

**Preformed ZnS Nanoflower Prompted Evolution of CuS/ZnS p-n Heterojunction for
Exceptional Visible Light Driven Photocatalytic Activity**

**Chanchal Mondal,^a Ankit Singh,^a Ramkrishna Sahoo,^a Anup Kumar Sasmal,^a Yuichi
Negishi,^b Tarasankar Pal*,^a**

^aDepartment of Chemistry, Indian Institute of Technology, Kharagpur-721302, India

^bDepartment of Applied Chemistry, Tokyo University of Science, Tokyo 1628601, Japan

E-mail: tpal@chem.iitkgp.ernet.in

Supporting Information

Supporting information S1:

Materials

All the reagents were of AR grade. Zinc sulfate [$\text{ZnSO}_4 \cdot 2\text{H}_2\text{O}$], Copper sulfate [$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$] and thioacetamide, methylene blue were purchased from E-Merck. Beakers and other glasswares (capacity 15 mL) were obtained from Blue Star India and they were properly cleaned with aqua regia, water and dried prior to their use.

Analytical Instrument

Powder X-ray diffraction (XRD) was carried out using a PW1710 diffractometer, a Philips, Holland, instrument. The XRD data were analyzed by adopting the help of (JCPDS) software.

Reflectance spectra were done employing DRS (Diffuse Reflectance Spectra) mode with a Cary model 5000 UV-vis-NIR spectrophotometer.

All absorption spectra for the degradation reaction were monitored using a chemito spectrophotometer (India) and taking the solutions in a 1 cm quartz cuvette.

Field emission scanning electron microscopy (FESEM) was carried out with a supra 40, Carl Zeiss Pvt. Ltd. Instrument, and an EDAX machine (Oxford link and ISIS 300) attached to the instrument was used to obtain the nanocrystal composition.

Transmission electron microscopy (TEM) was done with an H-9000 NAR instrument, Hitachi, using an accelerating voltage of 300 kV.

The chemical state of the surface of the nanomaterial was attained by X-ray photoelectron spectroscopy (XPS) measurements, performed by a VG Scientific Escalab MK II spectrometer equipped with a Mg Kr excitation source (1253.6 eV) and a five-channeltron detection system.

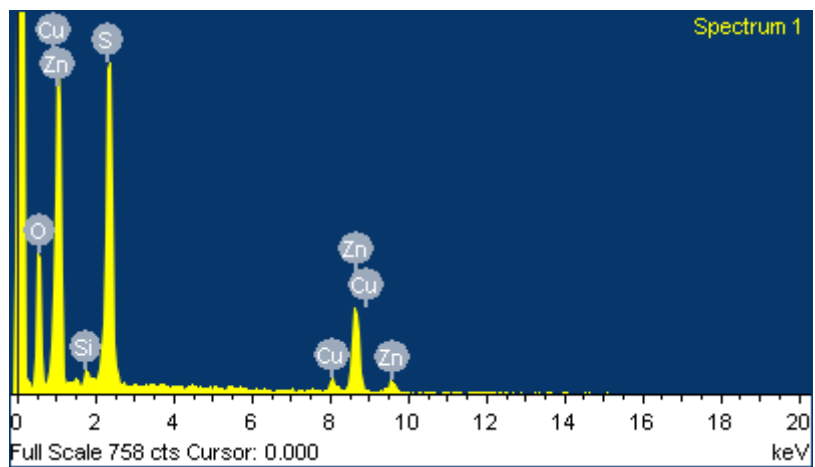


Figure S1: EDS spectrum of CuS/ZnS nanocomposite.

