Molecular Dynamics of Charged Wet TiO_2 Anatase (001) Surface Functionalized by Ru Ions

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Understanding photoinduced electron transfer mechanisms in TiO_2–based materials is significant for materials optimization and device design in high efficiency photovoltaics and photocatalysts. To investigate the photoinduced charge transfer process happening on the TiO_2 surface, in both experiment and theoretical calculation, TiO_2 functionalized by transition metals or metal oxides have been intensively studied.

A photoexcitation in such materials launches the sequence of intermediate steps. In the intermediate states, the fragment of TiO_2 material does exist in "charged" state. In such "charged" regions one expects some variation of the properties of the material. Several key properties of the materials are modified upon variation of total amount of electrons in agiven spatial region.

Here we theoretically monitor the charged wet TiO_2 anatase (001) surface functionalized by Ruthenium ion sat ambient temperatures. The model system represented by $Ti_{30}Ru_2O_{64}^{x}$ $8H_2O$, with x standing for the number of electrons variation in this system, ranging as $-4<x<+4$. We computationally simulate properties of this model in equilibrium and at ambient temperatures, by launching *ab initio* molecular dynamics[1]. All modeling is done using density functional theory (DFT) with PBE functional, implemented in VASP software package[2].

Our results show that, the density of state, absorption spectra, and fluctuation spectra were changed in certain range. As the system ($Ti_{30}Ru_2O_{64}$ $8H_2O$) loses electrons, the electron occupation on the HOMO is decreasing; while the system gains electrons, HOMO has been fully occupied and few electrons start to move to LUMO, showing the trend of electron occupation on LUMO. Thermal fluctuations of ions induce nonradiative relaxation of any photoexcitation. According to our data the rates of nonradiative relaxation are also affected by variation of the total charge of the model. Our simulation point out the possibilities of those properties variation, and our results benefit the understanding of electrons transfer on TiO_2 surface when doped by ruthenium and their derivatives ions. This work would advance the knowledge in TiO_2 based materials designing and provide theoretical evidence in high efficiency photodevices promotion.

1. Alavi, S., Ab Initio Molecular Dynamics. Basic Theory and Advanced Methods. By Dominik Marx and Jürg Hutter. *Angewandte Chemie International Edition* **2009,***48* (50), 9404-9405.
2. Kresse, G.; Furthmüller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B* **1996,***54* (16), 11169-11186.