



# Arrays of CZTS sensitized ZnO/ZnS and ZnO/ZnSe core/shell nanorods for liquid junction nanowire solar cells



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## ABSTRACT

Copper–zinc–tin–sulfide ( $\text{Cu}_2\text{ZnSnS}_4$  or CZTS) is an important p-type semiconductor material for solar cell applications. A unique architecture for liquid junction solar cell made of ZnO/Al:ZnO/ZnS or ZnSe/CZTS core/shell vertically aligned nanorods array is reported. Over fluorine-doped tin oxide (FTO) coated glass, vertically aligned Al-doped zinc oxide nanorods (VANR) were grown over ZnO seed layer. It was followed by surface transformation of ZnO nanorods to ZnS or ZnSe through solubility constant ( $K_{sp}$ ) difference induced anion exchange in a  $\text{S}^{2-}$  or  $\text{Se}^{2-}$  solution to produce ZnO/ZnS and ZnO/ZnSe core-shell (CS) structures. Separately, CZTS nanoparticles were synthesized from high temperature arrested precipitation and subsequently used for sensitization of ZnO/ZnS CS-VANR nanostructures.  $\text{Cu}_2\text{S}$  and polysulfide were employed as counter-electrode and electrolyte respectively for fabrication of liquid junction solar cells. FE-SEM, HRTEM, X-ray diffraction and Raman spectroscopy techniques were employed for microstructural, morphological and compositional characterization of different component materials. The  $J$ – $V$  measurements of the solar cell correspond to a several fold higher power conversion efficiency than similar device with thin film multilayer planar configuration involving same amount of materials. The aligned core/shell nanorods configuration offers an increase in the interfacial area by several folds, shorter pathway for charge transport and efficient photon absorption.

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## 1. Introduction

Chalcogenide solar cells based on  $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$  (CIGS) or CdTe have crossed the bench mark of 20% power conversion efficiency [1–3], resulting in widespread commercialization of these technologies. However, to meet the ever-growing energy needs of the world, issues related to scarcity and cost of precursors: In, Ga and Te cast doubts over long-term sustainability of these technologies. It is estimated that if all the In resources in the world would be used in fabricating commercial photovoltaic modules, it will account for only 70 GW of power generation [4,5]. The toxicity of Cd is also another hindrance in the pursuit of CdTe based thin film solar cells [6,7].

As a replacement for CIGS based compounds, exploratory research for alternative compositions involving environment-

friendly, earth-abundant and inexpensive precursor elements has led to the development of  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) p-type absorber semiconductor material. CZTS has high light absorption coefficient of the order  $> 10^4 \text{ cm}^{-1}$  [8,9], and direct band gap energy value of  $\sim 1.5 \text{ eV}$  [10,11]. The highest values of power conversion efficiency (PCE) reported for CZTS and CZTSe based solar cells are 8.4 [12] and 12.6% [13], respectively. Despite a high efficiency and other advantages associated with vacuum processing, drawbacks including high production cost of vacuum equipment, elevated synthesis temperatures, use of toxic gases ( $\text{H}_2\text{Se}$  or Se) and material waste [14–16], research focus has shifted to devise facile, solution based processing routes for CZTS nanocrystals and films. One of the approaches to overcome these issues involves using colloidal nanoinks of CZTS for subsequent absorber layer application under ambient or less severe processing conditions [17–21]. This heterojunction configuration, however, lowers the power conversion efficiency mainly by poor p–n junction due to small grain size and high series resistance arising from large number of grain boundaries in the path of current flow.

Solar cells with enhanced efficiencies maybe fabricated through incorporation of one-dimensional (1-D) nanostructures

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including nanowires, nanotubes, and nanorods. These offer great potential to improve conversion efficiency by expediting photon absorption, increasing electron mobility, and enhancing electron collection efficiency in solar cells [22–24]. Nanowire morphology of I–III–VI chalcopyrite materials can offer pathways for continuous charge carrier transport without dead ends, which is an advantage over random p–n junctions. In such devices, however, the charge carriers have to move long distances, on the order of absorber and buffer layers thicknesses, to reach the counter electrodes. This problem can be overcome through application of the absorber, buffer and window layers via facile solution synthesis in the 1-D core/shell structure configuration [25]. In this case the only disadvantage would be limited light absorption capabilities due to difficulty in producing absorber shells with greater thickness values [24].

Solar cells fabrication by employing solution processing techniques for all component layers, eliminating any needs of vacuum processing, is thus an attractive research domain to reduce extensive equipment costs. Recently, results from fabrication and testing of superstrate solar cell configurations based on vertically aligned nanorod arrays of ZnO/CdS core/shell structures coated with CZTS nanoparticles have been reported [26,27]. Although CdS is the most commonly used composition as buffer layer and has been an integral part of solar cells with record conversion efficiency, its drawbacks include inability to transmit full solar spectrum due to a relatively low band gap value ( $\sim 2.4$  eV), greater electron affinity as compared to CZTS or CIGS, enhanced carrier recombination rate at the relatively wider band gap absorber/CdS interface and serious environmental problems associated with CdS layer [28].

