

Supporting Information

Facile hydrothermal synthesis of CuO@ZnO heterojunction nanostructures for enhanced photocatalytic hydrogen evolution

Characterization

Crystallographic phases were studied on X-ray diffraction (XRD) D8 Advance Bruker with CuK α . The scan range was $2\theta = 20^\circ$ to 70° . Morphological and compositional studies were done with HRTEM (JEOL 2100 LaB6) operating at 200 kV where sample was dispersed in ethanol and a little was dropped on copper grid coated with carbon and dried. It was equipped with a CCD camera. Field emission scanning electron microscopic (FESEM) characterization was done on FEI Nova Nano SEM-450. The Brunauer–Emmett–Teller (BET) measurements by Nitrogen adsorption/ desorption isotherms were performed to investigate the surface characteristics at 77 K using a surface area analyzer (Quantachrome Instrument, USA; Model No. NOVA 1000e). The optical properties were characterized by using UV-vis diffuse reflectance spectroscopy (DRS) Perkin Elmer Lambda 750. XPS analysis was done on a KRATOS AXIS 165 with Mg K α irradiation. About 10^{-9} Torr pressure was maintained in the spectrometer. Electrochemical Impedance Spectroscopy (EIS) studies were carried out in a computer-controlled potentiostat/galvanostat (CHI 608E, CH Instrument, USA). Linear sweep voltammetry (LSV) and electrochemical impedance studies in a three-electrode photoelectrochemical (PEC) cell were carried out on a scanning potentiostat (Metrohm, Autolab). 2.5 mg of photocatalyst powder was dissolved in 1ml of ethanol and 20 μ L of Nafion (5 %) solution by ultrasonication. Indium tin oxide (ITO) coated PET (2 x 5 cm² area) was used as substrate on which 500 μ L of prepared solution was injected and dried for 6 hrs. For reference, calomel electrode is used and a

platinum wire as the counter electrode. 0.1 M Na₂SO₄ as aqueous electrolyte were used. LSV scan were performed between – 0.6 V to 1.0 V vs saturated calomel electrode (SCE) at scan rate of 2 mV s⁻¹. For photocurrent measurements, the same ITO substrate electrode was used as photoanode. A LED ((model no. HP-FL-20W-F-Hope LED Opto-Electric Co., Ltd.) was used as the incident light source and placed at 10 cm distance from the electrochemical cell. Shimadzu GC-2014 with Molecular Sieve/5Å packed column with thermal conductivity detector using N₂ as carrier gas was employed for Gas analysis.

