The Quest for Photocatalytic Systems with Broadband Solar Absorption

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Since the first discovery of photocatalytic splitting of water by Fujishima and Honda in 1972, the semiconductor catalysts have played a central role in the conversion of solar energy and the degradation of organic pollutants.[1] Over the past few decades, the development of semiconductor photoelectrochemical systems for efficient solar energy conversion has become the goal of numerous research efforts. Titanium dioxide (TiO_2) is perhaps the best investigated photocatalyst in water detoxification and air pollution control by utilization of solar energy. However, the photoactivity of TiO_2 with a bandgap energy of 3.2 eV is hampered by the requirement of illumination with wavelength of less than 387 nm, which only accounts for less than 5% of the solar energy. Another drawback associated with the TiO_2 system is its relatively high recombination rate of photoexcited charge carriers, thereby resulting in a decrease in process efficiency.[2] To solve these problems, a variety of strategies have been developed to achieve efficient photocatalysts featuring absorption over broad wavelength ranges.

One commonly used approach for enhancing the absorption efficiency of photocatalysts in the visible spectral region involves bandgap engineering by doping metal and non-metal species into TiO_2 host lattices. For example, the bandgap of the nitrogen-doped TiO_2 can be narrowed by 0.72 eV as a result of the hybridization of N($2p$) and O($2p$) energy states.[3] The incorporation of other non-metal (such as C and S) and metal elements (including Fe, Cu, Mn, Co, Pt, Ru, and Au) is also used to activate photocatalytic reactions under visible light.[4] However, the improvement of the photocatalytic activity by this approach is rather limited because the doping process often enables enhanced charge carrier recombination. To boost solar energy efficiency, dye-sensitized solar cells have also been exploited to enhance the light absorption in the visible region.[5] Alternatively, semiconducting nanomaterials

with narrow bandgaps, tunable optical absorption, and high photostability can be utilized as sensitizers for visible light. Importantly, the coupling of semiconductor sensitizers with TiO_2 in form of heteronanostructures could extend the energy range of photoexcitation and significantly improve the photocatalytic efficiency by increasing the charge separation.[6] Despite considerable efforts in developing heteronanostructured photocatalysts, the search for photocatalysts with broadband solar absorption covering the entire visible-NIR range remains a formidable challenge.[7]

Writing in *Advanced Materials*, Liu and co-workers[8] now describe an intriguing material design that allowed them to trap the light within a remarkable wavelength range. The material is based on a hybrid system comprising Bi_2WO_6 nanoplatelets and TiO_2 nanobelts. Bi_2WO_6 is chosen as the photocatalyst because of its narrow bandgap (2.8 eV) that matches closely with the energy of visible light.[9] The authors found that the Bi_2WO_6 nanoplatelets also possess good photocatalytic properties under NIR irradiation. It was believed that the presence of oxygen vacancies in the Bi_2WO_6 nanoplatelets raises the Fermi level and reduces the band edge, allowing for interband transitions and carrier creation.[8] Transmission electron micrograph of the hybrid semiconductor system shows the formation of a hybrid heteronanostructure with Bi_2WO_6 nanoplatelets grown epitaxially onto the surface of the TiO_2 nanobelt (**Figure 1**a). The Bi_2WO_6/TiO_2 nanostructure exhibits a broadband enhancement of the light absorption and much improved photocatalytic performance for the degradation of methyl orange dyes (Figure 1b,c).

The improvement in the photocatalytic performance of the hybrid nanomaterials is partly attributed to the enlarged surface area of the TiO_2 nanobelt because of the conformal growth of Bi_2WO_6 nanoplatelets. Apart from the increased surface area, one must take into account the synergetic effect imparted by combining the two components. A more likely explanation is that the modification of the TiO_2 nanobelt with Bi_2WO_6 effectively suppresses the recombination rate of photogenerated charge carriers.