Among alternative cadmium-free buffer layer compositions, zinc sulfide (ZnS) and zinc selenide (ZnSe) have been extensively explored for CIGS/Se based solar cells. ZnS is a high band gap energy material ( $E_g$  3.8 eV) with high transmittance in the visible range [29], higher quantum efficiency of the device at short wavelengths with an associated increase in the short-circuit current ( $J_{sc}$ ) of the device and a large band offset between CIGS and ZnS [30]. A power conversion efficiency of 18.6% was reported for CIGS solar cell incorporating ZnS(S, O, OH) buffer layer [31], whereas ZnS has already found its use as a standard buffer layer in commercial CIGS modules [32]. When conduction band alignment is considered for buffer-absorber interface, ZnS has been found to cause current blocking owing to a high barrier formation towards CZTS, both theoretically [33] and experimentally [34], in CZTS based solar cells. The device quality is explained in terms of the buffer/absorber heterojunction interface through critical parameters namely valence band offset (VBO) and conduction band offset (CBO) values that strongly affect charge transfer across the buffer/absorber interface. It is noteworthy that CdS/CZTS heterojunction interface has a CBO of  $-0.30$  to  $0.35$  eV with a negative value indicative of cliff-like behavior [35]. Due to smaller CBO values for selenides than sulfides, ZnSe is anticipated to promote better performance attributes in solar cells incorporating ZnSe buffer layer.

In this paper, we propose and present preliminary data from fabrication and testing of solar cells with superstrate configuration employing core/shell vertically aligned nanorod arrays (CS-VANR), polysulfide electrolyte and  $\text{Cu}_2\text{S}$  counter-electrode. Using fluorine-doped tin oxide (FTO) glass substrates, vertically aligned arrays of Al:ZnO were grown with subsequent encapsulation of individual nanorods via step-by-step application of different component layers with certain functionalities using low temperature, liquid processing routes. The solar cell configuration reported in this study is anticipated to reduce the extent of charge carrier recombination through reduction in the length of charge flow path and enhancement in light absorption due to a greater number of

grain boundaries in the direction of incident photons. The incorporation of mesoporous CZTS absorber layer is an addition to the benefits of the 1-D assembly and is specialty of the present report. Using ZnS and ZnSe as the buffer layers and exploiting two different buffer/absorber interfaces in the cell structure, the effect of buffer layer composition on the  $J$ - $V$  characteristics of the solar cells was also investigated.

## 2. Experimental work

### 2.1. Materials

Fluorine-doped tin oxide (FTO) coated glass slides were used as substrates for this work. All the precursor chemicals and organic solvents were procured from Sigma-Aldrich and were used as received without any further treatment.

### 2.2. Solar cell fabrication

Following thorough cleaning of the FTO substrates, the initial zinc oxide (ZnO) blocking layer was applied via spin coating a sol containing 200 mM zinc acetate in 20 mL methanol and 0.41 mL acetylacetone after it was magnetically stirred at  $60^\circ\text{C}$  for 2 h and aged for 24 h at room temperature. Afterwards, the samples were heat treated at  $400^\circ\text{C}$  for 0.5 h. To produce aligned arrays of aluminum-doped zinc oxide (Al:ZnO) nanorods, the FTO/*i*-ZnO samples were then immersed into an equimolar aqueous solution (25 mM each) of zinc nitrate and hexa-methylene-tetra-amine along with an uncoated aluminum foil at  $90^\circ\text{C}$  for 3 h. After cleaning, the samples were exposed to the ultraviolet (UV) radiation for  $\sim 30$  min in order to induce oxygen vacancies for increased electrical conductivity [36]. Subsequent layer of ZnSe or ZnS to obtain FTO/*i*-ZnO /Al:ZnO/buffer configuration was obtained via ion exchange method [24,37]. The samples were then washed with deionized water and absolute ethanol and finally dried with air blow.

Nanocrystals of the composition  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) were synthesized from high temperature arrested precipitation in oleylamine. For this purpose, halides of copper, zinc and tin were dissolved in oleylamine in molar ratios of 2:1:1 and heated to  $170^\circ\text{C}$  for 30 min to obtain a clear solution. Separately, another solution was prepared by adding S powder to oleylamine. Both solutions were mixed with Cu:Zn:Sn:S molar ratio of 2:1:1:4 and the resulting mixture was heated to  $230^\circ\text{C}$  for 1.5 h to ensure complete chemical reaction between precursors. The solution was later cooled and further purified by pouring into cold methanol. The nanocrystals so obtained were washed several times and separated in a centrifuge followed by overnight vacuum drying at  $40^\circ\text{C}$  and annealing in inert atmosphere at  $500^\circ\text{C}$  for 1 h. The annealed nanoparticles were dispersed in ethanol and spin coated at 1500 rpm to obtain FTO/*i*-ZnO /Al:ZnO/buffer/CZTS in the form of aligned arrays of core/shell nanorods, where buffer is either ZnS or ZnSe. Eventually, the nanostructured configuration was annealed at  $400^\circ\text{C}$  for 1 h under  $\text{N}_2$  gas flow and used as photoanode in the solar cell. To make the counter-electrode, a copper strip was immersed in a polysulfide aqueous solution containing one molar S and  $\text{Na}_2\text{S}$  along with 100 mM NaOH for 5 min [38], causing  $\text{Cu}_2\text{S}$  formation at the surface. The solar cell was fabricated by joining and bonding the  $\text{Cu}_2\text{S}$  counter electrode surface with VANR array assembly with the inter-electrode spacing filled with the polysulfide electrolyte of the same composition as that used to make the  $\text{Cu}_2\text{S}$  counter-electrode from copper.

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