

## Insights into the photocatalytic mechanism of mediator-free direct Z-scheme g-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>MoO<sub>6</sub>(010) and g-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>WO<sub>6</sub>(010) heterostructures: A hybrid density functional theory study

Opoku F  
Govender K  
Van Sittert CGCE  
Govender PP

### ABSTRACT:

Graphite-like carbon nitride (g-C<sub>3</sub>N<sub>4</sub>)-based heterostructures have received much attention due to their prominent photocatalytic activity. The g-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>WO<sub>6</sub> and g-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>MoO<sub>6</sub> 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-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>MoO<sub>6</sub>(010) and g-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>WO<sub>6</sub>(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 Bi<sub>2</sub>WO<sub>6</sub> and Bi<sub>2</sub>MoO<sub>6</sub>. In this study, we systematically calculated energy band structure, optical properties and charge transfer of the g-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>MoO<sub>6</sub>(010) and g-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>WO<sub>6</sub>(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-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>MoO<sub>6</sub>(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-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>WO<sub>6</sub>(010) interface ( $-1.16 \text{ eV}\text{\AA}^{-2}$ ). Therefore, our results show that the g-C<sub>3</sub>N<sub>4</sub> interaction with Bi<sub>2</sub>MoO<sub>6</sub> is stronger than Bi<sub>2</sub>WO<sub>6</sub>, which is also verified by the smaller vertical separation (3.25 Å) between Bi<sub>2</sub>MoO<sub>6</sub> and g-C<sub>3</sub>N<sub>4</sub> compared to the g-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>WO<sub>6</sub>(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-C<sub>3</sub>N<sub>4</sub> 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.