

Rapid Synthesis of CuInTe₂ Ultrathin Nanoplate with Enhanced Photoelectrochemical Property

Xiao Zhang,^a Lei Yang,^a Zenglong Guo,^a Ge Su,^a Rongjie Gao,^a Wei Wang, Bohua Dong,^{*a} and Lixin Cao,^{* a}

Institute of Materials Science and Engineering, Ocean University of China, 238 Songling Road, Qingdao, 266100 P. R. China

*To whom correspondence should be addressed. E-mail: dongbohua@ouc.edu.cn, caolixin@ouc.edu.cn

Experimental Section

I. Materials and Methods

Copper(I) iodide (CuI, 99.95%), Indium(III) acetate (In(OAc)₃, 99.99%), Tellurium (Te, 99.999%), Trioctylphosphine (TOP, 90%) 1-dodecanethiol (DDT, 98%), and 1-octadecene (ODE, 90%). All reagents were used without further purification.

Synthesis of Cu-In precursor. 0.2 mmol of CuI and 0.2 mmol of In(OAc)₃ were mixed with 2 mL of DDT in the presence of 4 mL of ODE in a 50 mL three-neck flask. The mixed solution was degassed at room temperature until the bubbling subsided, then the temperature was increased to 90 °C under a flow of high purity nitrogen and the mixed was degassed again at 90 °C for half an hour.

Synthesis of Te precursor. 0.2 mmol Tellurium powder is dissolved in 0.4 ml TOP at 90 °C under a flow of high purity nitrogen.

Synthesis of CuInTe₂ Nanoplates. 5 mL octadecene (ODE) in a 50 mL three-neck flask were degassed and quickly heated up to desired temperature under nitrogen at a rate of 20 °C min⁻¹. In a typical synthesis, 0.4 mL of Te precursor (0.02 mmol) was

added into the 6.0 mL Cu-In precursor (0.02 mmol) in a 50 mL three-neck flask at 30 °C under nitrogen flow, resulting the Cu-In-Te solution. Next, the obtained Cu-In-Te solution was quickly injected into the above-mentioned 5 mL ODE at 230 °C. The reaction temperature was then remained at 230 °C for further growth. It has to be noted that the reaction was maintained 230 °C only for 1 minute. Then, the solution in three-neck flask was kept in an ice bath to quench the reaction. The contents of the reaction mixture were added with alcohol and transferred into centrifuge tubes, the CuInTe₂ nanoplates were precipitated by the centrifugation at 7000 rpm for 6 min. The nanoplates were washed with 1:5 (v:v) cyclohexane:ethanol for several times. A part of the sample was dispersed in cyclohexane, the rest of products were dried in 60 °C in the vacuum drying oven.

Characterization. Transmission electron microscopy (TEM) measurements were obtained using a JEOL JEM 1200 transmission electron microscope at an acceleration voltage of 100 kV. High resolution transmission electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS) data were collected using a FEI Tecnai G2 F20 field emission electron microscope an acceleration voltage of 200 kV. The samples for TEM and EDS measurements were prepared by depositing one drop of hexane solution diluted products on a carbon-coated copper/nickel grid and drying at room temperature. The nanoplate sizes of the samples were measured using Nano Measurer software from the TEM micrographs, and the corresponding size distribution histograms were obtained based on the statistics of measurement results. Powder X-ray diffraction (XRD) patterns were obtained using a BRUKER D8 ADVANCE X-ray diffractometer fitted with Cu K α radiation over the 2 θ range from 20° to 70°, and the scanning speed was 4° min⁻¹. The samples were obtained at different reaction conditions and washed by cyclohexane three times and dropped onto a clean glass plate and dried. XPS measurements were performed on a Kratos Amicus X-ray photoelectron spectrometer with an exciting source of Mg with the working power of 180 W.

