Electronic supplementary information (ESI)

Efficient Hydrogen/Oxygen Evolution and Photocatalytic Dye Degradation and Reduction of Aqueous Cr(VI) by Surfactant Free Hydrophilic Cu_2ZnSnS_4 Nanoparticles

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Turn over frequency (TOF): Calculation of TOF is carried out based on an earlier report by Popczun et al.[1] on CoP NPs.

TOF Calculations:

Molar mass = 439.47 $g.mol^{-1}$

Density of CZTS = 4.56 $g.cm^{-3}$

Volume = 96.37 $ml.mol^{-1}$

Current Density at 1.5V = 16.2 x 10^{-3} $A.cm^{-1}$

Current Density at 900 mV = 2 x 10^{-3} $A.cm^{-1}$

Catalyst loading = 15.9 $mg.cm^{-2}$

BET Surface area 15 $m^2.g^{-1}$ = 150 $cm^2.mg^{-1}$

Average surface atoms per 1 square centimeter

$$\left(\frac{3\ X\ 6.023\ X\ 10^{23}}{96.37}\right)^{2/3} atom.cm^{-2} = 7.05\ X\ 10^{14}\ atom.cm^{-2}$$

Surface atoms per tested area

$$15.9\ mg.cm^{-2}\ X\ 150\ cm^2.mg\ X\ 7.05\ X\ 10^{14}\ atom.cm^{-2} = 1.68\ X\ 10^{18} atom.cm^{-2}$$

Turn over Frequency (TOF)

$$\frac{1\ turnover\ X\ 16.2\ X\ 10^{-3} A.cm^{-2}\ X\ 1mol\ \ X\ 6.023\ X\ 10^{23} e^{-}.mol^{-1}}{2e^{-}\ X\ 96485C\ X\ 1.68\ X\ 10^{18} atom.cm^{-2}} = 0.030\ s^{-1}.atom^{-1}$$

Exchange Current Density (*i*) Calculations: The Exchange Current Density (*i*) for the as-synthesized CZTS in the electrochemical reaction is calculated as below:

$$\text{Exchange Current Density } (i) = \frac{RT}{nF\theta A}$$

where R is gas constant, T is temperature, n is number of electron transfer during the reaction, F is Faraday constant, θ is interfacial reaction resistance and A is area of the working electrode. Values for various parameters used in the reaction are given below as:

R = 8.314 $J.K^{-1}.mol^{-1}$

T = 298 K

n = 2

F = 96485 $C.mol^{-1}$

θ = 37 Ω (As calculated from EIS)

A = πr^2 = 3.14 x 0.2 x 0.2 cm^2 (0.2 cm is the radius of circular glassy carbon electrode)

Putting all the values in above equation we get

$$\text{Exchange Current Density } (i) = \frac{8.314\ J.K^{-1}.mol^{-1} \text{ X } 298\ K}{2 \text{ X } 96485.33\ C.mol^{-1} \text{ X } 37\ \Omega \text{ X } 0.1256\ cm^2}$$

