

Electronic Supplementary Information

Oxygen-deficient photostable Cu₂O for enhanced visible light photocatalytic activity

Mandeep Singh^{a,†}, Deshetti Jampaiah^{a,†,*}, Ahmad E. Kandjani^b, Ylias M. Sabri^b, Enrico Della Gaspera^c, Philipp Reineck^d, Martyna Judd^e, Julien Langley^e, Nicholas Cox^e, Joel van Embden^c, Edwin L. H. Mayes^f, Brant C. Gibson^d, Suresh K. Bhargava^b, Rajesh Ramanathan^a, Vipul Bansal^{a,*}

^aIan Potter NanoBioSensing Facility, NanoBiotechnology Research Laboratory, School of Science, RMIT University, Melbourne VIC 3000, Australia

^bCenter for Advanced Materials and Industrial Chemistry, School of Science, RMIT University, Melbourne VIC 3000, Australia

^cSchool of Science, RMIT University, Melbourne VIC 3000, Australia

^dARC Centre of Excellence for Nanoscale BioPhotonics, School of Science, RMIT University, Melbourne VIC 3000, Australia

^eResearch School of Chemistry, Australian National University, Canberra VIC ACT 30002601, Australia

^fRMIT Microscopy and Microanalysis Facility, School of Science, RMIT University, Melbourne VIC 3000, Australia

[†]*Equal contributing authors*

^{*}*E-mail: vipul.bansal@rmit.edu.au; jampaiah.deshetti@rmit.edu.au*

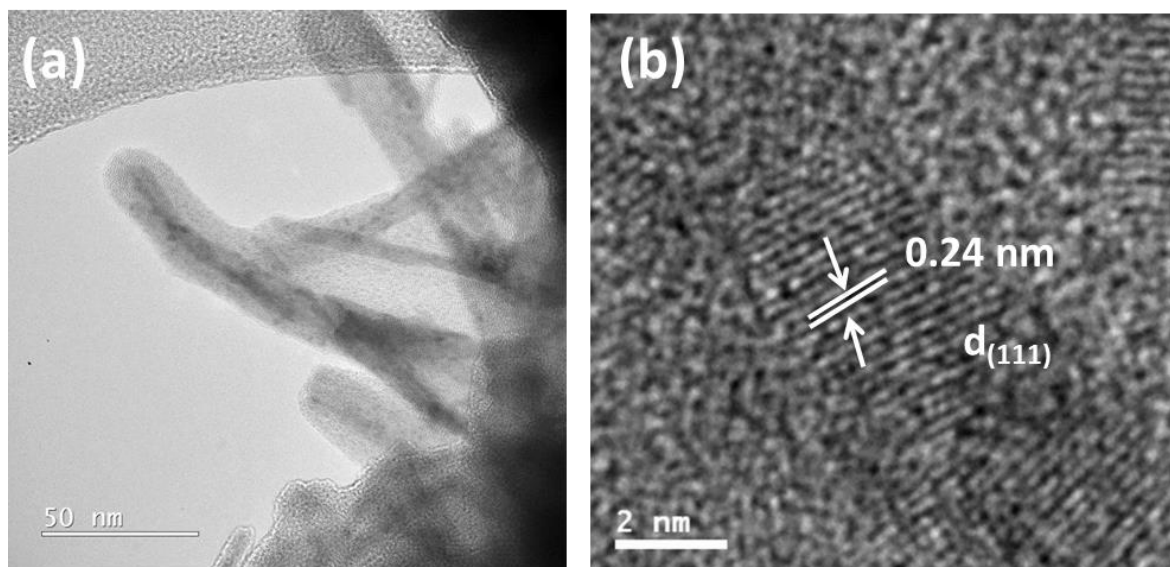


Fig. S1 HR-TEM images of Cu₂O nanotubes formed after 10 sec of reaction at room temperature.

