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Computational design of materials for solar hydrogen generation

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Photocatalysis has a great potential for the production of hydrogen from aquerous solution under solar light [1]. In this talk, two different approaches toward the computational materials desing for solar hydrogen generation will be presented. Tin (Sn), which has two major oxidation states, Sn^{2+} and Sn^{4+}, is abundant on the earth's crust. Recently, visible-light responsive photocatalytc H_2 evolution reaction was identified over a mixed valence tin oxide Sn_3O_4 [2]. We have carried out crystal structure prediction for mixed valence tin oxides in different atomic compositions under ambient pressure condition using advanced computational methods based on the evolutionary crystal-structure search and density-functional theory. The predicted novel crystal structures realize the desirable band gaps and band edge positions for H_2 evolution under visible light irradiation. It is concluded that multivalent tin oxides have a great potential as an abundant, cheap and environmentally-benign solar-energy conversion photofunctional materials [3]. Transition metal doping is effective for sensitizing $SrTiO_3$ under visible light. We have theoretically investigated the roles of the doped Cr in STO based on hybrid density-functional calculations [4]. Cr atoms are preferably substituting for Ti under any equilibrium growth conditions. The lower oxidation state Cr^{3+}, which is stabilized under an n-type condition of STO, is found to be advantageous for the photocatalytic performance. It is firther predicted that lanthanum is the best codopant for stabilizing the favorable oxidation state, Cr^{3+}. The prediction was validated by our experiments that La and Cr co-doped STO shows the best performance among examined samples [5]. This work was supported by the Japan Science and Technology Agency (JST) Precursory Research for Embryonic Science and Technology (PRESTO) and International Research Fellow program of Japan Society for the Promotion of Science (JSPS) through project P14207. [1] H. Tong, S. Ouyang, Y. Bi, N. Umezawa, M. Oshikiri, J. Ye, *Adv. Mater.* **24**, 229 (2012). [2] Maidhily Manikandan, Toyokazu Tanabe, Peng Li, Shigenori Ueda, Gubbala V. Ramesh, Rajesh Kodiyath, Junjie Wang, Toru Hara, Arivuoli Dakshanamoorthy, Shinsuke Ishihara, Katsuhiko Ariga, Jinhua Ye, Naoto Umezawa, and Hideki Abe, "Photocatalytic Water Splitting under Visible Light by Mixed-Valence Sn_3O_4" *ACS Applied Materials & Interfaces*, **6**, 3790 (2014). [3] Junjie Wang, Naoto Umezawa*, and Hideo Hosono, "Mixed Valence Tin Oxides as Novel van der Waals Materials: Theoretical Predictions and Potential Applications" *Adv. Energy Mater.* 2015,DOI: 10.1002/aenm.201501190 [4] P. Reunchan, N. Umezawa, S. Ouyang, J. Ye, *Phys. Chem. Chem. Phys.* **14**, 1876 (2012). [5] P. Reunchan, S. Ouyang, N. Umezawa, H. Xu, Y. Zhang, and J. Ye, *Journal of Materials Chemistry A*, **1**, 4221 (2013).