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# Plasmonic effect in *pn*-junction solar cells based on layers of semiconductor nanocrystals: Where to introduce metal nanoparticles?

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## ABSTRACT

We have introduced metal nanoparticles in *pn*-junction solar cells to study plasmonic effect in such devices. Here, the junction was based on a layer of copper–zinc–tin–sulfide (CZTS) nanocrystals as a *p*-type semiconductor and another layer of copper-diffused silver indium disulfide (Cu@AgInS<sub>2</sub>) nanocrystals as an *n*-type material in sequence. We introduced silver nanoparticles at different locations of *pn*- and also of *np*-junctions: (i) in the *p*-layer, (ii) in the *n*-layer, (iii) in both the layers, and (iv) at the interface between the layers of *p*- and *n*-type nanocrystals. The results in both *pn*- and *np*-junctions show that the devices with metal nanoparticles in *p*-type layer evidenced a substantial increase in energy conversion efficiency of solar cells as compared to other devices and the control device without any silver nanoparticles. We have inferred that the presence of silver nanoparticles in the depletion layer might have narrowed down the width of the region; metal nanoparticles in the *n*-layer acted as electron-traps to localize them hindering electron-transport and thereby reducing the efficiency of such plasmonic solar cells. Our results have shown that while introducing metal nanoparticles in solar cells, they should be placed only in the *p*-layer so that transport of electrons in plasmonic solar cells remains unaffected.

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## 1. Introduction

It may be recalled that the active layer of organic photovoltaic (OPV) devices is in general a bulk-heterojunction (BHJ) of an electron-donating and an electron-accepting material [1]. In such devices, low carrier mobility of electrons and holes alike limited the thickness of the active layer resulting in poor light absorption and accordingly a lower energy conversion efficiency ( $\eta$ ) as compared to devices based on contemporary materials. Quantum dots (QDs) of inorganic semiconductors were therefore introduced in OPVs to form hybrid BHJ devices, so that the advantages of the two types of semiconductors could be clubbed [2,3]. A typical example of hybrid BHJ device is II–VI semiconductor QDs, such as CdS, CdSe, and so forth in a conjugated polymer matrix. The research in this direction progressed further with the formation of *pn*-junctions between a layer of a *p*-type and an *n*-type inorganic semiconductor QDs [4–7]. Under an illumination, the *pn*-junctions acted as solar cells due to

the depletion region which separated the charge carriers through a drift of minority carriers through the junction.

The research on OPVs progressed laterally with the inclusion of metal nanoparticles in BHJ for increased light-trapping through plasmonic enhancement [8]. In a plethora of reports, the metal nanoparticles acted as sub-wavelength antenna and scattering centers and thereby increasing the cross-section of absorption and effective path length of incident photons, respectively, within the device [8–20]. They also increased the electrical conductivity of the active layers leading to an increase in  $\eta$  of OPVs [9–19]. Concentration [14,15], shape and size of the metal nanoparticles [16,17], their location in the active layer [18,19], and so forth have been considered to optimize the plasmonic enhancement. In hybrid BHJ, a singular report on plasmonic effect evidenced enhancement in  $\eta$  upon addition of gold nanoparticles; the active layer in such systems had been CdSe QDs in a matrix of a polymer of (a derivative of) dithiophene–benzothiadiazole in the form of a bulk-heterojunction [20].

The range of roles the metal nanoparticles play in plasmonic solar cells is wider than simply increasing the quantum of light absorption. Measurements based on photoinduced charge extraction with a linearly increasing voltage (photo-CELIV [21]) in BHJ OPVs evidenced a significant enhancement in carrier mobility due

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to carriers traversing through metal sub-network and, in contrary, a decrease in the total extracted carriers due to trapping of carriers [22]. The photo-CELIV measurements could however not distinguish the sign of the carriers that were trapped in metal nanoparticles.

In this work, we aimed to extend the domain of plasmonic enhancement effect to *pn*-junction devices between a layer of a *p*-type and an *n*-type semiconductor QDs. We chose silver nanoparticles at different locations of *pn*- and also *np*-junctions. Such systems would allow us to identify the (nature of) carriers, which may be trapped by metal nanoparticles in plasmonic solar cells. Copper–zinc–tin–sulfide (CZTS), an I<sub>2</sub>–II–IV–VI<sub>4</sub> quaternary semi-conducting compound having a kesterite structure and copper-diffused silver indium disulfide (Cu@AgInS<sub>2</sub>) nanocrystals absorbing in the near-IR region have been chosen as the *p*- and the *n*-type nanocrystals, respectively, in forming the junctions. While neither of the materials contains toxic elements, the CZTS nanocrystals were moreover grown with earth-abundant elements.

## 2. Experimental

### 2.1. Materials

Indium(III) acetate (99.99%), oleylamine, 1-octadecane, pyridine, tetrabutylammonium borohydride (TBABH) and oleic acid were purchased from Sigma-Aldrich Company. While zinc chloride anhydrous (ZnCl<sub>2</sub>), isopropanol, HPLC-grade toluene, and ethanol were from Merck, tin(IV) chloride anhydrous (SnCl<sub>4</sub>) was purchased from Strem Chemicals, Inc. Copper(II) chloride dihydrate (CuCl<sub>2</sub> · 2H<sub>2</sub>O, 99.9%) and sulfur powder were obtained from Loba Chemicals. Finally, silver acetate (98%) and HPLC-grade acetonitrile were purchased from Avra Synthesis Pvt. Limited. and Ranbaxy Fine Chemicals Limited, respectively. The materials were used without further purification.

