

Supporting Information

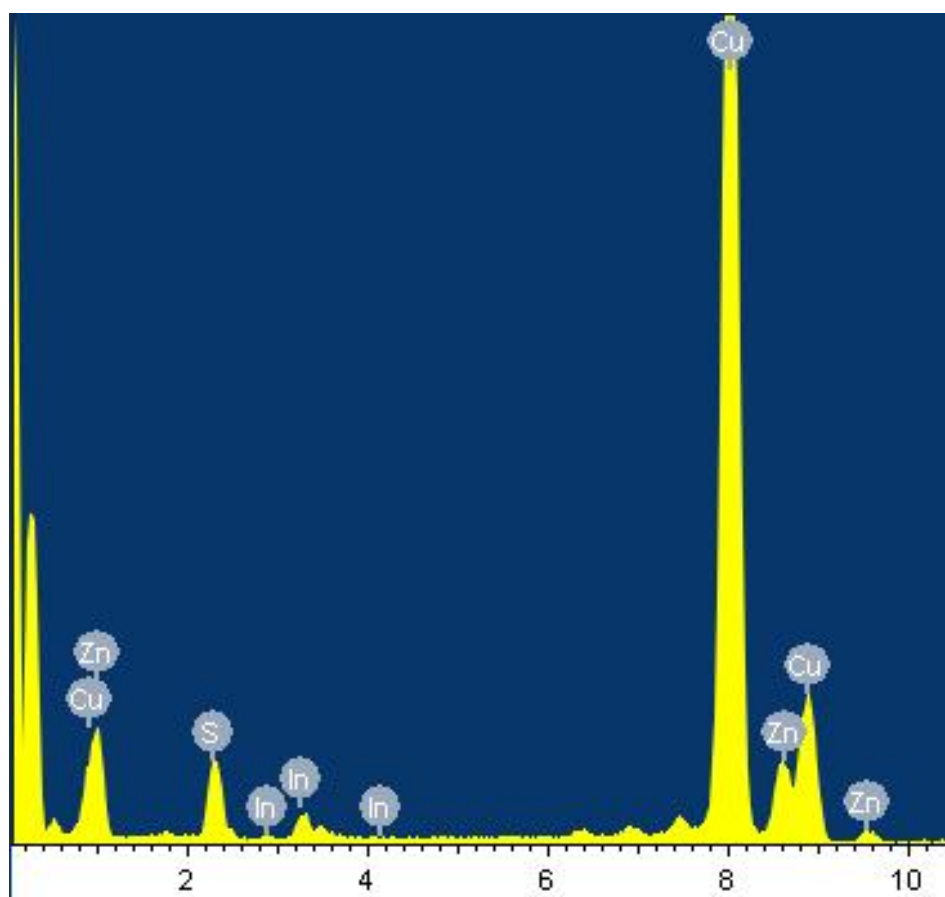
CuInZnS-Decorated Graphene Nanosheets for Highly Efficient Visible-Light-Driven Photocatalytic Hydrogen Production