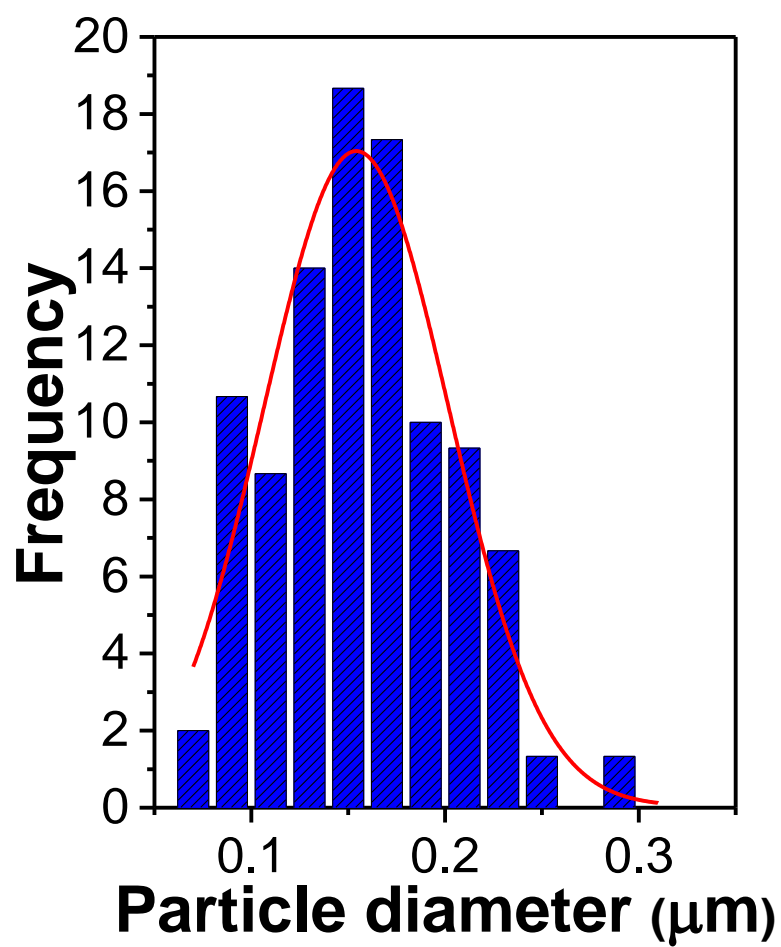


Fig. S2 Particle size distribution of as-synthesised Cu₂O nanoparticles, as determined by SEM.

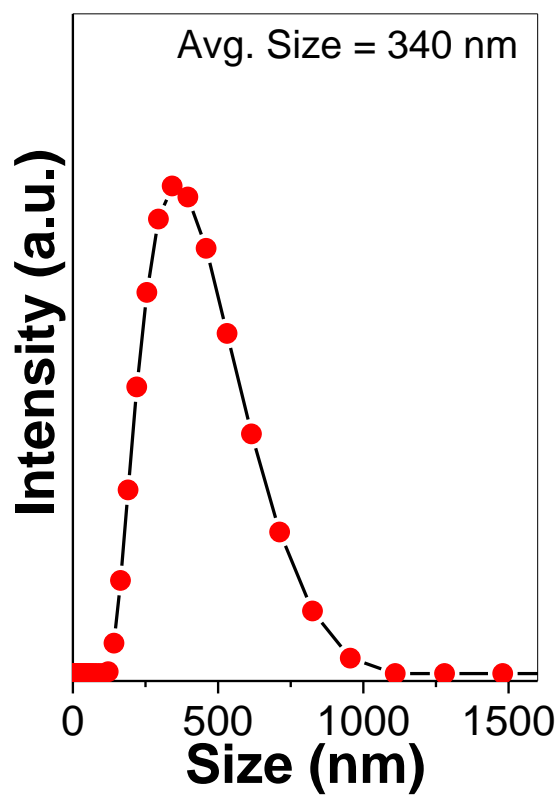


Fig. S3 Hydrodynamic diameter of as-synthesised Cu₂O nanoparticles in water, as determined by DLS.