$$i = 0.00276\ J.C^{-1}.\Omega^{-1}.cm^{-2}$$

$$i = 0.00276\ V.\Omega^{-1}.cm^{-2}$$

$$i = 0.00276\ A.cm^{-2}$$

$$i = 2.76\ mA.cm^{-2}$$

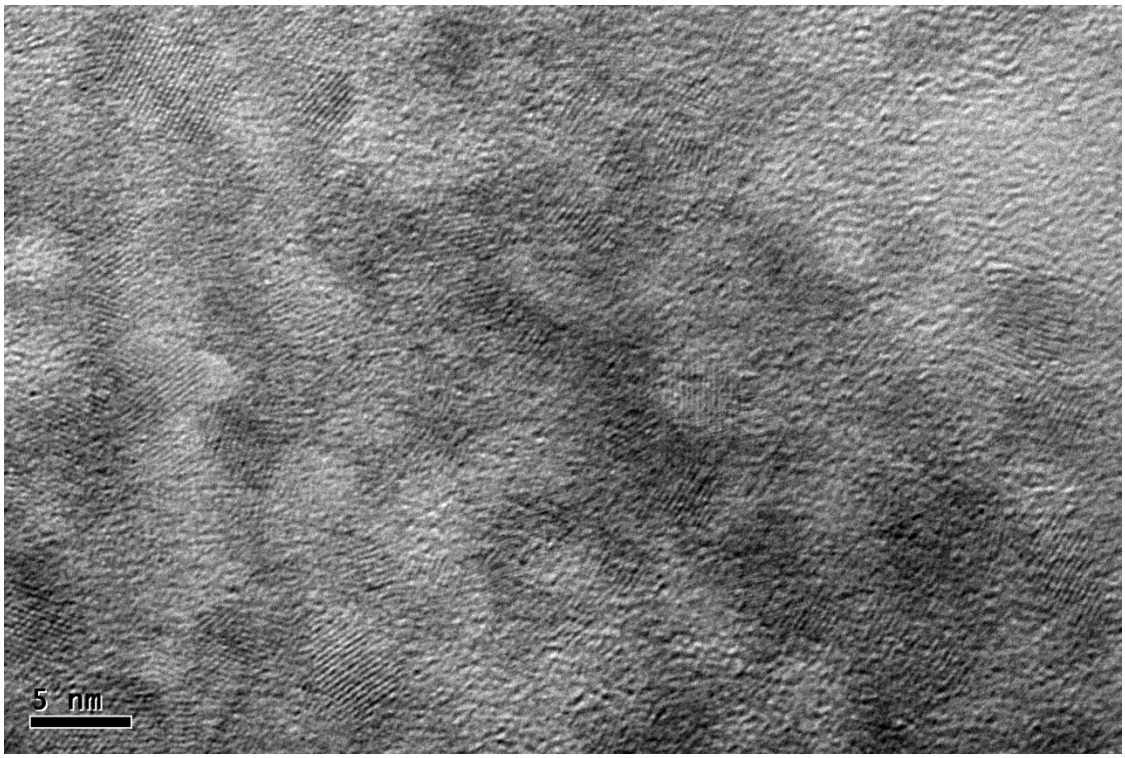

Fig. S1 HRTEM image of as-synthesized CZTS nanoparticles.

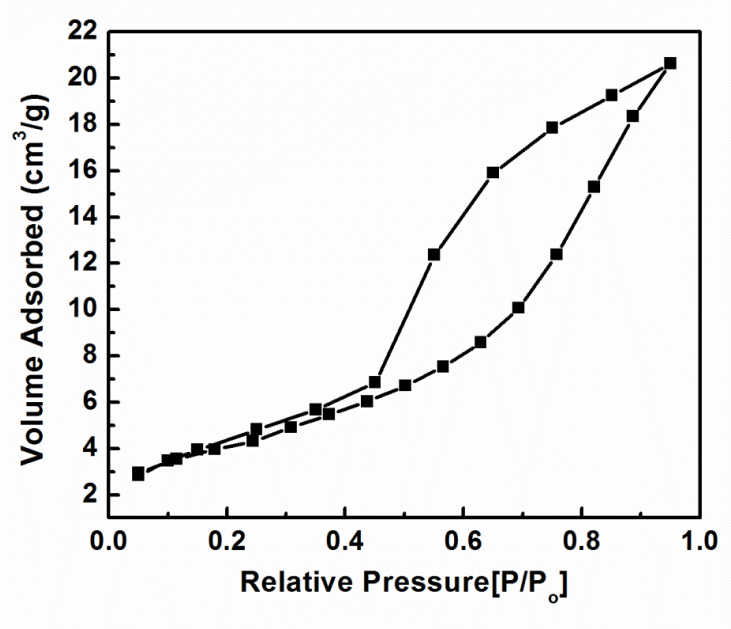

Fig. S2 Nitrogen adsorption−desorption isotherms at 77 K of the as-synthesized CZTS sample.

