$SrTiO_3$-based photocatalysts sensitive to visible light

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Strontium titanate ($SrTiO_3$) is a well-known photocatalyst with activity similar to titanium dioxide under UV light [1)-3)]. $SrTiO_3$ has a cubic perovskite structure and is represented as ABX_3 ternary compound. It is an advantage that three elements of $SrTiO_3$ would be substituted by different dopant elements, which make it capable of doping visible light sensitized element and counter-doping for charge compensation. These kinds of co-doped visible light sensitive $SrTiO_3$ have been reported, such as the one whose X site was substituted by nitrogen as the visible light sensitized element and A site by lanthanum as the counter dopant[4)]. Recently $AgNbO_3$ has been reported to be a water-splitting material under visible light irradiation with sacrificial reagent[5)]. Its valence band consists not only of O2p orbitals as ordinary oxide semiconductors, but also of Ag4d orbitals, hence its band gap is smaller than that of other niobates without silver atoms such as $NaNbO_3$. The valence band of $SrTiO_3$ is formed by O2p orbitals, thus it is expected that Ag4d forms the valence band mixing with O2p, as is $AgNbO_3$, by introducing Ag^+ at Sr site in $SrTiO_3$, which leads to band gap narrowing and visible light absorption. As counter ions, we chose pentavalent metal cathions, M= Ta, Nb, V. Seeing a different point of view, those are $SrTiO_3$-$AgMO_3$(M=Ta, Nb, V) solid solutions.

$SrTiO_3$-$AgMO_3$ (M=Ta, Nb, V) powders were prepared by two-step solid-state reaction of $SrTiO_3$ and $AgMO_3$ (M=Ta, Nb, V). $AgTaO_3$ and $AgNbO_3$ were prepared by solid-state reaction from mixture of oxide components and $AgVO_3$ by precipitation method[6)]. They were mixed with reagent $SrTiO_3$ in certain ratio, and then sintered at 970□C for 5 hours under O_2 flow. The obtained powders were washed by nitric acid for 20 minutes to remove reduced silver. The crystalline phases of them were investigated by XRD. UV-Vis absorption spectra for these samples were measured using the diffuse reflection method. The photocatalytic activities of the powders were evaluated by the decomposition of gaseous 2-propanol (IPA) under visible light irradiation under the some absorbed photon number.

Figure 1 shows the UV-Vis absorption spectra of $SrTiO_3$-$AgMO_3$ (M=Ta, Nb, V) solid solutions represented as $(Sr_{0.97}, Ag_{0.03})(Ti_{0.97}, Ta_{0.03}) O_3$, $(Sr_{0.97}, Ag_{0.03})(Ti_{0.97}, Nb_{0.03}) O_3$, and $(Sr_{0.995}, Ag_{0.005})(Ti_{0.995}, V_{0.005}) O_3$. Each solid solution shown here was confirmed to have the homogeneous $SrTiO_3$ structure according to XRD measurements. Compared to $SrTiO_3$, there emerged new absorption shoulders in visible light region for all solid solutions. The absorption edge of $SrTiO_3$-$AgVO_3$ solid solution showed a slight red-shift, indicating that the band gap narrowed. Figure 2 shows the changes of acetone and CO_2 concentrations generated by the decomposition of IPA as a function of time in the presence of the prepared photocatalysts under visible light irradiation. The injected IPA concentration was 300 ppm. The acetone and CO_2 evolution rates in the presence of $SrTiO_3$-$AgMO_3$ (M=Ta, Nb, V) solid solutions were faster than those in the presence of $SrTiO_3$. From these experiments we have supposed that isolated Ag4d band whose energy level was higher than O2p valence band might be formed and the excitation from this isolated band might be responsible for visible light sensitivity. And for $SrTiO_3$-$AgVO_3$ solid solution, in addition to Ag4d isolated band, V3d orbitals would mix Ti3d orbitals, resulting in the formation of conduction band, whose minimum energy level became lower. Thus, both Ag4d and V3d were responsible for visible light sensitivity. Further details are under examination.

References

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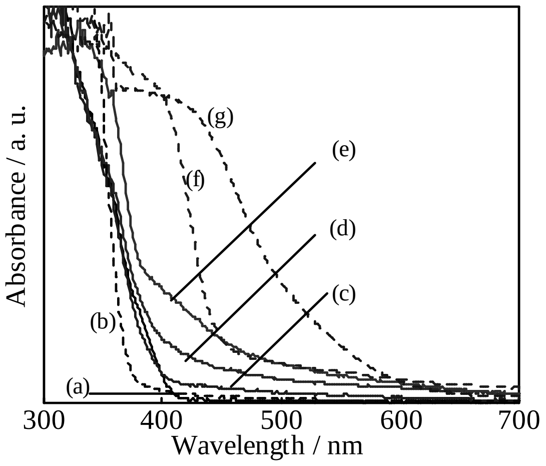

Fig. 1 UV-Vis absorption spectra for $SrTiO_3$, $AgMO_3$ (M=Ta, Nb, V) and their solid solutions
(a)$SrTiO_3$ (b)$AgTaO_3$ (c) $(Sr_{0.97}, Ag_{0.03})(Ti_{0.97}, Ta_{0.03})O_3$
(d) $(Sr_{0.97}, Ag_{0.03})(Ti_{0.97}, Nb_{0.03})O_3$
(e) $(Sr_{0.995}, Ag_{0.005})(Ti_{0.995}, V_{0.005})O_3$ (f) $AgNbO_3$
(g)$AgVO_3$

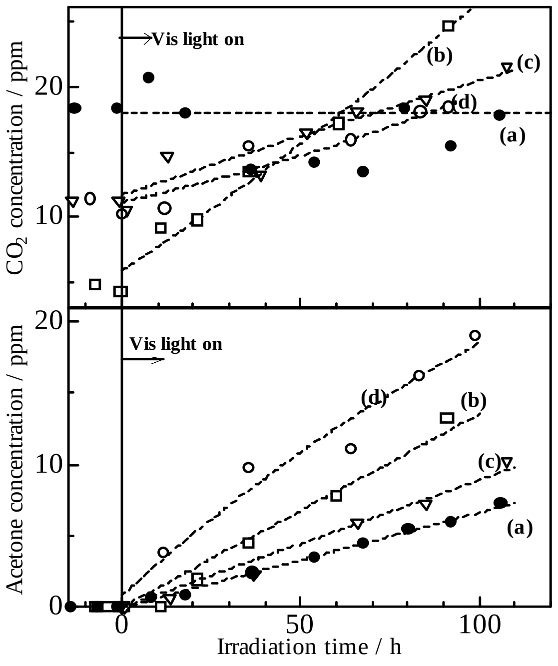

Fig. 2 Change of acetone and CO_2 concentrations generated by the decomposition of IPA in the presence of
(a) $SrTiO_3$ (b) $(Sr_{0.97}, Ag_{0.03})(Ti_{0.97}, Ta_{0.03})O_3$
(c) $(Sr_{0.97}, Ag_{0.03})(Ti_{0.97}, Nb_{0.03})O_3$
(d) $(Sr_{0.995}, Ag_{0.005})(Ti_{0.995}, V_{0.005})O_3$