To better understand the origin of the enhanced photocatalytic activity in Bi_2WO_6-modified TiO_2 nanobelts, the energy transfer process of the charge carriers needs to be considered. As shown in **Figure 2**, both TiO_2 and Bi_2WO_6 can be photoexcited by irradiation with UV light. Consequently, electrons are excited across the band gap of the semiconductor where no electron states exist. At the interface, the electron produced in the TiO_2 nanobelt transfers to the conduction band

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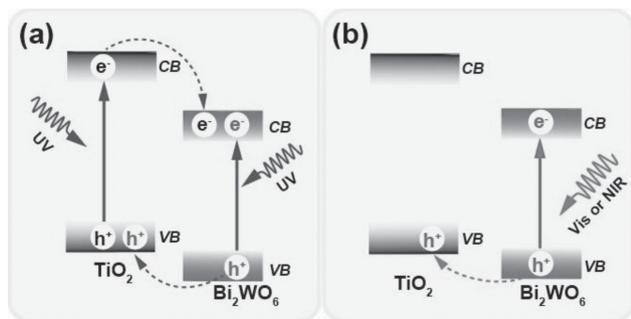3 Research Link, Singapore, 117602, Singapore
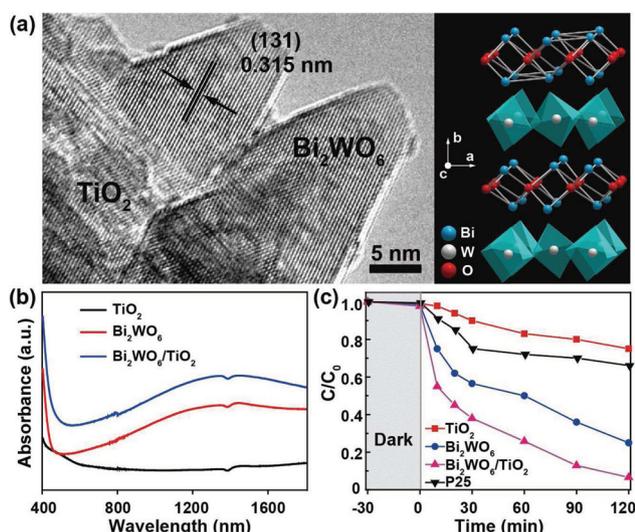
Figure 1. a) The HRTEM image of Bi_2WO_6/TiO_2 heteronanostructures. (Inset) The crystal structure of Bi_2WO_6 showing layers of corner-sharing WO_6 octahedral sheets and bismuth oxide sheets. b) The absorption spectra of TiO_2 nanobelts, Bi_2WO_6 nanoplatelets, and Bi_2WO_6/TiO_2 heteronanostructures. c) Photocatalytic performance for the degradation of methyl orange in the presence of P25, TiO_2 nanobelts, Bi_2WO_6 nanosheets, and Bi_2WO_6/TiO_2 heterostructures, respectively. Reproduced with permission.[8] Copyright 2013, John Wiley &Sons.

of the Bi_2WO_6, while the photoinduced hole in the Bi_2WO_6 particle migrates to the TiO_2 valence band. The transfer of charge carriers between the TiO_2 nanobelt and the Bi_2WO_6 particle increases the charge separation and thus efficiency of the photocatalytic process (Figure 2a). In contrast, when irradiated with visible-NIR light, only Bi_2WO_6 can be excited to generate an electron to the conduction band owing to its small bandgap (Figure 2b). The photogenerated hole in the

valence band of Bi_2WO_6 can be easily transferred to that of TiO_2 because of their close energy levels, while the electron produced in the Bi_2WO_6 conduction band from the excitation process remains in the Bi_2WO_6 particle, thereby enabling the separation of charge carriers.

One of the major further challenges will be to improve the photocatalytic activity of TiO_2/Bi_2WO_6 nanostructure under NIR excitation. An even greater challenge will be to understand the interplay between surface and electronic characteristics at the interface of the composite structure. Achieving these ambitious goals may require the integration of spectral converting nanomaterials[10–13] to the existing semiconductor systems. All in all, however, the work of Liu and co-workers work should provide a new direction for the development of broadband photocatalysts.

Figure 2. The proposed photoexcited charge transfer processes in the Bi_2WO_6/TiO_2 photocatalyst under a) UV and b) visible-NIR irradiation, respectively.

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