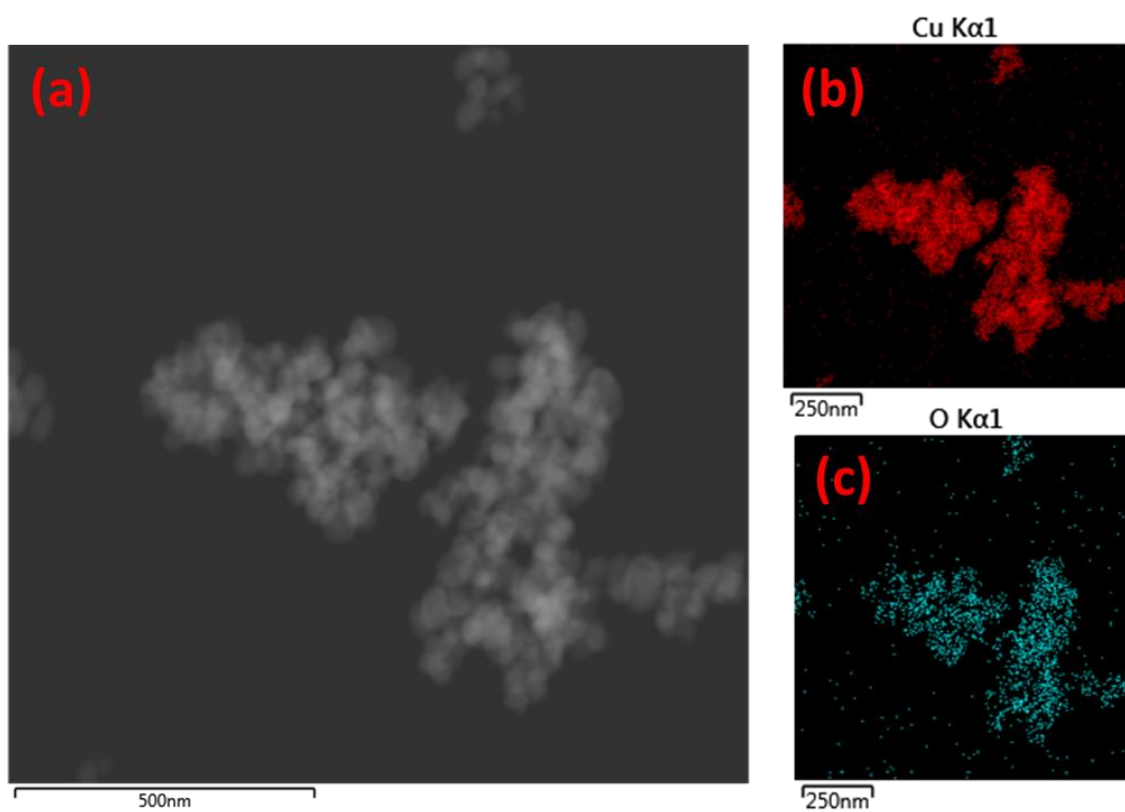


Fig. S4 EDX mapping of as-synthesised Cu_2O nanoparticles obtained on a nickel TEM grid.

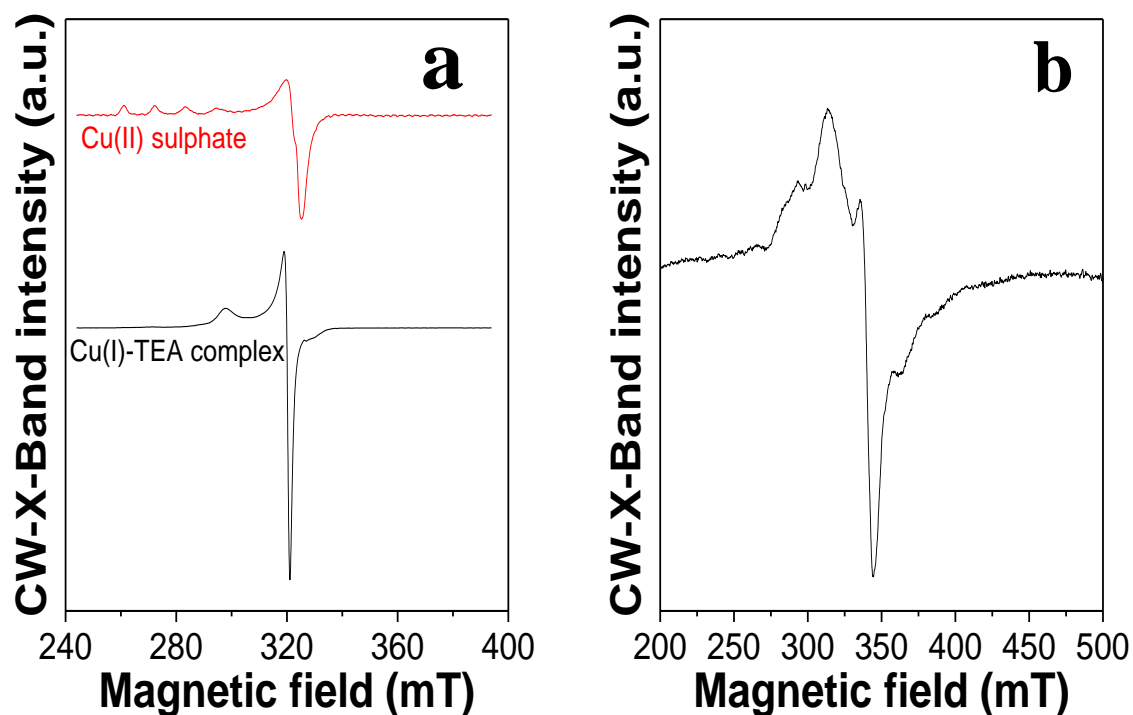


Fig. S5 (a) Low-temperature (20 K) CW-X-Band EPR spectra of the Cu(I)-TEA complex and CuSO_4 standard. The spectra have been scaled for clarity. Instrument settings: microwave power – 63 μW ; and field modulation amplitude – 2.0 mT; (b) Room-temperature CW-X-Band powder EPR spectra of oxygen-deficient Cu_2O nanoparticles. The baseline (EPR spectrum of the empty resonator) is subtracted from the obtained trace. Instrument settings: microwave power – 6.3 mW; and field modulation amplitude – 1.0 mT.

