Supporting Information

Blue-LED activated photocatalytic hydrogenation of nitroarenes with Cu_2O/CuO heterojunctions

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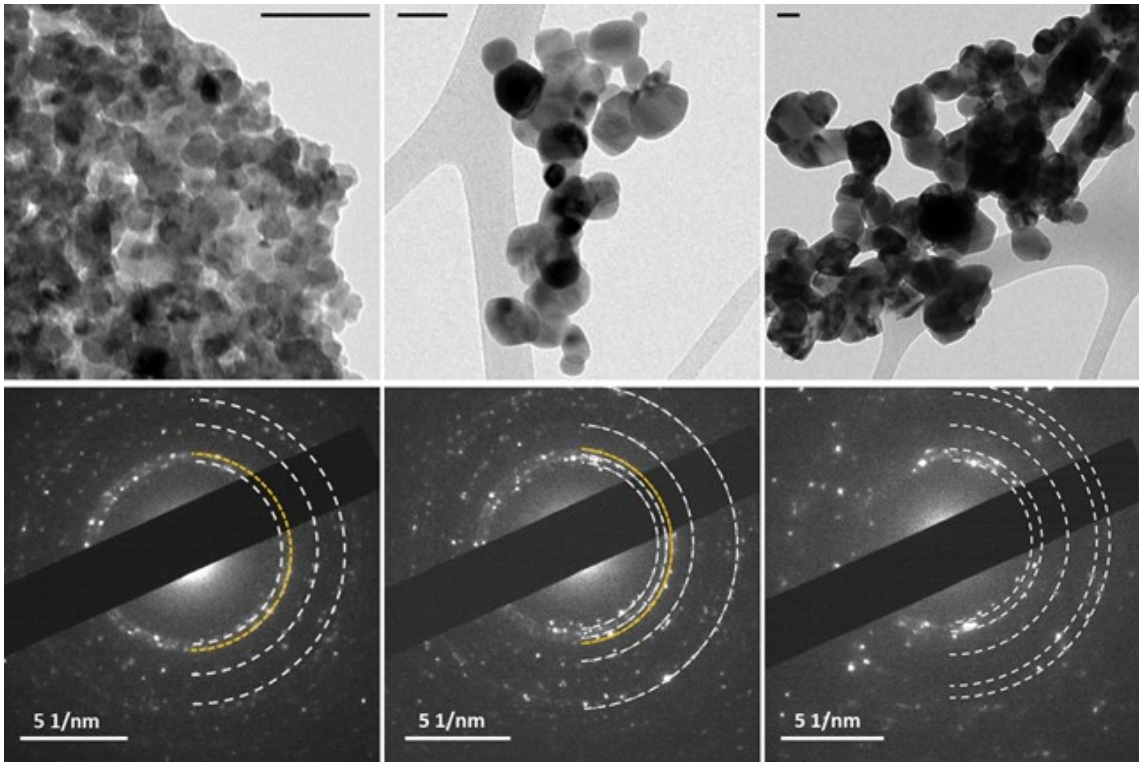


Figure S1. (top row) TEM micrographs of samples (left) Cu_2O/CuO = 0.42, (center) Cu_2O/CuO = 0.15 and (right) Cu_2O/CuO = 0.01. The scale bar represents 50 nm. (bottom row) The corresponding SAED patterns in which gold rings correspond to Cu_2O while white rings to CuO.

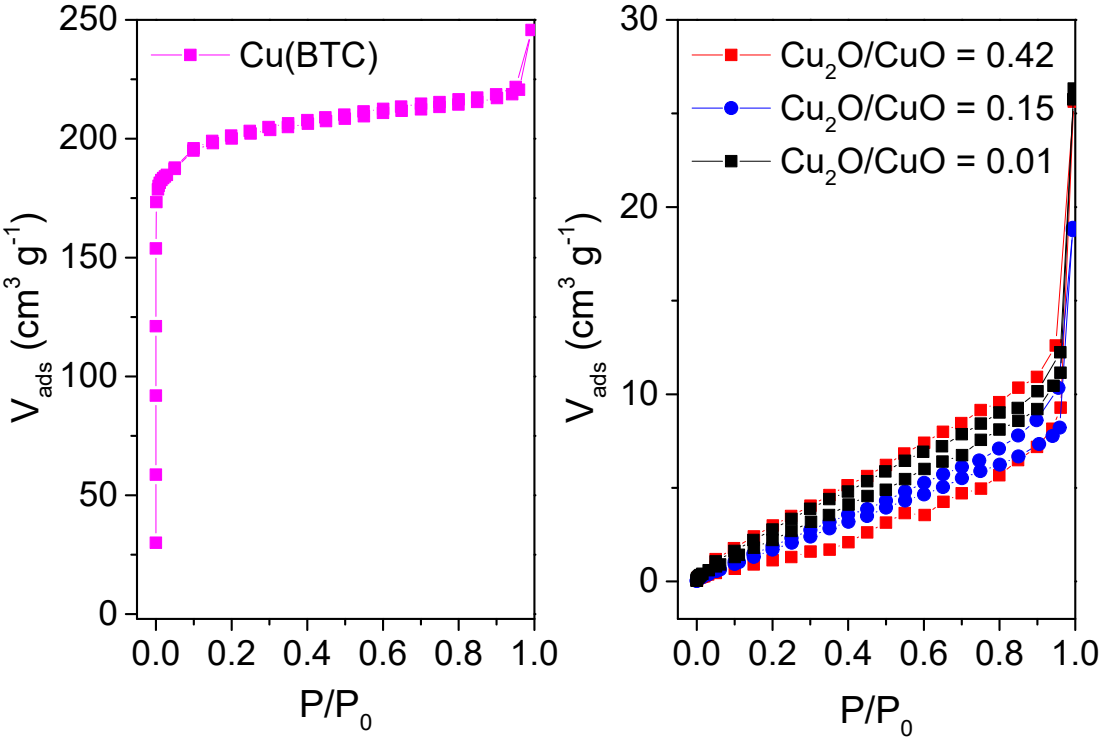


Figure S2. N_2 adsorption/desorption isotherms of the (left) MOF precursor and (right) the different catalysts.

