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Highly Selective Photocatalytic CO_2 Reduction on TiO_2-Passivated InP in Ionic Liquids GUANGTONG ZENG, JING QIU, SHERMIN ARAB, ZHEN LI, STEPHEN CRONIN, University of Southern California — Lowering the overpotential required to drive the photocatalytic reduction of CO_2 to useful products is a very important challenge. In this article, we use an ionic liquid $[EMIM]BF_4$ co-catalyst to improve the selectivity and efficiency of CO_2 reduction to CO on TiO_2-passivated InP. Here, the InP surface is passivated using a thin film of TiO_2 deposited by atomic layer deposition (ALD), which improves the photoconversion efficiency by as much as 17X compared to bare InP. We believe there are three mechanisms of enhancement in this photocatalytic system. Firstly, the TiO_2 deposited by ALD is n-type due to oxygen vacancies, and forms a pn-junction with the underlying p-type InP photocathode, resulting in a built-in potential which reduces electron-hole recombination through charge separation. Secondly, the Ti^{3+} active sites formed on the TiO_2 surface lower the energy of the CO_2^- intermediate through the formation of an intermediate complex. Thirdly, the $[EMIM]^+$ ions in solution also stabilize the CO_2^- intermediate, further lowering the energy barrier of this reaction. Here, we use a non-aqueous ionic liquid solution, which prohibits hydrogen formation and enables highly selective CO_2 reduction with a Faradaic efficiency of 46%. This general approach of passivating narrower band gap semiconductors with TiO_2 and utilizing a non-aqueous ionic liquid solution allows a wide range of materials to be considered for photocatalysis, enabling more efficient photocatalysts to be developed.

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