Effects of metal cation-doping into a layered perovskite oxynitride $K_2LaTa_2O_6N$ on its characteristics

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Solar-driven photocatalytic water splitting is a potential method for large-scale H_2 production. Certain layered perovskite oxides exhibit higher photocatalytic activity for overall water splitting owing to the unique 2D structure. Among the layered perovskite photocatalysts, $K_2LaTa_2O_6N$ is one of the promising photocatalysts that exhibited stable photocatalytic activity under visible light irradiation.[1] However, its activity is not satisfactory at present. The insufficient activity of Ta-based oxynitride photocatalyst is mainly attributed to the formation of Ta^{4+} species which can act as recombination center of photogenerated charge carrier. To suppress the formation of Ta^{4+}, aliovalent cation doping into 3D-perovskite oxynitride has been actively explored.[2] However, cation doping into layered oxynitride has not been attempted. Therefore, in this study, we attempted to dope aliovalent cations (Mg^{2+}, Al^{3+}, Ga^{3+}, Zr^{4+}, Mo^{6+}, W^{6+}) into layered oxynitride $K_2LaTa_2O_6N$.

The photocatalytic activity of Pt-loaded $K_2LaTa_2O_6N$:*M* (*M* represents doped element) for H_2 evolution was evaluated in an aqueous NaI solution. Cations were doped at 1 mol% to Ta site. As shown in **Fig. 1**, samples doped with lower-valence cations (Mg^{2+}, Ga^{3+}, Al^{3+}) relative to Ta^{5+} exhibited higher H_2 evolution activity under visible light irradiation compared to the undoped sample. In particular, $K_2LaTa_2O_6N$:Ga exhibited the highest activity. Ta oxidation state was estimated by XPS analysis. Although there are differences, the trend of Ta^{5+}/Ta^{4+} ratio did not affect the photocatalytic activity. On the contrary, the trend of the specific surface area of $K_2LaTa_2O_6N$:*M* obtained by BET method was almost consistent with the order of activity as shown in **Fig. 1**. Furthermore, increasing the concentration of doped Ga up to 10 mol% was found to further improve the H_2 evolution activity of $K_2LaTa_2O_6N$:Ga. The detailed results of the photocatalytic activity and materials characterization will be discussed in the presentation.

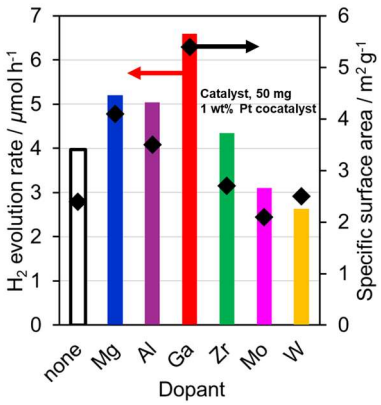

Fig. 1 H_2 evolution activity and specific surface area of $K_2LaTa_2O_6N$:*M*.

1) T. Oshima et al., *Angew. Chem., Int. Ed.* **2020**, *59*, 9736-9743.
2) K. Obata et al., *ChemPhotoChem* **2023**, *7*, e202200293.