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Supporting Information

Photocatalytic upcycling of marble waste into acetic acid by Copper Sulfide nanoparticles

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1. Experimental

Materials and Reagents

All the chemicals and reagents used were of analytical grade and without further purification unless stated. Cupric Nitrate trihydrate $(Cu(NO_3)_2).3H_2O$ (CDH), Sodium Sulfide fused flakes (Na_2S) (Thermo Fischer), 30 % w/v H_2O_2 (CDH) and De-Ionized water (Vartika Chemicals) were used. Marble dust (MD) was collected from Advance Research lab for Tribology, MNIT Jaipur, India.

Synthesis of CuS nanoparticles

In the first step, a 0.1 M $Cu(NO_3)_2).3H_2O$ solution was prepared by dissolving approximately ~0.94 g of the $Cu(NO_3)_2).3H_2O$ salt in 50 mL of distilled water. A saturated solution of sodium sulfide (Na_2S) was then added dropwise to this solution under continuous stirring until precipitation occurred, while maintaining the pH at ~10.2. The resulting precipitate was centrifuged and filtered using Whatman filter paper, followed by multiple washes with deionized water to remove impurities. Finally, the product was dried in a hot air oven at 60 °C, yielding a dark green-colored CuS nanopowder and named as CuS-NPs.

Instrumentation

X-ray diffractometer instrument (Panalytical X Pert Pro) was used to analyze powder X-ray diffraction (PXRD). Transmission electron microscopy (TEM) images was recorded using a Tecnai G2 20 (200 kV) X-ray photoelectron spectra (XPS) were performed using an ESCA+ omicron nanotechnology Oxford instrument. The ^1H, ^{13}C NMR spectra were recorded using a JEOL ECS-400 spectrometer operating at 400 MHz. High-resolution Mass spectra (HRMS) were recorded on a Xevo G2-S Q-TOF (Waters, USA) mass spectrometer.

Photoreduction of Marble Dust to AcOH

The photocatalytic reduction of marble dust (carbonate) to AcOH was conducted in a borosilicate glass reagent bottle under control illumination of monochromatic light source. The marble dust served as the source of carbonate for CO_2 generation. 400 mg of CuS nanoparticles (photocatalyst) and 200 mg of marble dust were dispersed in 20 mL of an aqueous solution containing 1:1 v/v H_2O_2 (30% w/v) and deionized (DI) water. The suspension was irradiated under various light sources-including monochromatic 525 nm LED light, incandescent bulb light, and natural sunlight-to evaluate photocatalytic performance under different conditions.

The mixture was magnetically stirred in a borosilicate glass reactor under continuous irradiation for 4 hours. After that the reaction mixture was centrifuged and distilled in a distillation assembly to isolate the catalyst and remaining solid, and the liquid part were used for the product analysis. The product (AcOH) obtained was analyzed by ^{1}H NMR and verified by ^{13}C NMR and HRMS spectroscopy. Reaction parameters such as catalyst loading, H_2O_2 concentration, irradiation time, and light source were systematically optimized to maximize AcOH yield.

2. UV-Vis absorbance spectra of CuS-NPs solid powder

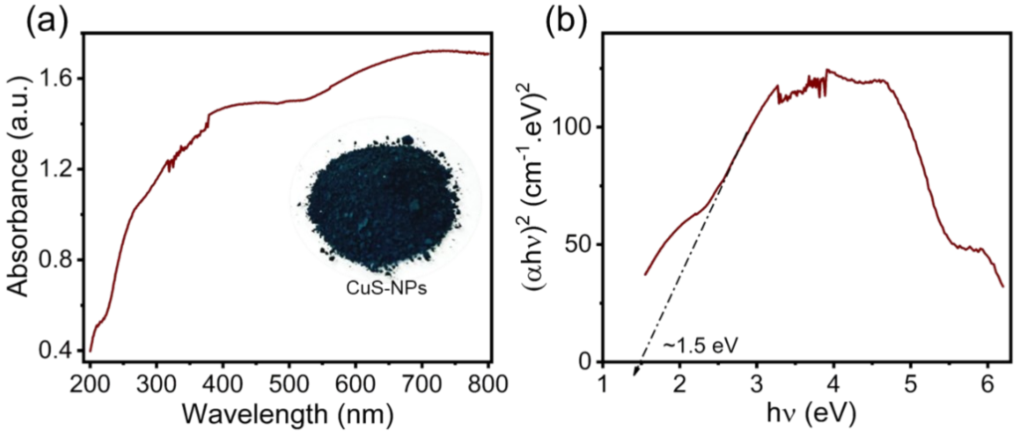

Figure S1: (a) UV-Vis absorbance spectra of CuS-NPs solid powder with digital photo of CuS-NPs (inset) and (b) Direct band gap analysis of CuS-NPs by Tauc plot.