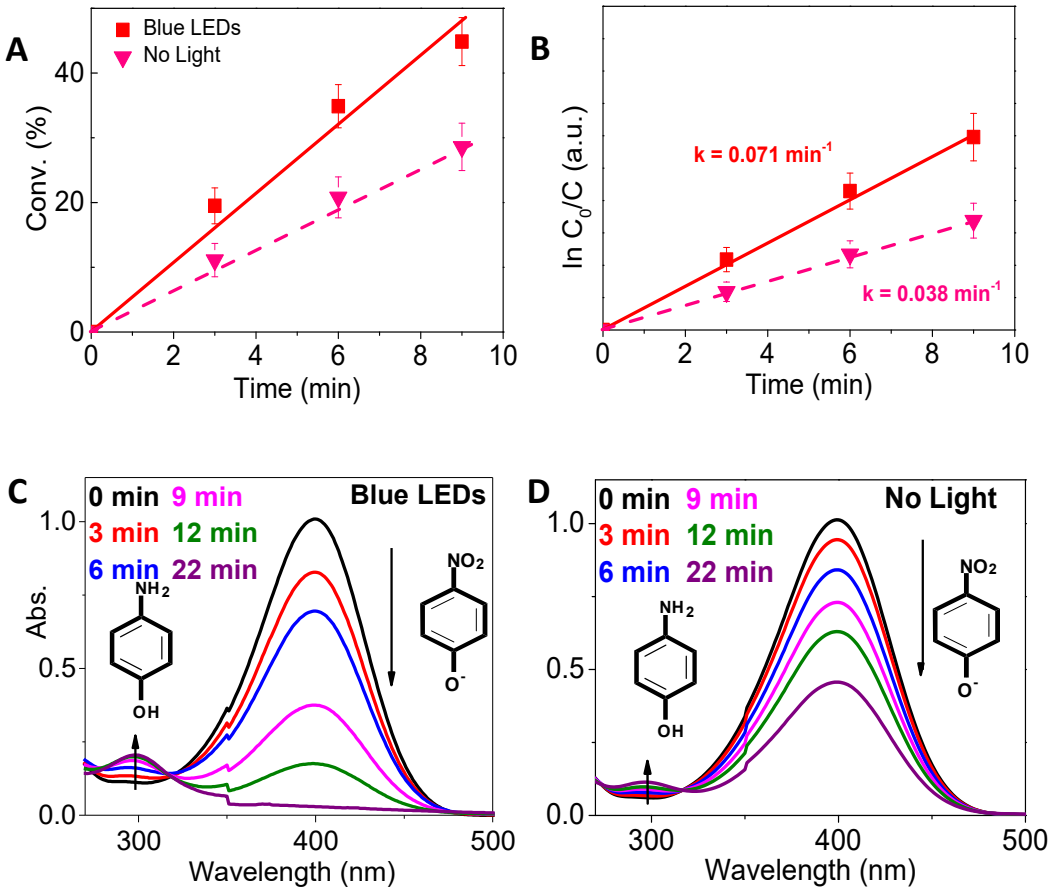


Figure S3. Performance of Cu_2O/CuO = 0.42: (A) Conversion vs Time plot for 4-nitrophenol reduction with and without irradiation in 9 minutes. (B) Rate constant comparison between irradiated and non-irradiated nitroreduction. (C) Uv-vis spectra evolution for 4-nitrophenol photoreduction and (D) reduction. As it has been elsewhere described,[1] at the start of the reaction there is an induction time, ca. 3 min, in which no conversion was found. This is attributed to the rearrangement of the surface atoms of the catalysts. The induction time has been removed from the plots for clarity.

