HERFD-XANES and vtc-RIXS study of mesoporous TiO_2 as an efficient interfacial charge-transporting layer for photo-electrochemical water splitting

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Abstract

Introduction: Most of the current energy need is fulfilled by the fossil fuels; the connected CO_2 release contributes to global warming. Inexpensive possibilities for the production of renewable fuels are thus required to meet future energy needs. Methods relying on abundant solar energy, water and transition metal/oxides (semiconductors) are the most promising for developing the future energy technologies. In this study we explore solar energy based water splitting using earth abundant photo-catalysts for producing renewable hydrogen fuel.

Methods: A solution based technique for the fabrication of a photo-electrochemical device to split water is presented in this study. P-type boron doped Si nanostructured photo-electrodes are functionalized with mesoporous TiO_2 and decorated with hematite nanorods to report efficient solar hydrogen generation. Photo-electrochemical (PEC) performance of the functionalized photo-electrodes was studied using linear sweep voltammetry (LSV), electrochemical impedance spectroscopy and Mott-Schottky. PEC data presented in this study is performed in aqueous NaCl and phosphate electrolyte at neutral pH. Neutral pH electrolytes are an eco-friendly approach compared to acidic and alkaline electrolyte. Changes in the electronic structures of functionalized photo-electrodes were studied at ID-26 ESRF high brilliance beam line using X-ray absorption (HERFD-XANES) and valence-to-core resonant inelastic X-ray scattering (vtc-RIXS) and compared with as-synthesized photo-electrodes. HERFD-XANES and vtc-RIXS were acquired at both the Ti and Fe K-edge.

Results and Discussion: The preliminary PEC data suggest better photocurrent density in aqueous NaCl electrolyte compared to phosphate buffer. However, the onset potential shift is more anodic in phosphate buffer compared to aqueous NaCl electrolyte. This is attributed to the Cl^- ion adsorption on the surface of hematite nanorods resulting in better ionic charge transfer for water splitting reaction. HERFD-XANES and vtc-RIXS reveals significant changes in the electronic structure of mesoporous TiO_2. Such significant changes were not observed at the Fe K-edge.

Conclusion: We presented here an inexpensive solution based approach to functionalize the Si nanostructured photo-electrodes In addition; we also demonstrate here the importance of synchrotron based high-energy X-Ray spectroscopy techniques (HERFD-XANES and vtc-RIXS) to characterize the interfacial charge-transporting layer in order to develop better and efficient Si nanostructured photo-electrodes.