Photocatalytic O$_2$ evolution with the visible-light-driven photocatalysts M$_3$V$_2$O$_8$ (M = Mg, Zn)

DEFA WANG $^1$, ZHIGANG ZOU $^2$ and JINHUA YE $^{1,3,*}$

$^1$ Ecomaterials Center, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
$^2$ Photoreaction Control Research Center (PCRC), National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
$^3$ Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency (JST), Japan

Received 3 February 2004; accepted 21 April 2004

Abstract—Photocatalytic O$_2$ evolution from aqueous AgNO$_3$ solution with M$_3$V$_2$O$_8$ (M = Mg, Zn) was carried out under visible light irradiation. The M$_3$V$_2$O$_8$ powder samples synthesized by a solid-state reaction method were characterized by X-ray diffraction and UV-Vis diffuse reflectance spectroscopy. M$_3$V$_2$O$_8$ had similar crystal structures and band gaps. However, the photocatalytic activity of O$_2$ evolution for Zn$_3$V$_2$O$_8$ was much higher than that for Mg$_3$V$_2$O$_8$. It was suggested that the Zn-3d orbital hybridized with the O-2p orbital in constructing the valence band of Zn$_3$V$_2$O$_8$, whereas there was no such hybridization involving in the valence band of Mg$_3$V$_2$O$_8$. The different photocatalytic properties could be ascribed to their different electronic structures.

Keywords: Photocatalysis; O$_2$ evolution; electronic structure; visible light; Mg$_3$V$_2$O$_8$; Zn$_3$V$_2$O$_8$.

INTRODUCTION

In recent years, photocatalytic decomposition of water using solar energy and semiconductors has attracted increasing attention [1, 2]. From the viewpoint of efficient solar energy conversion, it is necessary to develop visible-light-driven photocatalysts because the visible light accounts for 43% of the whole solar energy, while the UV light occupies merely about 4%. One way to achieve a narrow band gap semiconductor is to lower the bottom level of conduction band. Since the V-3d band is usually located below the analogous d band of the other transition metals in the energy spectrum [3], vanadium-containing oxides can, thus, be considered as promising candidate of visible-light-driven photocatalysts. Up to now, several

*To whom correspondence should be addressed. E-mail: jinhua.ye@nims.go.jp
vanadates, such as BiVO₄ with a deformed scheelite structure [4, 5], and InVO₄ [6, 7], composed of VO₄ tetrahedra and InO₆ octahedra, have successfully been developed as visible-light-driven photocatalysts for O₂ and/or H₂ evolution in the presence of sacrificial reagents AgNO₃ and CH₃OH, respectively. Previous studies have shown that the V-3d level seems to locate at a very critical position, which may be less or more negative than the potential for H₂ evolution. Theoretical calculations of the electronic structures [3] further verified that the In-5s contributed to the conduction band of InVO₄, while the relatively weak localized Bi-6s contributed to the valence band of BiVO₄. As a consequence, BiVO₄ [4] showed a higher O₂ evolution rate and InVO₄ [6] showed a higher H₂ evolution rate, respectively.

The role of d electron states in defining the electronic properties of several II–VI semiconductors has been extensively discussed by Wei and Zunger [8]. They have concluded that the p-d hybridization repels the top edge of valence band upwards without affecting the bottom edge of conduction band. Sampath et al. [9] have studied the electronic structure of ZnGa₂O₄ by means of the self-consistent tight-binding linearized muffin-tin orbital method with the atomic sphere approximation. It also shows that the hybridization of Zn-3d with O-2p orbitals shifts the valence band edge upwards. Recently, Kato et al. have reported a water splitting photocatalyst, AgMO₃ (M = Nb, Ta), in which the hybridized orbital of Ag-4d and O-2p forms the valence band at a more negative level than O-2p orbital [10]. Calculation on the electronic structures of MGa₂O₄ (M = Sr, Zn) by Ikarashi et al. [11] shows that a strong mixing of Zn and Ga orbitals appears in constructing the conduction band of ZnGa₂O₄, which accounts for the narrower band gap of ZnGa₂O₄. On the contrary, there is no such hybridization in SrGa₂O₄. Obviously, the substitution of tetrahedral site atoms also plays a role in the electronic structures and thus the photophysical and photocatalytic properties.

In our previous studies of M₂.₅VMoO₈ (M = Mg, Zn) [12], we found that the hybridization of O-2p and Zn-3d orbitals in Zn₂.₅VMoO₈ favored the photocatalytic O₂ evolution compared with Mg₂.₅VMoO₈. In this paper, a new series of polycrystalline powder photocatalysts M₃V₂O₈ (M = Mg, Zn) were synthesized by a solid-state reaction method and the hybridization effect of p-d orbitals on electronic band structures and photocatalytic activities of O₂ evolution in M₃V₂O₈ were further discussed.

EXPERIMENTAL

Polycrystalline M₃V₂O₈ (M = Mg, Zn) powder samples were prepared by the solid-state reaction method. Reagent grade oxides MgO, ZnO and V₂O₅ (Wako, Japan) in the stoichiometric ratio of M₃V₂O₈ were mixed carefully with addition of ethanol and then calcined at 600°C in an alumina crucible in air for 40 h. After pelleting, the samples were calcined, with intermittent grindings, for 80 h at 780°C for Zn₃V₂O₈ and 1000°C for Mg₃V₂O₈, respectively.