Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for "Growth and photoelectrochemical properties of ordered $CuInS_2$ nanorod arrays"

Xia Sheng, Lei Wang*, Yeping Luo, Lantao Chang, Hui Zhang, Jiazheng Wang and Deren Yang

State Key Laboratory of Silicon Materials and Department of Materials Science and Engineering, Zhejiang University

Hangzhou 310027, People's Republic of China

Synthesis of $CuInS_2$ nanorod arrays

$CuInS_2$ nanorod arrays in this paper are synthesized via annealing Cu-In intermetallic compound precursor thin films under H_2S and N_2 atmosphere. Firstly, Cu-In alloy particles are made by the commonly used polyol method. Briefly speaking, appropriate amount of $InCl_3 \cdot 4H_2O$ and $CuCl_2 \cdot 2H_2O$ are reduced by $NaBH_4$ at 140 ^oC in a high-boiling-point alcohol diethylene glycol (DEG). Polyvinylpyrrolidone (PVP) is used as stabilizing agent. The reaction is a fast process lasting for about 3-5 min. And then the particles are separated by centrifugation and washed by ethanol. The particles appear $Cu_{11}In_9$ and In phases co-existence normally. Typical scanning electron microscopy (SEM) image and X-ray diffraction (XRD) pattern of the Cu-In alloy particles are shown in Fig. s1. Secondly, the obtained Cu-In alloy particles are made into inks by dissolved in organic solvent and ultrasonic for well dispersed. Glasses, ITO glasses, Mo plates and Si wafers are used as substrates, respectively. Precursor thin films are fabricated by inks drop-casting on the substrates and dying under 80 ^oC. Finally, the precursor thin films are annealed at 500 ^oC for 30 min under N_2+H_2S (30% H_2S) atmosphere. The annealing process in the experiment is a rapid treatment process (RTP).

* Corresponding author: e-mail: phy_wangl@zju.edu.cn, Phone: +86 571 87951667, Fax: +86 571 87952322

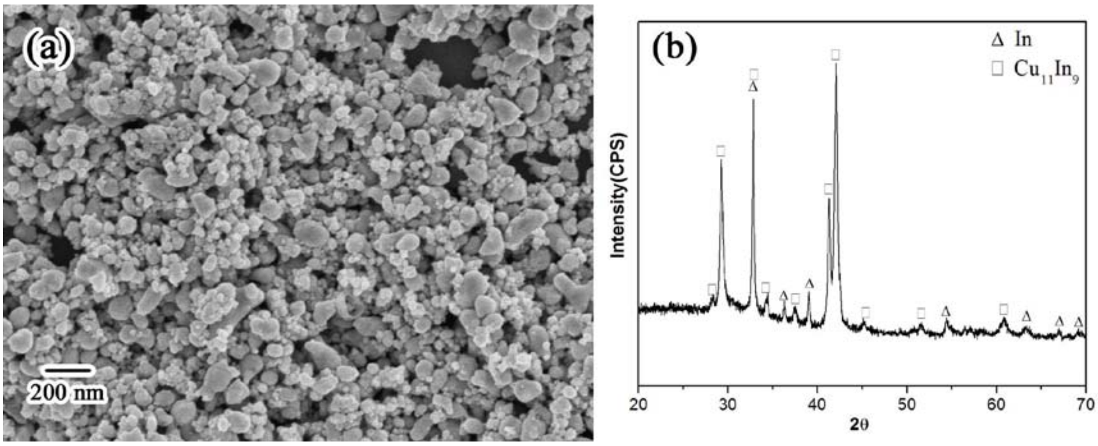

Fig. s1 (a) SEM image and (b) XRD pattern of Cu-In alloy particles

The important key to this experiment is the molar ratio of In and Cu in the Cu-In alloy particles is slightly larger than 1:1. It is found that only the In rich precursor thin films, that is the Cu-In alloy particles exist a separate In phase, can be annealed to form $CuInS_2$ nanorod arrays. Otherwise, the Cu rich precursor films with only $Cu_{11}In_9$ phase will turn to normal films (Fig. s2). Further experiments are carried out using In particles annealing under the same condition, In_2S_3 nanorods are obtained. Typical SEM image, transmission electron microscopy (TEM) image, XRD pattern and energy dispersive X-ray spectroscopy (EDS) pattern are shown in Fig. s3.