Photoelectrochemical Measurements. Photoelectrochemical measurements were performed using a CHI 760E working station (CH Instrument, Inc.) in a three-

electrode electrochemical cell, with CuInTe₂ nanoplates as the working electrode, a Pt electrode as a counter electrode and an Ag/AgCl electrode as a reference electrode. The electrolyte was an aqueous solution with 0.5 M NaOH. A 300 W Xe lamp was used as the white light source. The light power density at the sample surface was measured to be 100mW/cm². To prepare working electrode, an active layer was prepared by spin-coating nanoparticles and nanoplate dispersed in cyclohexane (1 mL with a concentration of 0.5 mg mL⁻¹) onto the FTO layer at 3000 rpm. As a proof-of-concept application of the as-prepared ultrathin 2D nanocrystals, the obtained nanoplates were used in PEC application. For comparison, nanoparticles were also examined in the PEC test. The particle loading was 0.25 mg/cm² as same as nanoplate loading.

Supporting Table and Figures

Table S1. The Bohr radius of CuInS₂, CuInSe₂ and CuInTe₂

Sample	CuInS ₂	CuInSe ₂	CuInTe ₂
Bohr radius	4.09 nm	8.85 nm	4.02 nm

We have calculated the Bohr radius of CuInTe₂. The Bohr radius is calculated by equation from (**Chem. Mater.** **2003**, *15*, 3142-3147):

$$r_B = r_H \epsilon_{dot} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right]$$

Where r_H is the hydrogen Bohr radius, ϵ_{dot} is the dielectric constant of the bulk material, m_e^* and m_h^* are the reduced masses of the electron and hole. Values for CuInS₂ ($m_e^*=0.16$, $m_h^*=1.3$, and $\epsilon_{dot}=11.0$), CuInSe₂ ($m_e^*=0.09$, $m_h^*=0.73$, and $\epsilon_{dot}=13.4$), and CuInTe₂ ($m_e^*=0.14$, $m_h^*=0.78$, and $\epsilon_{dot}=9.026$) are obtained from Ref 1 (**Chem. Mater.**, **2003**, *15*, 3142-3147) and Ref 2 (**Mater. Lett.**, **1999**, *40* 66-70). The Bohr radius of CuInS₂, CuInSe₂ and CuInTe₂ are calculated summarized in Table S1:

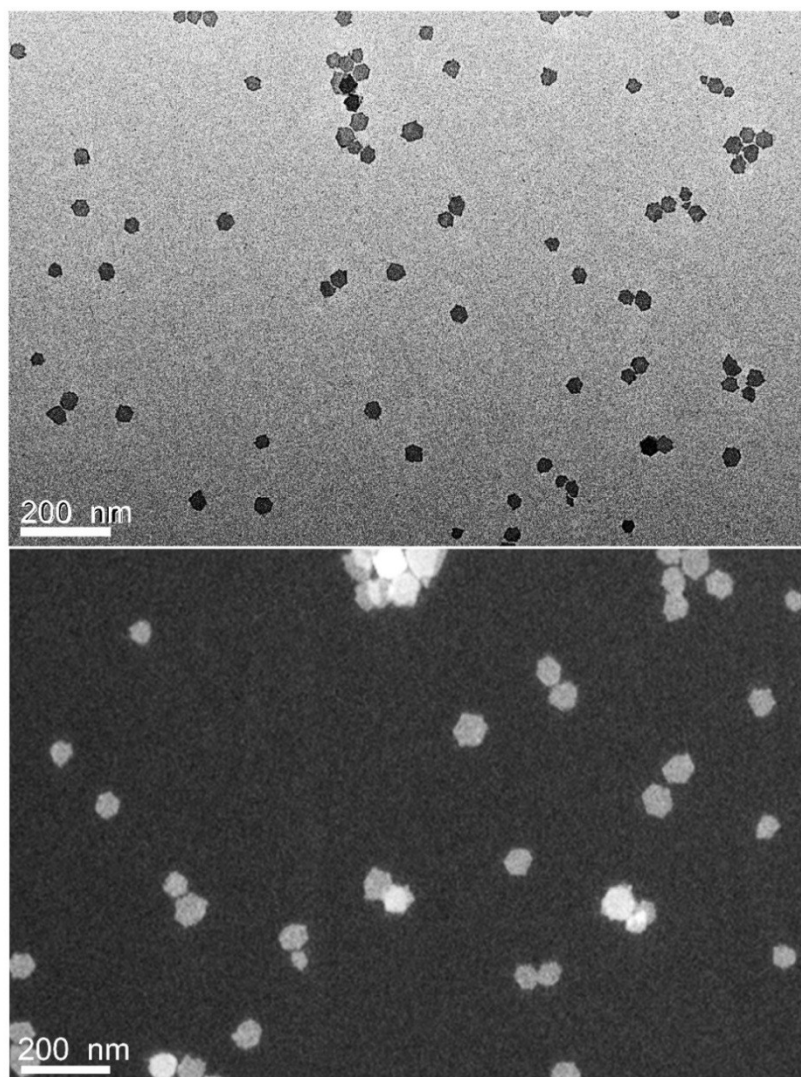


Figure S1. (a) Typical TEM image and (b) HAADF-STEM image of CuInTe₂ nanoplates.

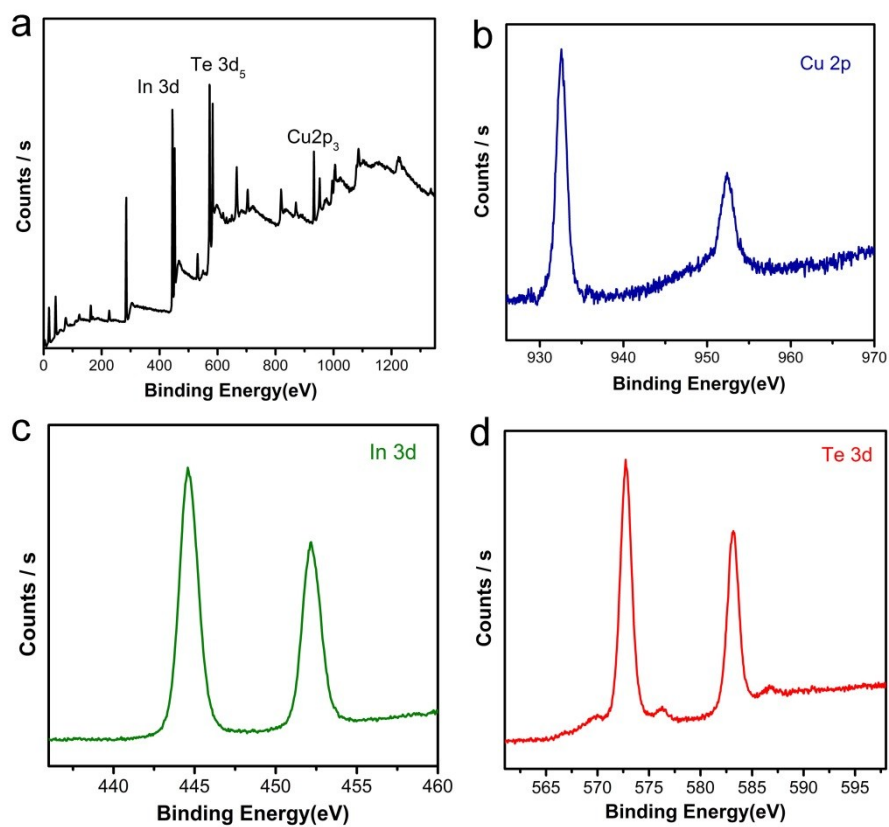


Figure S2. The XPS spectrum of CuInTe₂ nanoplates.

