Development of novel visible-light-driven photocatalysts by Ag(I)- and Cu(I)-substitution in layered perovskite oxides by molten salt treatments

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Abstract: Development of visible-light-driven photocatalysts is an important research topic toward highly efficient solar water splitting. Ag(I)- and Cu(I)-substitution is a useful method for sensitization of photocatalysts with wide band gap to visible light. In the present study, we have successfully developed novel visible-light-driven photocatalysts by Ag(I)- and Cu(I)-substitution in various layered perovskite oxides by molten salt treatments. In particular, Ag(I)-and Cu(I)-substituted tantalates were active for sacrificial O_2 and H_2 evolution under visible light irradiation, respectively.

Keywords: Visible light response, Metal oxide, Molten salt treatment.

1. Introduction

Solar water splitting over photocatalysts for clean hydrogen production has been paid attention as a candidate of a solution to energy and environmental issues. Visible light response is required for the photocatalysts to utilize sunlight. We have reported that Ag(I)- and Cu(I)-substitution is a useful method for sensitization of photocatalysts with wide band gap to visible light.[1,2] Actually, Cu(I)-substituted $K_2La_2Ti_3O_{10}$ with a layered perovskite structure shows activities for sacrificial H_2 evolution under visible light irradiation. Thus, layered perovskite oxides are expected as a useful host of sensitization to visible light, because they show high activities for water splitting under UV irradiation.[3] In the present study, we developed novel Ag(I)- and Cu(I)-substituted photocatalysts with visible light response by molten salt treatments of various layered perovskite oxides to expand the library of the visible-light-driven photocatalysts.

2. Experimental

Layered perovskite oxides as hosts were synthesized by a solid-state reaction and a polymerized complex method. Ag(I)- and Cu(I)-substituted materials were synthesized by molten salt treatments of layered perovskite oxides. Crystal structures of the synthesized materials were confirmed by XRD measurements. The bulk composition of the Ag(I)- and Cu(I)-substituted layered perovskite oxides was determined by XRF. The photocatalytic O_2 and H_2 evolutions from aqueous solutions containing sacrificial reagents under visible light irradiation were carried out using a top-irradiation cell with a Pyrex window connected in a gas-closed circulation system. A 300 W Xe arc lamp with a suitable long-pass filter was employed as a light source.

3. Results and discussion

Various layered perovskite oxides with either Li^+ or K^+ in the interlayer were treated with molten $AgNO_3$ and CuCl. XRD measurement revealed that the host oxides kept the layered perovskite structure after substitution of Ag(I) and Cu(I) by molten salt treatments. The substitution rates of Ag(I) and Cu(I) to alkali metal ions were analysed by XRF. When K^+-containing oxides were used as a host, all K^+ ions were substituted with either Ag(I) or Cu(I). Although 100% substitution of Ag(I) was achieved for Li^+-containing oxides, the substitution rate of Cu(I) was around 10-30%. Regardless of the substitution rates, Ag(I)- and Cu(I)-substituted layered perovskite oxides possessed new absorption bands at a longer wavelength region than the corresponding non-substituted samples.

Figures 1 and 2 show XRD patterns and diffuse reflectance spectra of Ag(I)- and Cu(I)-substituted $K_2SrTa_2O_7$ (Ag(I)- and Cu(I)-$K_2SrTa_2O_7$), as the representative results. The Ag(I)- and Cu(I)-$K_2SrTa_2O_7$ showed similar XRD patterns to the $K_2SrTa_2O_7$ host, except for disappearance of 002 and 004-peaks in Ag(I)-$K_2SrTa_2O_7$. The similar disappearance of layer-derived XRD peaks is observed in the XRD pattern of $Ag_2La_2Ti_3O_{10}$ prepared by a molten $AgNO_3$ treatment of $K_2La_2Ti_3O_{10}$.[4] The substitution rates of Ag(I) and Cu(I) were 100%. The Ag(I)- and Cu(I)-$K_2SrTa_2O_7$ possessed absorption bands in a visible light region. The photocatalytic activities for sacrificial H_2 and O_2 evolution were evaluated under visible light irradiation. The Ag(I)-$K_2SrTa_2O_7$ was active for O_2 evolution, whereas the Cu(I)-$K_2SrTa_2O_7$ was active for H_2 evolution. Note that the Cu(I)-$K_2SrTa_2O_7$ showed the activity for sacrificial H_2 evolution using visible light up to 600 nm agreeing with the absorption edge in DRS.

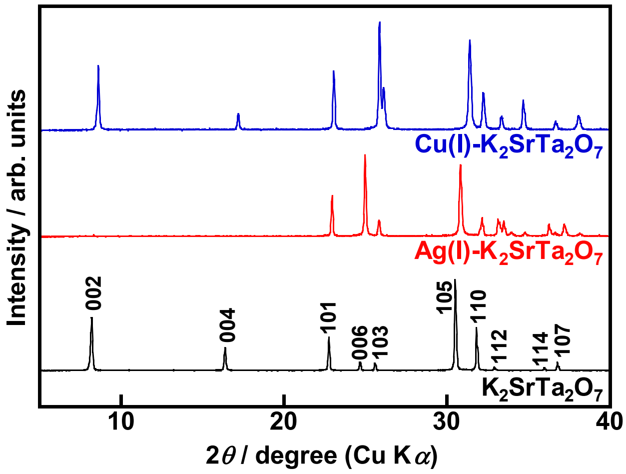

Figure 1. XRD patterns of non-, Ag(I)-, and Cu(I)-substituted $K_2SrTa_2O_7$.

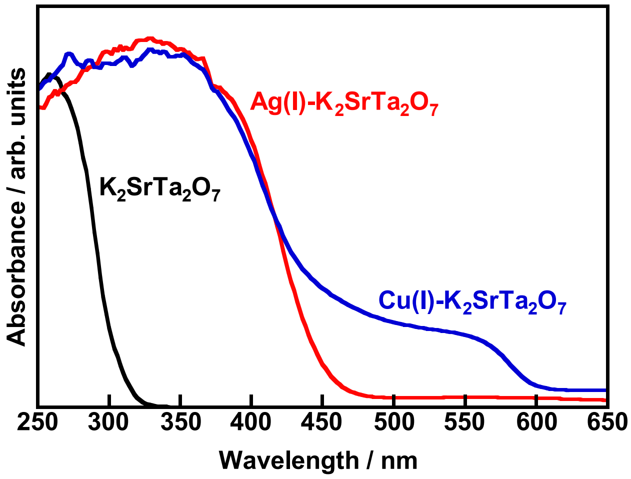

Figure 2. Diffuse reflectance spectra of non-, Ag(I)-, and Cu(I)-substituted $K_2SrTa_2O_7$.

4. Conclusions

Various layered perovskite oxides were treated with molten $AgNO_3$ and CuCl for Ag(I)- and Cu(I)-substitution, respectively. When K^+-containing oxides were used as a host, all K^+ ions were substituted with either Ag(I) or Cu(I). The Ag(I)- and Cu(I)-substituted samples possessed new absorption bands at a longer wavelength region than the corresponding non-substituted samples. Among them, the Ag(I)- and Cu(I)-substituted $K_2SrTa_2O_7$ showed activities for sacrificial O_2 and H_2 evolutions under visible light irradiation, respectively. In particular, Cu(I)-$K_2SrTa_2O_7$ responded to visible light up to 600 nm. Thus, we have successfully developed novel visible-light-driven photocatalysts by Ag(I)- and Cu(I)-substitution.

References

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