It is also proved in the experiments that the formation of $CuInS_2$ nanorod arrays is not related to the substrates. We obtain similar structures on glasses, ITO glasses, Mo plates and Si wafers respectively (Fig. s4). But only polished Si wafers can achieve free standing films (Fig. s5).

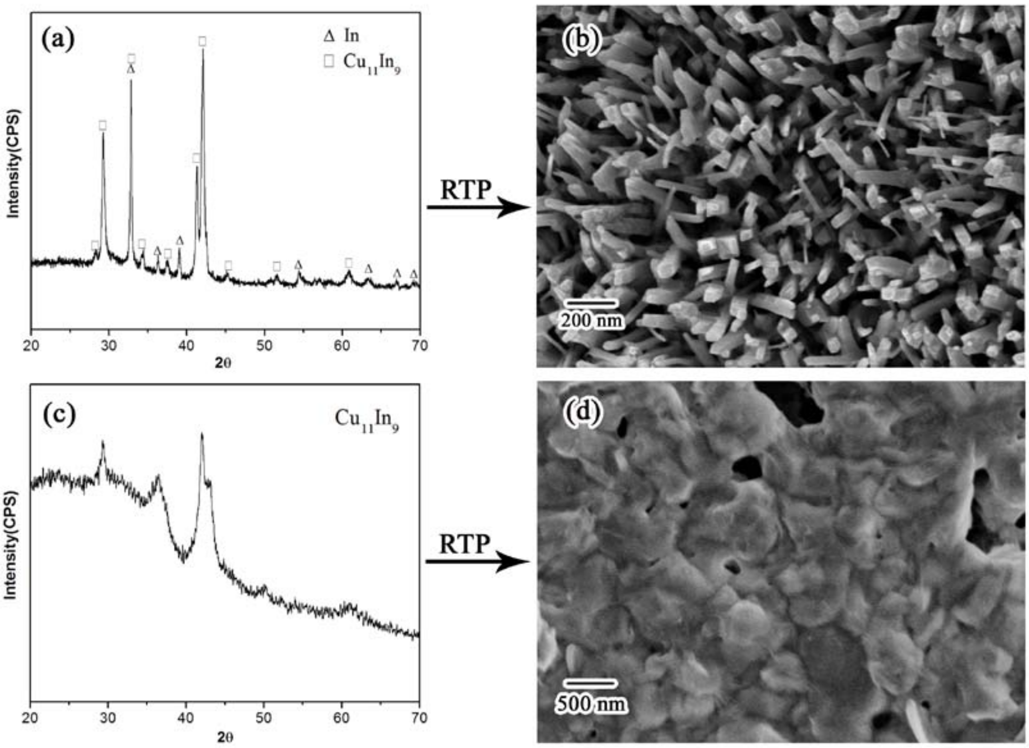

Fig. s2 Relationship of Cu-In alloy particles and thin films (a) XRD pattern of In-rich precursors; (b) SEM image of In-rich precursors after RTP; (c) XRD pattern of In-poor precursors; (d) SEM image of In-poor precursors after RTP.