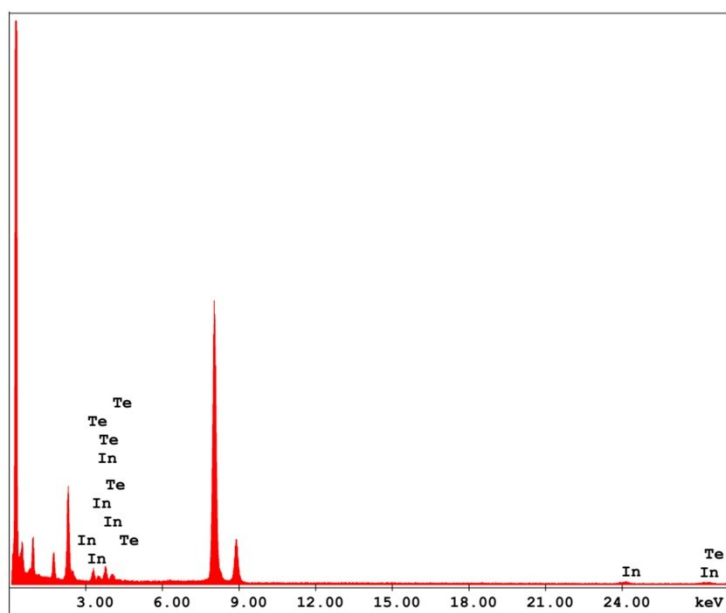


Figure S3. EDS spectrum of CuInTe₂ nanoplates.

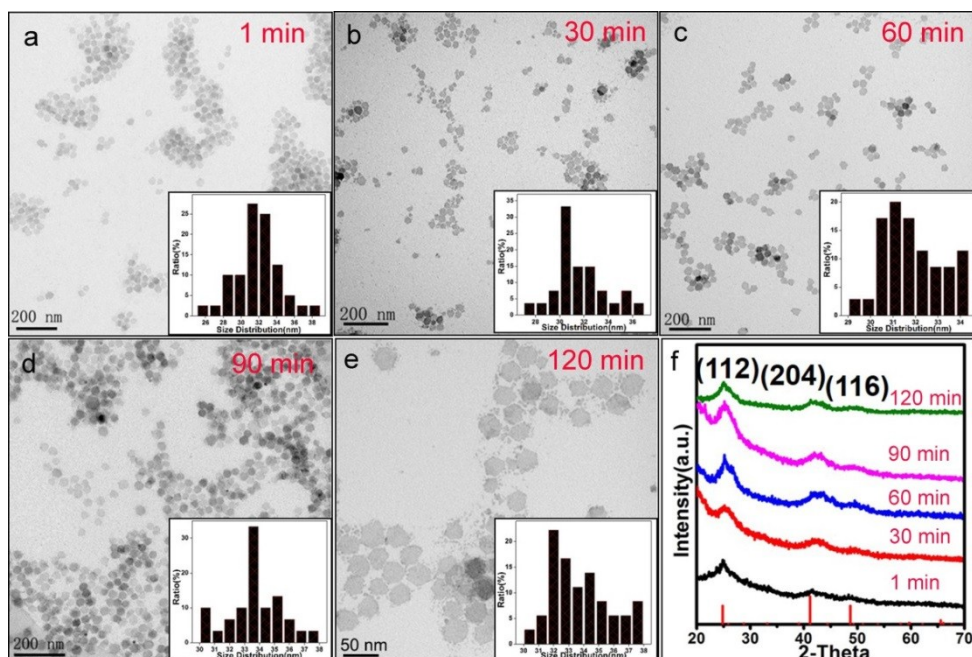


Figure S4. (a-e) TEM images of CuInTe₂ nanoplates under further annealing from 1 min to 120 min at the reaction temperature. (f) Corresponding XRD patterns of CuInTe₂ nanoplates.