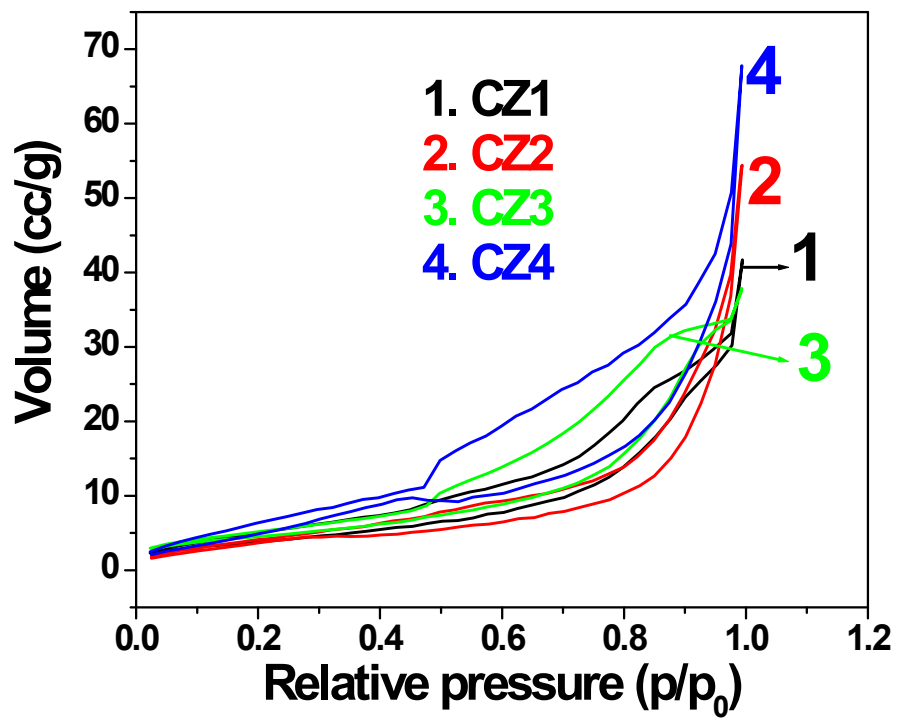


Figure S2: Nitrogen adsorption–desorption isotherm of composite materials CZ1, CZ2, CZ3, CZ4.

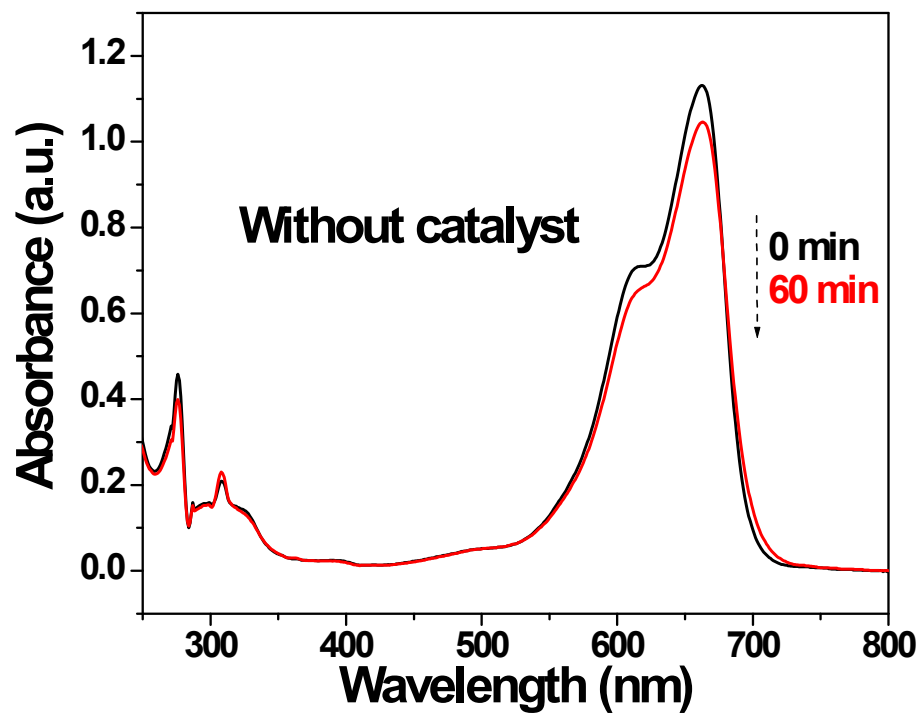


Figure S3: Photocatalytic degradation of 20 mL 2×10^{-5} M MB in absence of catalyst.

