DFT calculations of photocatalytic water splitting on $NaTaO_3$ (113) and $SrTaO_2N$ (001) surfaces

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Photocatalytic water splitting is considered as a promising route to produce clean hydrogen fuel. Since the famous work of Fujishima and Honda on TiO_2 [1], a large variety of metal oxides have been considered for visible-light photocatalysis, perovskite structured materials that hold particular promise due to their structural and chemical flexibility [2]. Oxynitride perovskites benefit from a smaller band gap compared to pure oxides, making them even more promising for photocatalytic water splitting.

In this work, we want to compare oxides and oxynitrides in terms of their surface chemistry. To this goal, we studied the photo-oxidation of water on the lowest–energy $NaTaO_3$ (113) and $SrTaO_2N$ (001) surfaces, using density functional theory (DFT). We found NaTaO termination to be the most stable for $NaTaO_3$ whereas. For $SrTaO_2N$ the SrO and TaON terminations have approximately the same surface energy. The two materials differ in their water adsorption behavior, $SrTaO_2N$ dissociating water without a barrier on both terminations, whereas for $NaTaO_3$ dissociative adsorption occurs only at the Ta site but it is not barrierless.

To describe the electrochemical process of water splitting as a function of the applied bias and pH on our surfaces, Nørskov's approach has been used [3].

Based on our results it is possible to rationalize the photocatalytic performance of oxynitrides compared to pure oxides going beyond the usual band-gap arguments, considering also the thermochemistry of the water-oxidation reaction on their surfaces.

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