

Insights into the photocatalytic mechanism of mediator-free direct Z-scheme g-C₃N₄/Bi₂MoO₆(010) and g-C₃N₄/Bi₂WO₆(010) heterostructures: A hybrid density functional theory study

Opoku F
Govender K
Van Sittert CGCE
Govender PP

ABSTRACT:

Graphite-like carbon nitride (g-C₃N₄)-based heterostructures have received much attention due to their prominent photocatalytic activity. The g-C₃N₄/Bi₂WO₆ and g-C₃N₄/Bi₂MoO₆ heterostructures, which follow a typical hetero-junction charge transfer mechanisms show a weak potential for hydrogen evolution and reactive radical generation under visible light irradiation. A mediator-free Z-scheme g-C₃N₄/Bi₂MoO₆(010) and g-C₃N₄/Bi₂WO₆(010) heterostructures photocatalyst are designed for the first time using first-principles studies. Moreover, theoretical understanding of the underlying mechanism, the effects of interfacial composition and the role the interface play in the overall photoactivity is still unexplained. The calculated band gap of the heterostructures is reduced compared to the bulk Bi₂WO₆ and Bi₂MoO₆. In this study, we systematically calculated energy band structure, optical properties and charge transfer of the g-C₃N₄/Bi₂MoO₆(010) and g-C₃N₄/Bi₂WO₆(010) heterostructures using the hybrid density functional theory approach. The results show that the charge transfer at the interface of the heterostructures induces a built-in potential, which benefits the separation of photogenerated charge carriers. The g-C₃N₄/Bi₂MoO₆(010) heterostructure with more negative adhesion energy ($-1.10 \text{ eV}\text{\AA}^{-2}$) is predicted to have a better adsorptive ability and can form more easily compared to the g-C₃N₄/Bi₂WO₆(010) interface ($-1.16 \text{ eV}\text{\AA}^{-2}$). Therefore, our results show that the g-C₃N₄ interaction with Bi₂MoO₆ is stronger than Bi₂WO₆, which is also verified by the smaller vertical separation (3.25 Å) between Bi₂MoO₆ and g-C₃N₄ compared to the g-C₃N₄/Bi₂WO₆(010) interface (3.36 Å). The optical

absorption verifies that these proposed Z-scheme heterostructures are excellent visible light harvesting semiconductor photocatalyst materials. This enhancement is ascribed to the role of g-C₃N₄ monolayer as an electron acceptor and the direct Z-scheme charge carrier transfer at the interface of the heterostructures. This work is useful for designing new types of Z-scheme photocatalyst and offers new insight into Z-scheme charge transfer mechanism for applications in the field of solar energy conversion.