

貴金属ドーピングした Ti 系ペロブスカイト光触媒**Noble-metal doped Ti perovskite photocatalysts**

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Photocatalytic oxides carry the promise of generating hydrogen fuel and raw materials for the chemical industry from water with the help of sunlight. While the photocatalytic Fujishima-Honda water splitting reaction has been known in TiO_2 for over 40 years, the energy conversion efficiency in sunlight has remained below a practical limit. The biggest reason for the low efficiency is the large bandgap of most oxides that are chemically stable in an electrolyte and have a suitable conduction and valence band alignment with water, resulting in a low light absorption rate in the visible part of the spectrum. A common approach to the band gap problem is doping, which can be used to obtain a narrower gap and improve visible light absorption. Rh and Ir are two suitable dopants for obtaining a hydrogen evolution photocatalyst by shifting the valence band edge in titanates, e.g., in SrTiO_3 , but despite a suitable electronic structure, the photocatalytic efficiency still remains low. This presentation reviews the behavior of noble-metal dopants, Rh, Ir, and Pt in SrTiO_3 and the photocatalytic activity of the doped thin films. The solubility of the different dopants in the SrTiO_3 lattice varies, affecting the achievable doping level and the microstructure of the materials. The electronic structure is discussed based on Rh- and Ir-doped SrTiO_3 . It is shown that subtle changes in the positions of the in-gap dopant-related electronic states result in dramatic changes in the photocatalytic activity. In addition to the offset of the main dopant states above the valence band top, unoccupied mid-gap states may also appear, depending on the valence of the dopant. Such states work as effective recombination centers, sharply reducing the photocatalytic response. A common feature for all materials used in this study is the strong localization of carriers at the dopant sites. Indeed, even at high doping levels, where visible light absorption is strong, the photocarrier extraction rate remains limited due to the short photocarrier diffusion length and the rapid loss of carriers to trapping and recombination. Thin film photocatalysts can be used to probe the photocarrier extraction depth by providing a reliable back electrode and a well-defined photocatalyst layer thickness. A typical carrier extraction depth for Rh: SrTiO_3 , for example, is less than 50 nm. Various strategies can be considered for improving the carrier extraction in self-organized nanostructures either on the photocatalyst surface or embedded in the crystal lattice. One particularly interesting technique is the use of self-organized metallic nanopillars embedded in the photocatalyst films, which function as charge extraction electrodes that can enhance the photocatalytic activity by reducing the average extraction depth of photocarriers.