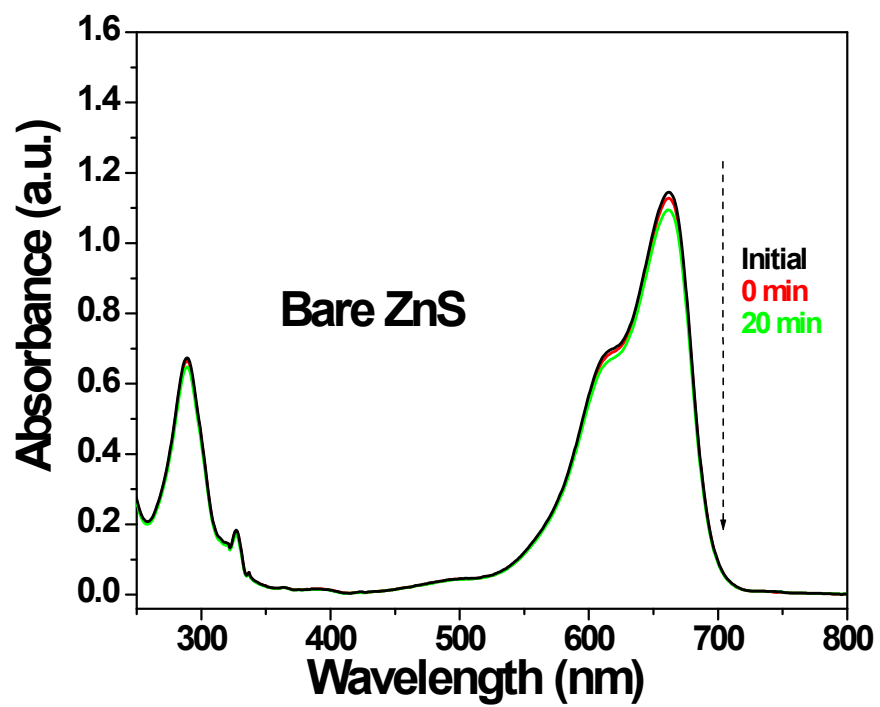


Figure S4: Photocatalytic degradation of 20 mL 2×10^{-5} M MB in presence of bare ZnS.

