

Photo-induced charge transfer mechanism in titanium-doped microporous silica for photocatalytic water-splitting applications

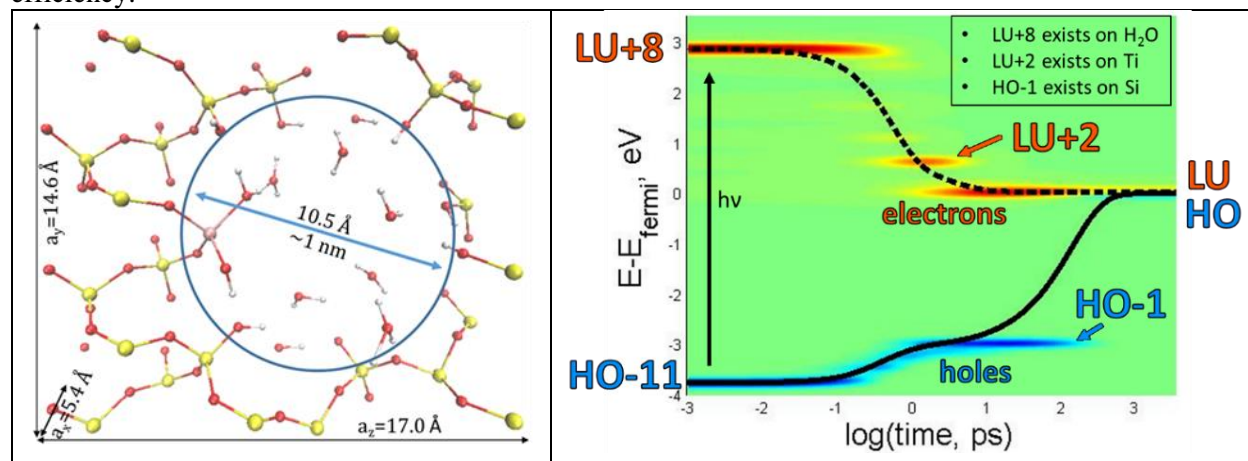
Wendi Sapp[†], Ranjit Koodali[†], Dmitri Kilin^{*‡}

[†]University of South Dakota, Vermillion, SD, USA

[‡]North Dakota State University, Fargo, ND, USA

Abstract

Solar energy conversion into chemical form is possible using artificial means. One example of a highly efficient scenario is solar energy used to split water into oxygen and hydrogen fuels. Efficient photocatalytic water-splitting remains an open challenge for researchers across the globe. Despite significant progress, several aspects of the reaction, including the charge transfer mechanism are not fully clear in this work. Density functional theory combined with density matrix equations of motion were used to identify and characterize the charge transfer mechanism involved in the dissociation of water. A simulated porous silica substrate, using periodic boundary conditions, with Ti⁴⁺ ions¹ embedded on the inner pore wall, and water molecules located within the pore and in the vicinity of the Ti atom, was found to contain electron and hole trap states that could facilitate a chemical reaction.² Simulation of excited state non-adiabatic dynamics allowed the identification of a particular trapping state, located within the silica substrate, which lengthens relaxation time, which may favor a chemical reaction. A chemical reaction would have to occur within the short time interval following the photoexcitation, therefore, the existence of a trapping state may encourage a chemical reaction. This provides evidence that the silica substrate plays an integral part in the electron/hole dynamics of the system, leading to the conclusion that both components (the photoactive materials and the support) of heterogeneous catalytic systems play an important role to optimize catalytic efficiency.



Left: A silicon dioxide slab was created, measuring $5.4 \times 14.7 \times 17.0 \text{ \AA}^3$. Si and O atoms were removed from bulk silica in a deliberate fashion in order to produce a cylindrical pore with a diameter of 10.5 \AA . On the inner surface of the pore, a Ti atom was added and capped with two hydroxyl groups, giving a tetrahedrally-coordinated Ti. **Right:** Photo-induced excited state dynamics for a typical excitation. (HO-11, LU+8) is shown in this distribution of electron and hole relaxations over time. The solid line represents the movement of the hole through orbitals over time. While the dashed line represents electron movement. Time is displayed in a logarithmic scale. A stable hole trap exists at HO-1, which lengthens the hole's relaxation rate compared to the electron. Also, this trap state may exist due to the energy gap law.³

- (a) Horiuchi, Y.; Toyao, T.; Takeuchi, M.; Matsuoka, M.; Anpo, M., *Physical Chemistry Chemical Physics* **2013**, *15* (32), 13243-13253; (b) Inerbaev, T. M.; Hoefelmeyer, J. D.; Kilin, D. S., *The Journal of Physical Chemistry C* **2013**, *117* (19), 9673-9692; (c) Fujishima, A., *Nature* **1972**, *238*, 37-38.
- Liu, I.-S.; Lo, H.-H.; Chien, C.-T.; Lin, Y.-Y.; Chen, C.-W.; Chen, Y.-F.; Su, W.-F.; Liou, S.-C., Enhancing photoluminescence quenching and photoelectric properties of CdSe quantum dots with hole accepting ligands. *Journal of Materials Chemistry* **2008**, *18* (6), 675-682.
- Englman, R.; Jortner, J., *Molecular Physics* **1970**, *18* (2), 145-164.