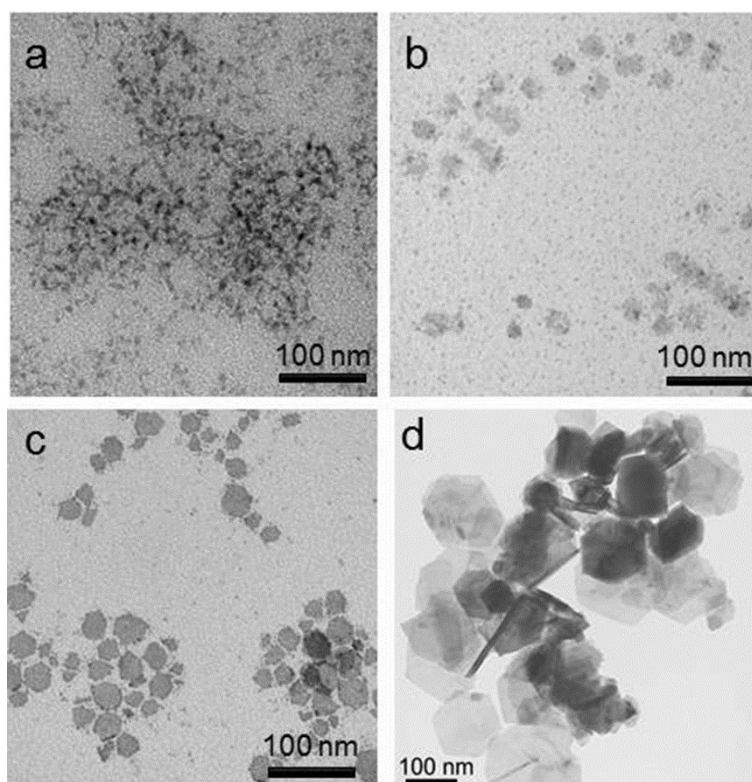


Figure S5. TEM images of CuInTe₂ nanoplates synthesized at different reaction temperature. (a) 150°C; (b) 170 °C; (c) 200 °C; (d) 240°C;

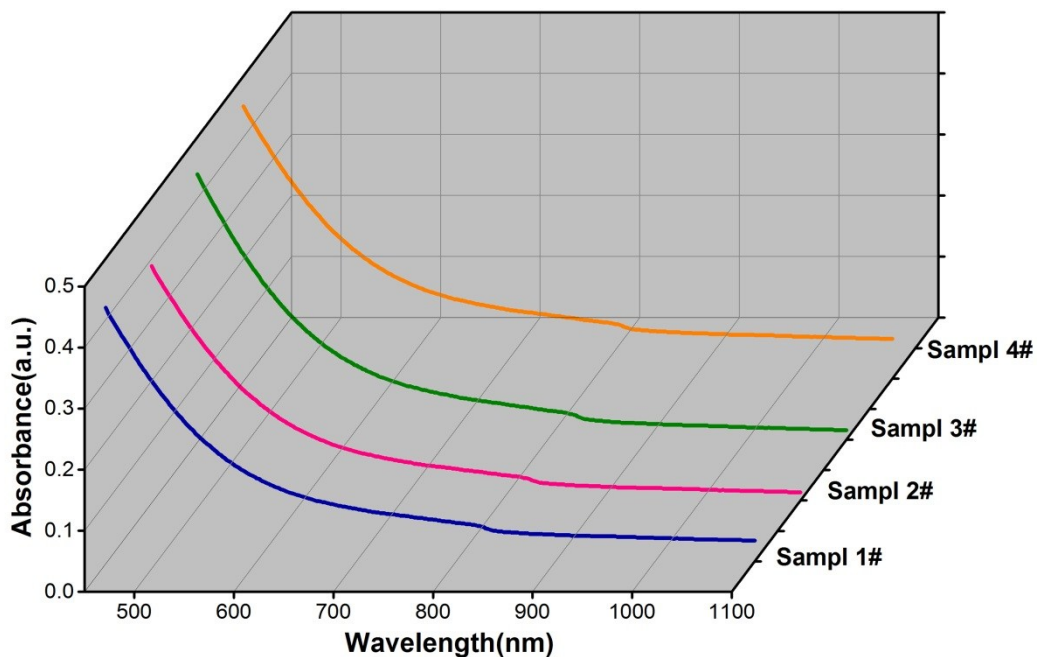


Figure S6. UV-vis-NIR absorption spectra of CuInTe_2 samples synthesized at different reaction temperature. (1#) 240°C; (2#)200 °C; (3#) 170 °C; (4#)150°C;

