

Electronic Supporting Information

Oleic Acid Induced Tailored Morphological Features and Structural Defects in CuO for Multifunctional Applications

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Table S1 Summary of the CuO synthesis parameters leading to tailored morphological features and information on corresponding dimensions.

Sample	Oleic Acid (mL)	Water:Hexane (mL)	Morphology	Dimensions*
1	0	50:0	Irregular Structures (IS)	t = 5 to 30 nm, L=100 to 800 nm
2	0.5056	50:50	Nano Feathers (NF)	t = 3 to 20 nm, L=200 to 1000 nm
3	2.5282	50:50	Solid/Hollow Hexagonal Sheets (HS)	t = 5 to 30 nm, L=50 to 350 nm
4	7.5840	50:50	Mega Hexagonal Sheets (MS)	t = 30 to 60 nm, L=400 nm to 2.5 μ m

**Here, t-Thickness and L-Edge Length.*

A0: Sensor Setup and Device Fabrication

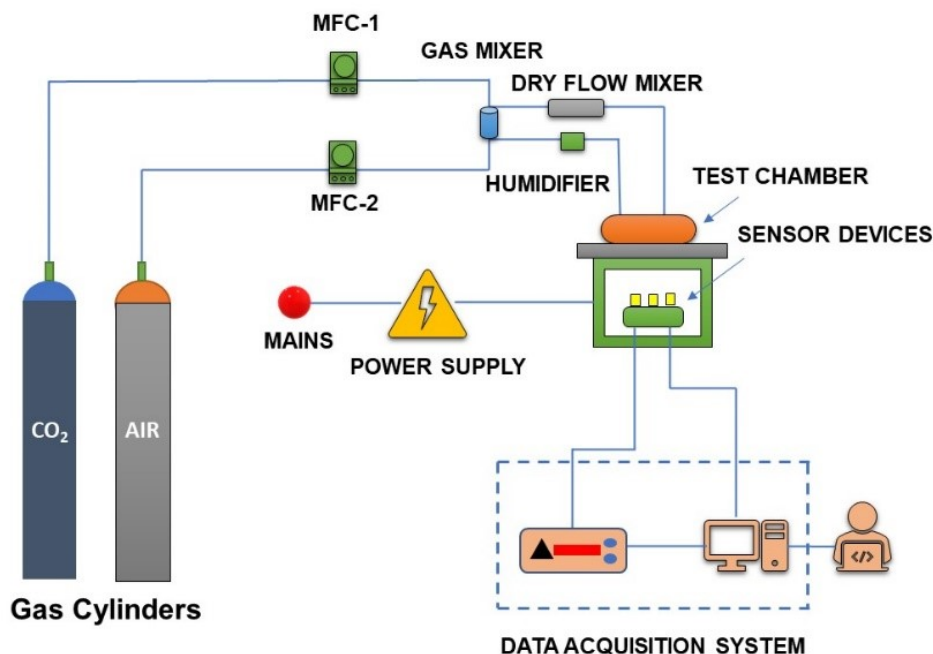


Fig. S1 Gas sensor assembly used for CO₂ sensing studies.

A calculated amount of 10 mg of as-synthesized powder was dispersed in a 15 mL Tarson tube containing 1 mL of ethanol to form a slurry using an ultrasonicator at room temperature. The steps involved in the sensor device fabrication are demonstrated in **Fig. 1** (see the main article). Four sensor devices were fabricated using CuO samples, namely CuO-MS, CuO-HS, CuO-NF, and CuO-IS, respectively. The sensor substrates used in the current study were washed with ethanol and distilled water before deposition of material. The dimensions of the substrate were 7 mm×14 mm with 7 interdigit pairs of fingers and rated operational for temperatures up to 600°C. In each case, the sensor element was prepared by drop-casting the slurry on an interdigitated (IDT) alumina sensor substrate coated with silver (Ag) fingers. Two silver wires of a specific length were attached that functioned as the electrical contacts for the sensor device using epoxy glue. Before each sensing test, the sensor device was preheated in synthetic dry air at 200°C for 7 to 9 h to stabilize the sensor surface and to remove any adsorbed residual organic species. The temperature was controlled by a flatbed ceramic heater kept underneath the sensor device that was coupled to a temperature controller utilizing a K-type thermocouple placed inside the sensor chamber for feedback.

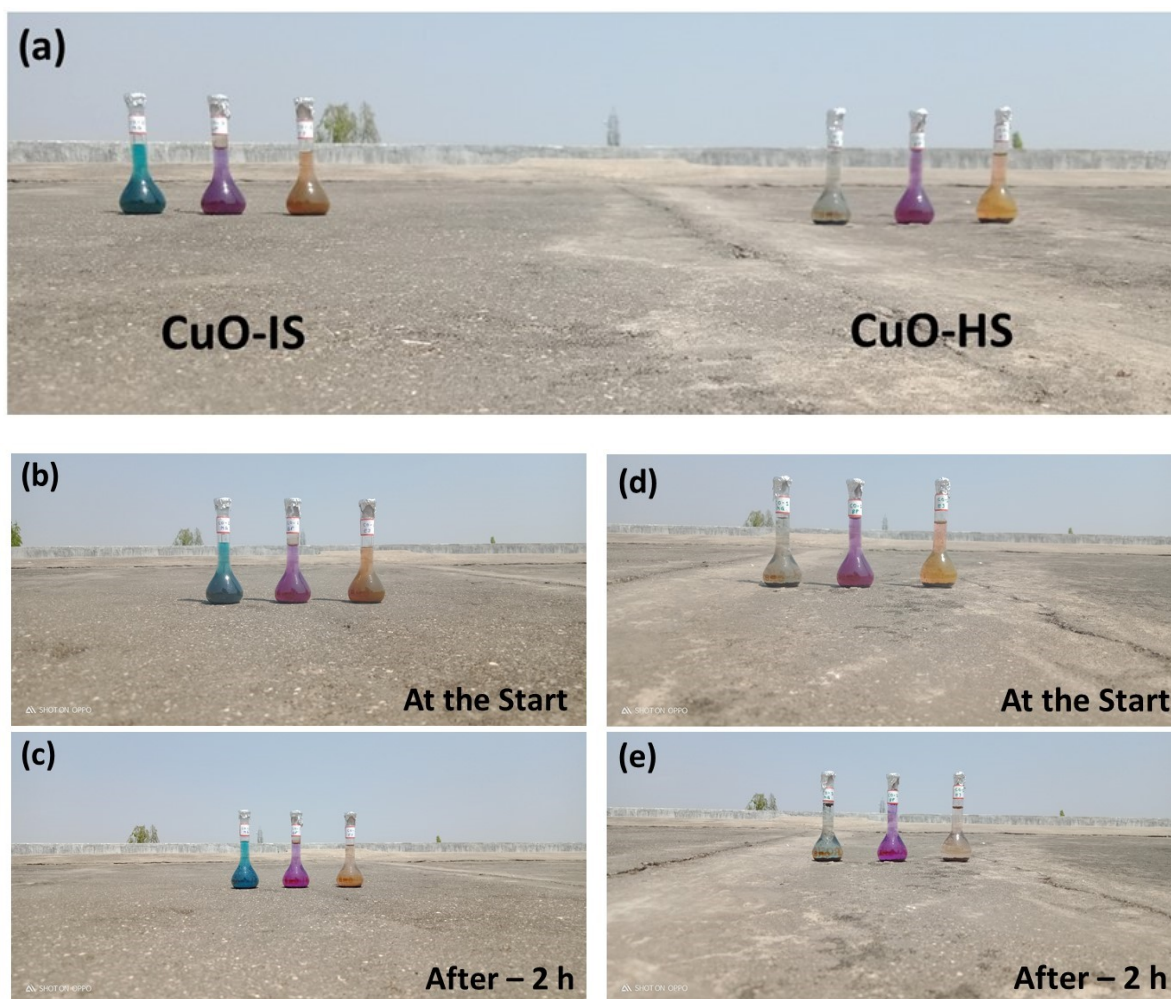


Fig. S2 (a-b) Images illustrating natural sunlight-induced degradation of malachite green, bromocresol purple, and eosin yellow dye solution carried out on institute's terrace at STP, where depicts for **(b-c)** CuO with irregular sheets/structures (CuO-IS) achieved without oleic acid-hexane solution and **(d-e)** CuO with hexagonal sheets synthesized by adding the oleic acid amount of 2.528 mL in 50 mL of hexane. Natural sunlight-induced dye degradation studies were carried out from 12th to 29th March 2021 on the main academic building terrace of G. S. Mandal's Marathwada Institute of Technology, Aurangabad, Maharashtra, India having co-ordinates as 19.8493°N, 75.3216°E. The tests were conducted daily for 3 h from 11 am to 2 pm and during this time, the light intensity measured using a lux meter was in the range of 70 to 100 mW/cm².