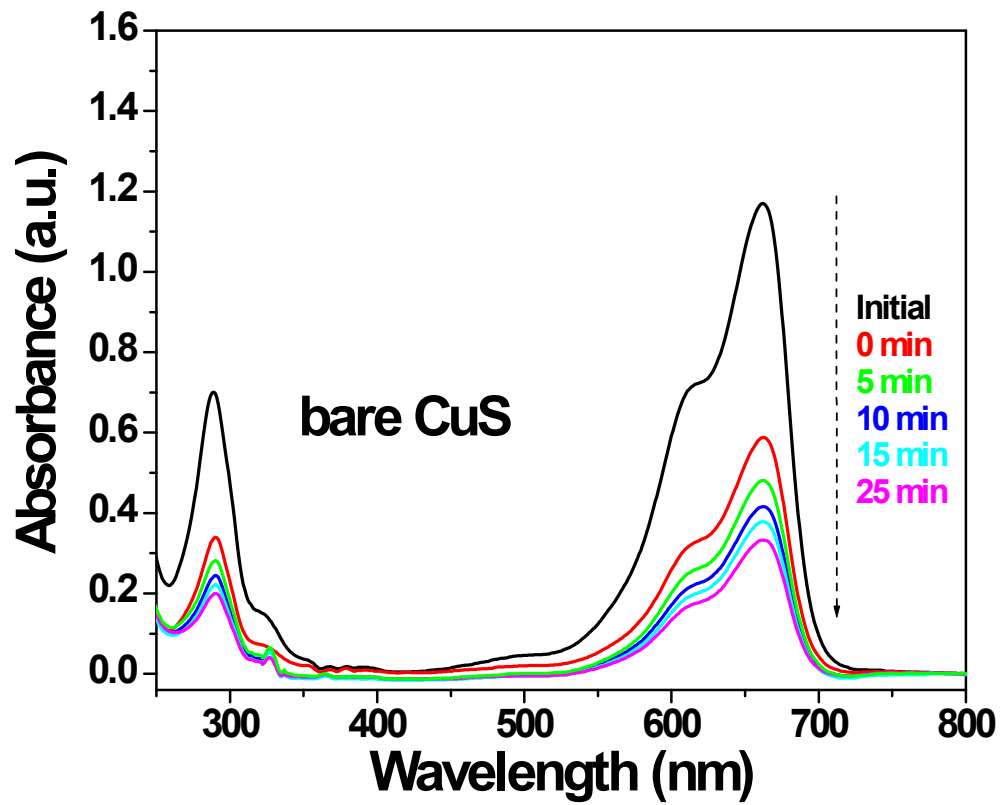


Figure S5: Photocatalytic degradation of 20 mL 2×10^{-5} M MB in presence of bare CuS.

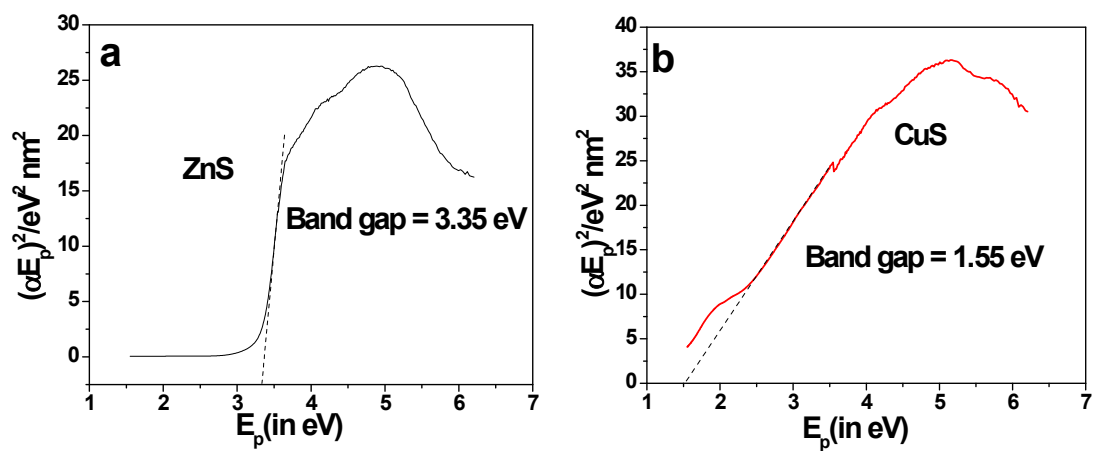


Figure S6: Band gap calculation of (a) ZnS nanoflower, (b) CuS nanomaterial.