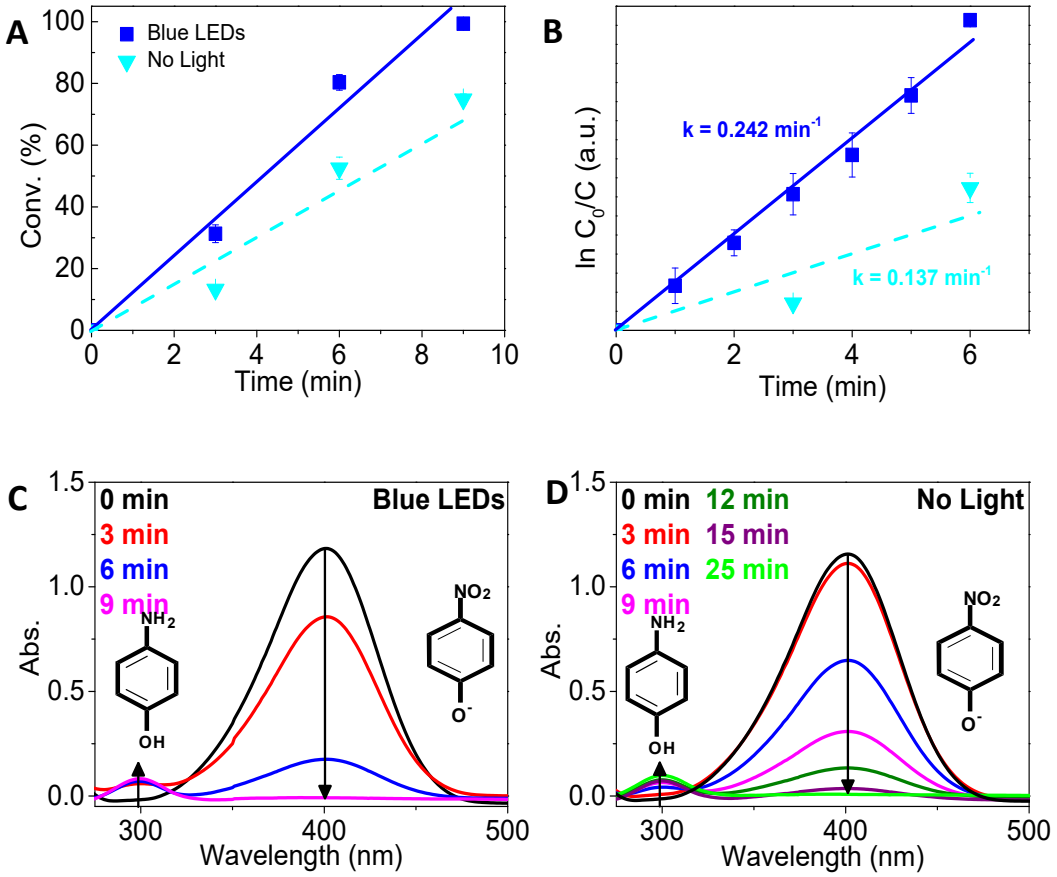


Figure S4. Performance of Cu_2O/CuO = 0.15: (A) Conversion vs Time plot for 4-nitrophenol reduction with and without irradiation in 9 minutes. (B) Rate constant comparison between irradiated and non-irradiated nitroreduction. (C) Uv-vis spectra evolution for 4-nitrophenol photoreduction and (D) reduction. As it has been elsewhere described,[1] at the start of the reaction there is an induction time, ca. 3 min, in which no conversion was found. This is attributed to the rearrangement of the surface atoms of the catalysts. The induction time has been removed from the plots for clarity.

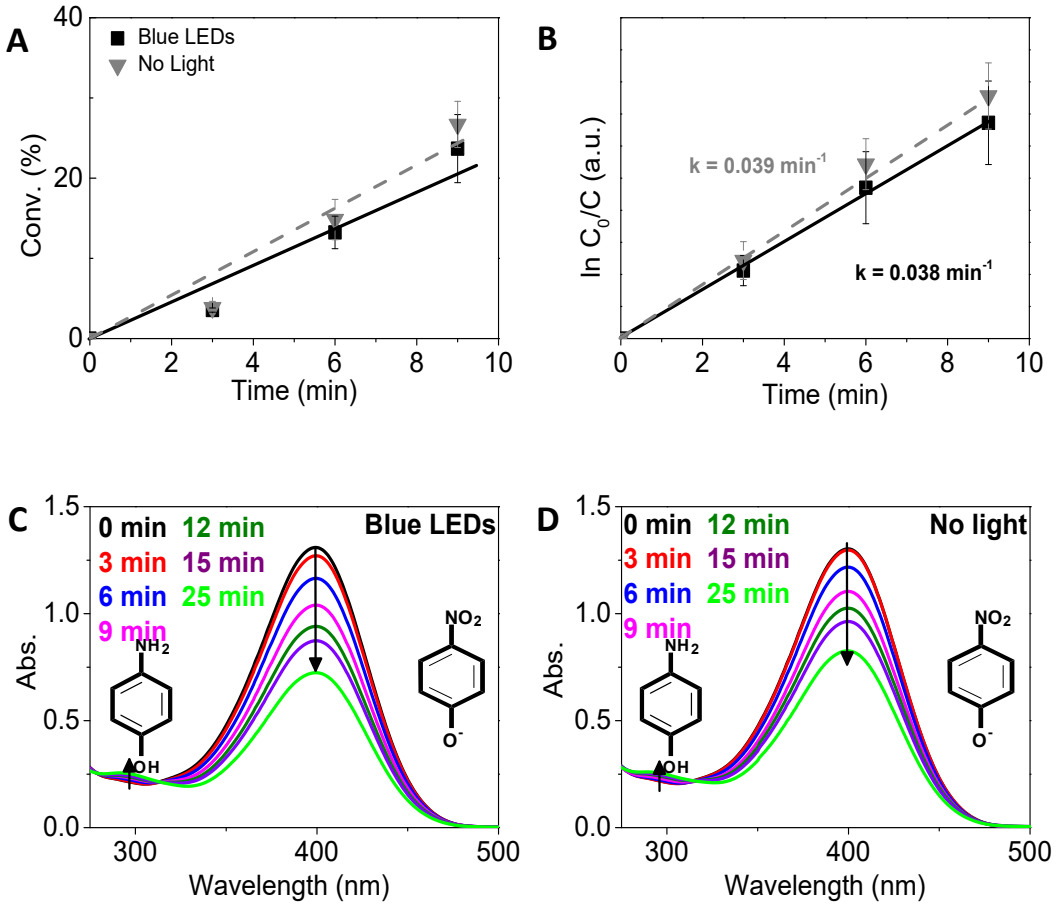


Figure S5. Performance of Cu_2O/CuO = 0.01: (A) Conversion vs Time plot for 4-nitrophenol reduction with and without irradiation in 9 minutes. (B) Rate constant comparison between irradiated and non-irradiated nitroreduction. (C) Uv-vis spectra evolution for 4-nitrophenol photoreduction and (D) reduction. As it has been elsewhere described,[1] at the start of the reaction there is an induction time, ca. 3 min, in which no conversion was found. This is attributed to the rearrangement of the surface atoms of the catalysts. The induction time has been removed from the plots for clarity.

