanorods. Figures 4(a)–(d) show the high resolution TEM images of Bi$_2$Te$_3$/T2 and Bi$_2$Se$_3$/T2. Plenty of monodisperse Bi$_2$Te$_3$ and Bi$_2$Se$_3$ QDs, mostly in form of hemisphere, with a similar diameter of $\sim 3$ nm can be found on the surface of TiO$_2$ nanorod. Apparently, the melting of QDs operates upon the annealing process at 350 °C, which is beneficial to the anchoring stability between QDs and TiO$_2$ nanorods. The intimate and firm decoration of QDs on TiO$_2$ with the formation of heterojunction will also assist the interfacial charge transfer of heterojunction and the cyclic performances.

Elemental mapping recorded on the surface of Bi$_2$Se$_3$/T2 by EDS technology illustrates the distribution of Bi and Se elements, as displayed in figures 3(e)–(g). Bi and Se elements almost homogeneously coat on T2 surface.

Figure 5 depicts UV–Vis absorption spectra of T2, Bi$_2$Te$_3$/T2 and Bi$_2$Se$_3$/T2 measured in the wavelength range of 380–480 nm. The bandgap of semiconductors can be estimated by extrapolating the Tauc plots of absorption spectra [35]. The absorption thresholds of Bi$_2$Te$_3$/T2 and Bi$_2$Se$_3$/T2 redshift to the visible region.
Figure 3. Top and cross-sectional SEM images of rutile TiO$_2$ nanorod arrays fabricated via a hydrothermal process at 160 °C for different reaction time of 2 h (a), (b), 6 h (c), (d), and 12 h (e), (f).

Figure 4. TEM images of TiO$_2$ nanorods sensitized by Bi$_2$Te$_3$ (a), (b), and Bi$_2$Se$_3$ (c), (d) QDs; and TEM EDS mapping images of Bi$_2$Se$_3$/TiO$_2$ (e), (f), (g).

upon the sensitization of metal chalcogens, and the coupled V$_2$VI$_3$/TiO$_2$ films become light yellowish with the surface deposition of Bi$_2$Te$_3$ or Bi$_2$Se$_3$ QDs. The calculated bandgap of T2, Bi$_2$Te$_3$/T2 and Bi$_2$Se$_3$/T2 were 3.04, 3.01 and 2.99 eV respectively. The narrowed bandgap that might be owing to the high absorption coefficient of V$_2$VI$_3$ QDs suggests the potential of heterojunctions to act as visible-light responsible photoanodes for the efficient PEC water treatment [36].

Figure 6 summarizes the PEC properties of photoanodes with and without the decoration of uniform V$_2$VI$_3$ QDs. Figure 6(a) shows the LSV curves of various photoelectrodes recorded under the simulated sunlight. For the pure rutile TiO$_2$ photoelectrodes, T2 shows the largest photocurrent owing to its distinct high-aspect-ratio 1D nanostructure with an appropriate density and relatively lower degrees in the aggregation and crystal fusion, compared with T3 that holds denser but fused nanorods. The difference in photocurrent suggests that $C_{Ti}$ and the resultant aligned nanostructure play significant roles in the PEC performances of photoelectrodes. The photocurrent density of T2 can be further increased greatly upon the decoration of V$_2$VI$_3$ QDs Compared to pristine TiO$_2$ (0.69 mA cm$^{-2}$), the current densities of Bi$_2$Te$_3$/T2 (0.86 mA cm$^{-2}$) and Bi$_2$Se$_3$/T2 (1.0 mA cm$^{-2}$) at 1.6 V$_{RHE}$ rise by ~30% and ~40%, respectively, implying
that surface modification can promote the separation of electrons and holes. Interestingly, Bi$_2$Se$_3$/T2 produced a larger photocurrent density, although Bi$_2$Se$_3$ shows a lower visible light absorption than Bi$_2$Te$_3$.

Figure 6(b) shows the transient photocurrents generated by T1, T2, T3, Bi$_2$Te$_3$/T2 and Bi$_2$Se$_3$/T2 under the simulated sunlight with light on/off circles under an applied potential of 1.0 V. After the light was on, the photocurrents of five samples increase to the highest value immediately, which implies their fast responses to the light irradiation. Then, the values of generated photocurrent keep constant, suggesting a stable energy output upon illumination. Three bare TiO$_2$ photoanodes deliver relatively lower photocurrents, which can be explained by the sluggish electron–hole separation kinetics. Consistent with LSV results, surface modification plays an important role in PEC performances. In particular, Bi$_2$Se$_3$/T2 exhibits the largest photocurrent as much as ~0.9 mA cm$^{-2}$, which was 50% higher than T2 (~0.6 mA cm$^{-2}$), implying that the heterojunction between TiO$_2$ and V$_2$VI$_3$ nanoparticles can significantly accelerate the charge carrier separation.