3. FESEM images of CuS-NPs

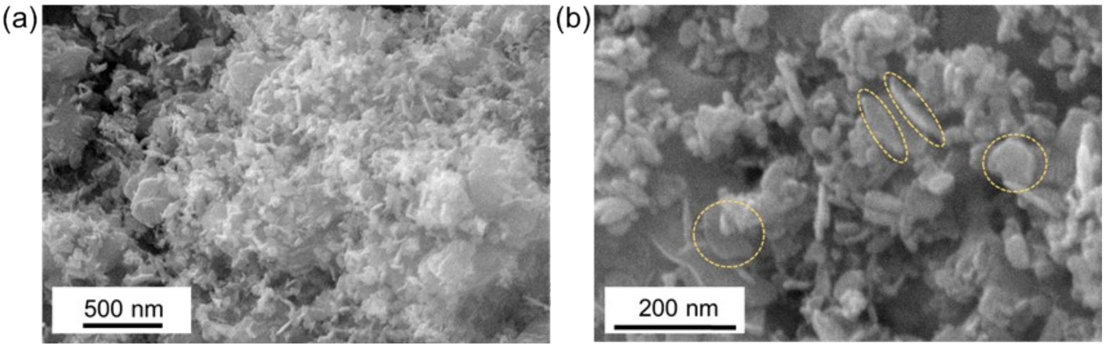

Figure S2: FESEM images of CuS-NPs (a) Low resolution; (b) High resolution.

4. Table S1: Detectable ^1H NMR peaks positions of internal standards and carbonate-reduced products.

Analytes	Detectable number of protons (splitting)	Peak position
Sodium formate (Internal standard for AcOH)	1 (s)	~8.42
AcOH	3 (s)	~1.88

5. LCMS analysis of photo-reduced product (AcOH)

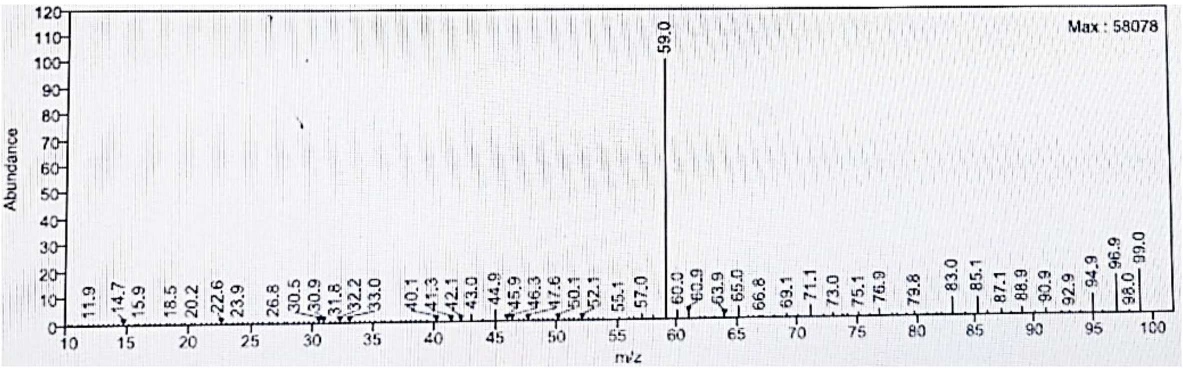

Figure S3: Liquid chromatography-mass spectrometry (LCMS) analysis showed an isolated peak with a value of 59 m/z of product AcOH.

6. Table S2: Percentage decrease in yield of AcOH with different scavengers.

S. No.	Scavenger Used	% Reduction in AcOH yield
1.	IPA	~97
2.	p-BZQ	~41
3.	$K_2S_2O_8$	~75
4.	Na_2EDTA	~82

7. Optimization of Marble Dust Loading.

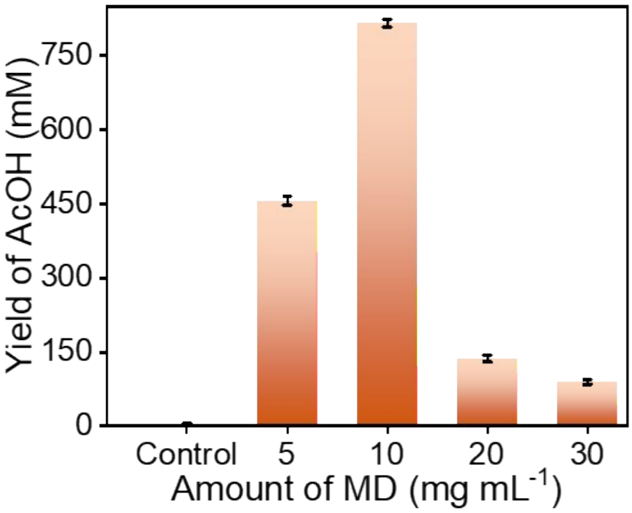

Figure S4: Loading variation of Marble dust vs yield of AcOH.