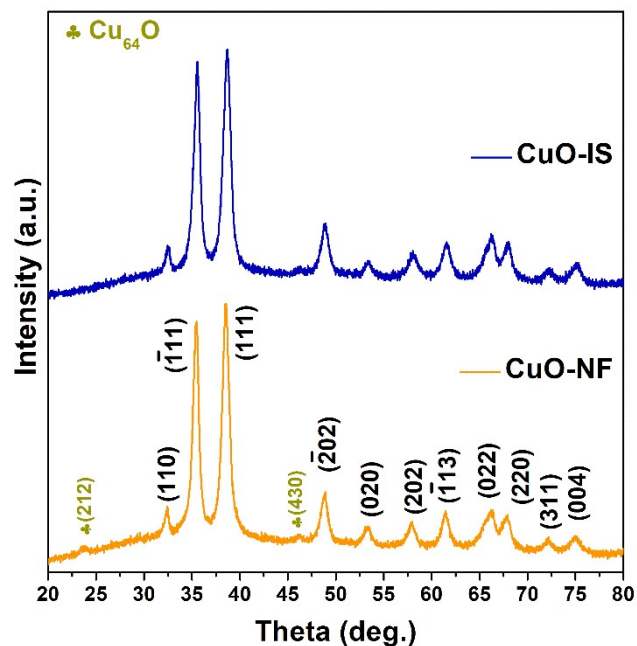


Fig. S3 X-ray diffraction patterns for CuO with irregular sheets/structures (CuO-IS) were achieved without oleic acid-hexane solution and CuO in the form of nano feathers (CuO-NF) achieved by adding the oleic acid amount of 0.5056 mL in 50 mL hexane. The intermediate phase of copper oxide (Cu_{64}O) in orthorhombic crystal structure was observed in minor percentage with JCPDS Card: 77-1898 and space group: Bmm2 (38). The data was collected in the 2θ range from 20 to 80° in a continuous scanning mode with a 0.01° sampling pitch and 5° min^{-1} scan rate.

A1: Thermal Stability and Nature of Chemical Bonds

Thermogravimetric differential thermal analysis (TG-DTA) in the range of 30 to 800°C was carried out to evaluate the phase stability of the nanomaterial at higher temperatures. The raw data was processed using the TA instrument's universal analysis software. The figures are provided in the main article. **Fig. 1c** illustrates the TG-DTA curve for the CuO-HS sample with a two-step decomposition process. The two weight-loss zones were observed in the temperature range 30–186°C, and 187–750°C, respectively. The initial weight loss of ~2.73% in the range 30–186°C corresponding to a DTA peak at 178°C is attributed to the evaporation of moisture (hydroxyl groups) and organic moieties.¹ The second weight loss of ~6.17% corresponding to three DTA peaks at 248°C, 639°C, and 669°C is due to the removal of organic matter from the precursor and solvents (oleic acid and n-hexane).²

The nature of chemical bonds in CuO-IS and CuO-HS samples was probed by Fourier Transform Infrared Spectroscopy (FTIR) and comparative data is shown in **Fig. 1d**. The sample preparation involved grinding the nanopowder with potassium bromide (KBr, IR spectroscopy grade, Sigma-Aldrich) in a 1:100 ratio and pressing it into highly thin translucent pellets followed by vacuum drying at 75°C before collecting the spectra. The pellets dimensions were diameter (D) = 1.2 cm and thickness (t) = 0.02 cm. The transmittance spectra collected for 64 scans with a resolution interval of 2 cm⁻¹, were corrected for baseline, atmospheric interference, and normalized before comparative evaluation. The characteristic bands observed at 478 cm⁻¹ and 596 cm⁻¹ are due to the Au and Bu mode of monoclinic CuO. Moreover, the Cu-O stretching vibration along the [101] direction is confirmed from the band at 478 cm⁻¹.³⁻⁵ The broad band between 3000 and 3700 cm⁻¹ is assigned to the stretching vibration of the O-H bonds and $\nu(\text{OH})$ species.⁵ A sharp band at 682 cm⁻¹ observed only for CuO-HS confirms the infrared active mode of CuO. This band is of much lower intensity for CuO-IS to be highlighted. Further, the analysis also showed peaks due to the use of oleic acid. Two bands at 2924 and 2854 cm⁻¹ are attributed to symmetric and asymmetric stretching of the CH₂ group and terminal groups -CH₃ and =CH corresponding to oleic acid.⁶ The broad bands between 1200 and 1700 cm⁻¹ are due to the physisorbed H₂O and CO₂ molecules on the surface of the sample.⁵ More specific absorption bands at 1623 and 1450 cm⁻¹ confirm the presence of carboxylate coordination and metallic asymmetric COO⁻ stretching, whereas the band at 1123 cm⁻¹ corresponds to symmetric COO⁻ stretching in the nanomaterial.⁶

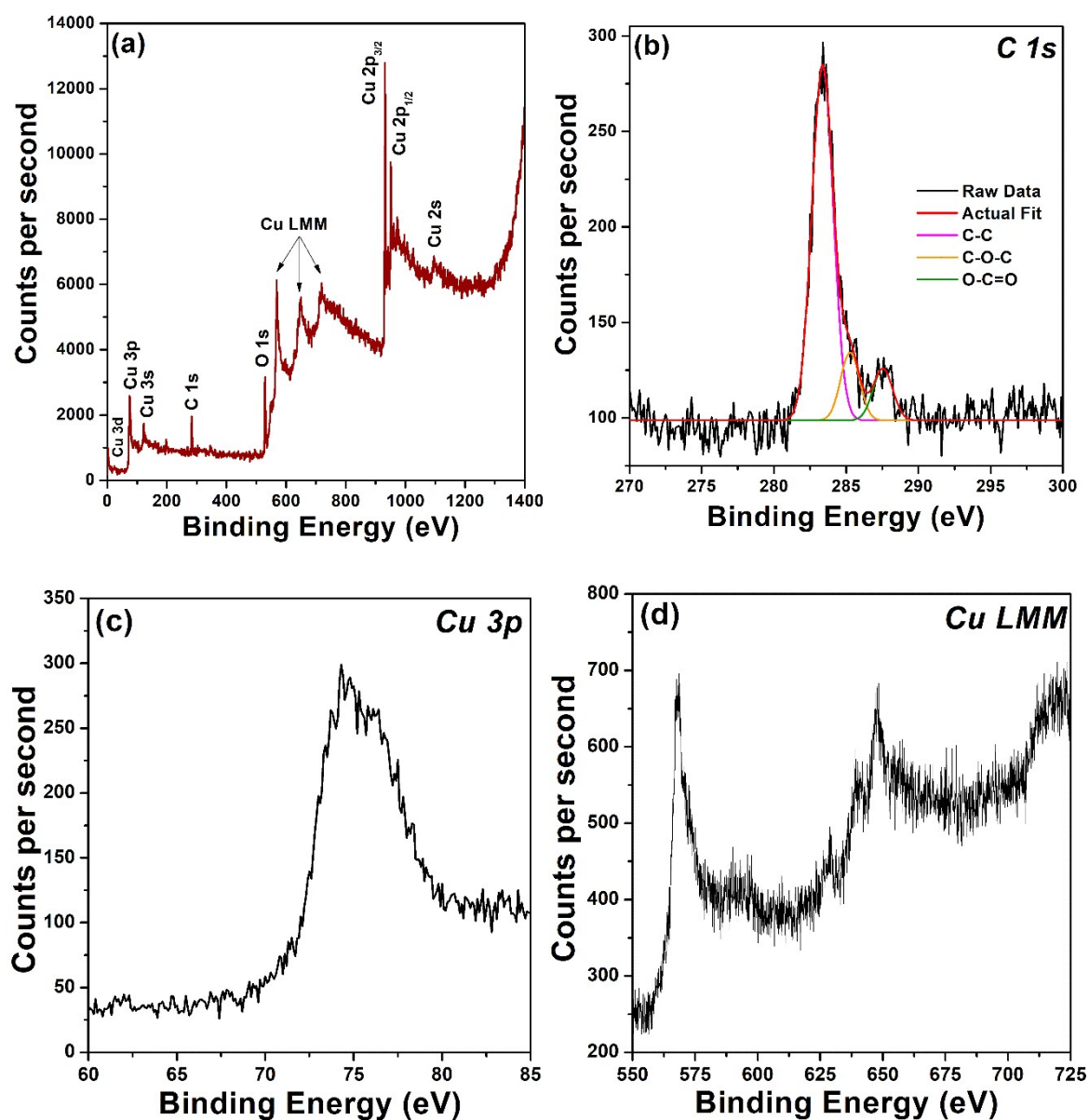


Fig. S4 X-ray photoelectron spectroscopy showing (a) wide scan survey spectrum and core levels of (b) C 1s, (c) Cu 3p, and (d) Cu LMM for CuO-HS sample.

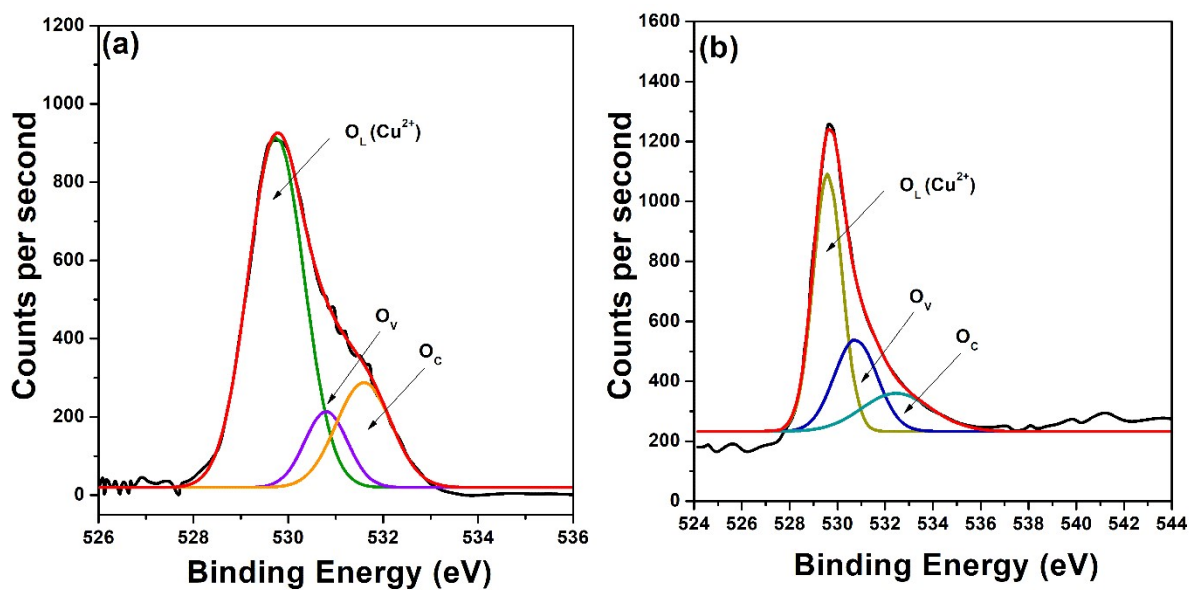


Fig. S5 X-ray photoelectron spectroscopy data illustrating core level O 1s for **(a)** CuO-NF and **(b)** CuO-MS.