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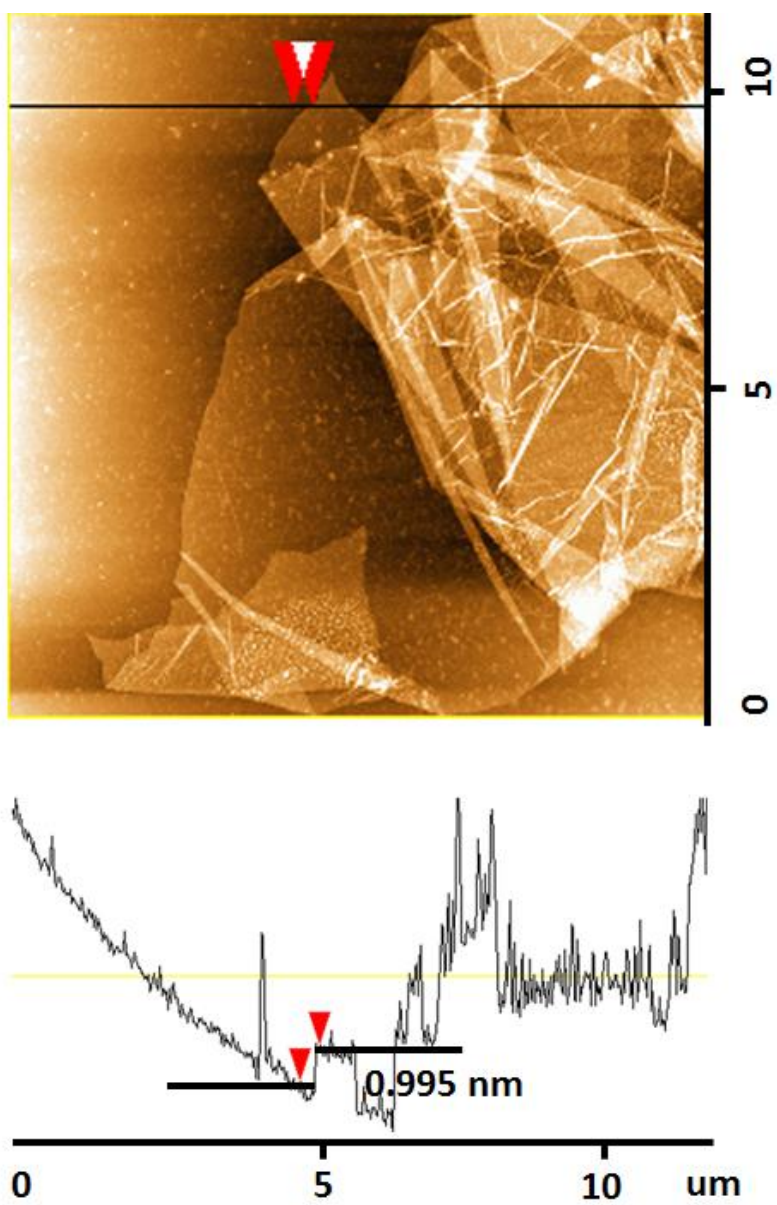
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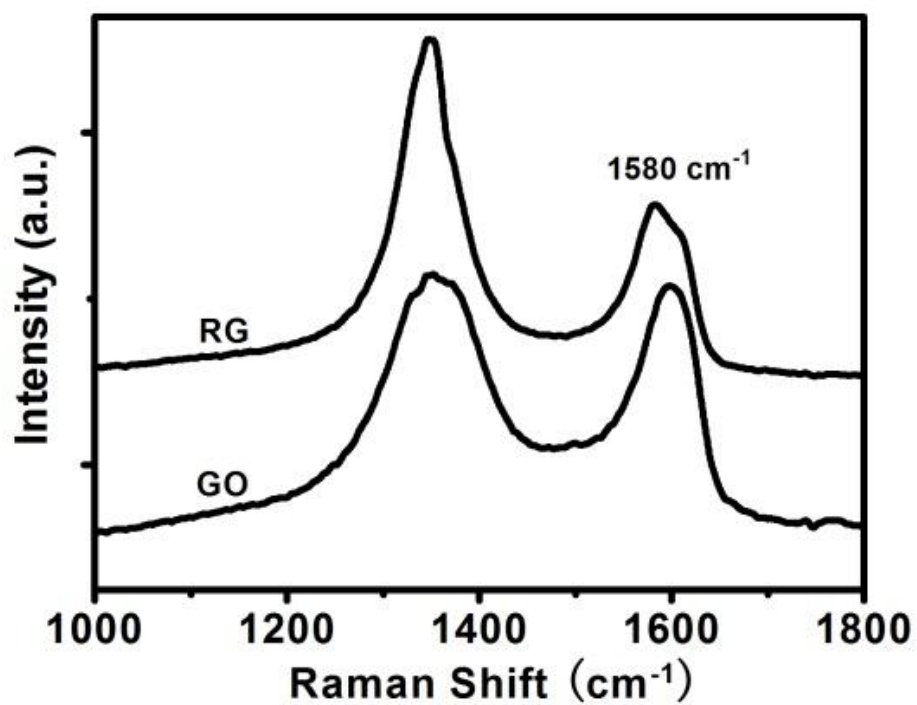
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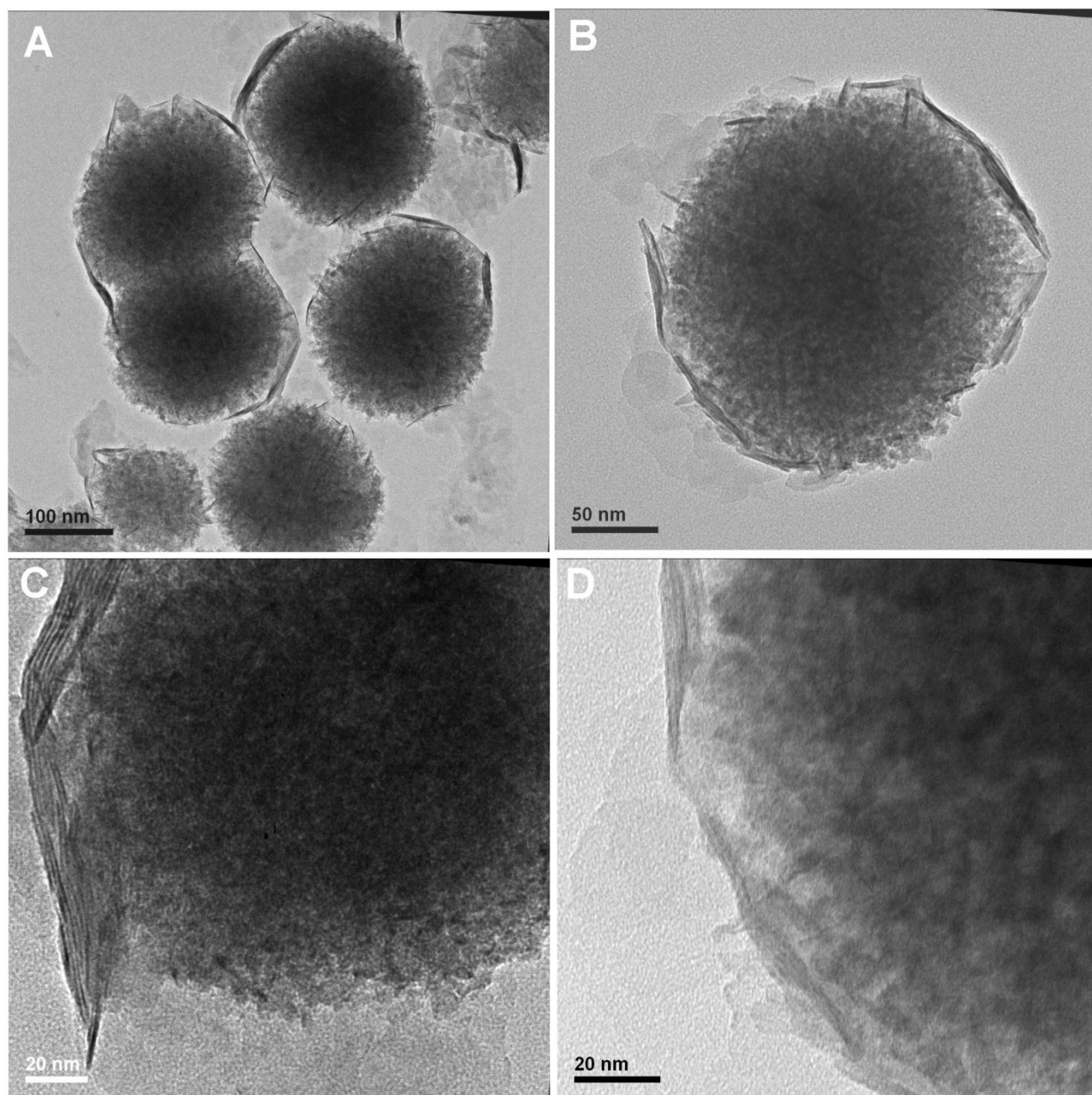
S-Figure 1 EDS spectrum of CIZS-rGO (CG2) nanocomposites.