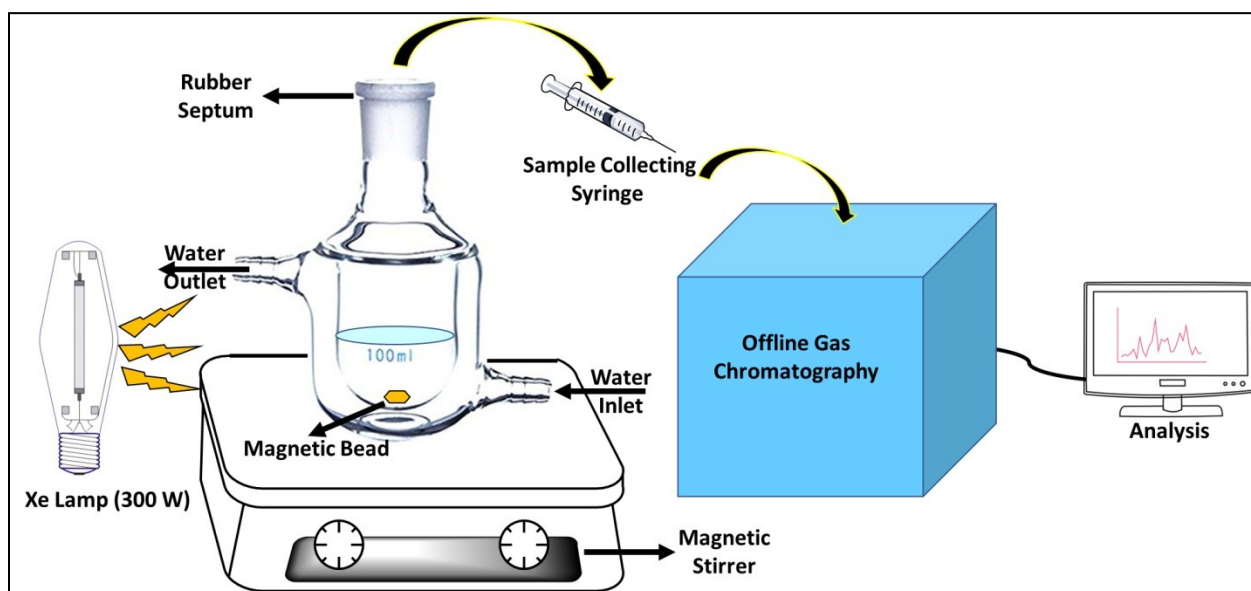


Figure S1. Schematic diagram demonstrating the apparatus for H₂ production.

