

The effect of ligand coverage on nanocrystal surface on the carrier collection efficiency of AgBiS₂ nanocrystal-based solar cells

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The semiconducting properties of colloidal nanocrystal assemblies make them attractive materials for developing emerging optoelectronic devices such as photovoltaics and LEDs. Recently, infrared absorbing AgBiS₂ colloidal nanocrystals (NCs) have been attracting much attention as photovoltaic materials for solution-processed solar cells.^{1, 2} To achieve good carrier transport properties of AgBiS₂ NC films, the choice of ligands is crucially important. In this work, we focused on halide ligands (I⁻, Br⁻, Cl⁻ and F⁻), with the aim of reducing the inter-nanocrystal distance as well as passivating the surface defects, thereby improving carrier transport property of the nanocrystal films. The coverage of the ligands on the AgBiS₂ NCs, and the influence on the resulted performance of the AgBiS₂ NC solar cells (ITO/AgBiS₂ NC dense layer/P3HT/Au)² were studied. The AgBiS₂ NC solar cells using I⁻, Br⁻, Cl⁻ and F⁻ ligands were denoted as I-SC, Cl-SC, Br-SC and F-SC, respectively.

The coverage of ligands was defined as the atomic ratio of the halides to the sum of Ag and Bi measured by X-ray photoelectron spectroscopy. The coverage values are 0.27, 0.17, 0.11 and 0.04 for I⁻, Br⁻, Cl⁻ and F⁻ treated AgBiS₂ films, respectively. This is chiefly due to the adsorption strength of halide anions on the NC surface, which is attributed to the kinetic energy required for desorption of halide anions under the attack of hydrogen protons in the methanol solvent. The weak adsorption of Cl⁻ and F⁻ may have resulted in insufficient passivation. Therefore, Cl-SCs and F-SCs are considered to have lower power conversion efficiency (PCE) compared to I- and Br-SCs. On the other hand, the strong adsorption of I⁻ might cause excess coverage of I⁻ on the surface of some AgBiS₂ NCs. The excess coverage of I⁻ has been reported to produce mid-gap states.³ The recombination process via the mid-gap states is thought to degrade the photoelectric conversion properties of I-SCs. When Br⁻ was used for ligand exchange, the highest carrier collection efficiency was achieved among the solar cells using the four ligands, as confirmed by the EQE spectra shown in Figure 1. As a result, the Br-SCs exhibited the highest PCE of 3.12%. These results indicate that the selection of ligand species and the control of coverage are extremely important to achieve good passivation of AgBiS₂ NCs.

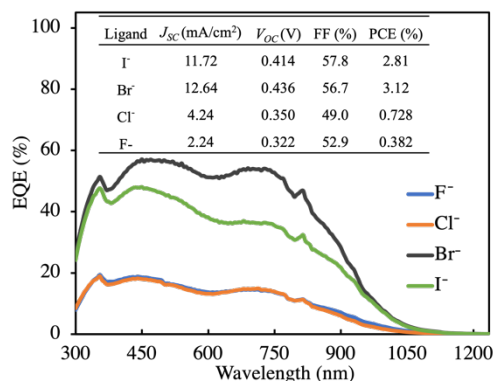


Figure 1. EQE spectra of the best performing I-SC, Br-SC, Cl-SC and F-SC. (Inset table: the corresponding solar cell performance).

[1] Bernechea, M.; Miller, N. C.; Xercavins, G.; Stavrinadis, D. So, A.; Konstantatos, G., *Nat. Photonics* 2016, 10, 521–525.

[2] Xiao, Y.; Wang, H.; Awai, F.; Shibayama, N.; Kubo, T.; Segawa, H., *ACS Appl. Mater. Interfaces* 2021, 13 (3), 3969–3978.

[3] Ju, M.-G.; Dai, J.; Ma, L.; Zhou, Y.; Zeng, X. C., *Nanoscale Advances* 2020, 2 (2), 770–776.