Table S2 XPS O 1s spectra curve fitting parameters.

Parameters	Oxygen Species	CuO-MS	CuO-HS	CuO-NF	CuO-IS
Binding Energy (eV)	O_L	529.59	529.80	529.71	529.66
Percentage (%)		53.27	43.75	68.46	97.35
Binding Energy (eV)	O_V	530.76	530.91	530.82	-
Percentage (%)		28.01	25.60	11.33	-
Binding Energy (eV)	O_C	532.45	532.50	531.96	-
Percentage (%)		18.27	30.64	20.24	-

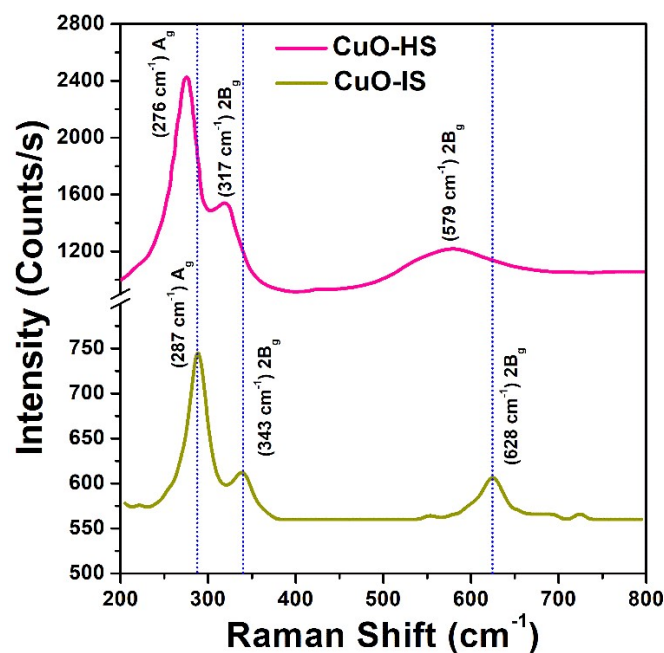


Fig. S6 Raman spectra were recorded at room temperature for CuO samples with irregular sheets/structures (CuO-IS) and hexagonal sheets (CuO-HS).

Lattice dynamics, electronic and vibrational properties of CuO nanoarchitectures were evaluated using Raman spectroscopy and comparative data is illustrated in **Fig. S6**. Confocal micro-Raman spectroscopy was performed using a Horiba Jobin-Yvon LabRam HR spectrometer with a laser source of 17 mW internal Helium-Neon at 632.8 nm. Briefly, in a unit cell of monoclinic structured tenorite CuO, out of six Cu–O bonds present, four are in the unit cell, and the other two are part of the primitive cell. A single Cu atom lies at the center of an oxygen parallelogram and every O atom shows a distorted tetrahedral copper coordination.⁷ CuO has twelve phonon branches, out of which three acoustic modes are of $A_u + 2B_u$ symmetry. From the remaining nine optical modes, three are Raman active ($A_g + 2B_g$), while the other six are infrared active ($3A_u + 3B_u$).⁸ For the CuO-IS sample, peaks at 287 cm^{-1} , 343 cm^{-1} , and 628 cm^{-1} are assigned to A_g and B_g modes, respectively. These wavenumber values are slightly lower than the values reported in the literature and could be due to grain size effects.⁹⁻¹⁰ In the case of the CuO-HS sample, peaks assigned to A_g and B_g modes shifted to lower wavenumber. The observed redshift and broadening of the peak at 579 cm^{-1} hints strongly at decreased grain size and the presence of crystal defects such as oxygen vacancies.¹¹

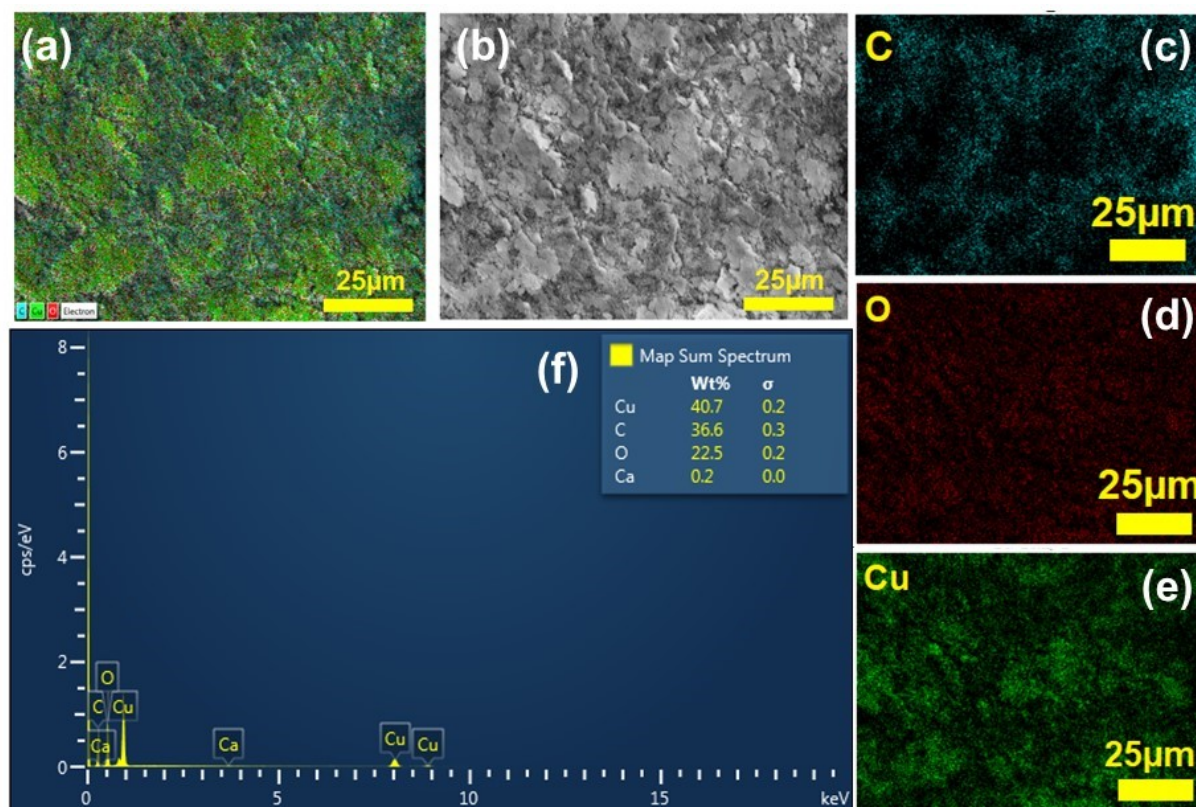


Fig. S7 Clockwise (a) EDAX layered image showing the uniform presence of copper (Cu), oxygen (O). The carbon (C) element detected is from the carbon tape used for sample preparation. (b) Electron micrograph in scanning mode recorded for CuO-NF sample depicting true area used for elemental quantification. Elemental mapping recorded for CuO-NF sample showing the consistent distribution of (c) carbon (C), (d) oxygen (O), and (e) copper (Cu) and (f) EDAX analysis.

