

Semiconductive Nature of Two-Dimensional Coordination Polymers Containing Ag-S Network

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Two-dimensional (2D) materials that include graphene and transition metal dichalcogenides are of significant interest due to their unique properties resulting from 2D nature. Of these, 2D coordination polymers (2D CPs) have attracted considerable attention over recent years because they show various interesting properties associated not only with 2D nature but also arising from both inorganic and organic blocks. Until now, our group focuses on sulfur-coordinated CPs (S-CPs) that exhibit semiconductive property and excellent photoconductivity and reports photocatalytic property for water splitting.¹ However, the reports about 2D S-CPs are quite limited in spite of their potential application.

Herein, we succeeded in synthesizing two 2D S-CPs of type $[\text{Ag}(\text{tzdt})]_n$ (KGF-24) and $[\text{Ag}_2(\text{tzdt})(\text{TFA})]_n$ (KGF-25) (Htzdt = 1,3-thiazolidine-2-thione, TFA = trifluoroacetic acid), and their crystal structure, band structure, and photoconductive property were discussed in detail. The S-CPs were obtained by solvothermal synthesis using CF_3COOAg and Htzdt at metal ion/ligand ratio of 1:1 for KGF-24 and at 2:1 for KGF-25, respectively (Figure 1). Single crystal X-ray structural analysis indicated that both KGF-24 and KGF-25 formed 2D layer structure comprising Ag-S network. The photoconductive properties were investigated by time-resolved microwave conductivity (TRMC) experiments, in which the maximum values of $\phi\Sigma\mu_{\text{max}}$ (ϕ = quantum yield of charge-carrier generation; $\Sigma\mu$ = sum of the hole and electron mobilities) were determined to be $3.6 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for KGF-24 and $2.2 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for KGF-25, which were comparable to those of other photoconductive S-CPs.¹ As a result of the first-principle calculations using CASTEP, it is likely that the Ag-S layer network contributes to the observed photoconductive property.

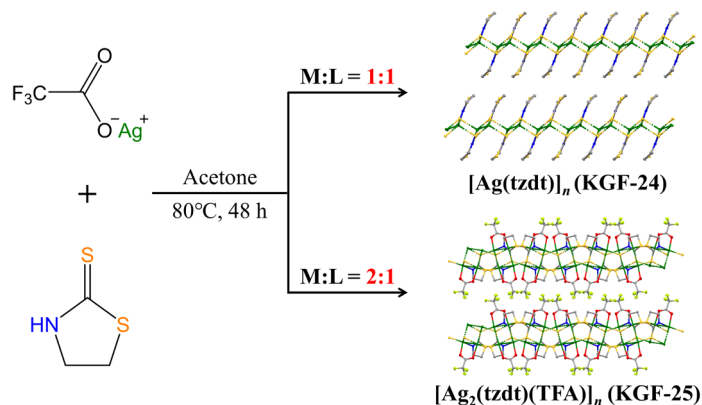


Figure 1. Synthesis of $[\text{Ag}(\text{tzdt})]_n$ (KGF-24) and $[\text{Ag}_2(\text{tzdt})(\text{TFA})]_n$ (KGF-25).

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