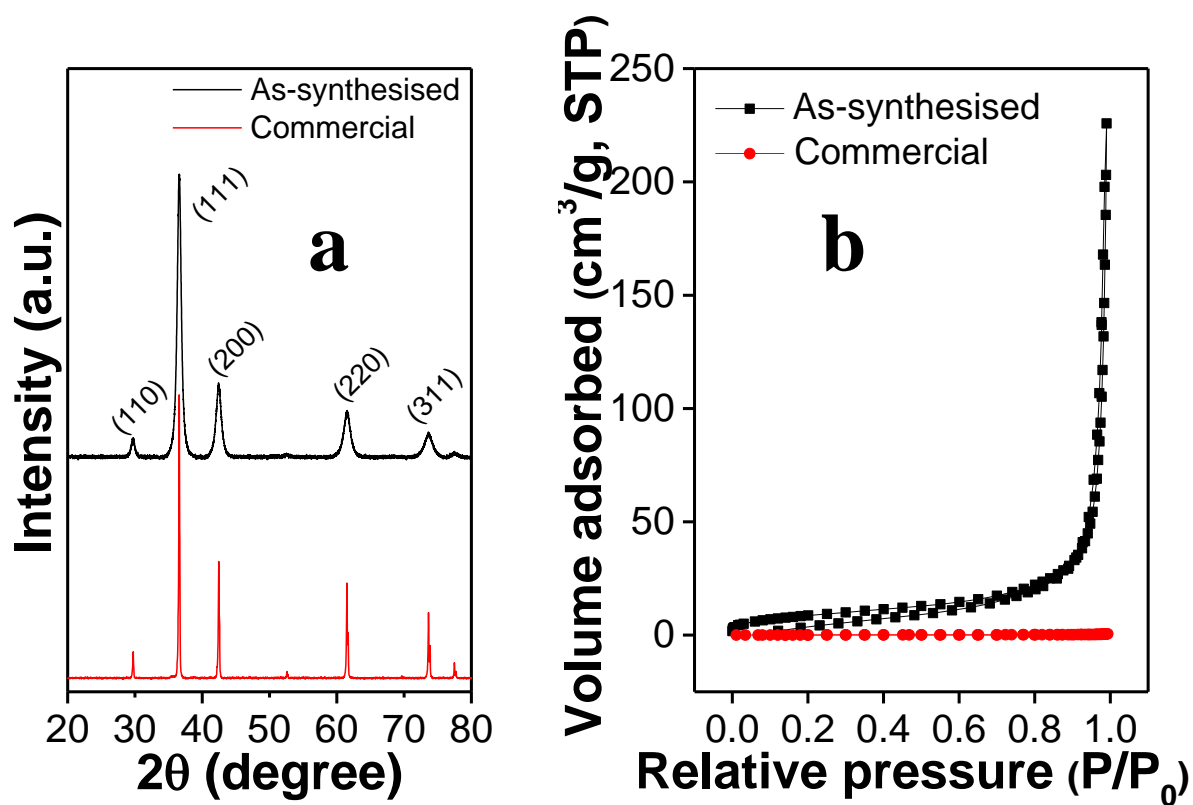


Fig. S6 (a) Powder XRD, and (b) N_2 sorption isotherms of as-synthesised Cu_2O nanoparticles and commercial Cu_2O .

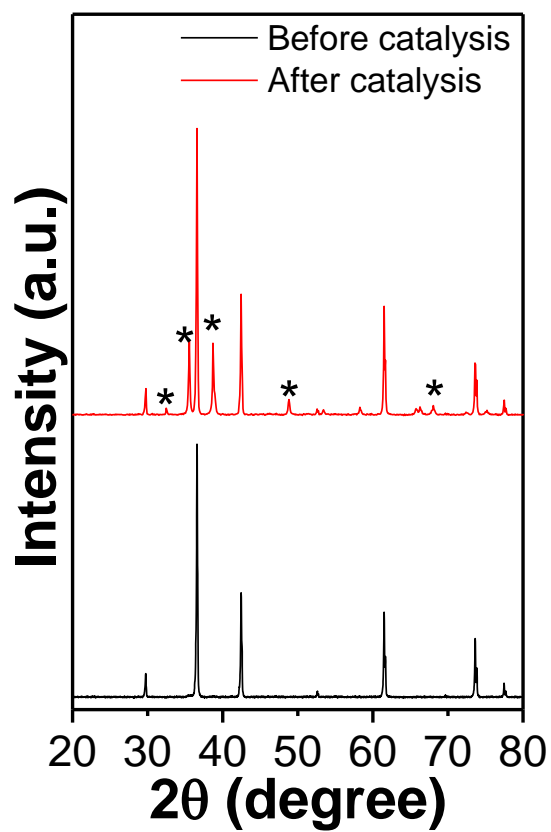


Fig. S7 XRD patterns of commercial Cu₂O nanoparticles before and after visible light-induced photooxidative degradation of methyl orange. The appearance of CuO signatures (marked with *) after photocatalysis reaction due to oxidation of commercial Cu₂O are noted.