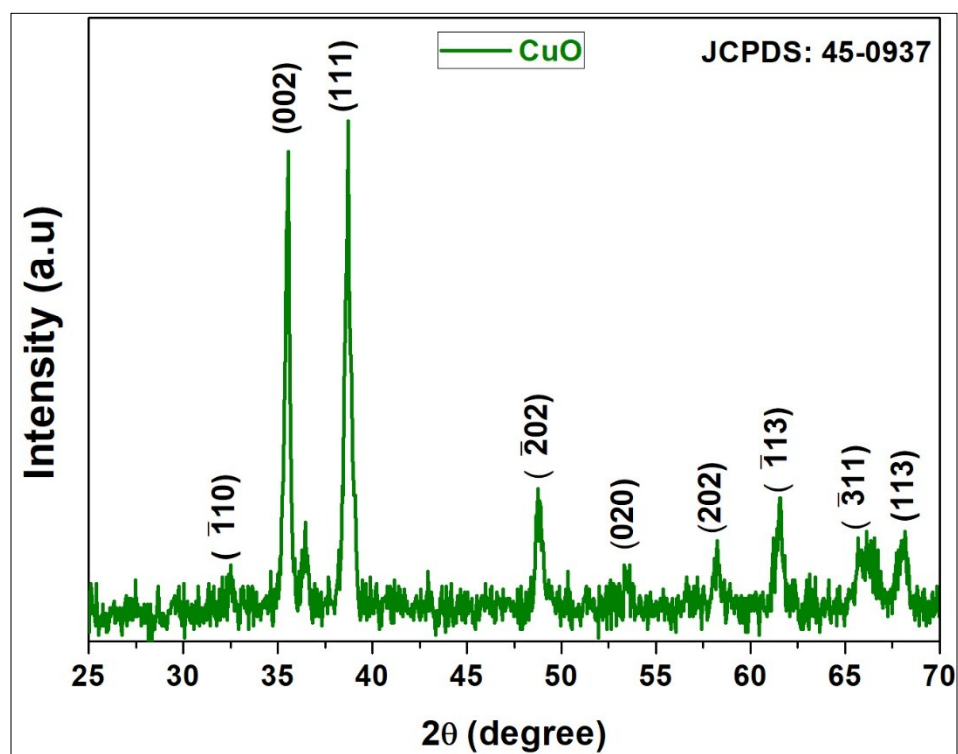


Figure S2. XRD pattern of CuO

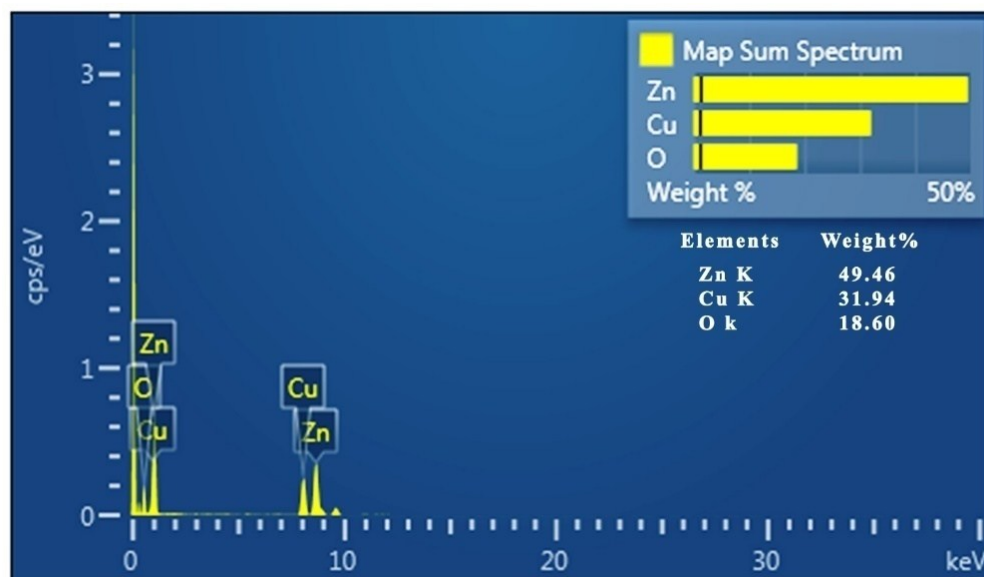


Figure S3. EDXS pattern for CuO@ZnO composite

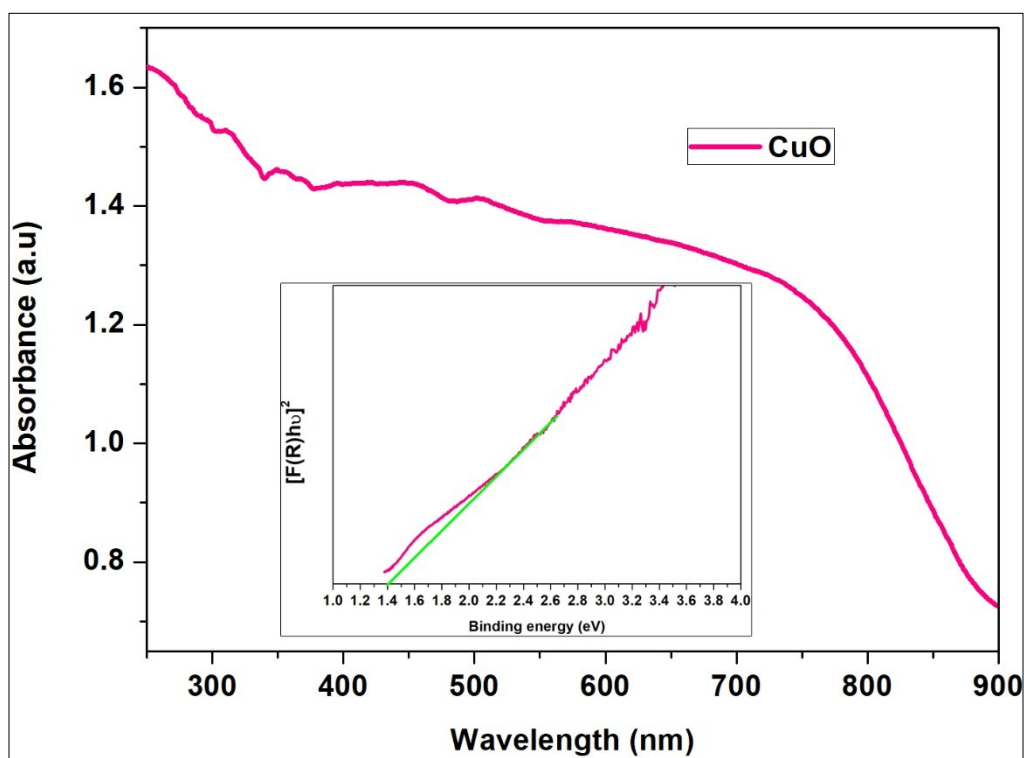


Figure S4. UV-DRS and Kubelka-Munk transformed reflectance spectra of CuO.

