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 photocatalytic systems for efficient solar energy conversion has become the goal of numerous research efforts. Titanium dioxide (TiO$_2$) is perhaps the best investigated photocatalyst material, as it was believed that the presence of oxygen vacancies in the TiO$_2$ nanobelt transfers to the conduction band and traps the electrons, inhibiting their recombination with the holes.

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] The field of advanced materials has significantly contributed to this area, with Liu and co-workers[8] now describing 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$_2$WO$_6$ nanoplatelets and TiO$_2$ nanobelts. Bi$_2$WO$_6$ 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$_2$WO$_6$ nanoplatelets also possess good photocatalytic properties under NIR irradiation. It was believed that the presence of oxygen vacancies in the Bi$_2$WO$_6$ nanoplatelets raises the Fermi level and reduces the band edge, allowing for interband transitions and carrier recombination. The modification of the TiO$_2$ nanobelt with Bi$_2$WO$_6$ effectively suppresses the recombination rate of photogenerated charge carriers.

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$_2$WO$_6$ 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$_2$WO$_6$ effectively suppresses the recombination rate of photogenerated charge carriers.

To better understand the origin of the enhanced photocatalytic activity in Bi$_2$WO$_6$-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$_2$WO$_6$ 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...
of the Bi₂WO₆, while the photoinduced hole in the Bi₂WO₆ particle migrates to the TiO₂ valence band. The transfer of charge carriers between the TiO₂ nanobelt and the Bi₂WO₆ particle increases the charge separation and thus efficiency of the photocatalytic process (Figure 2a). In contrast, when irradiated with visible-NIR light, only Bi₂WO₆ 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 Bi₂WO₆ can be easily transferred to that of TiO₂ because of their close energy levels, while the electron produced in the Bi₂WO₆ conduction band from the excitation process remains in the Bi₂WO₆ particle, thereby enabling the separation of charge carriers.

One of the major further challenges will be to improve the photocatalytic activity of TiO₂/Bi₂WO₆ 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.

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Figure 1. a) The HRTEM image of Bi₂WO₆/TiO₂ heteronanostructures. (Inset) The crystal structure of Bi₂WO₆ showing layers of corner-sharing WO₆ octahedral sheets and bismuth oxide sheets. b) The absorption spectra of TiO₂ nanobelts, Bi₂WO₆ nanoplatelets, and Bi₂WO₆/TiO₂ heteronanostructures. c) Photocatalytic performance for the degradation of methyl orange in the presence of P25, TiO₂ nanobelts, Bi₂WO₆ nanosheets, and Bi₂WO₆/TiO₂ heterostructures, respectively. Reproduced with permission.[8] Copyright 2013, John Wiley & Sons.

Figure 2. The proposed photoexcited charge transfer processes in the Bi₂WO₆/TiO₂ photocatalyst under a) UV and b) visible-NIR irradiation, respectively.