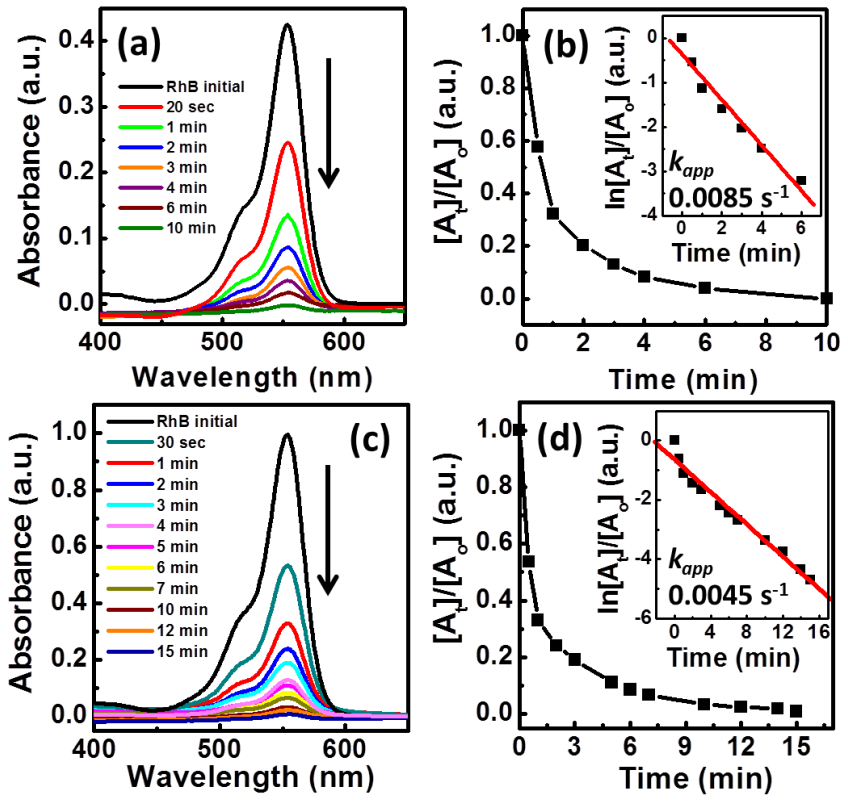

Fig. S3 Degradation (represented with downward arrow) in peak intensity of Rhodamine B at λ_{max} (554 nm) with various amount of CZTS for 50 ml of dye solution (c,d) CZTS = 10 mg, RhB = 0.004 mM. Degradation in peak intensity of Rhodamine B at λ_{max} (554 nm) CZTS = 25 mg, RhB = 0.01 mM.

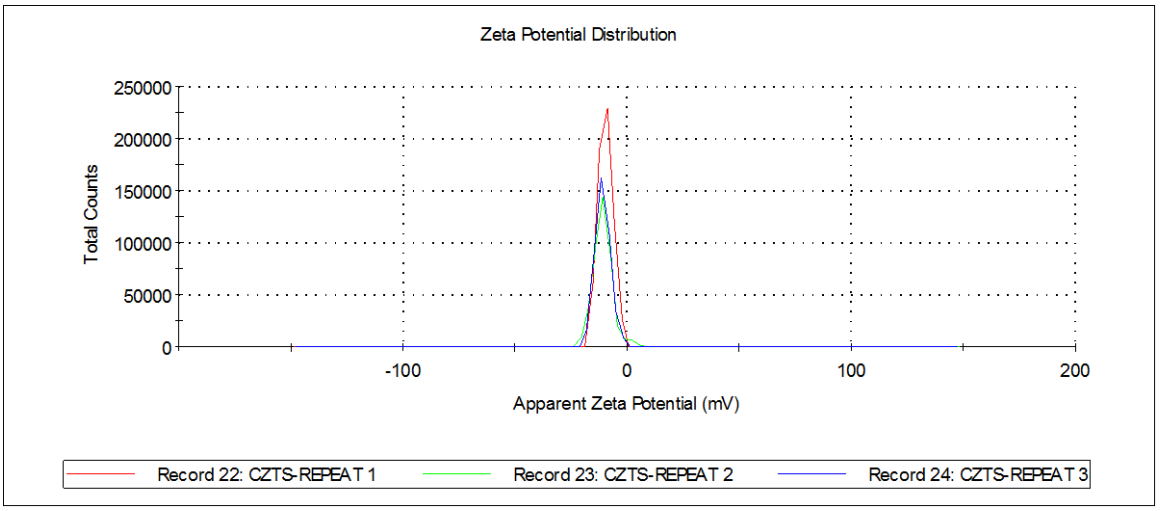

Fig. S4 DLS measurement on CZTS sample to examine the nature of the surface charge. The observed Zeta potential = –10.4 ± 0.8 mV.