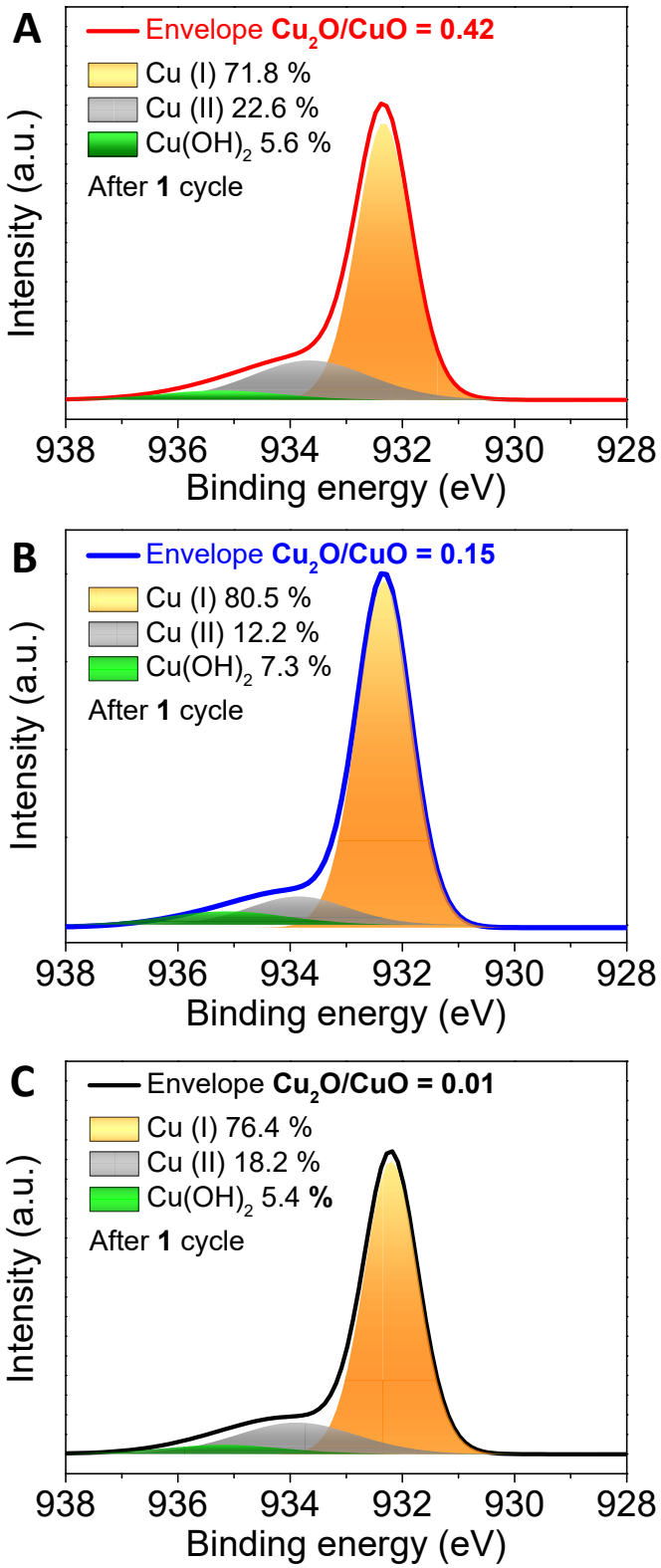


Figure S6. $Cu2p_{3/2}$ spectra of each catalyst after one photocatalytic cycle. (A) Cu_2O/CuO = 0.42; (B) Cu_2O/CuO = 0.15; (C) Cu_2O/CuO = 0.01.

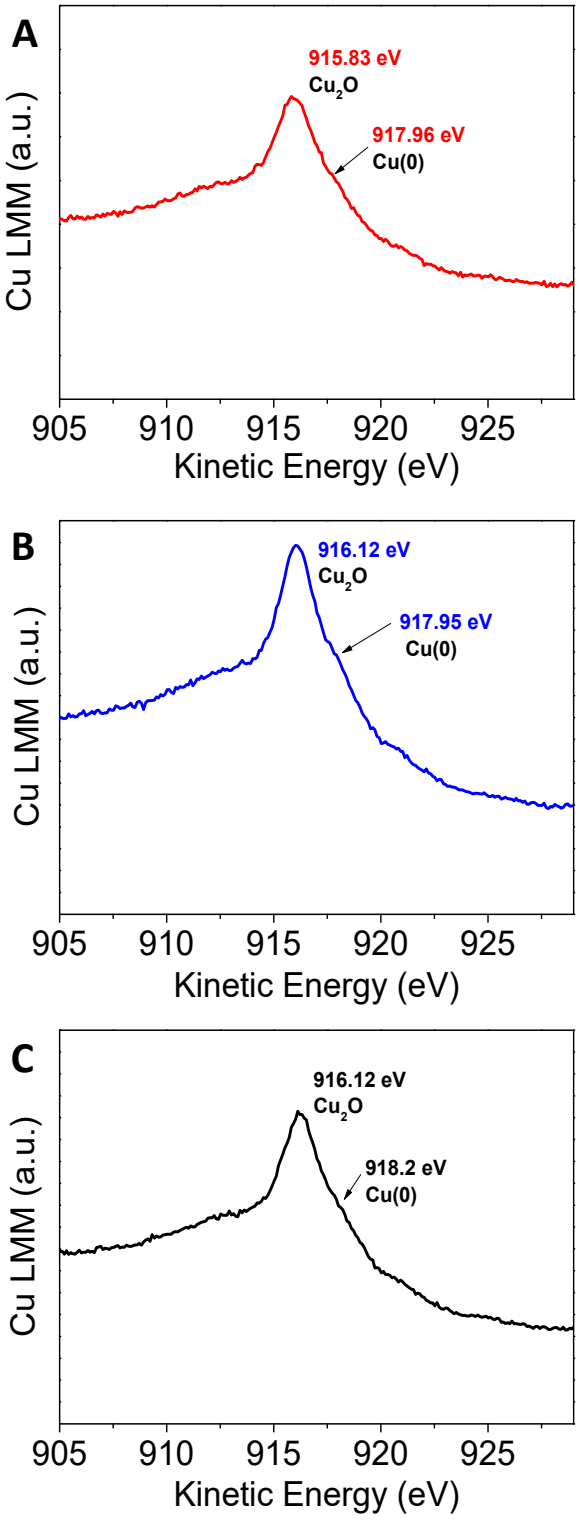


Figure S7. Cu LMM spectra of the catalysts after 1 cycle of photoreduction. (A) $Cu_2O/CuO = 0.42$; (B) $Cu_2O/CuO = 0.15$; (C) $Cu_2O/CuO = 0.01$. In the 3 spectra a well-defined peak can be observed around 916 eV with a small shoulder peak at 918 eV. The peak at 916 is attributed to Cu_2O and the shoulder at 918 is due to a small amount of metallic copper present in the samples.[2]