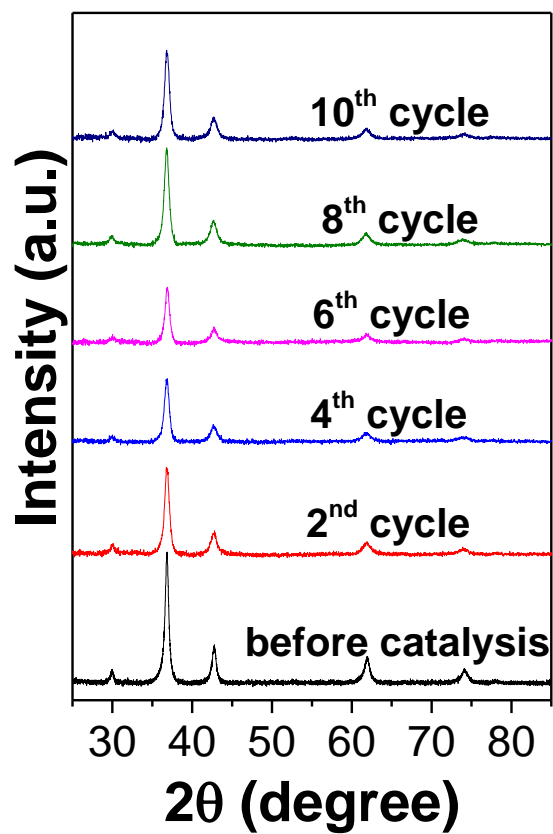


Fig. S8 XRD patterns of as-synthesised oxygen-deficient Cu₂O nanoparticles after repeated cycles of visible light-induced photo-oxidative degradation of methyl orange.

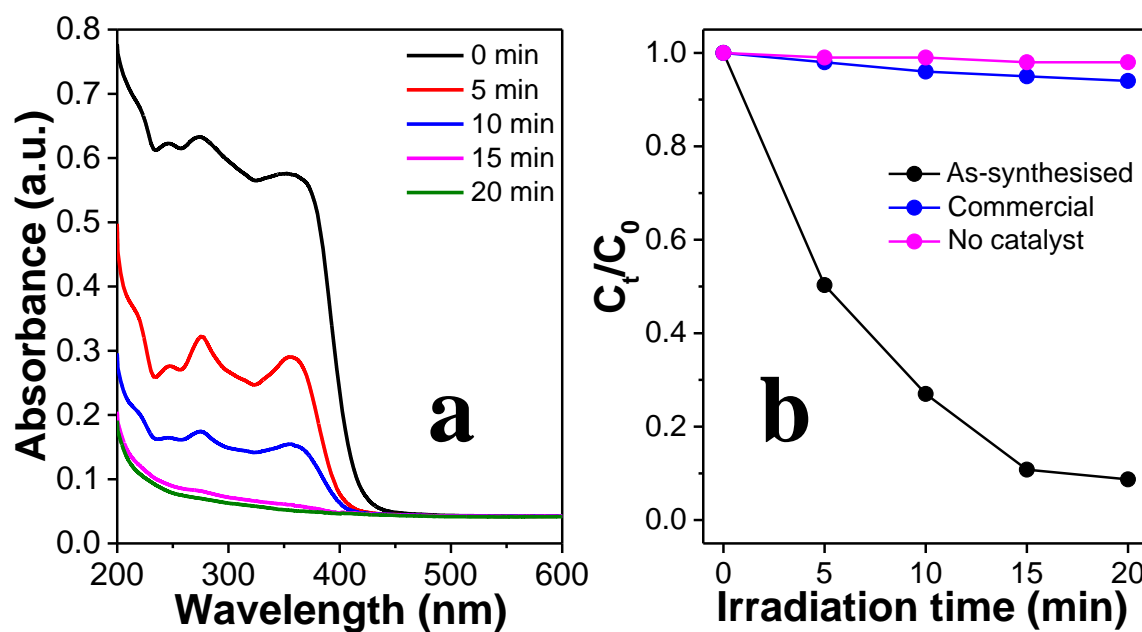


Fig. S9 (a) Photo-oxidation of tetracycline using oxygen-deficient Cu_2O , as evident from the UV-Vis absorption spectra of tetracycline after visible light photo-irradiation over 20 minutes; (b) plots of C_t/C_0 vs. irradiation time depicting the photodegradation of tetracycline in the presence of different catalysts.

