Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplemental Information for

"Nucleus-Coupled Electron Transfer Mechanism for TiO_2-Catalyzed Water Splitting"

Michael Lucking, Yi-Yang Sun,* DamienWest, and Shengbai Zhang*

Department of Physic, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, NY 12180, USA

Contact information:

suny4@rpi.edu (YYS); zhangs9@rpi.edu (SBZ)

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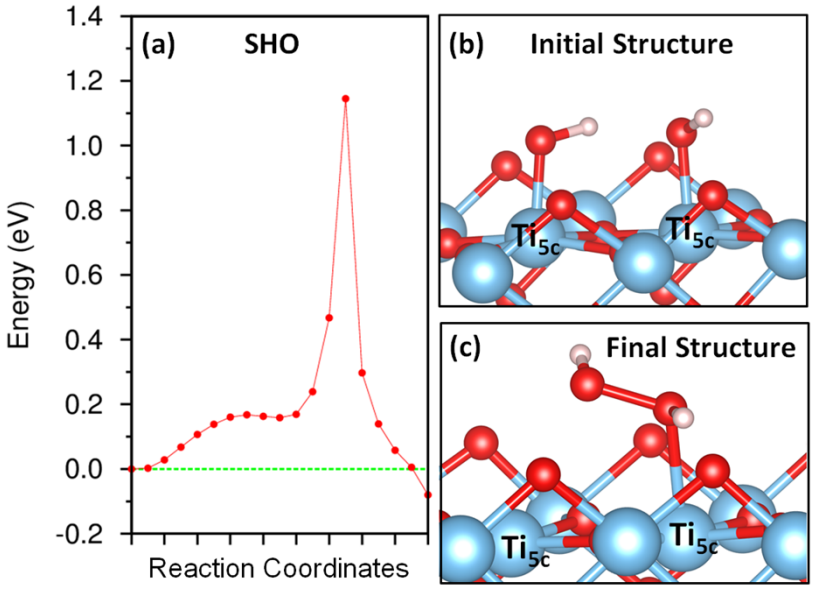

FIG. S1. (a) Potential energy curve for surface hydroxyl oxidation (SHO) mechanism as obtained using CI-NEB method. (b) and (c) show the initial and final structures of the reaction.

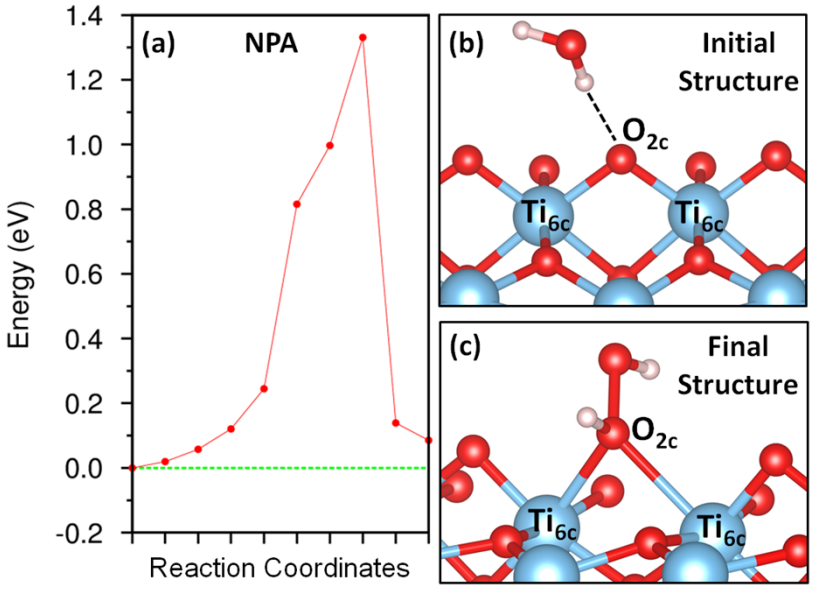

FIG. S2. (a) Potential energy curve for nucleophilic attack (NPA) mechanism as obtained using CI-NEB method. (b) and (c) show the initial and final structures of the reaction. Starting from the initial structure shown in (b), we also checked another two possible final structures. One is to form O_2 and two H on neighboring O_{2c} sites [i.e., the final structure in Figure 1(b) in the main text]. Another is to form HO_2 and one H on O_{2c} site. Both pathways involve the formation of a structure similar to the one shown in (c). Therefore, the barrier shown in (a) should represent at least the lower bound for the reaction barrier of the NPA mechanism.