EIS is a crucial technique for investigating the charge carrier transfer processes. Figure 6(c) shows the Nyquist plots of alternating current (A.C.) impedance of aligned TiO$_2$ nanorod photoanodes with and without surface decoration with Bi$_2$Se$_3$ and Bi$_2$Te$_3$ upon solar illumination and a 1 V imposed potential.
Charge carriers transfer generally occurs if the shape of the Nyquist plot is a semicircle, and the radius of the curves indicates the magnitude of the impedance [37, 38]. By coupling with V₂VI₃, the impedance of heterojunction photoanodes decreases dramatically. Further, the Nyquist plots can be fitted by utilizing the equivalent circuit as depicted in figure 6(c). Where, R₁ represents solution resistance; R₂ suggests charge transfer resistance and C₁ is double layer capacitance. The simulated R₂ of T₂, Bi₂Te₃/T₂ and Bi₂Se₃/T₂ are around 1301.0, 875.8 and 221.4 Ω, respectively. In particular, the TiO₂ photoanode decorated with Bi₂Se₃ accounts for the smallest impedance, which further demonstrates the faster charge transfer separation kinetics.

Mott–Schottky measurements were performed to obtain the flat band energy of photoanodes. As depicted in figure 6(d), all the curves show a positive slope, indicating n-type semiconductor properties [39]. The value of flat band energy is approximately equal to that of Fermi level (Eₚ) [40]. Herein Eₚ can be quantified by extrapolating the linear part of curves according to Mott–Schottky equation (Equation 2) shown below:

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 N} \left[ E - E_p \right] - \frac{kT}{e}$$

where Cᵢ is differential capacitance of the space charge region per unit area, e is the electron charge, ε₀ is the vacuum permittivity, ε is the dielectric coefficient of TiO₂, N is the electron donor concentration, and E is electrode potential. The Eₚ values of TiO₂, Bi₂Te₃/TiO₂ and Bi₂Se₃/TiO₂ represent −0.04, −0.09 and −0.09 eV, respectively. Thus, there is a negative shift in the energy of Fermi level after the sensitization of Bi₂Se₃ and Bi₂Te₃ QDs. As the Fermi level in n-type semiconductor can be used to determine the conduction band position, their band structures can be thus confirmed and listed in figure 7. For reference, the energy band structures of bare Bi₂Se₃ and Bi₂Te₃ were also calculated according to the reports by Rajamathi et al and Sharma et al [41, 42].

The PEC MO and MB bleaching experiments were carried out upon solar irradiation to explore the role of V₂VI₃ nanoparticles on the PEC activities of V₂VI₃/TiO₂ systems, and the results are summarized in figure 8.

Figure 8(a) shows the UV–Vis spectra of MO solution (5.0 mg l⁻¹) over the Bi₂Se₃/T₂ photoanode under the irradiation by a solar simulator. The intensity of the characteristic absorption peak at the wavelength of 507.5 nm gradually decreases with the proceeding of PEC decoloration by Bi₂Se₃/T₂. Figure 8(b) summarizes the PEC activity of different photoanodes in degradation of aqueous MO (5.0 mg l⁻¹) solution. The pH was set to 2.3 to improve the MO adsorption since it was reported that the optimal value for photo(electro)catalytic MO degradation is in the range of 2–3. Clearly, the QD-sensitized TiO₂ nanorod arrays exhibit the enhanced PEC bleaching in MO decoloration than that of pristine TiO₂ photoanodes. Under 1.0 V bias and after the simulated solar light irradiation for 240 min, ~91.8% and 76.5% MO can be

**Figure 7.** Estimated band structure of T₂, Bi₂Te₃/T₂, and Bi₂Se₃/T₂ nanorods.
Figure 8. (a) UV–Vis spectra of MO during PEC bleaching over T2 under a bias of 1.0 V over the irradiation time of sunlight; (b) PEC or photocatalytic (without bias) bleaching of MO over T2, Bi₂Te₃/T2, and Bi₂Se₃/T2 nanorod array photoanodes with a bias of 1.0 V and (c) their corresponding apparent reaction constants ($k_{app}$) and TOC removal after 240 min sunlight irradiation; (d) Cyclic PEC performances of Bi₂Te₃/T2, and Bi₂Se₃/T2 nanorod array photoanodes and (f) their corresponding $k_{app}$.