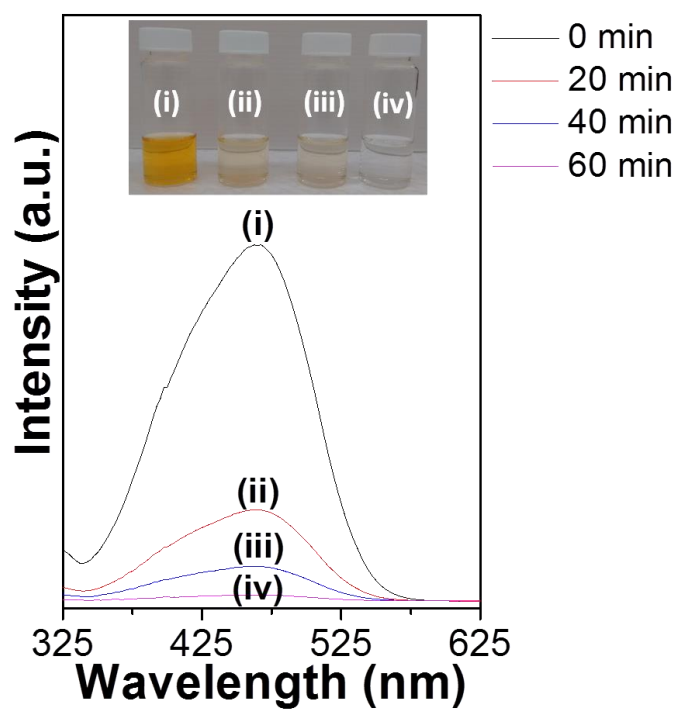


Fig. S10 Absorption spectra of MO over 1 h of exposure to simulated solar light in the presence of oxygen-deficient Cu_2O nanoparticles. Insets show the colours of the corresponding solutions.

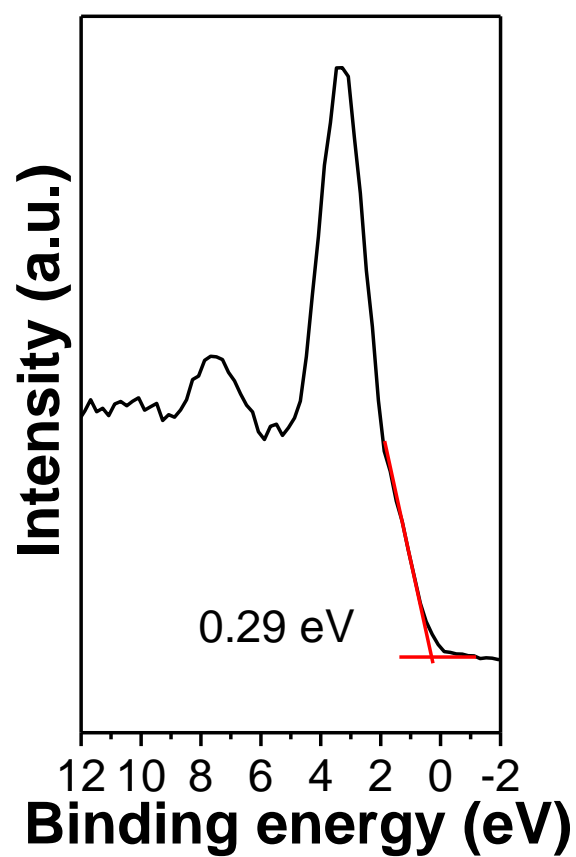


Fig. S11 Valence band XPS spectrum of oxygen-deficient Cu₂O nanoparticles.

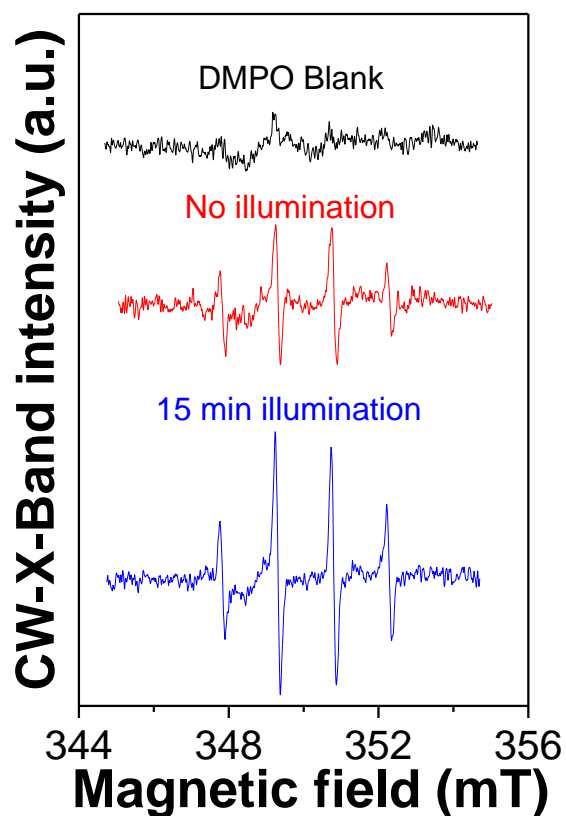


Fig. S12 Liquid solution CW-X-Band EPR Spectra of the DPMO-OH adduct generated by white light illumination of oxygen-deficient Cu_2O nanoparticles. Top trace: DMPO solution with no Cu_2O added; middle trace DMPO/ Cu_2O reaction mixture before exposure to light; bottom trace DMPO / Cu_2O reaction mixture after 15 min illumination. Instrument settings: microwave power – 200 mW; and field modulation amplitude – 0.1 mT.

