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Composition-Dependent Photoelectrochemical Property of Non-Stoichiometric Cu_2ZnSnS_4 (CZTS) Nanoparticles Synthesized in Hot Organic Solutions

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A semiconductor of copper zinc tin sulfide, Cu_2ZnSnS_4 (CZTS), has been of great interest as a light-absorbing material in photovoltaic applications because CZTS is composed of low-toxic and earth-abundant elements and has wide-range absorption from ultraviolet to visible light region with high absorption coefficient. So far, solar energy conversion efficiency up to ca. 7% has been reported for CZTS thin-film solar cell.[1] On the other hand, semiconductor nanoparticles have been attracted great attention for the construction of highly efficient quantum dot solar cells because of their tunable energy structure, carrier multiplication, and hot carrier extraction. In this study, we reported the solution phase synthesis of CZTS nanoparticles having various chemical compositions and investigated their photoelectrochemical properties.

The CZTS nanoparticles were prepared by the heat treatment of $Cu(CH_3COO)_2$, $Zn(CH_3COO)_2$, $Sn(CH_3COO)_4$ and S in dodecanethiol at 240 °C under N_2 atmosphere. The typical molar ratio of the metal acetates (Cu:Zn:Sn) in the reaction solution was set to be 0.50:0.25:0.25. By changing the ratio of precursors, CZTS nanoparticles having various chemical compositions were prepared. To the reaction solution was added ethanol, followed by the centrifugation at 15000 rpm, after the reaction solution was cooled to room temperature. CZTS nanoparticles were obtained as the precipitate and purified by reprecipitation using hexane and ethanol. The hexane solution of the particles was filtered before use.

Figure 1 shows TEM image of the resulting CZTS nanoparticles prepared in the molar ratio of Cu:Zn:Sn = 0.50:0.25:0.25. The particle diameter was determined to 2~3 nm from the image. XRD pattern of the particle was assigned the kesterite-type CZTS. Average diameter and crystal structure of the nanoparticles prepared were not varied, regardless of the molar ratio of Cu:Zn:Sn used in the preparation. Meanwhile, the chemical composition of the particles was changed depending on the ratio of precursors used. Consequently, we successfully controlled the composition of CZTS nanoparticles without changing diameter and crystalline structure.

The band gap energy (E_g) of the CZTS nanoparticles determined from absorption onset was dependent on the content of Zn in the particle (f_{Zn} = Zn/metal). Figure 2 shows absorption spectra of the particles having various f_{Zn}. The absorption onset was blue-shifted with increasing the Zn content in the particles. The E_g of CZTS particles increased from ca. 1.3 to 2.2 eV by changing f_{Zn} from 0.11 to 0.83 respectively. These results suggested that E_g of the nanoparticles prepared by the present method can be controlled in the wide-range of the visible light region.

CZTS nanoparticles were immobilized on an ITO electrode via spin-coating. Thus-obtained electrode was immersed in 0.2 M aqueous solution of $Eu(NO_3)_3$ and then irradiated by 300-W Xe lamp (λ >350 nm). Schematic illustration of the measurement system is shown in Figure 3. Cathodic photocurrent was observed at a more negative potential than 0.2~0.3 V vs. Ag/AgCl, for the paticles of f_{Zn} = 0.11~0.32. This indicates that the chemical composition of the particles little affect valence band position. Incident photon-to-current efficiency (IPCE) of the CZTS nanoparticles, measured under the potential application of -0.5 V vs. Ag/AgCl, significantly depended on the chemical composition of the particles. Optimal composition of the CZTS nanoparticle for the light energy conversion will be discussed in the presentation.

In summary, we successfully synthesized CZTS nanoparticles by the solution phase method and controlled their optical properties and light energy conversion properties by changing the chemical composition of the particles.

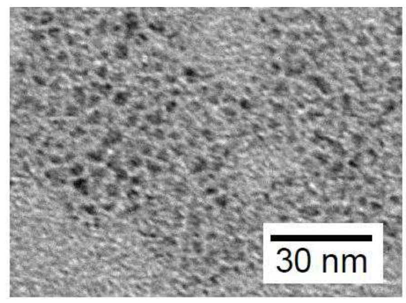

Figure 1. Typical TEM image of the CZTS nanoparticles prepared in the molar ratio of Cu:Zn:Sn = 0.50:0.25:0.25.

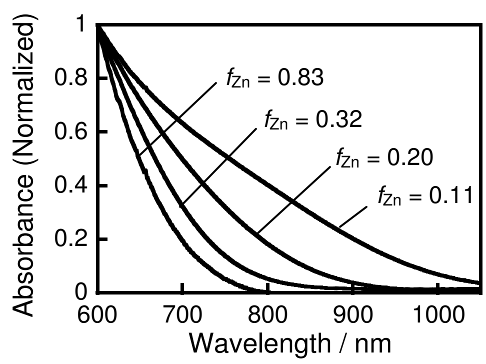

Figure 2. Absorption spectra of CZTS nanoparticles having various chemical compositions.

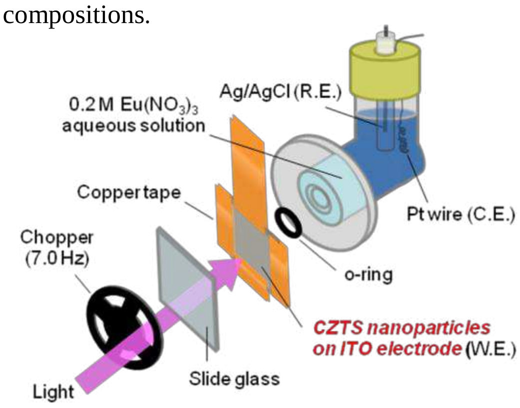

Figure 3. A schematic illustration of the system to measure the photoelectrochemical properties of the CZTS nanoparticles.

References

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