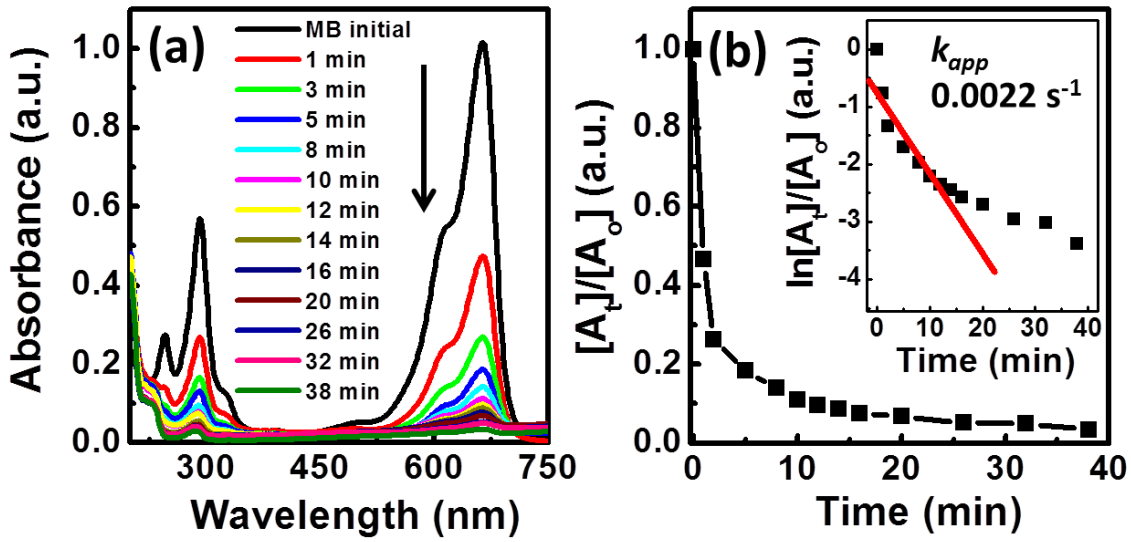

Fig. S5 (a) Degradation (represented with downward arrow) in peak intensity of Methylene Blue at λ_{max} (664 nm) with time, CZTS = 25 mg, MB = 0.01 mM. (b) $[A_t]/[A_o]$ vs. time and inset: $\ln[A_t]/[A_0]$ vs. time for the same reaction.

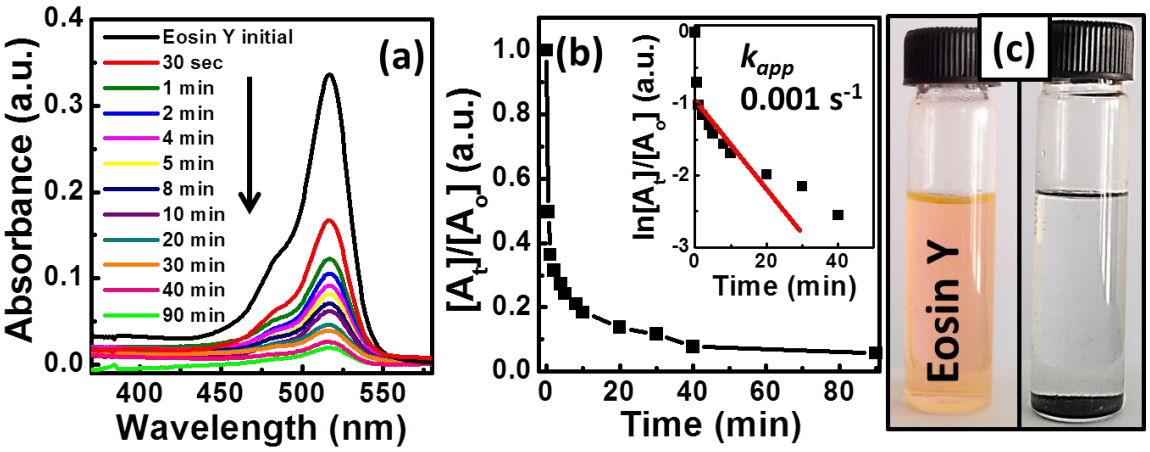

Fig. S6 (a) Degradation (represented with downward arrow) in peak intensity of Eosin Y at λ_{max} (519 nm), CZTS = 25 mg, Eosin Y = 0.002 mM. (b) $[A_t]/[A_0]$ vs. time and inset: $\ln[A_t]/[A_0]$ vs. time for the same reaction. (c) Change in color of the dye after the completion of the reaction.