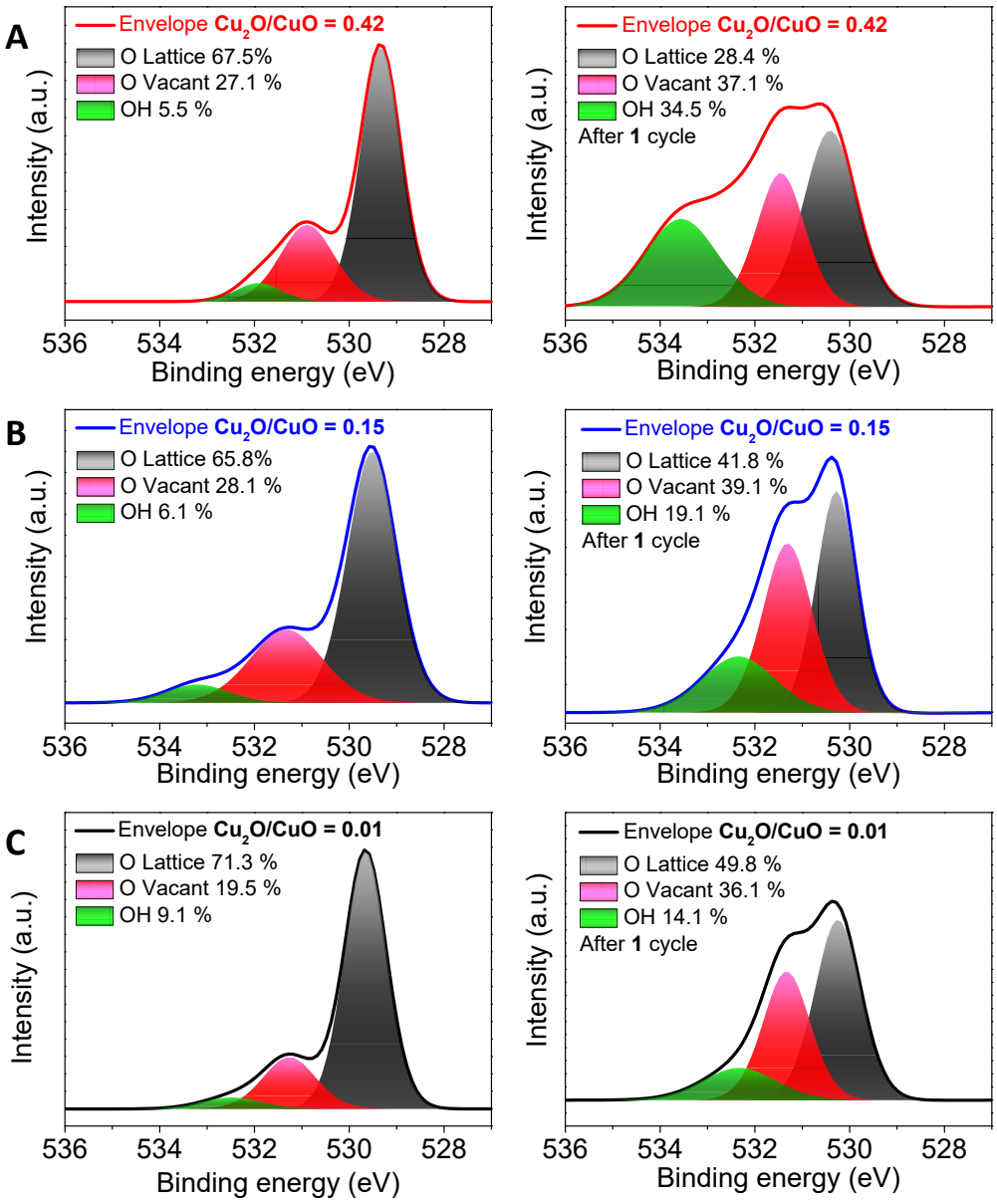


Figure S8. O1s XPS spectra of: (A) Cu_2O/CuO = 0.42, (B) Cu_2O/CuO = 0.15 and (C) Cu_2O/CuO = 0.01 before (left) and after (right) one photocatalytic cycle.

Table S1. Variation of distribution of oxygen on the catalysts' surface after 1 photocatalytic cycle. Data obtained through O1s XPS spectra deconvolution.