### 2.2. Growth of CZTS nanocrystals

CZTS nanocrystals were grown following a reported method with certain modifications [23,24]. The growth process was carried out in a three-neck round-bottom reaction-flask in a nitrogen environment. Copper, zinc, tin, and sulfur precursor salts (molar ratio=2:1:1:4) were added in 15 mL of oleylamine. They were dissolved through a thorough stirring process and rising the temperature of the flask to 120 °C. After a wait of 30 min, the temperature of the flask was further raised to 180 °C so that the nanocrystals started to grow. After 4 min, the reaction was stopped by cooling down the flask to 80 °C; at this stage 5 mL of toluene was injected into the reaction flask to stabilize the nanocrystals. Temperature of the reaction flask was finally lowered down to room temperature before separating and purifying them using toluene and isopropanol in sequence. The oleylamine-capped CZTS nanocrystals were finally redispersed in toluene (20 mg/mL) to use in the device-fabrication process.

### 2.3. Growth of copper-diffused silver indium disulfide (Cu@AgInS<sub>2</sub>) nanocrystals

Cu@AgInS<sub>2</sub> nanocrystals were grown following a reported synthesis process [25]. A stock solution of indium was formed by dissolving 1 mmol of indium acetate in 3.2 mL of oleic acid and 6.8 mL of octadecane in a nitrogen environment. The solution was warmed to obtain a light-yellow solution that indicated the formation of indium oleate. To form a stock solution of copper, 1 mmol of CuCl<sub>2</sub> · 2H<sub>2</sub>O was dissolved in 10 mL oleylamine under a similar condition. Likewise, silver acetate was dissolved in 1 mL oleylamine. The stock solutions of silver and indium were thoroughly mixed and degassed for 15 min. The temperature of the

reaction-flask was raised to 160 °C; at this stage, 2.5 mL of a sulfur stock solution, prepared by dissolving 0.3 mmol of sulfur in 2 mL of octadecane and 0.5 mL of oleylamine, was injected to the reaction flask. The light-yellow solution quickly turned into blackish-red indicating formation of AgInS<sub>2</sub> nanocrystals. For copper diffusion into AgInS<sub>2</sub> nanoparticles, a measured amount of copper stock solution was injected drop-wise to the reaction mixture; the temperature of the flask was raised to 180 °C so that the diffusion process occurred. After 2 min, the nanoparticles were separated and purified by using ethanol and toluene in sequence coupled with centrifugation; they were finally redispersed in toluene to use in the device-fabrication process.

### 2.4. Growth of silver nanoparticles

To grow silver nanoparticles [26], 1 mmol (17 mg) of silver acetate was dissolved in 4 mL toluene under a stirring condition. 200 μL oleylamine and 100 μL oleic acid were then added and mixed thoroughly. In a separate container (2 mL) 25 mg of tetrabutylammonium borohydride (TBABH) was mixed with 1 mL toluene and 100 μL oleic acid. The TBABH:oleic acid mixed solution was injected into the reaction-flask containing a silver acetate solution. The solution turned into golden yellow in color implying formation of silver nanoparticles, which were separated by centrifuging after addition of ethanol. The nanoparticles were finally redispersed in toluene (4 mg/mL) for the fabrication of plasmonic devices.

### 2.5. Characterization of the nanoparticles

CZTS, Cu@AgInS<sub>2</sub>, and silver nanoparticles were characterized by optical absorption spectroscopy, X-ray diffraction (XRD) patterns, transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), and scanning transmission electron microscopy (STEM) images, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The measurements were carried out with Shimadzu UV-2550 and Varian 5000 UV–vis–NIR Spectrophotometer, Bruker D8 Advanced X-ray Powder Diffractometer, JEM 2100 F Jeol TEM, Horiba Jobin-Yvon Raman triple grating spectrometer system model number T64000 using 514 nm excitation of Spectra Physics laser source (Model number Stabilite 2017), and an XPS instrument (Omicron: Serial number 0571), respectively. In addition, to substantiate the *p*- or *n*-type nature of CZTS and Cu@AgInS<sub>2</sub> semiconductor nanocrystals, tunneling current of an ultrathin film of the nanocrystals was recorded with a Nanosurf Easyscan2 scanning tunneling microscope (STM) under an ambient condition. Density of states of the nanocrystals enabled us to locate the conduction and valence band-edges of the semiconductor with respect to its Fermi energy. For STM measurements, voltage was applied with respect to the substrate electrode.

### 2.6. Device fabrication

Devices were fabricated on glass substrates coated with indium tin oxide (ITO) strips. ITO electrodes purchased from Thin Film Devices Inc. had a surface resistance of 15 Ω/square. They were cleaned following a standard protocol. To form *pn*-junction devices, layers of CZTS and Cu@AgInS<sub>2</sub> nanoparticles were formed in sequence. Both the layers were formed through a layer-by-layer technique so that the long chain surfactants could be removed by short-chain ligands. In practice, formation of a layer of each of the semiconductor nanocrystals was a multi-step process: (i) an ultrathin layer of a nanocrystal was spun followed by (ii) pyridine treatment to remove the long-chain oleylamine ligands with short-chain ones, and (iii) washing with anhydrous acetonitrile through spinning to remove the excess pyridine. The steps were repeated for a certain number of times to obtain a thin-film of the

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