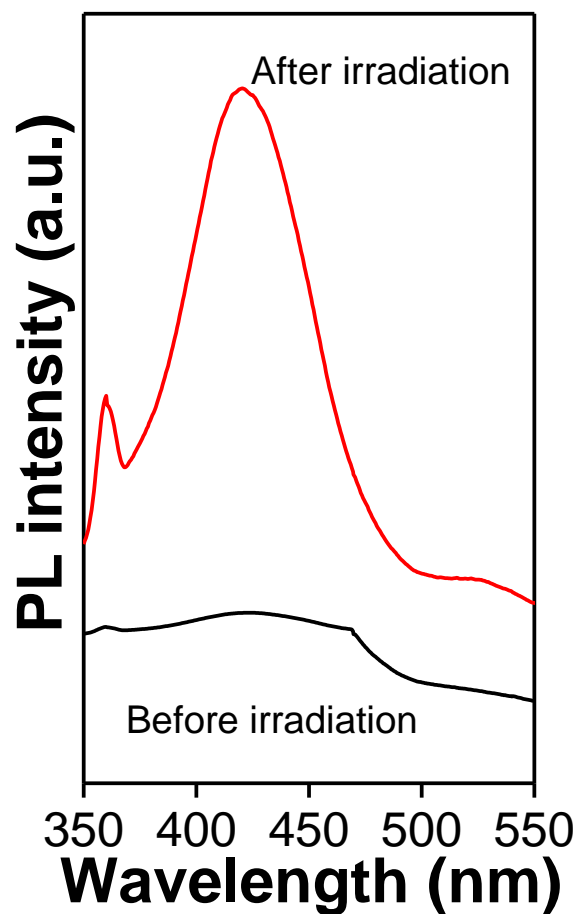


Fig. S13 Fluorescence spectra of 3 mM terephthalic acid (TA) obtained in the presence of oxygen-deficient Cu₂O nanoparticles at the λ_{ex} of 320 nm. Before photoexcitation, TA molecules remain non-fluorescent; however after 15 min of visible light photoexcitation, the OH[•] radicals generated by the photo-excited Cu₂O nanoparticles readily react with TA to produce highly fluorescent 2-hydroxy terephthalic acid (λ_{max} ~425 nm).

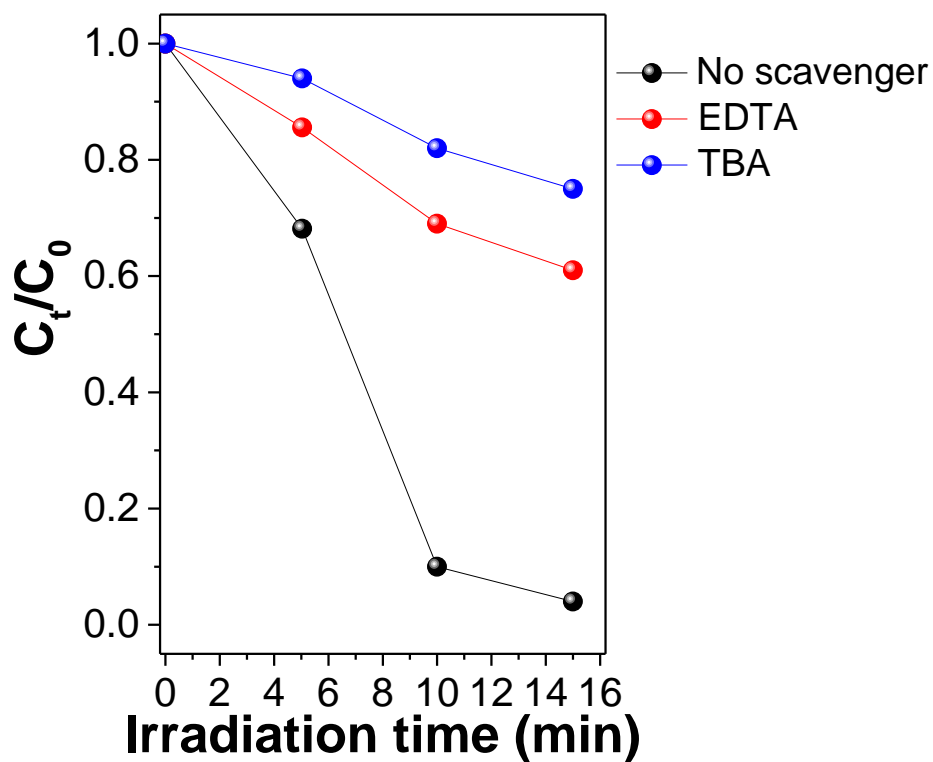


Fig. S14 Plots of C_t/C_0 versus irradiation time for oxygen-deficient Cu_2O nanoparticles-driven MO photodegradation in the presence of different scavengers. EDTA and TBA are able to suppress the photo-oxidation efficiency to 38% and 25%, respectively, in comparison to the control reaction involving no scavenger.