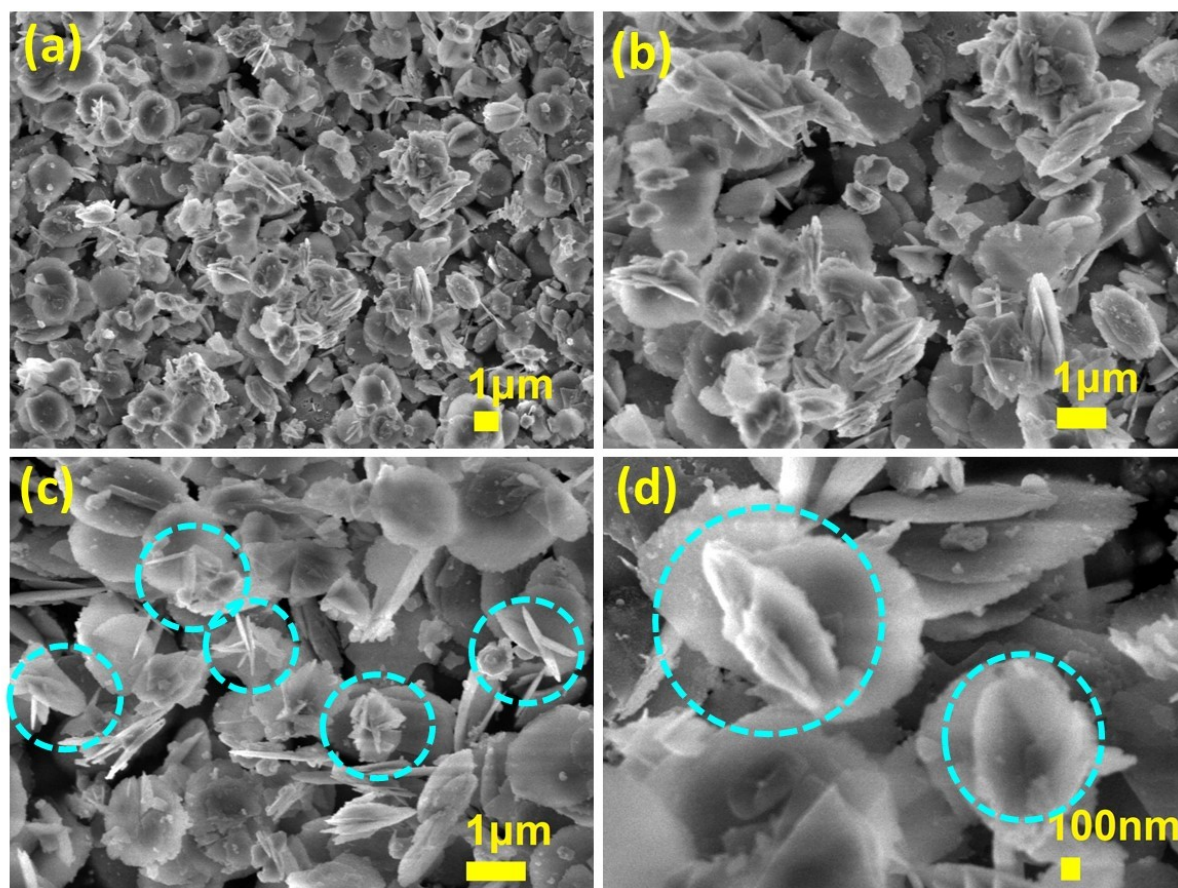


Fig. S8 (a-d) Scanning electron micrographs captured for CuO-MS. Here, the CuO-MS sample was synthesized by adding the oleic acid amount of 7.584 mL to a 50 ml hexane solution at room temperature.

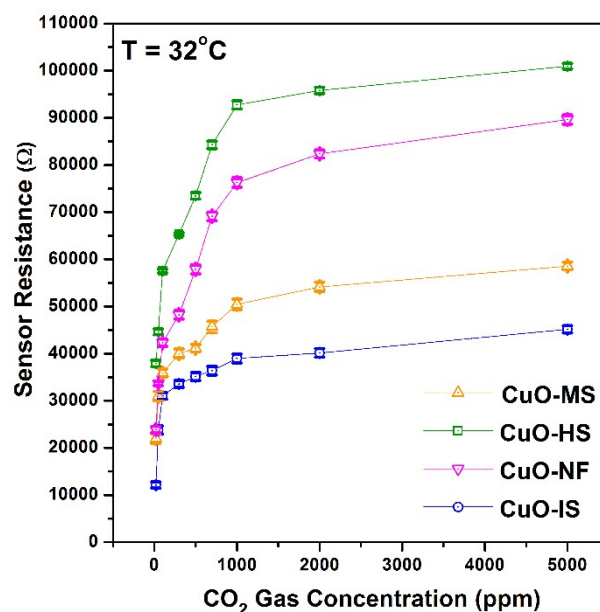


Fig. S9 Sensor characteristics of various CuO nanostructures depicting calibration curves fitted with error bars using standard deviation ($\pm\sigma$) measured for 3 dynamic transient runs.

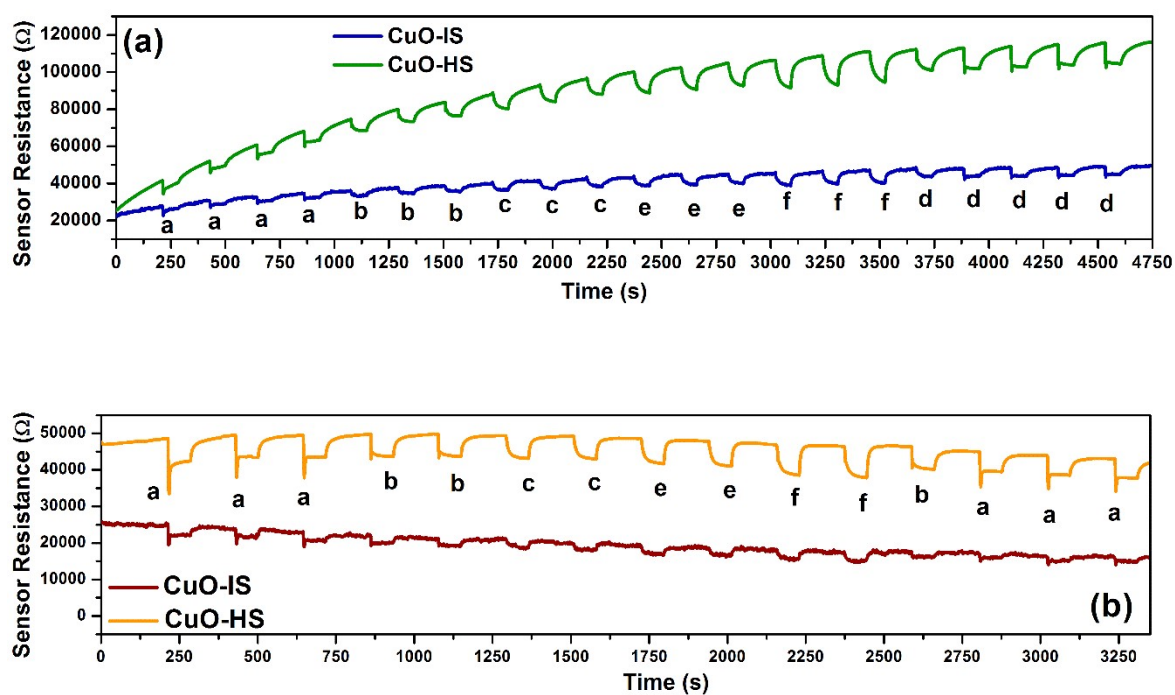


Fig. S10 Raw data illustrating dynamic transients at room temperature in (a) dry air and (b) humid condition.

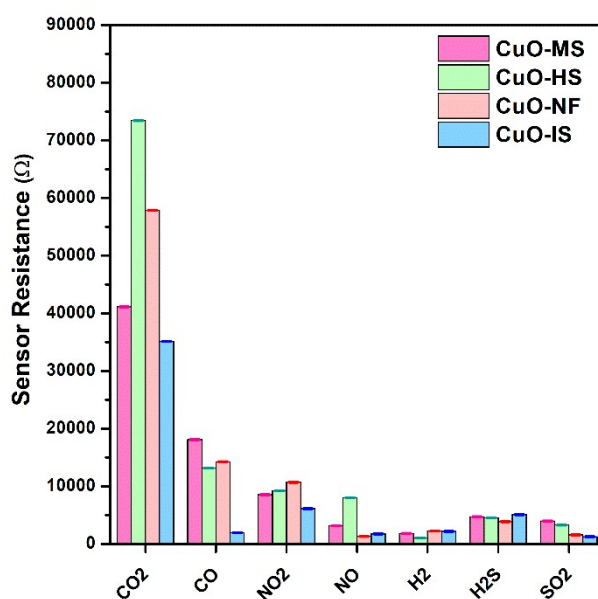


Fig. S11.a Selectivity, where the gas concentrations are, CO₂ (500 ppm), CO (50 ppm), NO₂ (500 ppm), NO (500 ppm), H₂ (250 ppm), H₂S (100 ppm), and SO₂ (50 ppm). The error bars are fitted with standard deviation ($\pm\sigma$) measured for 3 consecutive test cycles in a dry condition at 32°C.

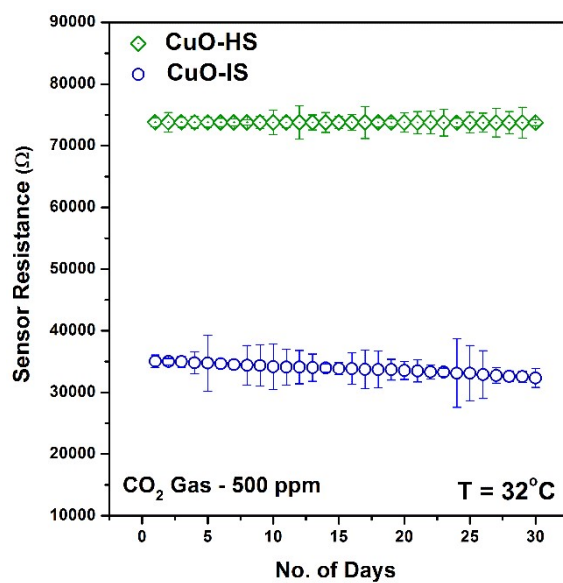


Fig. S11.b Long term repeatability data were collected at room temperature in dry condition with error bars fitted based on 17,000 datapoints tests carried out per day.

A2: Limit of Detection (LoD)

The theoretical limit of detection (LoD) is estimated using the following equation,¹² and the values are presented in Table S5,

$$LoD \text{ (ppm)} = 3 \times \frac{\text{Standard Deviation}}{\text{Slope}}$$

The slope is calculated from calibration curves from the linear portion fitted that is, 20-1,000 ppm (See ESI, **Fig. S9**). The standard deviation is taken for the set of sensor resistances in air based on 17,000 data points measured from the baseline of the dynamic response curve (**Fig. 6b**). The test was carried out continuously for 30 days, giving us long term repeatability data (See ESI, **Fig. S11.a**). Gas concentration ranged from 20 to 5,000 ppm and hence the experimental LoD is considered as 20 ppm.