	Initial			1st cycle		
	Lattice	**Vacant**	**OH**	**Lattice**	**Vacant**	**OH**
Cu_2O/CuO = 0.42	67.5 %	27.1 %	05.5 %	28.4 %	37.1 %	34.5 %
Cu_2O/CuO = 0.15	65.8 %	28.1 %	06.1 %	41.8 %	39.1 %	19.1 %
Cu_2O/CuO = 0.01	71.3 %	19.5 %	09.1 %	49.8 %	36.1 %	14.1 %

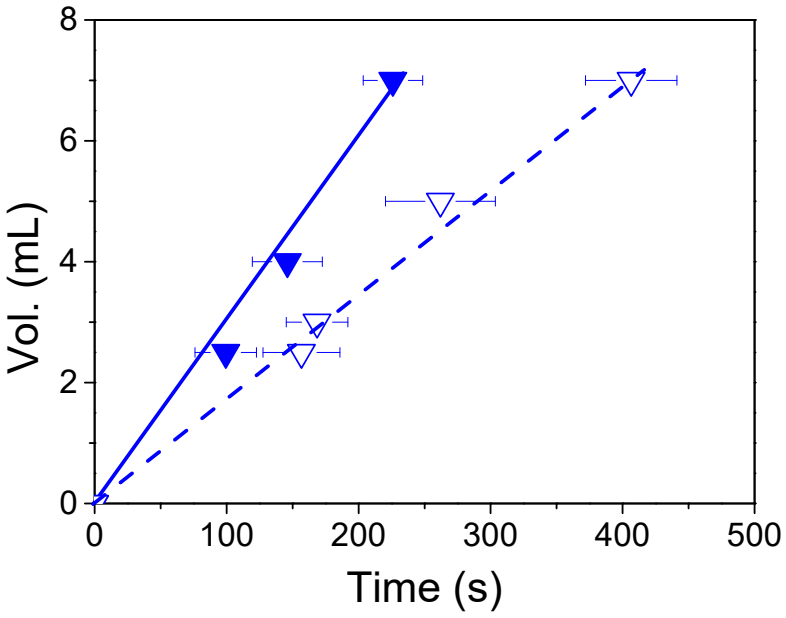


Figure S9. Volume of generated H_2 vs time plot using $Cu_2O/CuO = 0.15$ as catalyst. Solid line is for blue LEDS irradiated hydrolysis and dashed for non-irradiated.

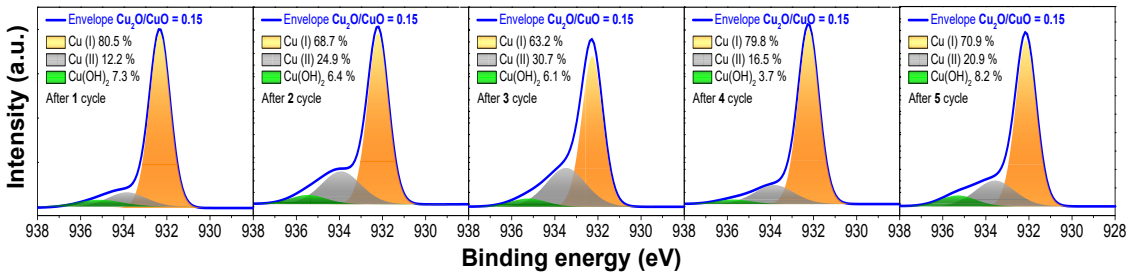
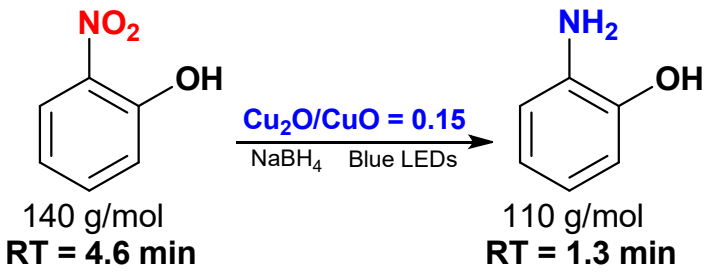


Figure S10. XPS Cu2p3 spectra of the best performing catalyst after each catalytic cycle.