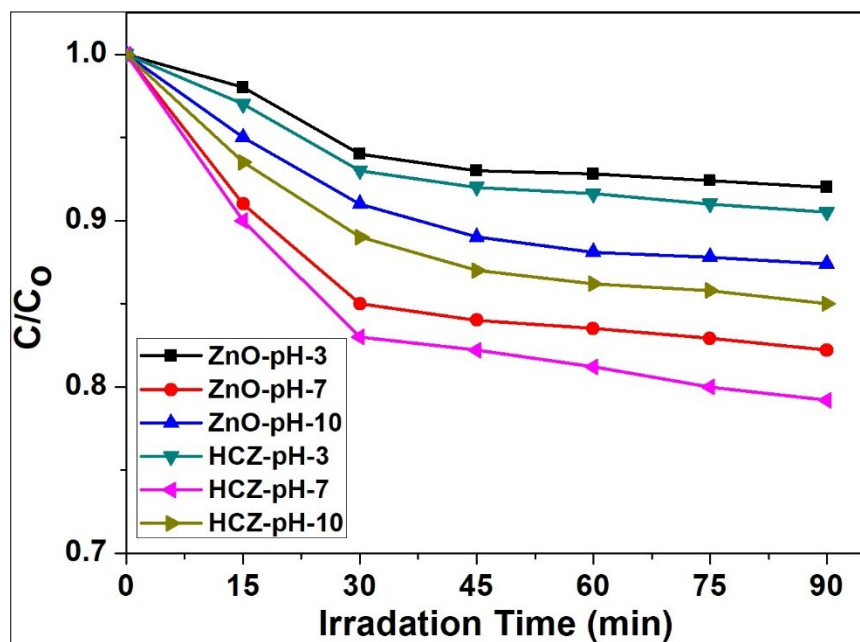


Figure S5. Adsorption-desorption equilibrium rate of MB under dark conditions versus time in the presence of various photocatalysts.

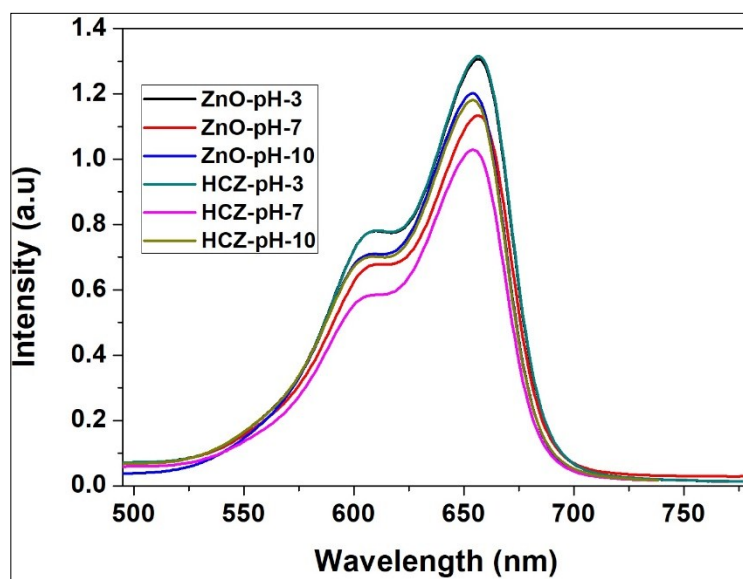


Figure S6. UV-vis absorption spectra of MB aqueous solution at 90-min dark adsorption-desorption equilibrium.

Table S1. Comparison table for the photocatalytic activity of different state of art photocatalyst with the CuO@ZnO photocatalyst.

Photocatalyst	Sacrificial agent	Light Source	Catalyst (mg/mL)	Amount of H ₂ ($\mu\text{mol h}^{-1} \text{g}^{-1} \text{cat}$)	Ref
ZnO	Na ₂ S + Na ₂ SO ₃	400 W Xe	20/75	341.9	1
ZnS/CdS	Triethylamine + ethanol	300 W Xe	25/100	375	2
ZnS/ZnO	Na ₂ S + Na ₂ SO ₃	Sunlight	10/10	374	3
Cu-ZnO	Methanol	500 W Xe	20/30	33	4
CuO/ZnO “corn-like”	Methanol+ H ₂ O	400W High Pressure Hg	10/10	1700	5
CuO@ZnO	Na ₂ S + Na ₂ SO ₃	300 W Xe	20/50	4604	Present Work

References

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