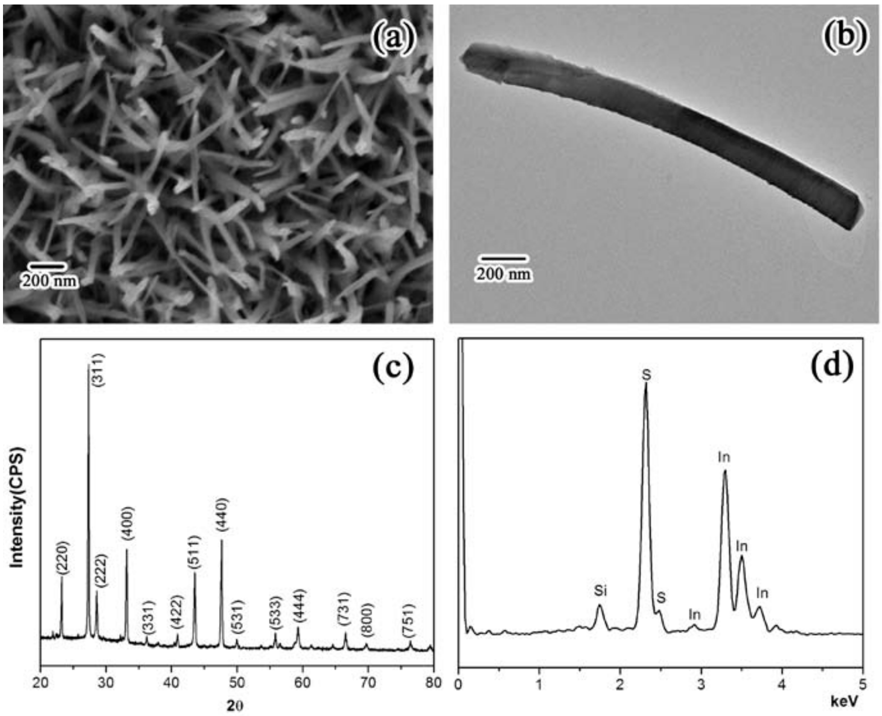

Fig. s3 (a) SEM image; (b) TEM image; (c) XRD pattern; (d) EDS pattern of the In_2S_3 nanorods.

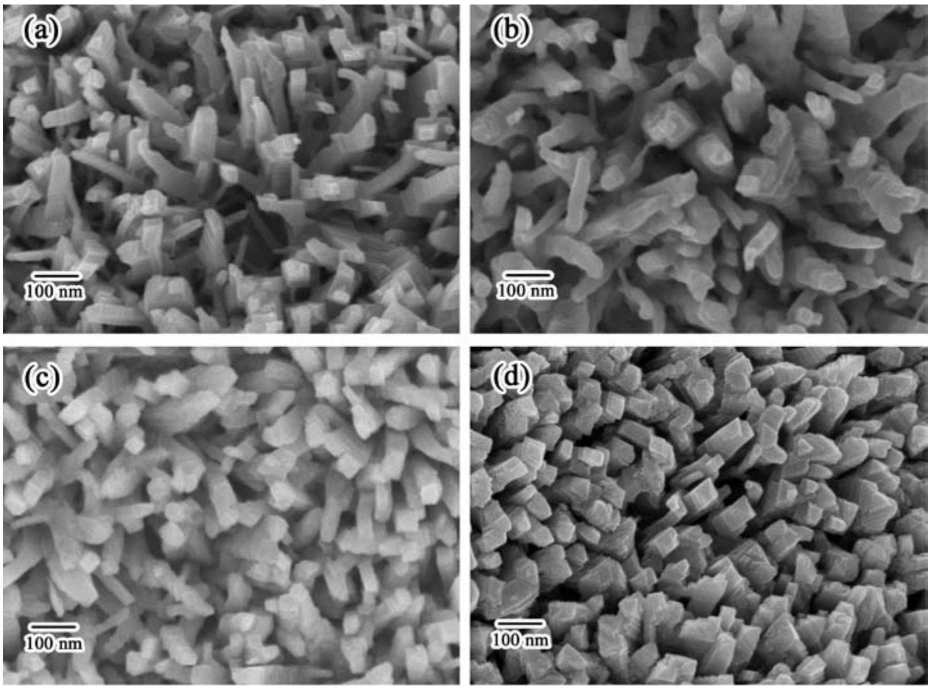

Fig. s4 SEM images of the $CuInS_2$ nanorod arrays obtained on different substrates (a) glass, (b) ITO glass, (c) Mo plate and (d) Si wafer.