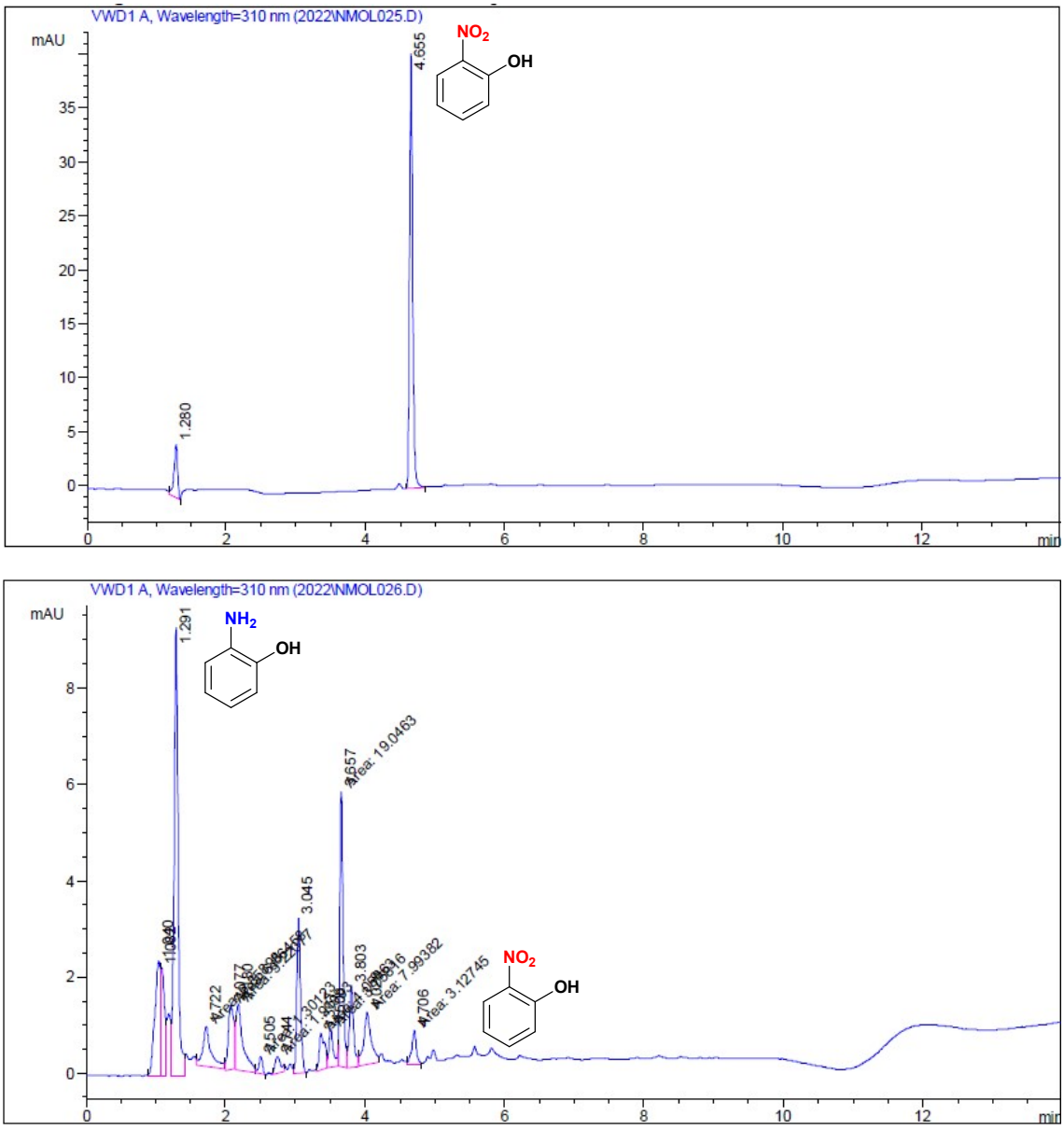
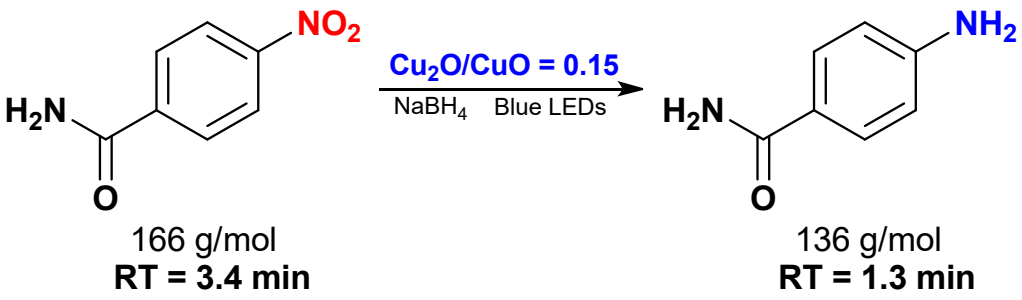


Figure S11. 2-nitrophenol 12 minutes photoreduction to 2-aminophenol. Chromatograms obtained from HPLC-MS of samples taken before photoreduction (above) and after reaction (below).