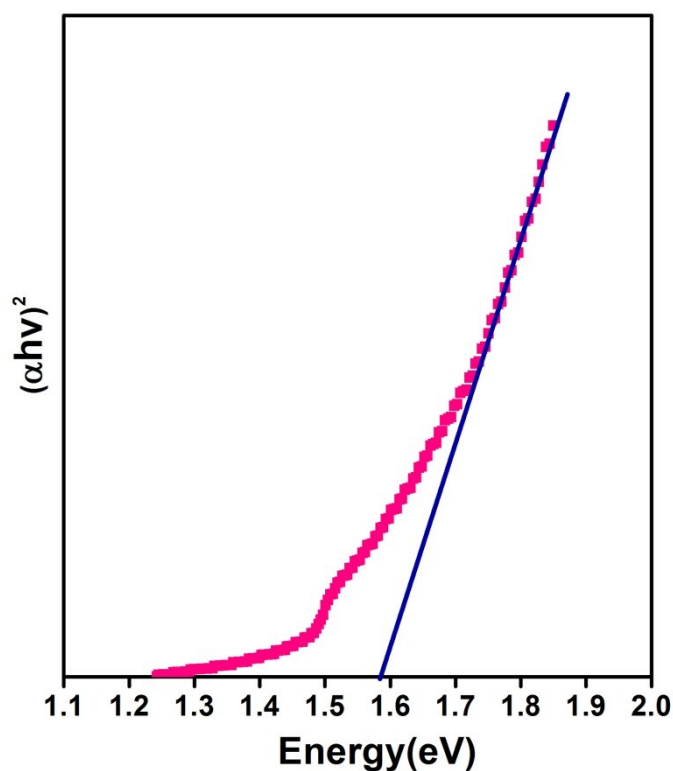


Figure S7. The band gap of CuInTe_2 sample synthesized at 230°C. The band gap of the CuInTe_2 nanoplates is approximated using the direct band gap method by plotting the absorbance squared versus energy, and extrapolating to zero.

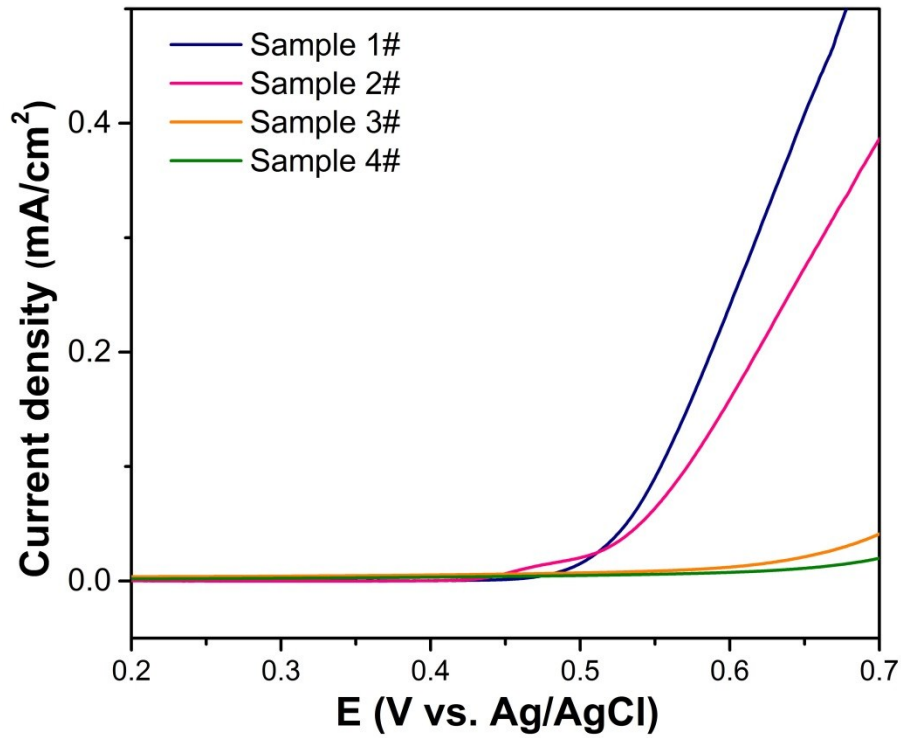


Figure S8. Linear sweep voltammetry (LSV) curves for CuInTe₂ samples under full-spectrum illumination. (1#) 240°C; (2#) 200 °C; (3#) 170 °C; (4#) 150°C;

