Support information for

Monodispersed Sphalerite $CuInSe_2$ Nanoplates and Highly (112) Oriented Chalcopyrite Thin Films by Nanoplates Ink Coating

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Experimental Section

Materials. Copper(II) chloride($CuCl_2$•$2H_2O$, 99%), indium(III) chloride($InCl_3$•$4H_2O$, 99%), selenium powder(Se, 99%), trithylene glycol(TEG, 99%), ethylenediamine($C_2H_8N_2$, 99%), polyvinylpyrrolidone(PVP, Mr=10000), absolute ethanol(CH_3CH_2OH, 99.7%) and high-purity nitrogen gas. All chemicals were purchased and directly used without further pretreatment.

Synthesis of CuInSe2 Nanoplates. 0.25 mmol $CuCl_2 \cdot 2H_2O$ (0.0426 g) and 0.25 mmol $InCl_3$•$4H_2O$ (0.07320 g) were dissolved into 10ml triethylene glycol in beaker with magnetic stirring for 1 h at room temperature to get a clear solution. 0.5 mmol Se (0.0395 g), 7.5 mmol ethylenediamine and 0.1 g PVP (Mr=10000) were poured into 40mL triethylene glycol in a three-necked flask to form Se precursor solution. The three-necked flask was installed at a heating mantle with magnetic stirring and attached to a condenser, and heated under nitrogen stream from room temperature to a given injection temperature of 210°C, 230°C, 250°C and 270 °C, respectively for four samples, where injection solution was quickly injected into anionic precursor solution in the three-necked flask with vigorous stirring. The reaction solution was refluxed at the temperature below 20℃ compared to the corresponding injection temperature for 20 min. The resultant solution was naturally cooled in the air to room temperature, and the synthesized products were abstracted by diluting the resultant solution with absolute ethanol of 5 multiple by volume and then high speed centrifugation. The abstracted products were washed ultrasonically with excess amounts of absolute ethanol followed by high speed centrifugation in centrifuge tubes for four times to finish products purification. The precipitated products were kept in a small sealed glass vessel for further use or dried into powder for characterization.

Preparation of $CuInSe_2$ Thin films. The precipitated $CuInSe_2$ products obtained by above synthesis process were used to prepare stable colloidal ink. Firstly, 5 mL absolute ethanol was added to the precipitated $CuInSe_2$ products in the glass vessel, and the vessel was ultrasonically treatment for 20 min to obtain a stable colloidal ink with CuInSe2 solid concentration about 4 mg/mL. The colloidal ink was applied to deposit $CuInSe_2$ thin films on clean glass slide substrates by layer-by-layer dip-coating. Dipping cycles consisted of immersing the substrates into the colloidal ink, and then drawing them from the ink to dry, and the dipping-drawing-drying cycle was repeated until the desired film thickness. The coated substrates were settled in a box made with light weight alumina brick and then in a tubular oven steaming Ar atmosphere to be annealed at 500°C for 20 min.

Materials Characterization. X-ray diffraction (XRD) was detected by Rigaku D/Max 2500V/PC X-ray powder diffractometer with Cu Kα radiation at 40 kV and 200mA and a scan rate of 8˚/min from 2θ 10˚ to 90˚. The observation of transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and Energy Dispersive X-Ray Fluorescence (EDX) analyses were performed using Tecnai G2 F20 field emission transmission electron microscope (FETEM). Absorption spectra were recorded by UV-3600 UV-vis absorption spectrometer with optics intergrating sphere. The morphology of the CIS NPs Thin film was characterized by using Hatchi s-4800 field emission scanning electron microscope (FESEM). Hall measurement was detected by Accent HL5500PC Hall effect measurement system.