Table S3 Summary of calculated values for evaluation of limit of detection (LoD)

Material	Standard Deviation (%)	Slope (%.ppm⁻¹)	Theoretical LoD (ppm)	Experimental LoD (ppm)
CuO-IS	2.384	60.6223×10 ⁻²	11.8	20
CuO-HS	0.3428	23.91646×10 ⁻²	4.3	20

A3: Natural Sunlight Induced Degradation of Dyes

CuO nanoarchitectures mediated dye mineralization in presence of natural sunlight involved the selection of three commonly found pollutants, namely bromocresol purple (BP), eosin yellow (EY), and malachite green (MG) and closely monitoring its degradation. The process depicted here can be imagined as wastewater treatment contaminated by several such dyes expelled from textile mills, manufacturing industries, and food processing units. Dye degradation observed for BP, EY, and MG in absence of photocatalysts was 1.31, 0.8, and 0.45% (**Fig. S12**). Dye degradation in minimal diminution observed without nanocatalysts dismisses the probability of the photocatalysis mechanism. In presence of natural sunlight, CuO-HS and CuO-IS could not degrade BP (**Fig. S13.a**). We anticipate that an extension of irradiation time could facilitate its degradation. Interestingly, the photocatalysts were able to disintegrate EY and MG in 3 h (**Fig. S14.a-S15.a**). In comparison to CuO-IS, the CuO-HS sample displayed remarkable degradation constant of 98 and 99% for EY and MG, respectively at the end of 3 h. Additional quantitative insights into the degradation process were carried out through kinetic analysis (**Fig. S13.b**, **Fig. S14.b**, and **Fig. S15.b**). In their role as photocatalysts, the CuO nanoarchitectures followed first-order degradation kinetics, wherein a decrease in dye concentration (C/C_0) versus irradiation time was observed. Here, C_0 and C are original dye concentrations after equilibration and final concentration at reaction time (t), respectively. The $\ln(C_0/C)$ plot of dye degradation versus light exposure time (t) showed linear replication of dye concentration following a Langmuir-Hinshelwood model for photocatalysis (**Fig. S13.c**, **Fig. S14.c**, and **Fig. S15.c**). The rate constant for first-order reaction (κ) was evaluated from the slope of the plot illustrating $\ln(C_0/C)$ as a function of irradiation time. Comprehensive documentation has confirmed that metal oxide semiconductor photocatalysts are highly susceptible to photocorrosion during the dye degradation process, thereby highlighting the importance of verifying the photostability of as-synthesized nanomaterials. Photostability and resistance to photocorrosion of CuO-HS and CuO-IS towards BP, EY, and MG were assessed for four consecutive cycles under comparable conditions (**Fig. S13.d**, **Fig. S14.d**, and **Fig. S15.d**). The average photocatalytic efficiency of CuO-HS tested successively for four runs of EY and MG degradation in presence of natural sunlight for 3 h was found to be 98.1% and 98.8% with a standard deviation of ± 0.365 and ± 0.218 , respectively. The steady loss in the photocatalytic efficiency ($\sim 2\%$) is attributed to the loss of nanomaterial during post-reaction harvesting and re-use over four runs. The dye decolorization sequence during the photocatalysis process reveals the decrease in color intensity as a function of irradiation time (**Fig. S16**).

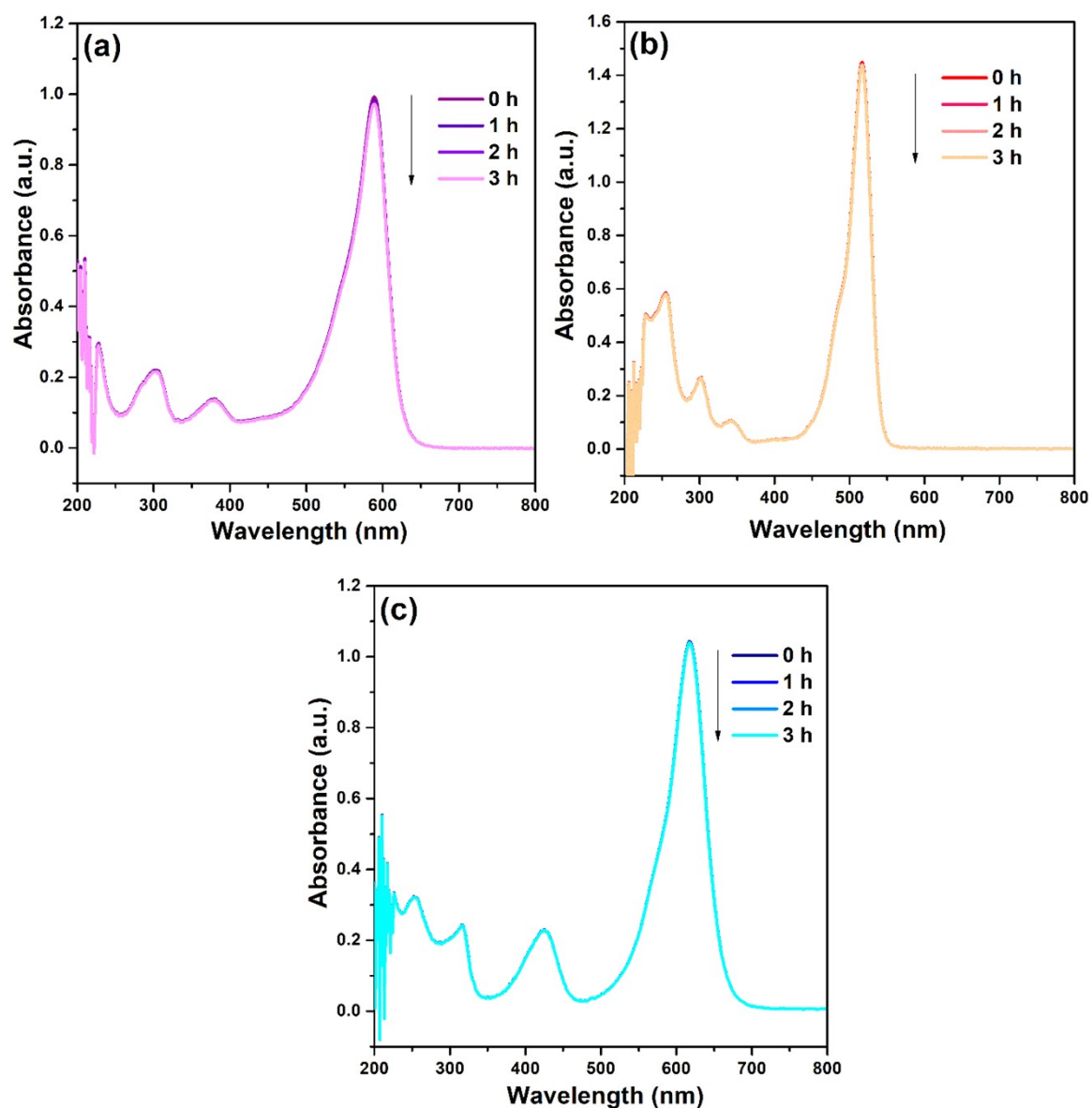


Fig. S12 UV-Vis absorbance spectra depicting the concentration change for dye solution under natural sunlight irradiation as a function of time with degradation profile in absence of nanocatalysts for **(a)** bromocresol purple (BP), **(b)** eosin yellow (EY), and **(c)** malachite green (MG).

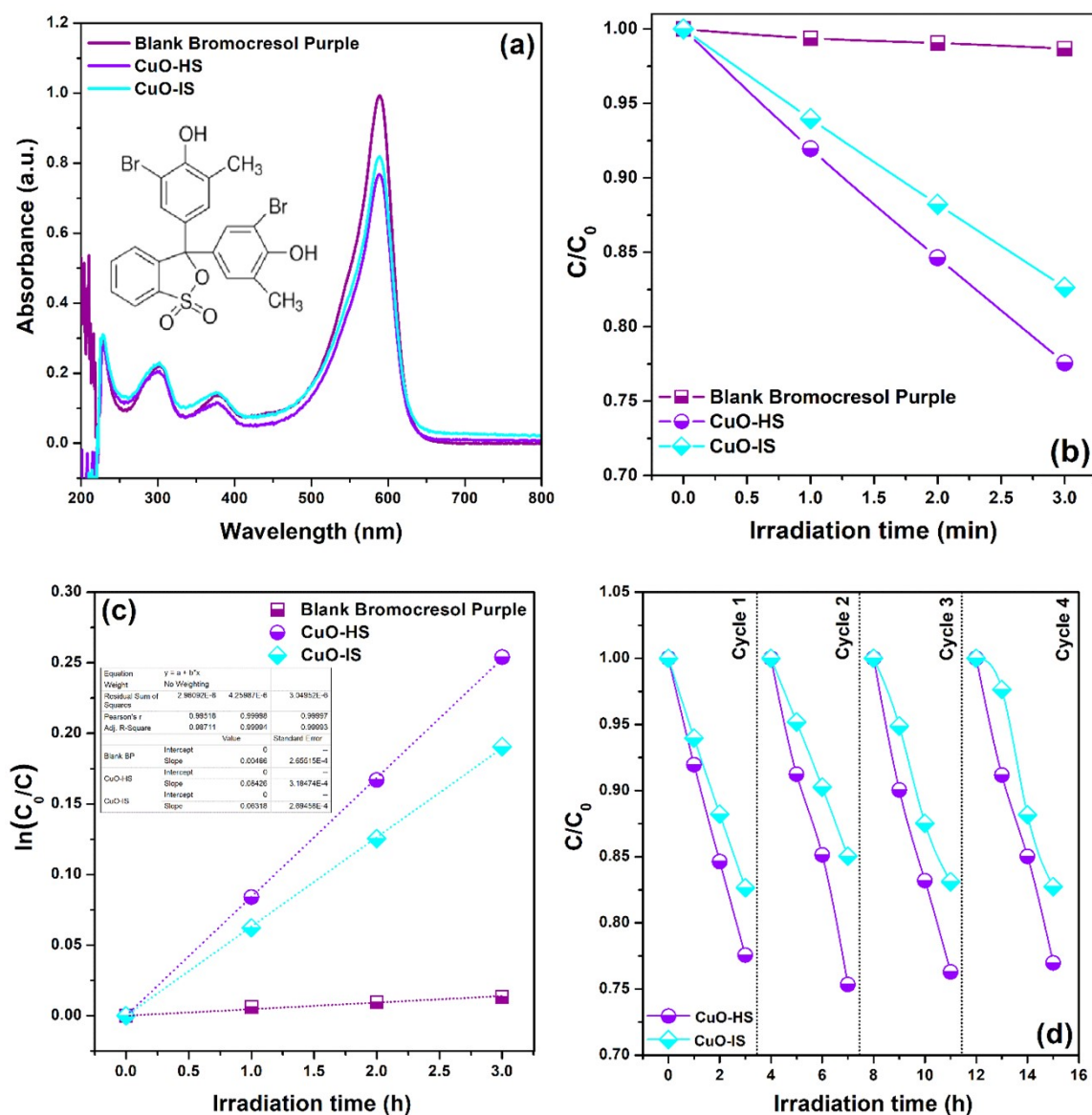


Fig. S13 UV-Vis absorbance spectra depicting the concentration change for bromocresol purple (BP) solution under natural sunlight irradiation as a function of time, where **(a)** degradation profile in presence of nanocatalysts after 3 h, **(b)** rate of photocatalytic degradation, and **(c)** kinetic plots, and **(d)** repeatability tests.