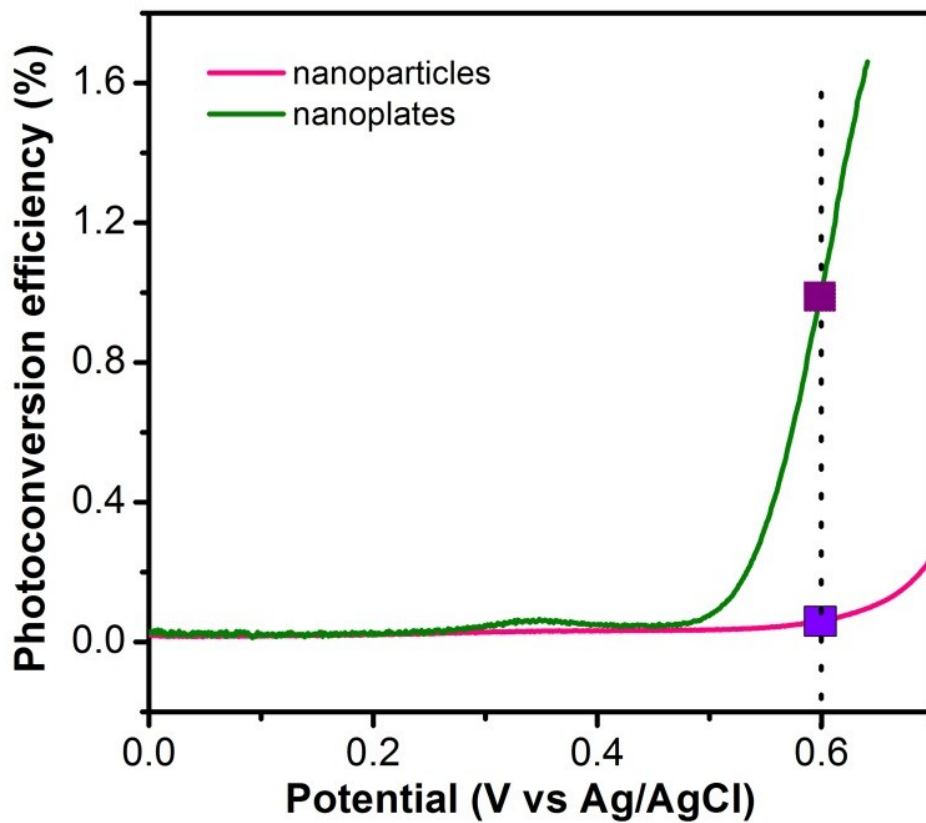


Figure S9. The photoconversion efficiency of nanoplate and nanoparticle

The corresponding photoconversion (light energy to chemical energy conversion) efficiencies which were calculated as follows

$$\varepsilon(\%) = \frac{|j_p|(1.23 - |E_b|)}{I_0} \times 100$$

Where j_p is the photocurrent density (mA/cm²) obtained under an applied bias E_B (V), and I_0 (100 mW/cm²) is the power density of incident light. The photoconversion efficiency of nanoplate at 0.6 V was about 1.01% which was 14.4 times the value of that of the nanoparticle (0.07%).