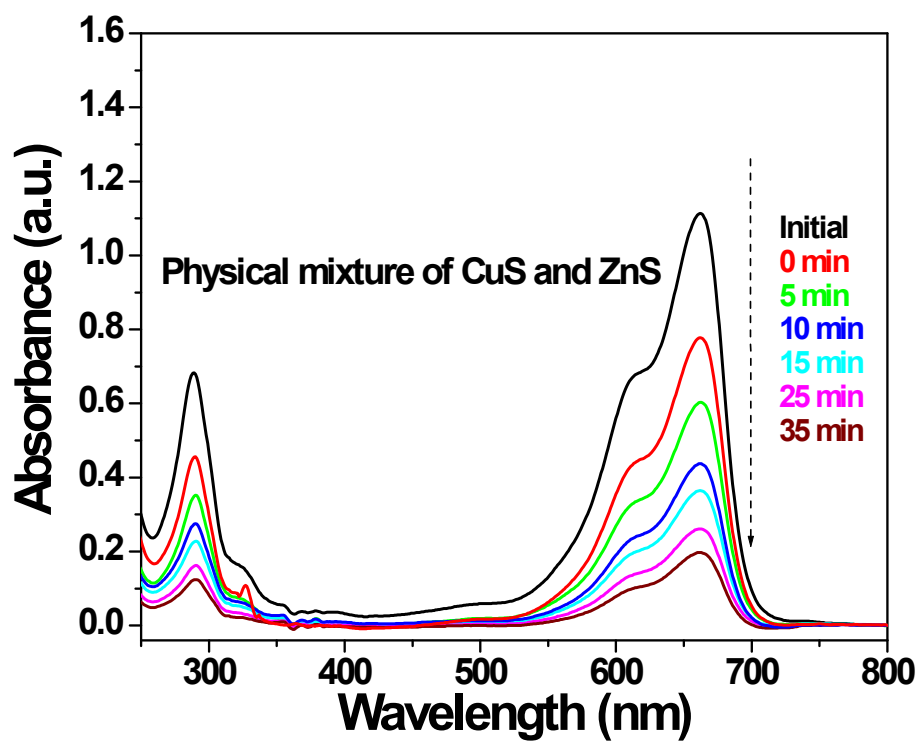


Figure S7: Photocatalytic degradation of 20 mL 2 x 10⁻⁵ M MB in presence of CuS and ZnS physical mixture.

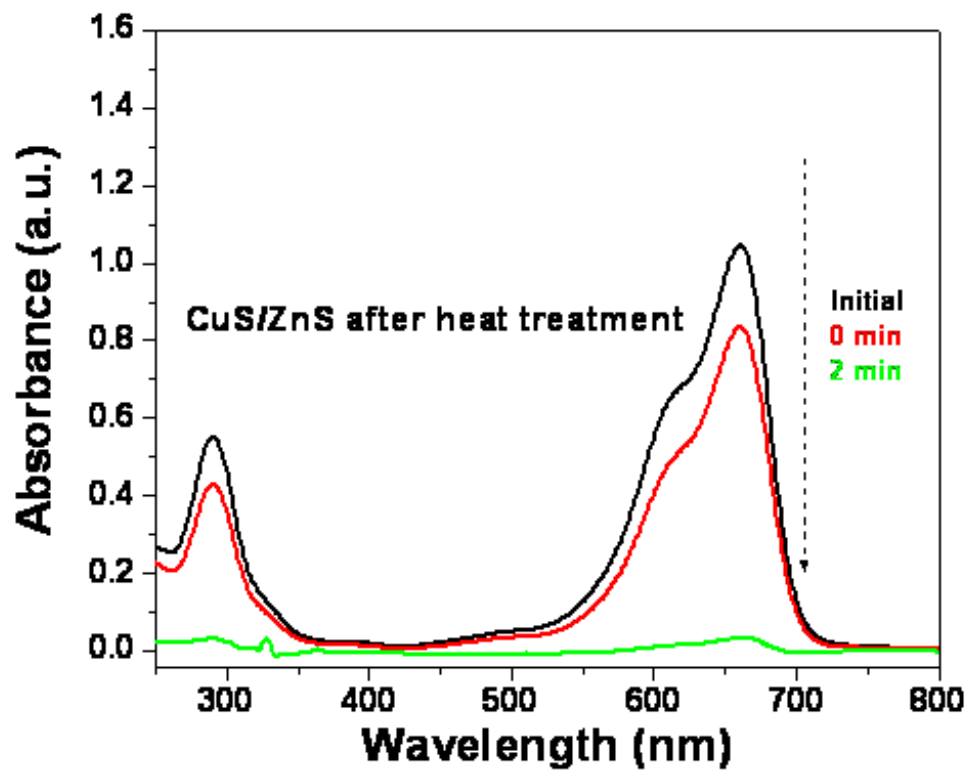


Figure S8: Photocatalytic degradation of 20 mL 2×10^{-5} M MB in presence of CZ2 (heated at 100°C).