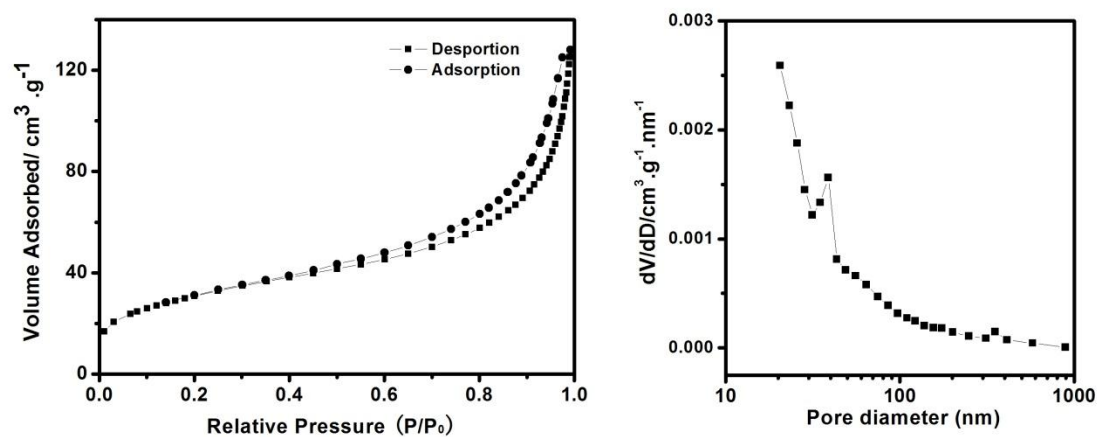
S-Figure 2 AFM image of graphene oxide nanosheet.