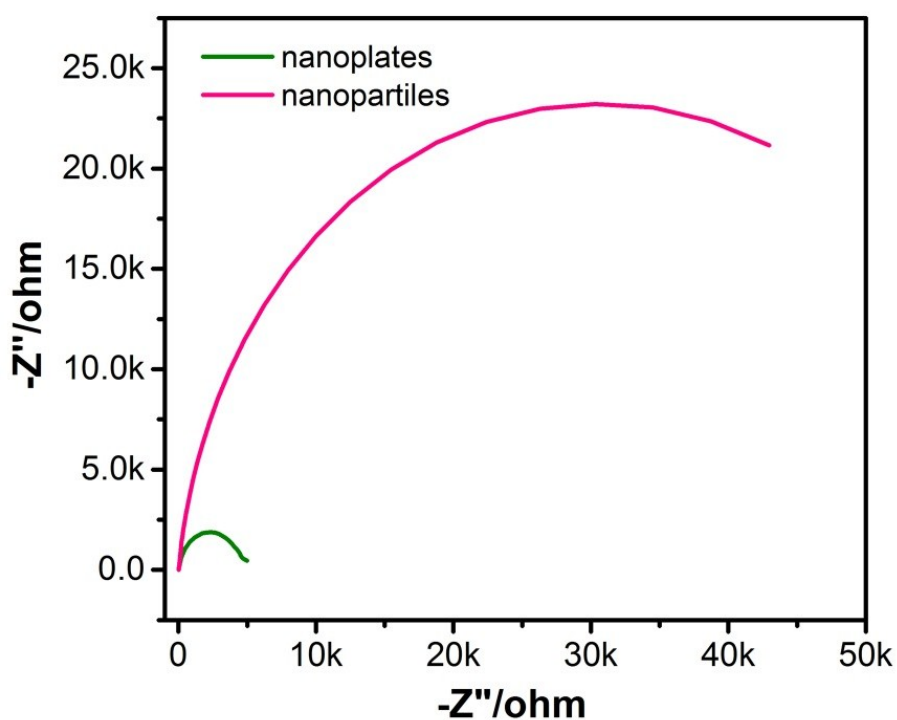


Figure S10. EIS curves of nanoplate and nanoparticles under full-spectrum illumination.

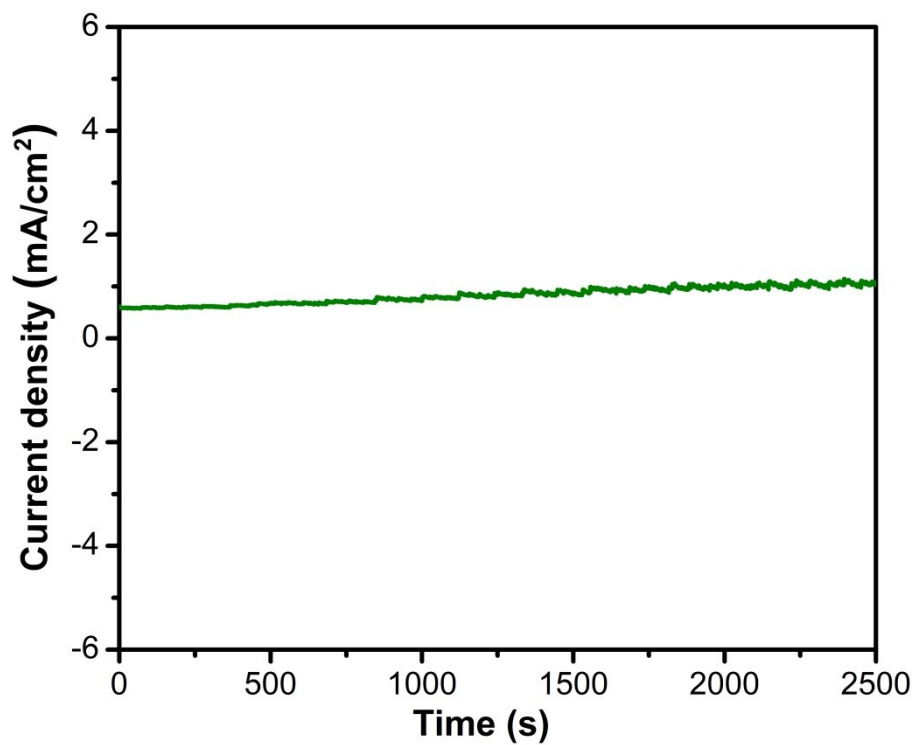


Figure S11. The photocurrent density vs. time ($I-t$) curves of CuInTe_2 nanoplates at a constant potential of 0.6 V vs. Ag/AgCl.