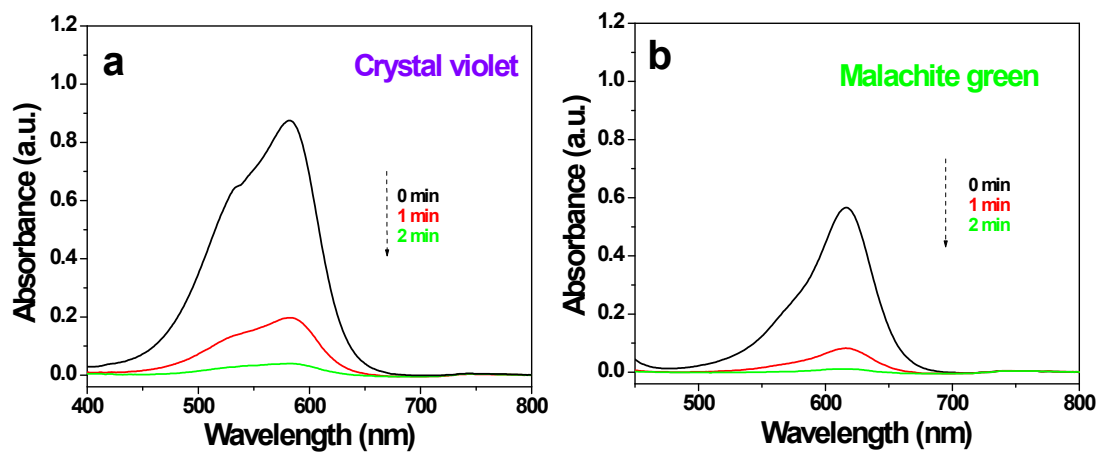


Figure S9: Photocatalytic degradation of (a) Crystal violet and (b) malachite green in presence CZ2 sample.

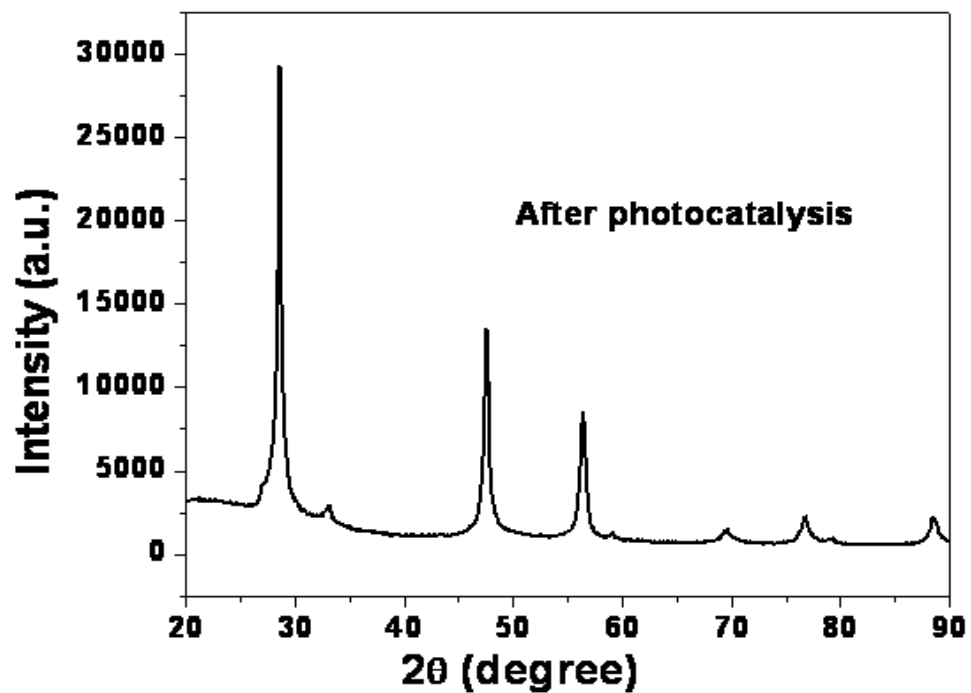


Figure S10: XRD pattern of CuS/ZnS after 4th cycle of operation.