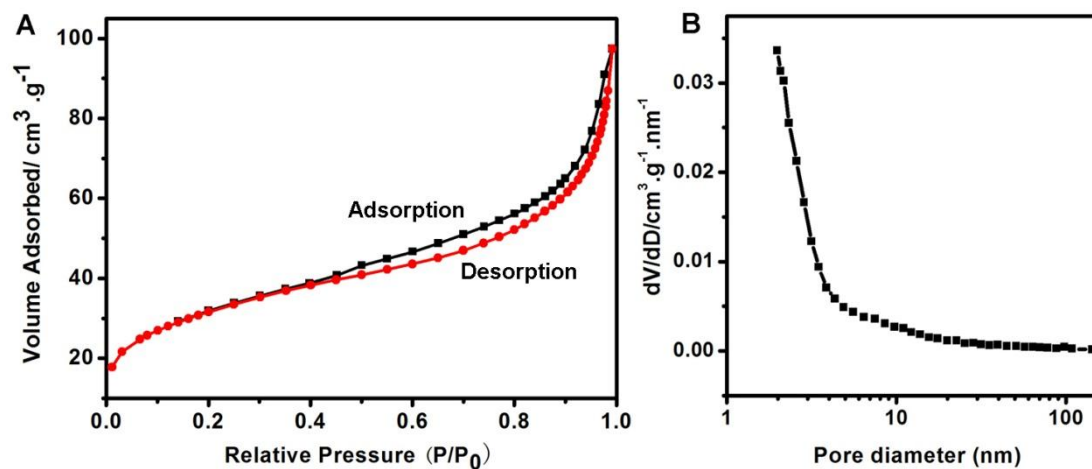
S-Figure 3 Raman spectra of graphene oxide and CIZS-rGO.



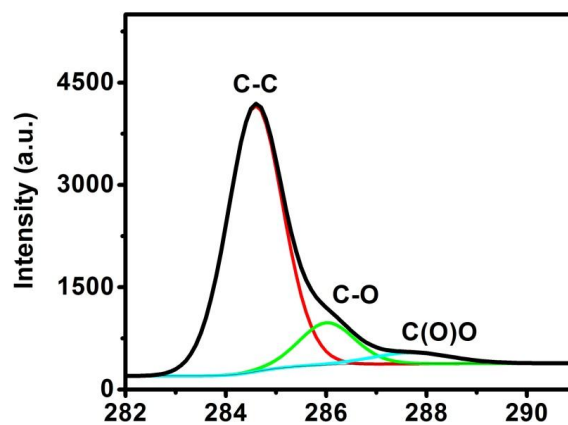
S-Figure 4 TEM images of pure $\text{Cu}_{0.02}\text{In}_{0.3}\text{ZnS}_{1.47}$ nanospheres.



S-Figure 5 Nitrogen adsorption-desorption isotherms (A) and corresponding pore size distribution curves (B) of pure CIZS nanospheres.