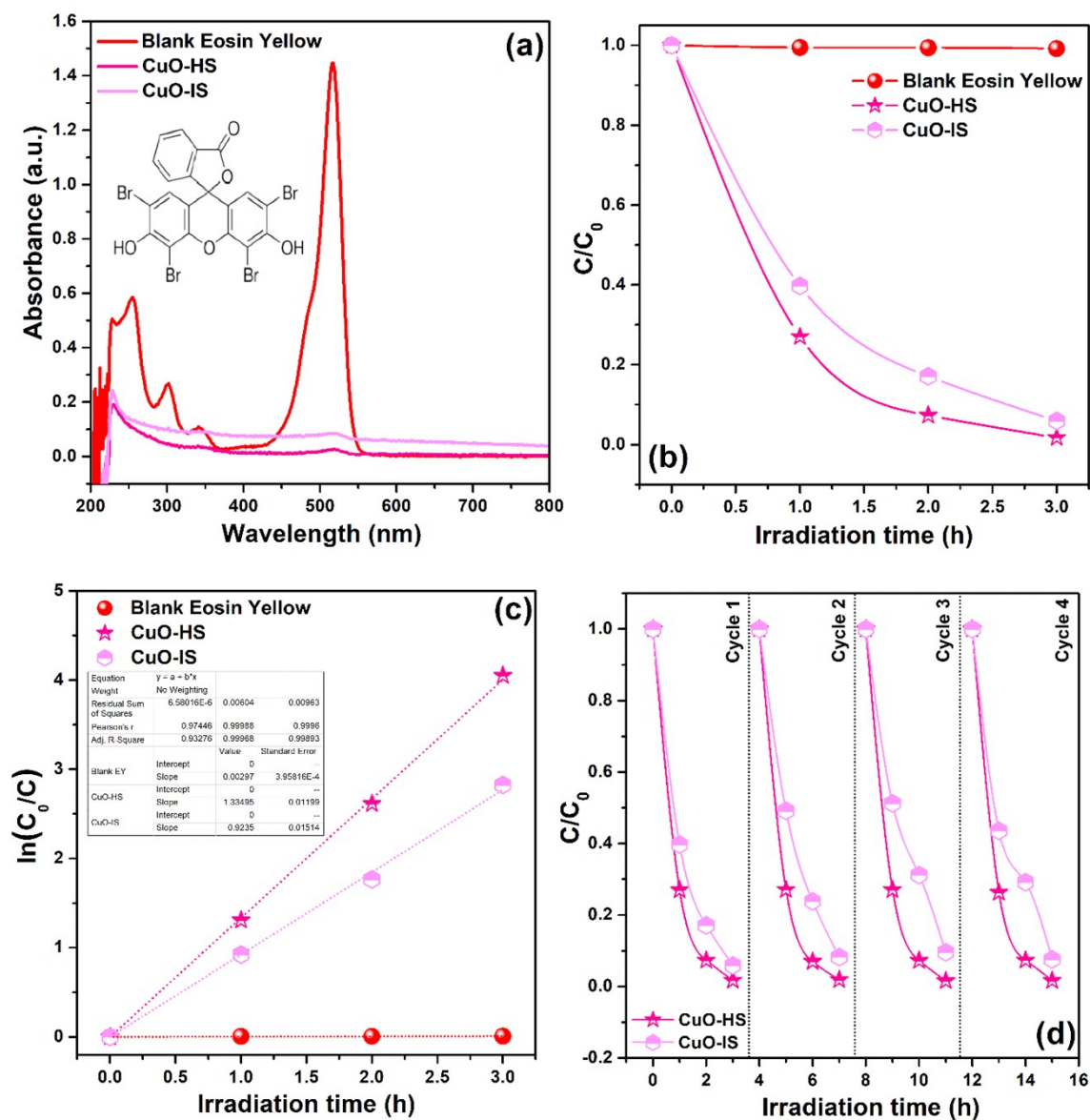


Fig. S14 UV-Vis absorbance spectra depicting the concentration change for eosin yellow (EY) under natural sunlight irradiation as a function of time, where **(a)** degradation profile in presence of nanocatalysts after 3 h, **(b)** rate of photocatalytic degradation, and **(c)** kinetic plots and **(d)** repeatability tests.

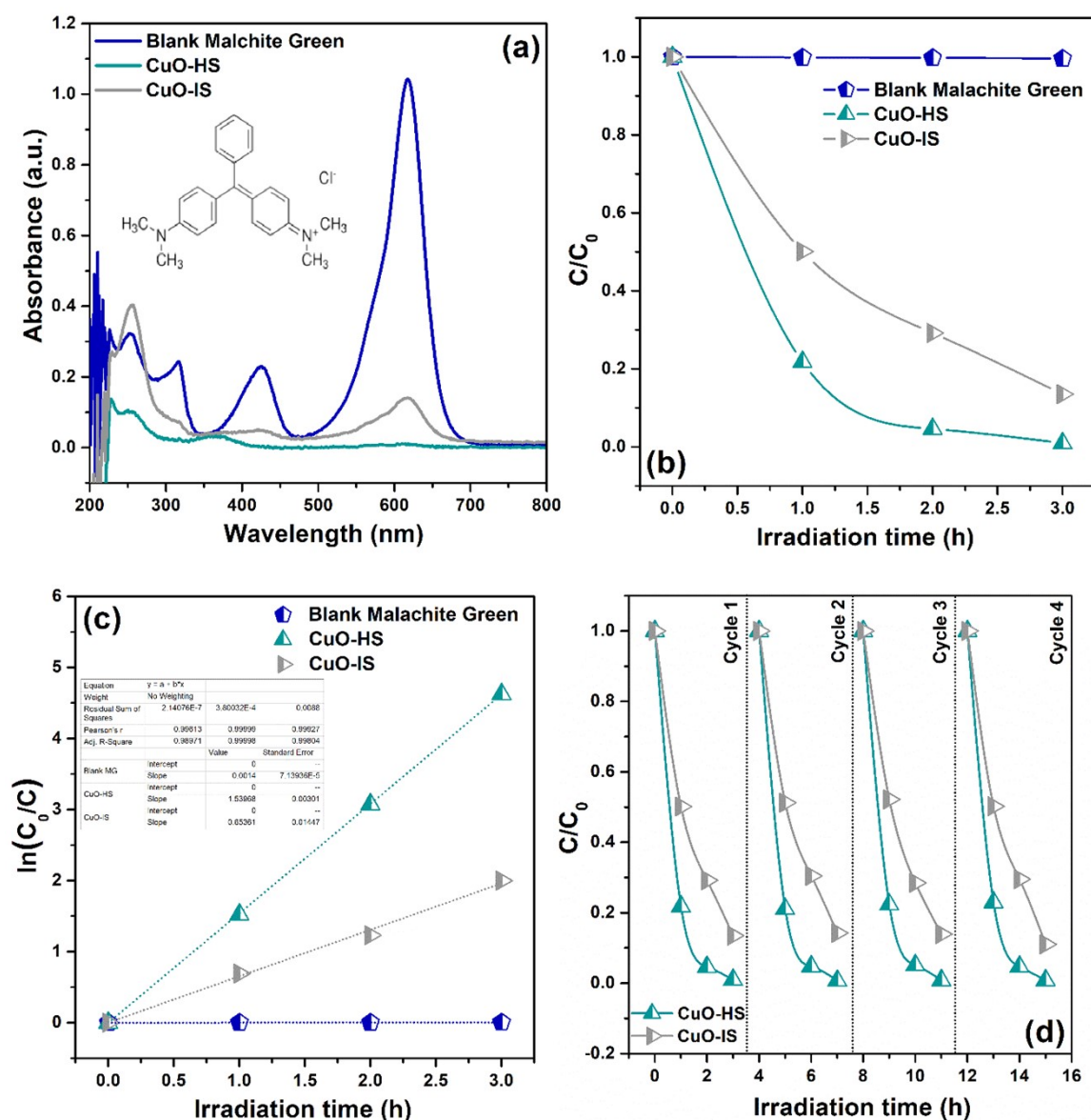


Fig. S15 UV-Vis absorbance spectra depicting the concentration change for malachite green (MG) under natural sunlight irradiation as a function of time, where **(a)** degradation profile in presence of nanocatalysts after 3 h, **(b)** rate of photocatalytic degradation, and **(c)** kinetic plots, and **(d)** repeatability tests.

