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Photocatalytic Water Splitting with a Novel Cr-doped $Ba_2In_2O_5/In_2O_3$ Nanocomposite Oxide Semiconductor

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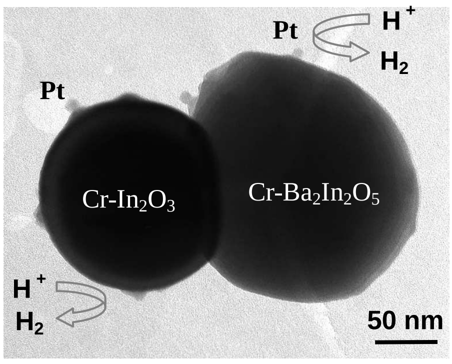
Photocatalytic water splitting to produce clean H_2 energy is one of the ideal solar energy conversion methods.[1, 2] Generally, the photocatalytic water splitting process with a semiconductor includes light-induced band gap excitation to form electrons in conduction band and holes in valence band and subsequent redox reactions to generate H_2 and O_2. In principle, this process can be realized either by one-photon excitation process using single-phase semiconductor or by two-photon excitation process (Z-scheme) using composite semiconductor. In both cases, the band edges of a photocatalyst must be suitable for the redox reactions of water splitting.

Most efforts have been made to develop single-phased photocatalysts for efficient water splitting. Up to now, however, the number of single-phase photocatalysts capable of stoichiometric water splitting is very limited probably due to the difficult modulation of the electronic structure of a semiconductor photocatalyst within a definite crystal structure. The rapid recombination of photo-excited electron/hole pairs is probably another reason that stoichiometric water splitting is hard to be realized even if the band edges of a single-phase semiconductor are suitable for evolution of both H_2 and O_2.

On the other hand, if these two semiconductors are integrated into one system, the redox reactions of both H_2 and O_2 evolution will be able to fulfill, and thus stoichiometric water splitting can be expected theoretically. Actually, designing composite semiconductor photocatalysts for the purpose of achieving efficient charge separation in a light energy conversion system has attracted much attention. However, in these composite semiconductor systems, the two semiconductors are simply coupled or mediated with a shuttle redox, the charge transportation between two semiconductors seems not fluent although the charge separation ability is improved.

In this report, we present a nanostructured Cr-doped $Ba_2In_2O_5/In_2O_3$ (C-BIO) oxide semiconductor as a novel composite photocatalysis system, in which the charge separation and transportation abilities have been improved by the formation of internal nanostructures and ohmic contact among different components. In addition, the role of the split Cr-3d orbitals has also been considered for the purpose of increasing the capacity of C-BIO to absorb visible light. The C-BIO powder samples synthesized by a solid-state reaction method were characterized with powder X-ray diffraction (XRD), energy dispersive spectrometry (EDS), high-resolution transmission electron microscopy (HRTEM) and UV-vis diffuse reflectance spectrometry. Figure 1 shows HRTEM image of Pt-loaded C-BIO. The photocatalytic activities of Pt or NiO loaded C-BIO and individual precursor materials were evaluated by H_2 evolution from aqueous CH_3OH solution under visible light and by water splitting under UV light irradiation, respectively. It was found that the composite C-BIO was a novel nanostructured photocatalyst for H_2 evolution with enhanced capability in comparison with individual raw materials. The overall band structure, charge excitation, separation, transportation and redox reactions for H_2 and O_2 evolution in C-BIO system were proposed.



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