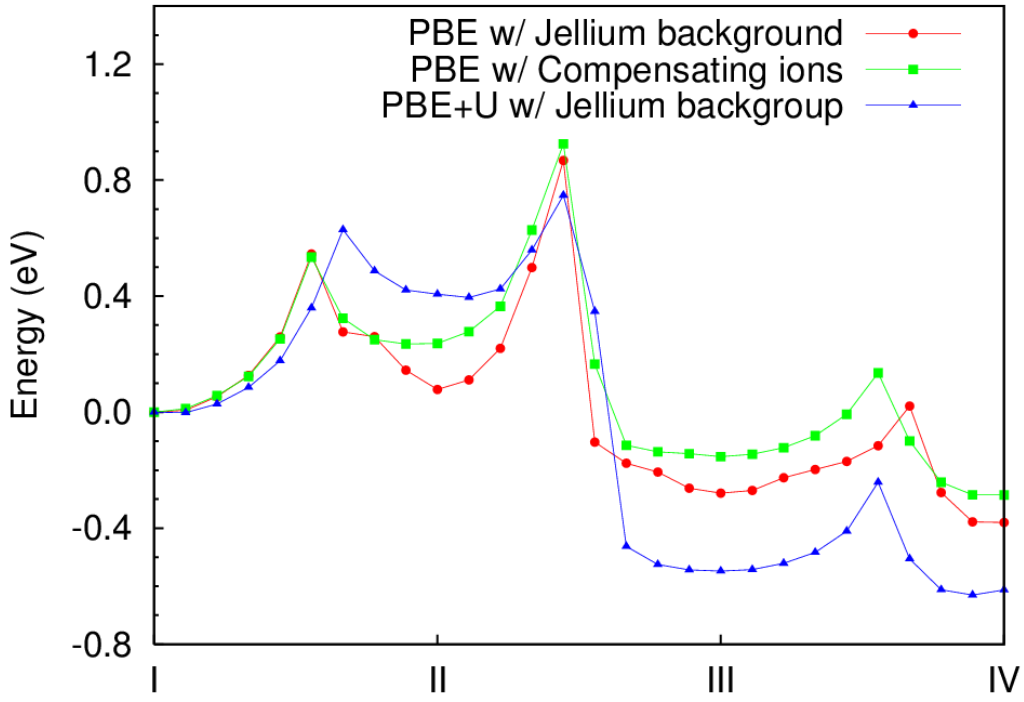

FIG. S3. Comparison of calculated reaction barriers using three different methods: I) using PBE functional in the calculation and uniform charge background (or Jellium background) for compensating the two introduced holes, which is the result shown in Fig. 2 in the main text; II) using PBE functional in the calculation and two OH^- ions for compensating the two introduced holes, where each OH^- ions are created by removing one H atom from a water molecule far from the reaction center; III) using PBE+*U* method and Jellium background.

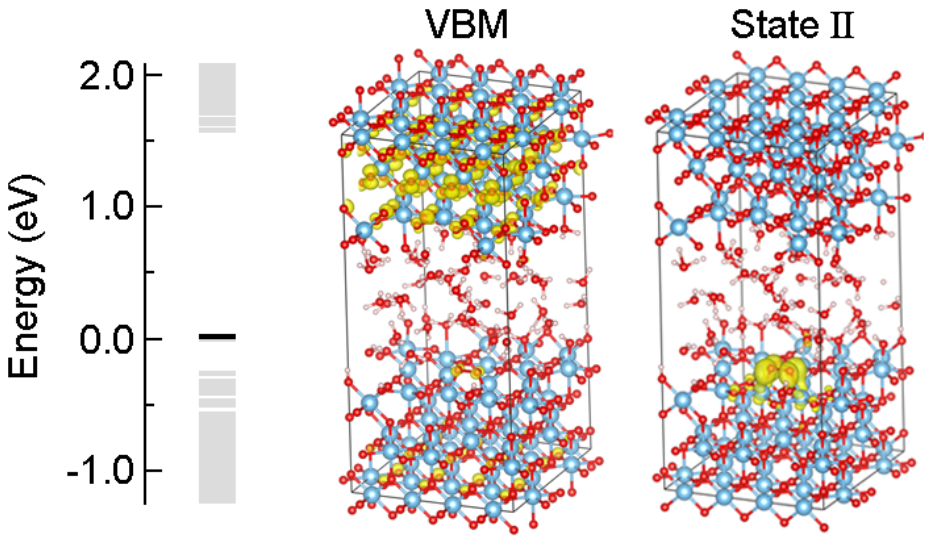

FIG. S4. The eigenvalue spectrum of Configuration IV (left panel). Because in this configuration, the π^*_{2p} state (i.e., State II in Fig. 3 in the main text) is already in the band gap (the state marked by a thick black line), we did not perform the projection of all the electronic orbitals onto the two O atoms forming O-O bond. Note that the VBM state of TiO_2 is only slightly lower than State II and cannot be differentiated from the eigenvalue spectrum. By inspecting the charge density plots (middle and right panels), the VBM state and State II can be clearly identified.