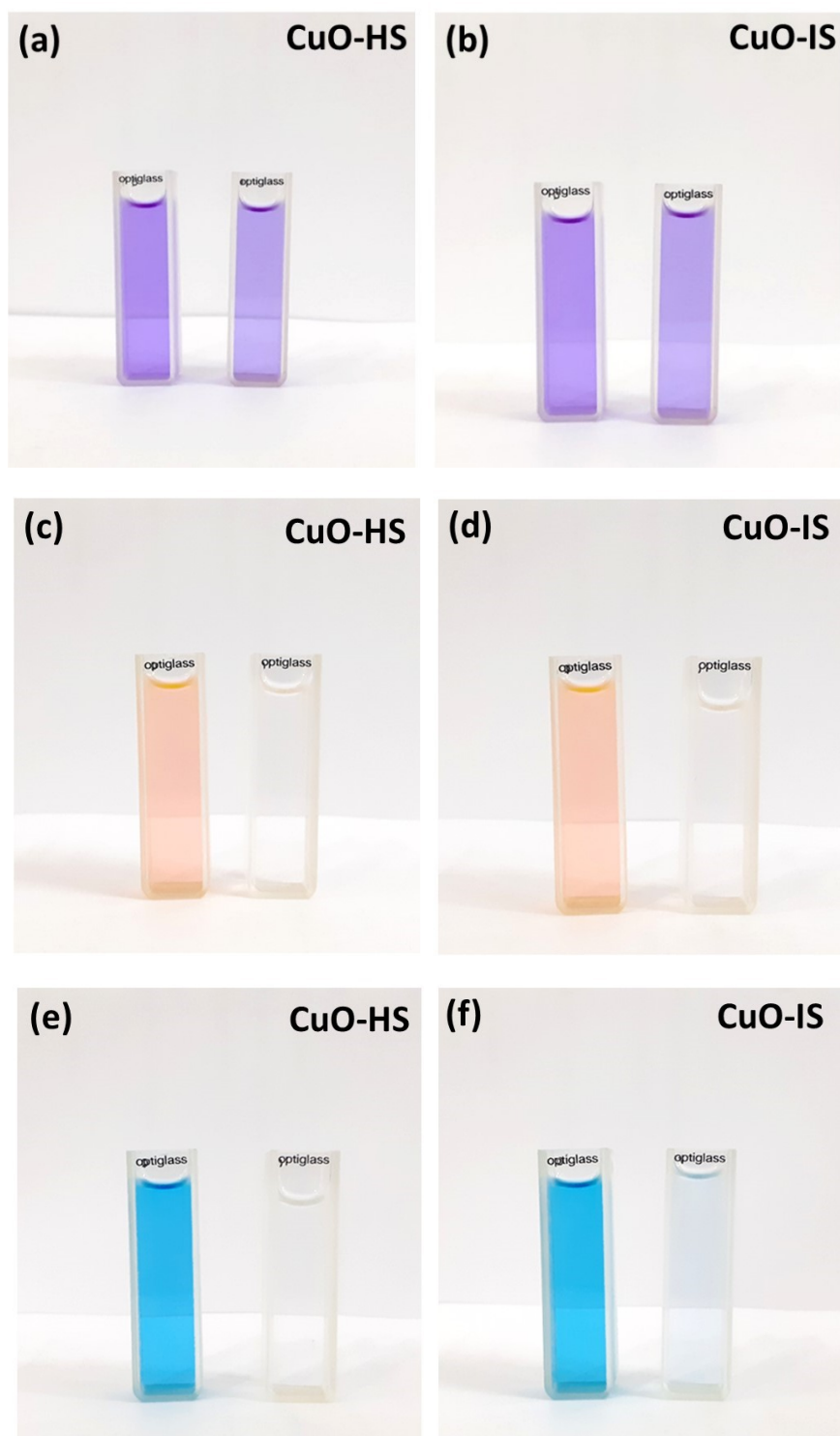


Fig. S16 Digital photographs showing decolorization sequence at the start and after 3 h exposure to natural sunlight for **(a-b)** bromocresol purple, **(c-d)** eosin yellow, and **(e-f)** malachite green.

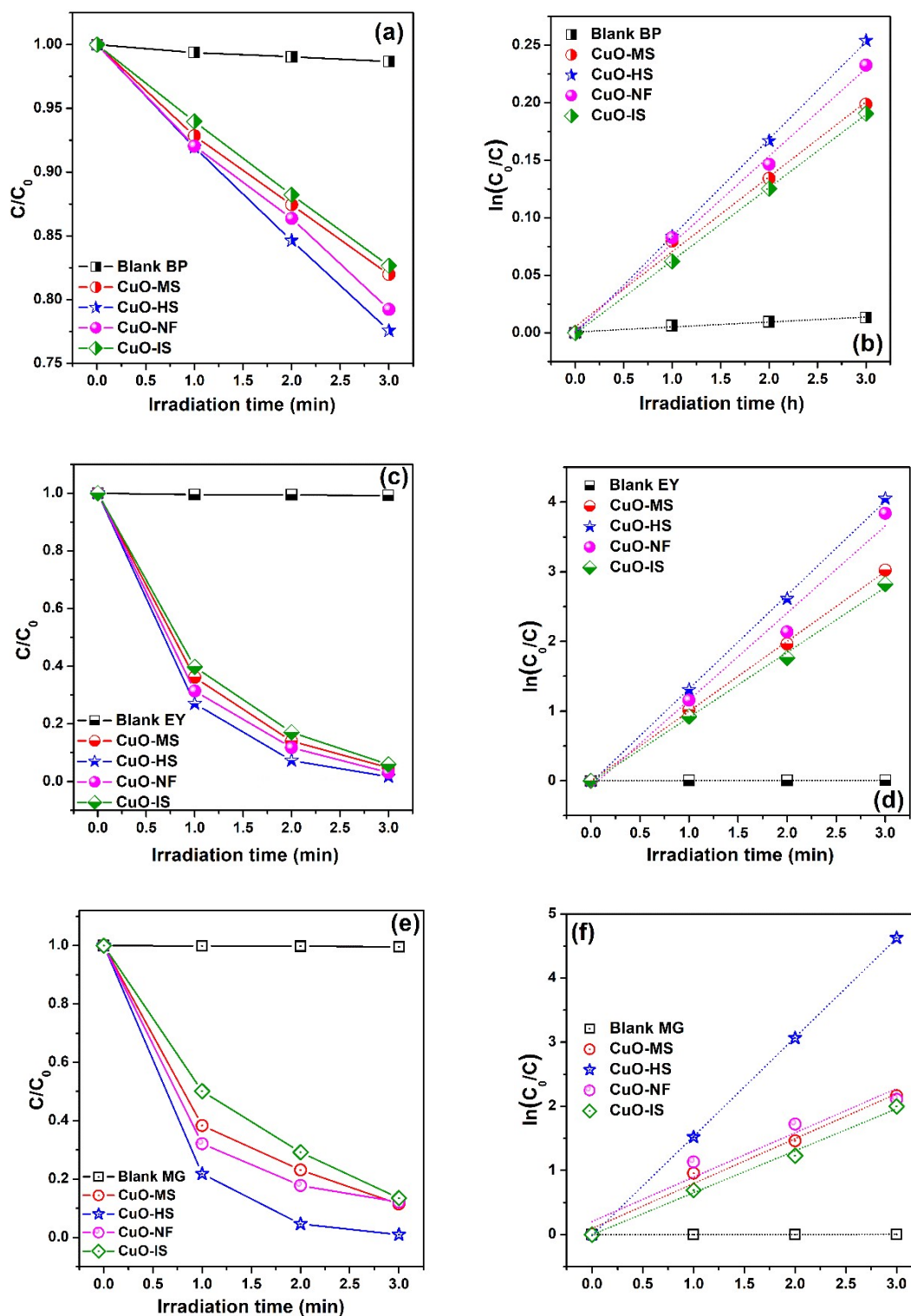


Fig. S17 UV-Vis absorbance spectra depicting the concentration change under natural sunlight irradiation as a function of time for the rate of photocatalytic degradation and kinetic plots for organic dyes, namely **(a-b)** bromocresol purple, **(c-d)** eosin yellow, and **(e-f)** malachite green.

Solar illuminated catalytic degradation induced by CuO nanostructures with respect to three randomly selected organic dyes were evaluated from the position of the conduction (CB) and valence band (VB) associated band gap energy (E_g). It is a widely accepted fact that the excitation of an electron from VB to CB of semiconductor nanocatalyst takes place based on certain conditions.¹³⁻¹⁴ And one of the important conditions is if the photon energy is equal to or greater than the bandgap (E_g). Assuming the conditions are met, the photon energy facilitates excitation of the electron (e^-) from VB to the CB, leaving behind the hole (h^+) in VB and the efficiency with which these two charge carriers are prevented from reunification governs, in general, the photocatalysis. The solid/hollow hexagonal particles (CuO-HS) synthesized in the present study showed a bandgap of 1.72 eV, which confirms its suitability for dye degradation under natural sunlight (**Fig. S18**). Upon excitation under suitable wavelengths, electron (e^-)-hole (h^+) pairs are generated. The photogenerated electrons have sufficient potential to reduce the molecular oxygen (O_2) to yield the superoxide anion ($O_2^{\bullet-}$). These $O_2^{\bullet-}$ radicals then undergo a series of reductive reactions to produce H_2O_2 and $OH^{\bullet}$ radicals. These $OH^{\bullet}$ radicals then participate in the photocatalysis of organic dyes by oxidizing them first followed by complete degradation, subsequently producing CO_2 and H_2O as end products. Oxygen vacancies present act as traps, thus lowering the charge recombination rate. Chemical reactions involved are as below:

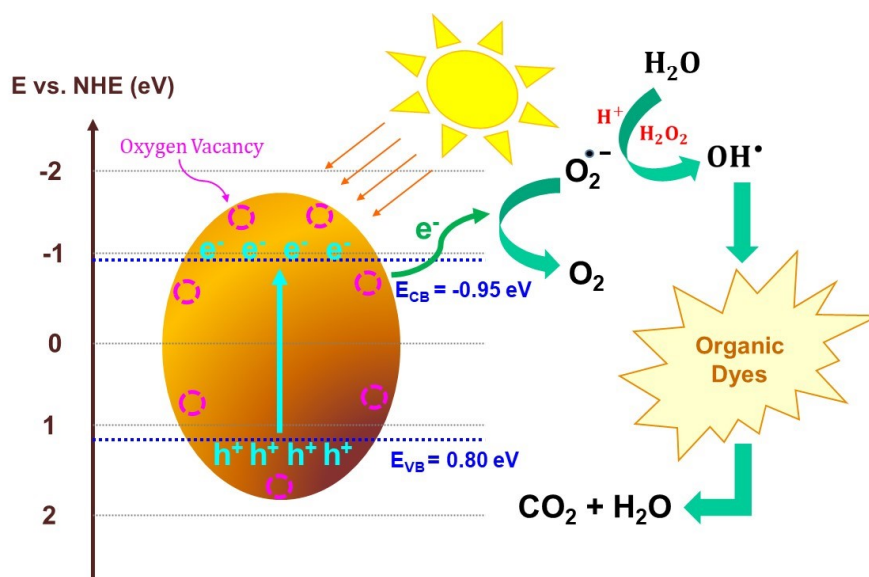
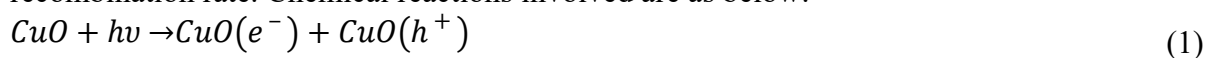


Fig. S18 Proposed charge transfer mechanism for organic dyes (bromocresol purple, eosin yellow, and malachite green) degradation in natural sunlight.

Table S4 Photocatalytic reduction of CO₂ gas to methanol in presence of artificial solar illumination under ambient conditions using various CuO nanoarchitectures.

Entry	Nanocatalyst	Reaction Precursor	Catalyst/mg	Light	Time (h)	Methanol Yield (μmol/g of catalyst)
1	Blank 1	CO ₂	None	Yes	3	None
2	Blank 2	CO ₂	25	None	3	None
3	Blank 3	N ₂	25	Yes	3	None
4	CuO-IS	CO ₂	25	Yes	3	16
5	CuO-NF	CO ₂	25	Yes	3	24
6	CuO-MS	CO ₂	25	Yes	3	53
7	CuO-HS	CO ₂	25	None	3	None
8	CuO-HS	N ₂	25	Yes	3	None
9	CuO-HS	CO ₂	25	Yes	3	19

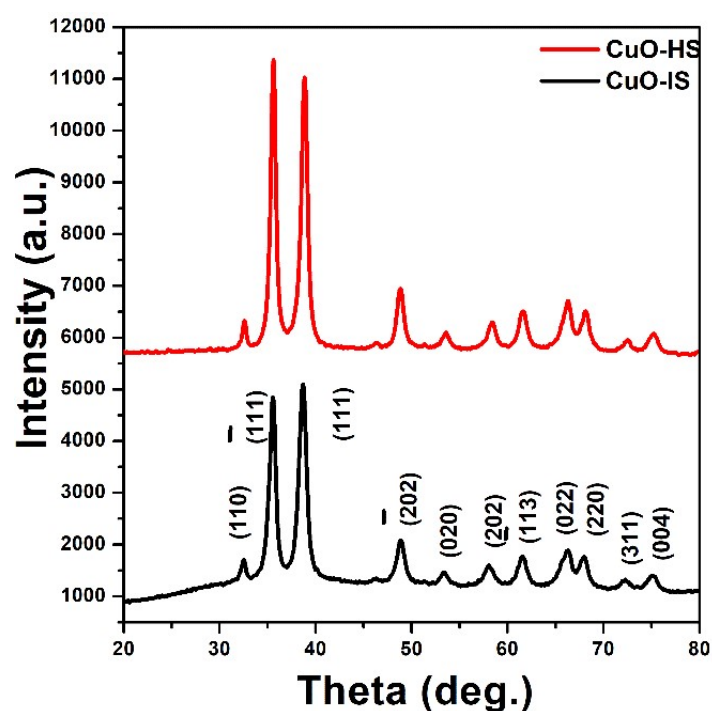


Fig. S19 X-ray diffractograms were recorded after 4 successive CO₂ photoconversion cycles in presence of artificial solar irradiation for CuO nanocatalysts.

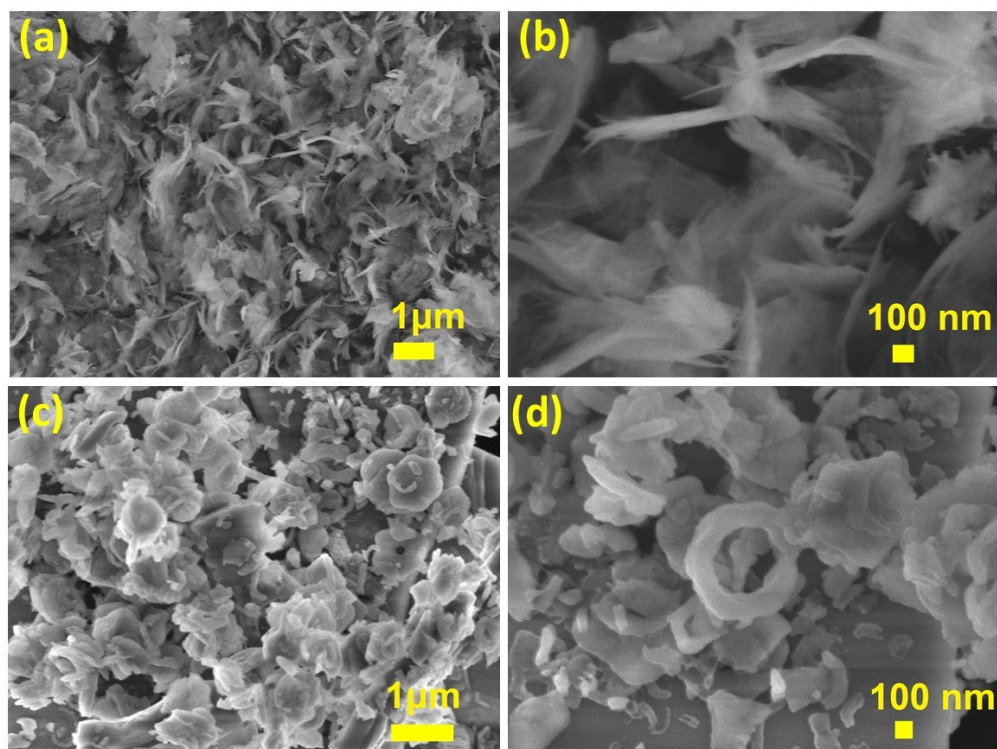


Fig. S20 Scanning electron micrographs captured after 4 consecutive CO₂ photoreduction runs in presence of artificial solar irradiation for **(a-b)** CuO-IS and **(c-d)** CuO-HS samples.

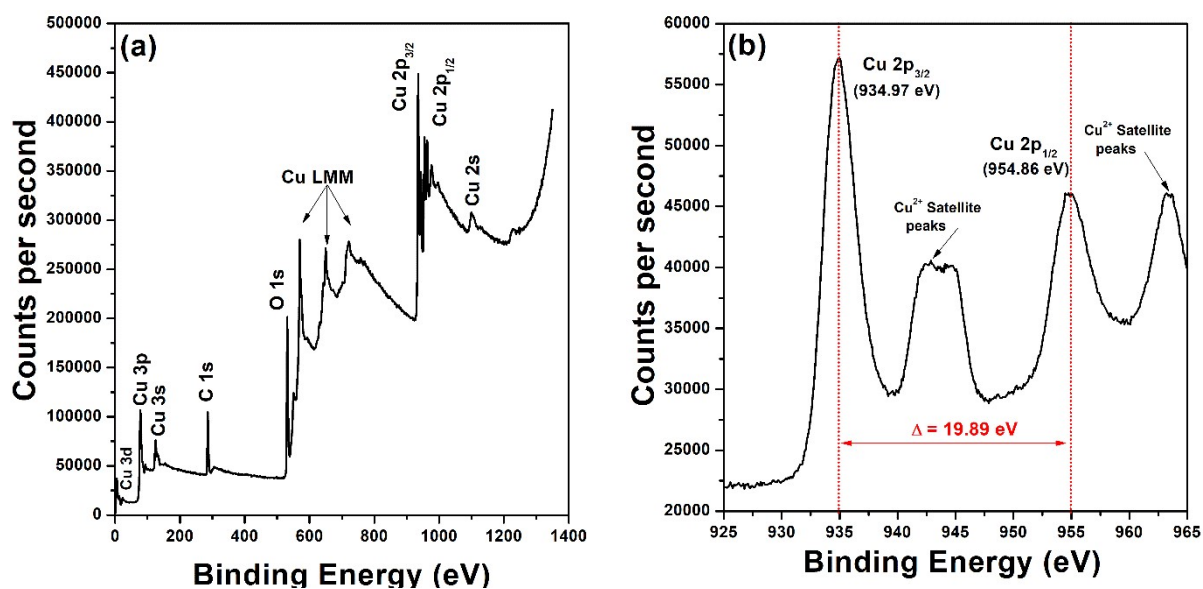


Fig. S21 X-ray photoelectron spectroscopy showing **(a)** wide scan survey spectrum and core levels of **(b)** Cu 2 p for CuO-HS sample after 4 consecutive CO₂ photoreduction run in presence of artificial solar irradiation.

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