Decolorated by Bi₂Se₃/T2 and Bi₂Te₃/T2, respectively; while merely 44.5% by T2. Without bias, this photocatalytic bleaching rate is even lower (24.3%). Similar trends in the PEC activity can be found in bleaching MB (10.0 mg l⁻¹): Bi₂Se₃/T2 > Bi₂Te₃/T2 > T2 by the descending order of PEC activity. After 120-min sunlight irradiation, ~79.4% of MO can be decolored over the Bi₂Se₃/T2 photoanode, which is much higher than 65.4% and 37.5% by Bi₂Te₃/T2 and T2, respectively.

The photocatalytic bleaching kinetics of azo dyes is well matched with a pseudo-first-order reaction [43]. The apparent rate constant ($k_{app}$) can be calculated by Equation 3.

$$\ln \frac{C_t}{C_0} = -k_{app} \times t_i$$  \hspace{1cm} (3)

where $C_0$ is the initial concentration of azo dye; $C_t$ is the concentration of azo dye upon solar irradiation for a certain time ($t_i$). As calculated, Bi₂Se₃/T2 shows the highest $k_{app}$ values, i.e. 0.0094 and 0.012 min⁻¹ during PEC bleaching of MO and MB, respectively, which are also 3.84 and 3.53 times as large as those of T2 (figures 8(c) and (f)).

The significant improvements in PEC activities imply the critical role of the anchored VₓVI₃ (V = Bi; VI = Se, Te). From optics point view, narrow-bandgap Bi₂Se₃ and Bi₂Te₃ improves the light-harvesting properties of photoanodes. Moreover, it is well known that Bi₂Se₃ and Bi₂Te₃ are representative topological insulators whose surface contains rich conducting states [44, 45]. When irradiated with sunlight, the excited TiO₂ electrons prefer to migrate along the surface of QDs rather than move into the bulk. Thus, the well dispersed Bi₂Se₃ and Bi₂Te₃ QDs are assumed to facilely extract the photinduced electrons, and the specially separated electrons possess great mobility for the subsequent photocatalytic and PEC applications.

Rajamathi et al reported that Bi₂Se₃ and Bi₂Te₃ themselves show photocatalytic activity in H₂ production from aqueous triethanolamine solution [41]. Their electrons might be derived from both metallic surface states and the photoexcited electrons at the bulk conduction bands. Moreover, the photogenerated electrons from VₓVI₃ and TiO₂ might be accumulated on the VₓVI₃ surface, leaving holes on TiO₂ surface for proceeding oxidation. It is also noteworthy that the sunlight irradiation on VₓVI₃ surface is accompanied with the heat transfer. Bi₂Se₃ and Bi₂Te₃ are both thermoelectric materials that can proceed energy conversions between heat and electricity. Quantifying the contribution of different factors and the exact interfacial charge carrier transfer pathway are in progress in our group.

The cyclic PEC performances of Bi₂Se₃/T2 and Bi₂Te₃/T2 were conducted to study their chemical and photocorrosion stabilities. Bi₂Se₃/T2 shows a slight loss (4.2%) in MO bleaching after four PEC cycles; while...
a significant loss (21.6%) occurs in Bi$_2$Te$_3$/T2. Future works will focus on the chemical stability of QDs under the oxidation and acid attack, the passivation of QD surface, and interfacial stability between TiO$_2$ and V$_2$VI$_3$ during the PEC applications to further boost the long-term PEC performances.

4. Conclusion

Vertically aligned V$_2$VI$_3$/TiO$_2$ (V = Bi; VI = Se, Te) nanorod photoanodes have been successfully synthesized by a wet-chemistry route. The surface sensitization of topologically insulating Bi$_2$Te$_3$ and Bi$_2$Se$_3$ QDs significantly increases the light response of rutile TiO$_2$ nanorod arrays in the visible region. The PEC properties of V$_2$VI$_3$/TiO$_2$ heterojunctions, including transient photocurrent, LSV and EIS, are significantly improved due to the efficient charge carrier separation and the enhanced visible light absorption. The fabricated rutile TiO$_2$ nanorod arrays with well-dispersed Bi$_2$Se$_3$ QDs exhibit the highest PEC activity and show the great potential for the oxidative mineralization of azo dyes. Future studies will focus on the charge transfer mechanism, the insight and exact role of topological insulators, and photochemical stability of the V$_2$VI$_3$/TiO$_2$ interfaces.

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