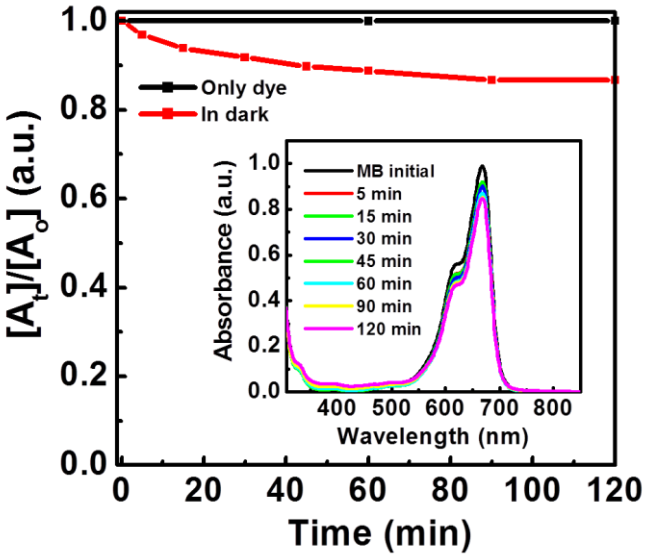

Fig. S7 Controlled experiment showing $[A_t]/[A_o]$ vs. time plot of MB in dark with CZTS = 25 mg, MB = 0.01 mM. Inset shows Absorbance vs. Wavelength plot for MB in dark.

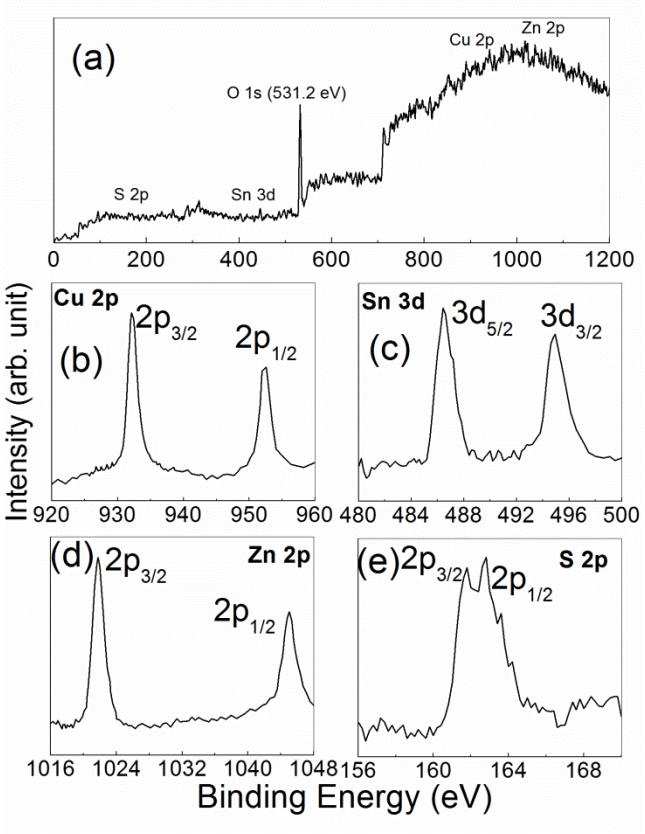

Fig. S8 (a) Full Scale XPS spectrum of as-synthesized Cu_2ZnSnS_4 nanoparticles. High-resolution XPS spectra of (b) Cu 2p, (c) Sn 3d, (d) Zn 2p, and (e) S 2p for CZTS recorded at room temperature.

1. E. J. Popczun, Read, C. W. Roske, N. S. Lewis and R. E. Schaak, *Angew. Chem. Int. Ed.* 2014, **53**, 5427.