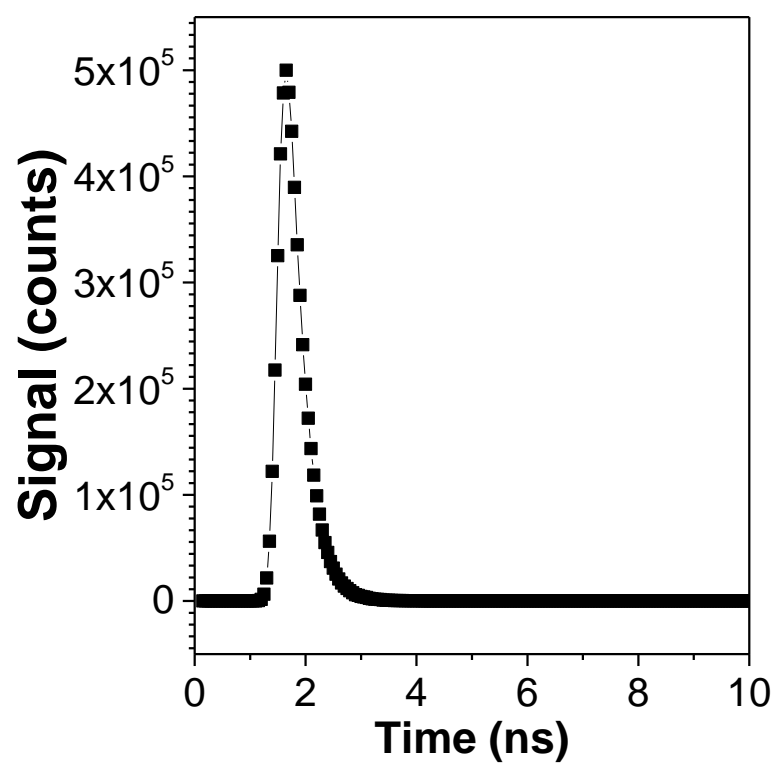


Fig. S15 Instrument response function (IRF) for the instrument used to acquire the time resolved PL spectrum of Cu_2O nanoparticles.

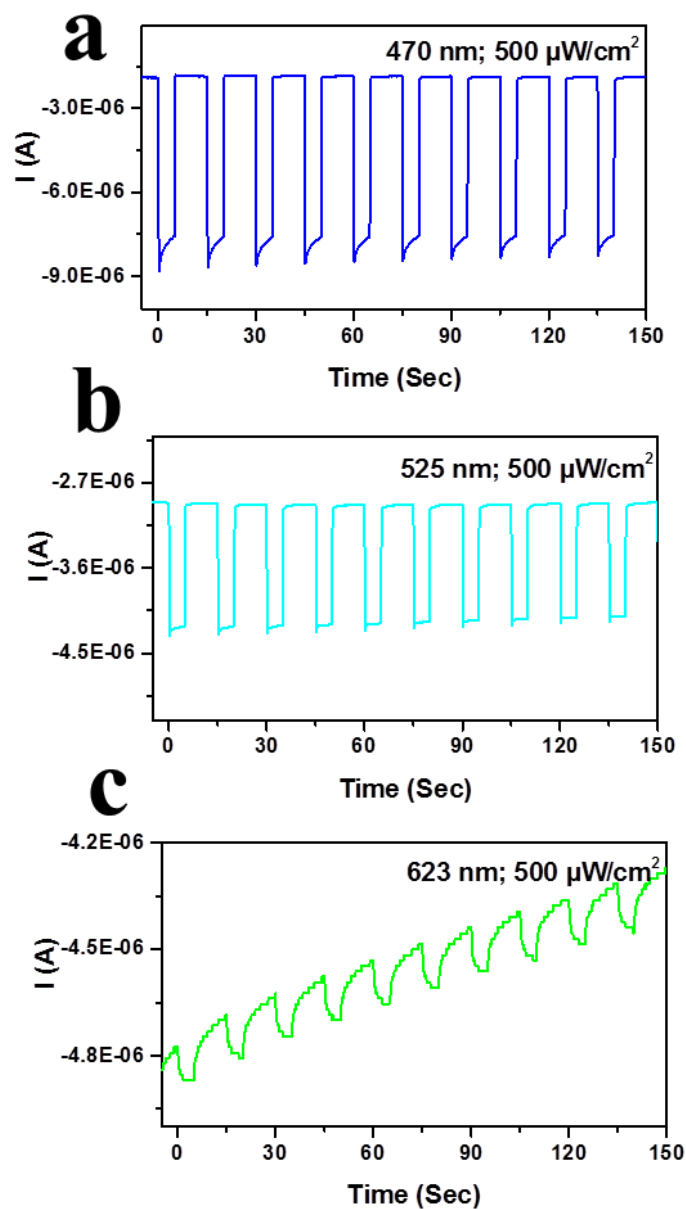


Fig. S16 The dynamic photocurrent response repeatability of the substrate over 10 exposure cycles of constant intensity of $500 \mu\text{W} \cdot \text{cm}^{-2}$ for wavelengths of **(a)** 470 nm, **(b)** 525 nm, and **(c)** 623 nm.