



量子物理学・ナノサイエンス第 270 回セミナー

Hopping, Recombination Dynamics and Interface Interactions of Surface Polarons on TiO₂

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表面科学およびナノサイエンス、特に酸化物表面研究の分野において、走査プローブ顕微鏡等を用いた研究展開で著名な Thornton 先生が来日される機会に、本学にてセミナーをお願いいたしました。聴講を歓迎いたします。

Electron polarons are thought to play an important role in energy related processes at TiO₂ interfaces. In particular, small electron polarons initially associated with bridging oxygen vacancies on TiO₂(110) have been shown to be involved in key physical and chemical properties. Here we look at the hopping behaviour of these polarons using STM and show that they can be manipulated with an STM tip [1]. The polarons are still present after the surface is hydroxylated. For this termination we have investigated the electron hole recombination processes using time-resolved femtosecond pump-probe photoemission spectroscopy (TRPES) [2,3]. This employed an XUV probe following an infra-red or UV pump. When an infra-red pump is employed, electrons in polaronic band gap states (BGS) are excited to the bottom of the conduction band. The subsequent recapture time of 50±10 fs is determined by directly monitoring the intensity change of the BGS and hot electrons in TRPES spectra. When a UV pump is employed, electrons are excited either from the BGS to a resonance in the CB, or from the top of the valence band (VB) to the bottom of the CB. The same trapping of hot electrons is observed as for infra-red excitation. In addition, a long lifetime component (>1 ps) of the hot electron decay and the BGS recovery are observed, pointing to trap assisted electron-hole recombination. Finally, the interaction of water with the polarons is described. Water-oxide surfaces are ubiquitous in nature and of widespread importance to phenomena like corrosion as well as contemporary industrial challenges such as energy production through water splitting [4]. So far a reasonably robust understanding of the structure of such interfaces under certain conditions has been obtained. Considerably less is known about how overlayer water modifies the inherent reactivity of oxide surfaces. Here we address this issue experimentally for rutile TiO₂(110) using STM and photoemission, with complementary density functional theory calculations. Through detailed studies of adsorbed water nanoclusters and continuous water overlayers, we determine that excess electrons in TiO₂ are attracted to the top surface layer by water molecules. Our results suggest that adsorbate-induced surface segregation of polarons could be a general phenomenon for technologically relevant oxide materials, with consequences for surface chemistry and the associated catalytic activity [5].

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3. State-selective dynamics of TiO₂ charge-carrier trapping and recombination, *J. Phys. Chem. Lett.* **10**, 5265-5270 (2019).
4. Structure of a model TiO₂ photocatalytic interface, H. Hussain, G. Tocci, T. Woolcot, X. Torrelles, C.L. Pang, D.S. Humphrey, C.M. Yim, D.C. Grinter, G. Cabailh, O. Bikondoa, R. Lindsay, J. Zegenhagen, A. Michaelides, G. Thornton, *Nature Materials* **16**, 461-466 (2017).
5. Visualization of water-induced surface segregation of polarons on rutile TiO₂(110), *J. Phys. Chem. Lett.* **9**, 4865-4871 (2019).

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