

# Dissipative carrier dynamics for photocatalysis

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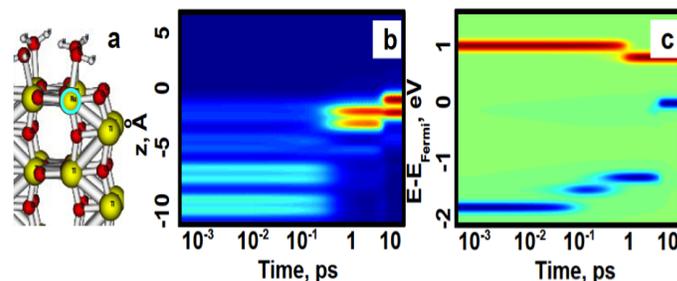
High surface-area semiconductor nanorods decorated with RuO<sub>2</sub> as a surface functional component are investigated. Main attention is focused on the most important and least explored study of photoexcited hole relaxation process. DFT-based simulation approach for the charge transfer dynamics at the interface of the RuO<sub>2</sub> nanocatalyst and TiO<sub>2</sub> nanorod is applied. TiO<sub>2</sub> nanorod is modeled as a periodic anatase (100) slab functionalized with RuO<sub>2</sub> nanocatalyst. In this model, a photoexcitation promotes a non-equilibrium state of a material, so that the electronic states are recalculated for each atomic configuration along molecular dynamics trajectory produced during the simulation to compute the coupling between the electronic and nuclear degrees of freedom. Photon-to-exciton conversion efficiencies and photo-excited charge carriers lifetime are estimated. According to computed dynamics, hole excitation relaxes to valence band maximum faster than electronic one towards to conduction band minimum. This leads to creation of positively charged areas on the nanorod's surface that is an important prerequisite for oxidation catalysis. Our computation identifies optimal composition and morphology of nanocatalyst for such applications as water splitting for hydrogen production or solar cells.

We identify the structure-property relationship using DFT-based modeling. Modeling is used to determine which structures provide less heat loss, longer lifetime of charge carriers, and better photon-to-electron conversion ratio. An output of DFT electronic structure of atomic models is fed to an original electron dynamics code to reveal several aspects of non-equilibrium dynamics: (i) photoinduced rearrangement of charge density in time and space [1, 2], and (ii) dynamics of the excitonic energy transfer between subunits of the model [3], see Fig. 1.

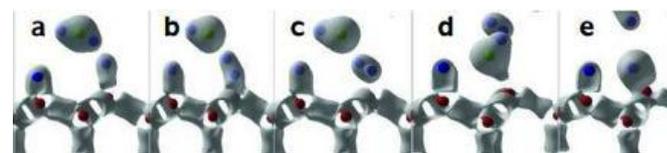
The following values are calculated: (i) rate of energy relaxation, and (ii) space-time charge evolution, and (iii) lifetime of an excited state. For successful light-induced charge separation, an electronic excitation should be long-lived and the rate of backward charge transfer should be much slower than the same value for the charge-separating process. In real systems there are other channels that reduce charge separation effectiveness such as hole recombination with an electron coming from an electrolyte or substrate [4].

We examine chemical stability of adsorbed ions in a model of the excited state. To address chemical stability, we identify conditions leading to unstable configurations and repulsive interatomic interactions. Various concentrations of adsorbates, total charge of the model, temperature, and whether the model is in an excited state is considered. A thermalized mixture of H<sub>2</sub>O molecules and H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> ions in the vicinity of the nanocatalyst on a substrate in an excited or charged electronic state is modeled using DFT. We calculate ab initio molecular dynamics using VASP software. This method gives electron density, accurate interatomic forces, bonds,

and velocities which are recalculated at each time step. Results for a test model show water dissociation facilitated by collision with a semiconductor surface as shown in Fig. 2; video).



**Figure 1.** (a) Minimalistic atomic model of a titania/ruthenia nanocatalyst. (b) Dynamics of non-equilibrium charge density distribution in space for valence bandwith. Colors from blue to red symbolize charge density values from 0 to 1. (c) Dynamics of charge density distribution as a function of energy with red, green, and blue areas showing the distribution for gain, no-change, and loss, respectively, in comparison with the equilibrium distribution; red areas correspond to electron, and blue areas correspond to holes.



**Fig.2.** Snapshots of the reaction pathway for dissociation of H<sub>2</sub>O and hydroxylation of Si surface. For animation see <http://youtu.be/E-ks5zGOxmQ>. Red, green, and blue spheres correspond to Si, O, and H atoms. Grey clouds represent isosurfaces of total charge density.

The catalytic properties of the materials used in a photoelectrochemical cell are critical for maximizing energy yield from an absorbed solar photon. These catalytic properties are dictated by the size, shape, and crystalline structure of the material being used, as well as the solution environment that surrounds the catalytic layer. Our computational modeling method aid in the interpretation of available experimental results, as well as predict outcomes of experiments that have not yet been performed. It is also possible that this method will be able to guide development of entirely novel energy materials for photocatalysis by optimizing desired optical and electronic characteristics. The method can serve as a basis for suggesting novel experimental probes, including femto-second spectroscopy.

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