

Nanosheet Photocatalysts for Water Splitting

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Hydrogen production from water using solar energy is an ultimate goal of renewable energy research. Splitting water into hydrogen and oxygen using the energy of photoexcited carriers generated in semiconducting powders, which are generally called photocatalysts, is one approach. Although the barriers that must be overcome for practical application remain high, the efficiency for hydrogen production has gradually improved. Photocatalytic technology is now capable of overall water splitting using the visible part of the solar spectrum. Interestingly, the oxidation and reduction reactions both proceed on the same small particles, with diameters ranging from several hundred nanometers to several micrometers. This is accomplished by loading co-catalyst nanoparticles on the surface of the semiconducting particles. These co-catalysts are thought to act as reduction or oxidation sites, but many aspects of the reaction mechanism and reaction site remain unclear. Partly, this is because the structure is too complex to easily determine the water adsorption sites and charge separation conditions for the photoexcited carriers, and the polycrystalline cocatalyst nanoparticles are randomly deposited on the various crystal faces of the semiconducting power. Therefore, much simpler crystal systems and/or surface conditions are necessary in order to investigate the effects of a co-catalyst on a photocatalyst.

Our research has focused on two-dimensional semiconducting oxide nanocrystals with a thickness of around 1 nm, which are called nanosheets [1]. Nanosheets provide an ideal photocatalyst structure for determining the reaction mechanisms. Nanosheets can be obtained by exfoliating a

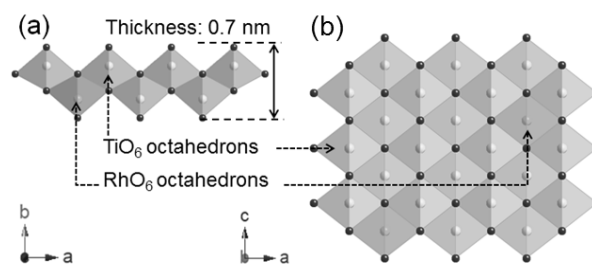


Fig.1 Structural model of Rh-doped titania nanosheet; (a) sectional view, (b) top view.

layered oxide material, in which all the single-crystal layers have the same thickness, and expose the same crystal face to the reaction solvent, except at the edges. For example, for a $\text{Ca}_2\text{Nb}_3\text{O}_{10}$ nanosheet, the exposed crystal face is a (001) face. In the case of nanosheet, all dopants are present very close to the surface, because the thickness of the nanosheet is approximately 1 nm. Therefore, most of the dopants in a nanosheet can be expected to be directly involved in the catalytic reaction and cause a significant improvement in photocatalytic activity in the same manner as co-catalyst loading. However, there is no clear evidence that the dopants function as a photocatalytic reaction center. If the environment surrounding the reaction center can be clearly imaged, the accuracy of the proposed mechanism will be more improved. Therefore, direct observation of dopant atoms in a crystal is a powerful tool for understanding reaction mechanisms. In this work, we prepared Rh-doped titania single-crystal nanosheets with a uniform thickness of 0.7 nm as shown in Fig.1. The atomic number of the dopant element (Rh, $Z = 45$) is sufficiently greater than that of the main constituent element (Ti, $Z=22$). We attempted the direct observation of single Rh atoms in the lattice, which are believed to function as the photocatalytic reaction centers. Finally, we discuss the possibility of a photocatalyst with a two-dimensional structure, and present new insights into role of the co-catalyst for the photocatalytic reaction.

REFERENCES

- [1] S. Ida, N. Kim, E. Ertekin, S. Takenaka, T. Ishihara, *J. Am. Chem. Soc.* 137(2015), 239.