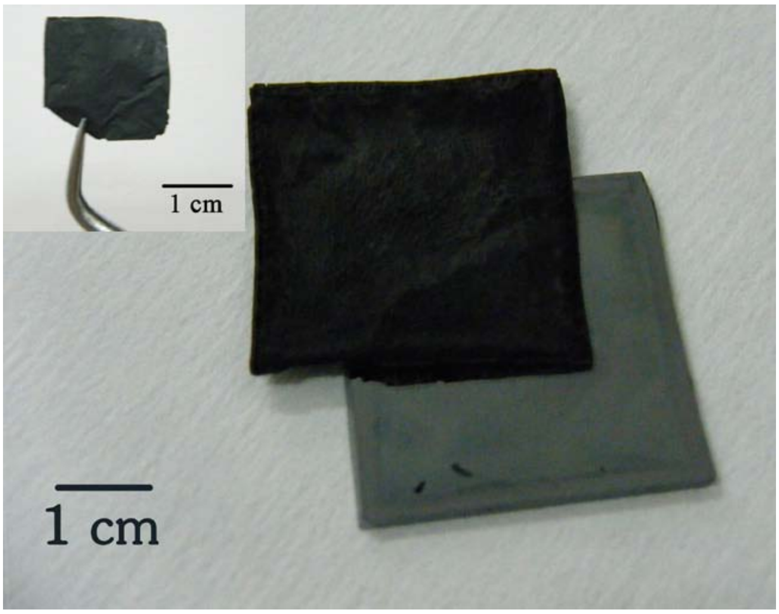

Fig. s5 photos of a free standing thin film.

Optical properties of $CuInS_2$ nanorod arrays

The optical properties of the obtained $CuInS_2$ nanorod arrays are also characterized by UV transmittance spectra.

The fundamental absorption spectrum can be used to determine the energy gap

(E_g) of the semiconductor. As a kind of allowed direct optical transition α can be expressed by following formula:

$$\alpha = (A / h\upsilon)\ (h\upsilon - E_g)^{1/2}$$

where A is a constant and E_g is the energy gap. The band gap is obtained by extrapolating the linear portion of the plots of $(\alpha hv)^2$ versus hv to α^2=0. The plot of $(\alpha hv)^2$ versus hv of the $CuInS_2$ nanorod arrays are shown in Fig. s6a. The band gap E_g is calculated to be 1.46 eV, which corresponds to the band gap of normal $CuInS_2$ thin films.

Compared with normal thin films, nanorod array structures have better light trapping effect. Fig. s6b shows the reflectance of two kinds of the thin films. In the visible spectral region, the one with nanorod array structures has lower reflectance.

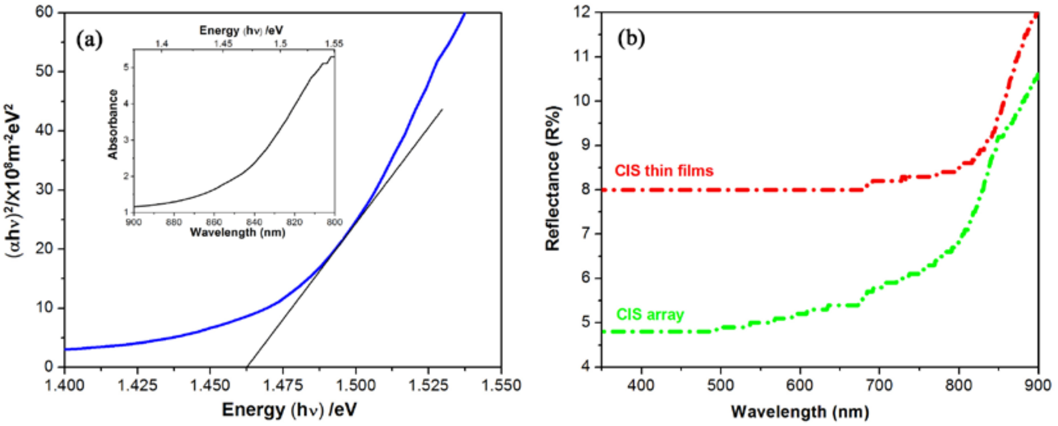

Fig. s6 (a) $(\alpha hv)^2$ against photo energy (hv) of $CuInS_2$ nanorod arrays; insert: absorbance of $CuInS_2$ nanorod arrays; (b) reflectance of $CuInS_2$ nanorod arrays and normal $CuInS_2$ thin films.