S-Figure 6 Nitrogen adsorption-desorption isotherms (A) and corresponding pore size distribution curves (B) of samples CIZS-rGO composites (CG2) solid powders.



S-Figure 7: XPS spectra of C 1s of CG2 nanocomposites after hydrogen production.

Flatband potential measurements

The flatband potential was measured by impedance spectroscopy with Mott-Schottky plot. 15 mg of the CuInZnS powder was sonicated in 1 mL of ethanol to obtain a homogenous mixture. An appropriate amount of suspension was drop-casted on a conductive fluorine-tin oxide (FTO) glass with adhesive tapes which act as spacers attached on the 4 sides of the substrate. The substrate was then heated at 80 °C for drying and the adhesive tape attached on the top side of the substrate was removed. Electrical contact was formed by applying silver paint on the top uncoated area of FTO and sticking copper tape on the silver paint. Three electrodes were used for the impedance measurements which include the working electrode (CuInZnS film), counter electrode (Pt plate) and reference electrode (Ag/AgCl, saturated KCl). 0.1 M of NaOH solution was used as the electrolyte. The measurements were carried out by Gamry electrochemical impedance spectroscopy and the potential was systemically varied between +0.2 to -1.4 V with frequency of 10, 50 and 100 Hz.

Mott-Schottky graph was plotted by measuring the apparent capacitance as a function of potential under depletion condition at the semiconductor-electrolyte junction based on the following equation 1:

$$\frac{1}{C_{sc}^2} = \frac{2}{e\epsilon\epsilon_0N} \left(E - E_{fb} - \frac{kT}{e} \right) \quad (1)$$

where C_{sc} = capacitance of the space charge region, e = electron charge (1.602×10^{-19} C), ϵ = dielectric constant of the semiconductor, ϵ_0 = permittivity of

free space ($8.85 \times 10^{-14} \text{ Fcm}^{-1}$), N = donor density (electron donor concentration for n-type semiconductor or hole acceptor concentration for p-type semiconductor), E = applied potential, E_{fb} = flatband potential, k = Boltzmann constant ($1.38 \times 10^{-23} \text{ JK}^{-1}$) and T is the absolute temperature.

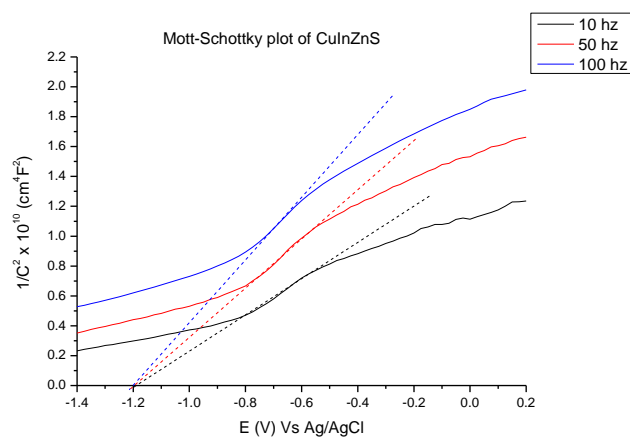
By extrapolating the $(1/C^2)$ versus E graph to the potential axis, the flatband potential can be determined. From S-Figure 6, the flatband potential of CuInZnS is $-1.2 \text{ V vs. Ag/AgCl}$. To convert the potential to be against the normal hydrogen electrode (NHE), 0.197 V has to be added according to the following equation:

$$E(\text{NHE}) = E(\text{Ag/AgCl}) + 0.197 \text{ V}$$

Hence, the flatband potential of CuInZnS is -1.003 V vs. NHE at pH 12.57 and to convert it to be at pH 7, the following equation is used:

$$E_{\text{F}}(\text{pH}) = E_{\text{F}} + 0.059 (\text{pH}_0 - \text{pH})$$

Thus, the flatband potential of CuInZnS is -0.67 V vs NHE at pH 7.



S-Figure 8 Mott-Schottky plot obtained at different frequencies for CuInZnS film electrode with Ag/AgCl, saturated KCl reference electrode and Pt counter electrode immersed in 0.1 M NaOH electrolyte with pH 12.5.