

# Preparation of (Cu,Ag)<sub>2</sub>ZnSnS<sub>4</sub> Solid Solution Nanocrystals for Efficient Solar Energy Conversion

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Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS), a multinary chalcogenide with p-type semiconductor property composed of earth-abundant and non-toxic elements, has been intensely studied as a new type of photovoltaic materials owing to their optimal properties for solar energy conversion, such as high absorption coefficient and band gap energy of 1.4-1.5 eV. Recently, Kudo and co-workers reported that the photocatalytic activity for hydrogen evolution was greatly enhanced by the formation of solid solution between CZTS and Ag<sub>2</sub>ZnSnS<sub>4</sub> (AZTS).<sup>[1]</sup> The hydrogen evolution rate under visible-light irradiation of bulk CZTS-AZTS photocatalyst particles was 150 times higher than that of pure CZTS particles due to the negative shift of conduction band potential by making solid solution.

In our previous papers, we successfully synthesized CZTS nanocrystals (NCs) of ca. 5 nm in diameter via thermal decomposition of precursors in hot organic solution and investigated their photoelectrochemical properties depending on the particle size and composition.<sup>[2-4]</sup> So far, a lot of studies have been reported for the preparation of solid solution semiconductor NCs for application to photoenergy conversion systems, but such attempt has not been carried out for CZTS-AZTS. In this study, we prepare the solid solution NCs of CZTS-AZTS uniformly dispersed in organic solution and investigate their photoelectrochemical properties.

CZTS-AZTS solid solution ((Cu<sub>1-x</sub>Ag<sub>x</sub>)<sub>2</sub>ZnSnS<sub>4</sub>; CAZTS) NCs were prepared via thermal decomposition of corresponding metal diethyl dithiocarbamate precursors in hot oleylamine under N<sub>2</sub> atmosphere.

Photoelectrochemical properties of thus-obtained NCs immobilized on ITO electrodes were measured in an aqueous solution containing 0.2 mol dm<sup>-3</sup> Eu(NO<sub>3</sub>)<sub>3</sub> as an electron scavenger.

The X-ray diffraction patterns of CAZTS NCs were assignable to kesterite crystal structure similar to that of CZTS, in which individual peaks were shifted to lower angles with an increase in the Ag content in NCs. These indicated that the obtained NCs were composed of uniform solid solution between CZTS and AZTS. TEM measurement revealed that CAZTS NCs had a polygonal shape with average diameter of ca. 10 nm, regardless of *x* value. The optical bandgap of CAZTS NCs dispersed in chloroform, estimated from absorption onset energy, was enlarged with an increase in Ag content from 1.1 eV (*x* = 0) to 2.0 eV (*x* = 1.0).

CAZTS thin films were prepared onto ITO electrodes by spin-coating CAZTS NC chloroform solutions at 1000 rpm for 10 second, followed by the heat treatment at 300°C. The irradiation ( $\lambda > 350$  nm) to thus-obtained films induced cathodic photocurrents except for NCs of *x* = 1.0 (AZTS), the magnitude being increased with negative shift of the electrode potential. The observed behavior was similar to that of a p-type semiconductor photoelectrode. In contrast, AZTS NCs-immobilized ITO electrodes exhibited an anodic photocurrent like as an n-type semiconductor as reported in our previous paper.<sup>[5]</sup> The action spectra of the photocurrent were in good agreement with the absorption spectra of CAZTS NPs used, indicating that CAZTS NPs effectively worked as photovoltaic materials driven by the irradiation of visible and near-IR lights.

## REFERENCES

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