

The Role of Small Polarons in the Photoelectrochemical Properties of Hematite

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Hematite, owing to its ideal physical properties, chemical stability, and abundance on Earth, has become a potential candidate as a photoanode in solar water-splitting device applications. However, the high photogenerated charge recombination due to its low efficiency of charge separation as a consequence of poor electronic transport and collection at the back contact has hindered its commercial application. Based on the limitations of hematite, this study describes germanium as a potentially ideal element that combines the beneficial improvement in charge transfer efficiency and morphology control toward high hematite-based photoanode performance. Our experimental results demonstrated that the addition of Ge enhanced the charge mobility, leading to a superior charge separation efficiency than the pristine hematite photoanode. Moreover, photoelectrochemical measurements performed at different wavelengths shows the Ge interferes with the formation of small polarons, making the charges more mobile (delocalized), thus favoring the process of photoinduced charge separation. The combined role played by Ge addition resulted in a significant improvement in the photoelectrochemical performance from 0.5 to 3.2 mA cm⁻² at 1.23 VRHE by comparing the pristine and Ge-hematite-based photoanodes.

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