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Adsorption of Water on Cocatalyst Surfaces for Photocatalytic Water Splitting

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Photocatalytic water splitting is a promising technology for using solar energy to produce directly hydrogen (green hydrogen (GH₂)), GH₂ is considered to as environmentally friendly and renewable energy based fuel. However, only a few semiconductor materials have been developed as efficient photocatalyst, amongst them photocatalysts based on Al:SrTiO₃.⁽¹⁾ A typical photocatalyst consists of three components: i) a semiconductor absorbing light and generating electron/hole pairs which migrate to ii) co-catalysts driving the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) and iii) a protective overlayer blocking the reaction of the produced H₂ and O₂ back to H₂O, i.e. blocking the backreaction. (2, 3) Co₃O₄ can be used as OER co-catalyst and Rh NPs as HER co-catalyst SrTiO₃ (STO) while Cr₂O₃ as overlayer to block the backreaction. One of the questions which is not well understood is the contribution of the adsorption process of H₂O onto the photocatalyst in driving the H₂O splitting reaction. Does H₂O adsorb as water onto the photocatalyst or does it turn into e.g. OH⁻ as a first step in the H₂O splitting process. In the present work this question is investigated. This question is investigated with electron spectroscopy. Firstly, X-ray Photo-electron Emission Spectroscopy (XPS) is employed as a common technique to investigate the chemical compositions of the surfaces including the adsorbates. Secondly, Metastable Induced Electron Spectroscopy (MIES), the most surface-sensitive technology for analyzing the surface, to determine the electronic structure and thus the molecular composition of the outermost layer. It was found with XPS and MIES that on STO (100) water partially dissociates forming OH⁻ and H₂O on the surface. However, Rh NPs and Cr₂O₃ photodeposited on STO (100) resulted that only OH⁻ was detected for both materials. These observations may support the Rh NPs and Cr₂O₃ rules to enhance the overall photocatalysis water splitting.

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