Development of Visible-light-driven Oxide Photocatalysts by Band Engineering with Cu(I)

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Photocatalytic water splitting gathers much attention due to its potential for solar fuel production. The construction of highly active photocatalysts is required to realize practical photocatalytic solar hydrogen production. Therefore, development of new photocatalyst materials is still being an important subject. In general oxides such as TiO_2, valence bands composed of O2p orbital are located at deep position, ca 3 eV vs NHE [1]. It means that shallower valence bands composed of orbitals other than O2p are required for visible-light-driven photocatalysts capable of hydrogen evolution. In this work, we investigated into development of visible-light-driven oxide photocatalysts with the concept of valence band engineering by Cu(I) [2,3].

ATa_7O_{19} (A: Y, La) has the crystal structure, which is constituted of TaO_6 octahedra and TaO_7 pentagonal bipyramids, similar to $Cu_3Ta_7O_{19}$. It is expected from the similarity in structure that Cu(I)-substitution for ATa_7O_{19} according to the formula $A_{1-x}Cu_{3x}Ta_7O_{19}$ is one strategy to obtain Cu(I)-containing oxides.

In the $La_{1-x}Cu_{3x}Ta_7O_{19}$ system, the samples obtained were classified into two types; $LaTa_7O_{19}$-type (x = 0–0.6) and $Cu_3Ta_7O_{19}$-type (x = 0.8–1). UV-vis spectra revealed that band gaps of samples were significantly narrowed by substitution of Cu(I) as shown in Fig. 1. The narrow band gaps would be due to formation of shallow valence bands by Cu3d orbitals. Indeed, contribution of the Cu3d orbital to valence bands was clearly observed in XPS of the valence region.

All $La_{1-x}Cu_{3x}Ta_7O_{19}$ samples except for x = 0 exhibited photocatalytic H_2 evolution from an aqueous methanol solution under visible light. The activity strongly depended on the composition and kind of crystal structure as shown in Fig. 2. The $LaTa_7O_{19}$-type samples showed higher activity than $Cu_3Ta_7O_{19}$-type one. In the $LaTa_7O_{19}$-type samples, activity enhanced as increasing the content of Cu. The higher activities of the solid solutions than the native Cu(I)-tantalate $Cu_3Ta_7O_{19}$ (x = 1) are the interesting feature of this solid solution system, indicating usefulness of the substitution of Cu(I).

Solid solutions were also obtained in the $Y_{1-x}Cu_{3x}Ta_7O_{19}$ system like as $La_{1-x}Cu_{3x}Ta_7O_{19}$. $Y_{1-x}Cu_{3x}Ta_7O_{19}$ produced H_2 at higher rate than $La_{1-x}Cu_{3x}Ta_7O_{19}$ from an aqueous solution containing S^{2-} and SO_3^{2-} as sacrificial reducing agents.

Cu(I) ions in oxides sometimes undergo oxidation to Cu(II). However, XPS analysis confirmed that Cu(I) ions in $A_{1-x}Cu_{3x}Ta_7O_{19}$ survived from oxidation even after irradiation, indicating moderate stability of Cu(I) ions in $A_{1-x}Cu_{3x}Ta_7O_{19}$.

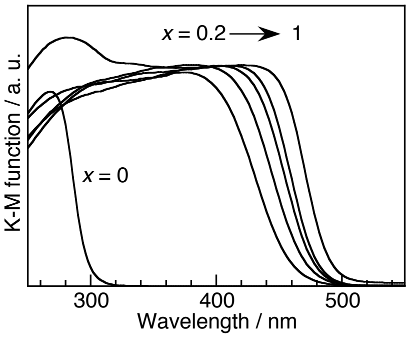

Fig.1 UV-vis spectra of $La_{1-x}Cu_{3x}Ta_7O_{19}$.

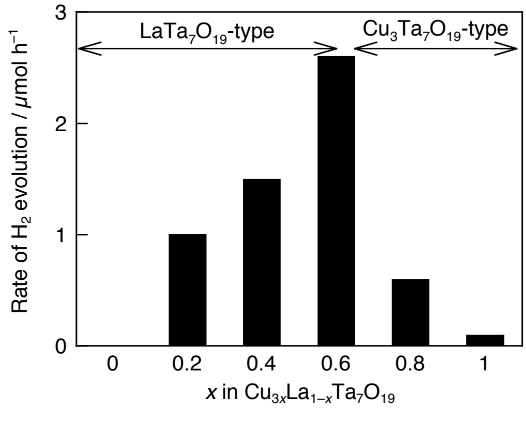

Fig. 2 Activity of $Pt/La_{1-x}Cu_{3x}Ta_7O_{19}$ for H_2 evolution under visible light.

REFERENCES

[1] D.E. Scaife, Sol. Energy, 25 (1980) 41.
[2] H. Kato, A. Takeda, M. Kobayashi, M. Hara, M. Kakihana, Catal. Sci. Technol., 3 (2013) 3147.
[3] H. Kato, T. Fujisawa, M. Kobayashi, M. Kakihana, Chem. Lett., 44 (2015) 973.