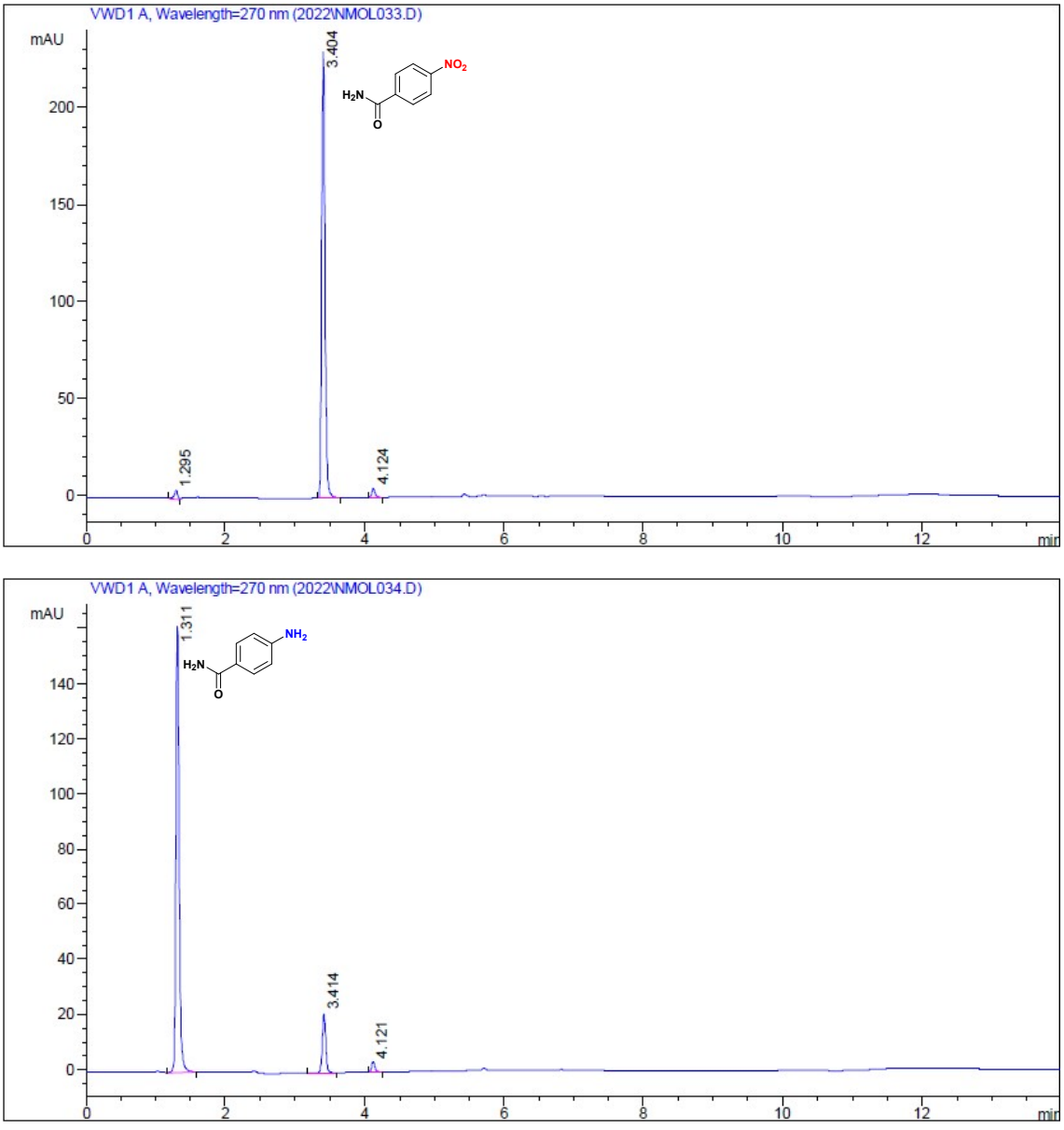


Figure S12. 4-nitrobenzamide 12 minutes photoreduction to 4-aminebenzamide. Chromatograms obtained from HPLC-MS of samples taken before photoreduction (above) and after reaction (below).

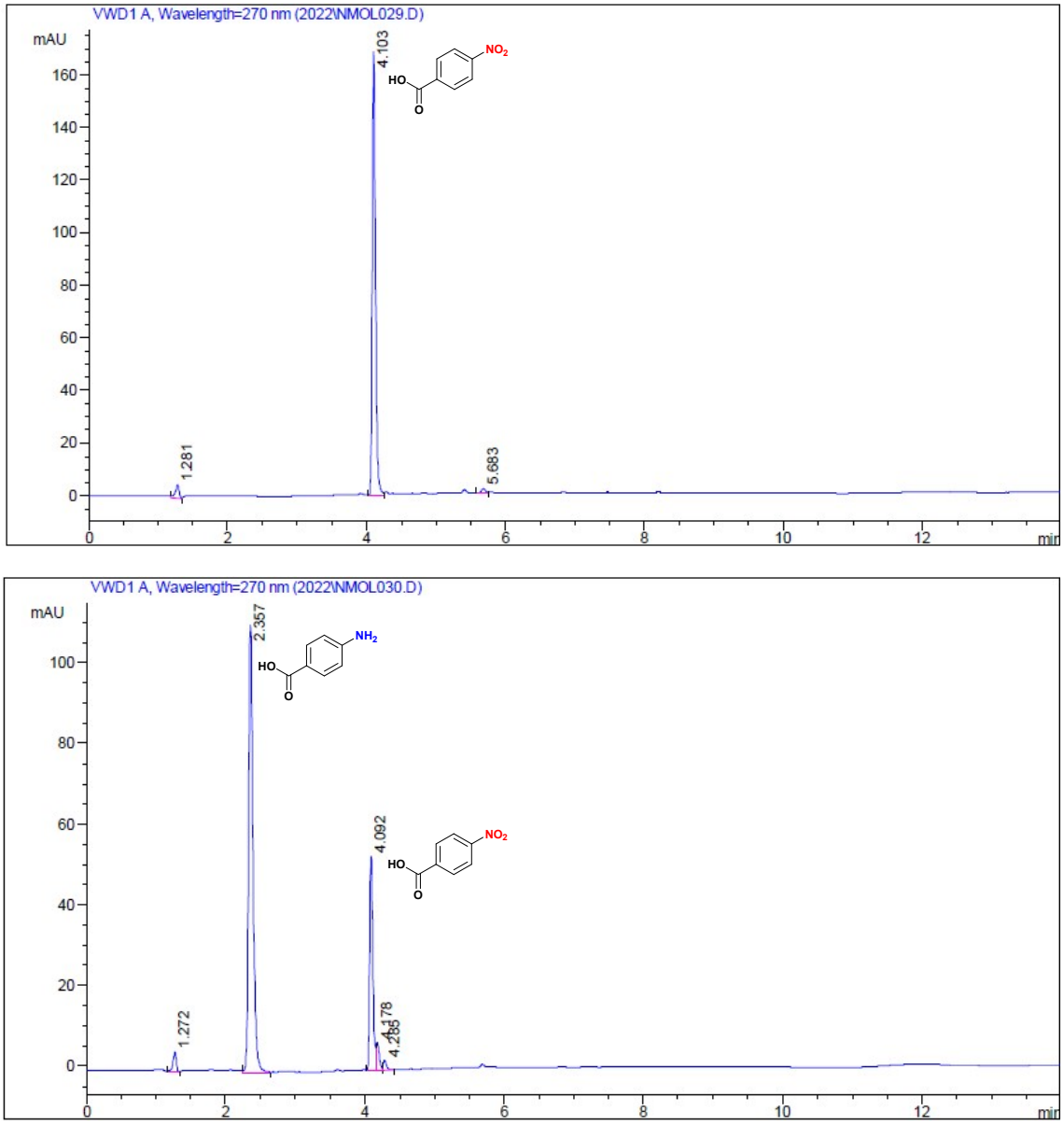


Figure S13. 4-nitrobenzoic acid 12 minutes photoreduction to 4-aminobenzoic acid. Chromatograms obtained from HPLC-MS of samples taken before photoreduction (above) and after reaction (below).

References

[1] T. Aditya, A. Pal, T. Pal, Nitroarene reduction: A trusted model reaction to test nanoparticle catalysts, Chem. Commun. 51 (2015) 9410–9431. https://doi.org/10.1039/c5cc01131k.

[2] P. S. and M. B. S. Poulston, P. M. Parlett, Surface Oxidation and Reduction of CuO and Cu_2O Studied Using XPS and XAES, Surf. Interface Anal. 24 (1996) 811–820. https://doi.org/10.1002/(SICI)1096-9918(199611)24:12<811::AID-SIA191>3.0.CO;2-Z