Photoexcitation of Bulk Polarons in Rutile TiO_2

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In recent years there has been considerable interest in the physics of polarons at reduced TiO_2 surfaces. This includes photoexcitation studies, which have proposed that polaron excitation may represent an alternative vector to band gap excitation in photocatalysis. Two photon photoemission spectroscopy (2PPE) is an ideal technique to investigate these polarons due to its ability to resolve individual electronic states. A number of 2PPE studies have shown that surface-localized polarons in rutile TiO_2(110) couple with excited electronic states ~2.6 eV above the conduction band minimum. [1-3] However, surface polarons are readily oxidized in ambient conditions, [4] likely leading to a minimal contribution in catalytic applications. In contrast, polarons in bulk TiO_2 remain protected and therefore offer intriguing potential. In this work, we present the first observation of bulk polaron photoexcitation by employing a novel technique that allows the bulk contribution to be isolated from the much stronger surface component.

We find that bulk polarons are less bound by 0.2 eV compared with polarons at the surface, consistent with our results of hybrid density functional theory calculations. Because the excited state is also shifted to higher energy, bulk polarons have the same photoexcitation resonance energy as at the surface (3.6 eV) with a threshold at 3.1 eV. This is degenerate with the band gap, suggesting that bulk polarons could also provide an additional contribution to the photoyield.

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