Supporting Information for

Tuning the Cu_xO Nanorod Composition for Efficient Visible light induced Photocatalysis

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S1. Transmittance and Reflectance spectra of Cu_xO NR samples

Figures S1 (a) and (b) below show representative optical transmission spectra $T(\lambda)$ and reflection spectra $R(\lambda)$ for a single phase Cu₂O NR sample (T = 150 °C), a mixed phase Cu₂O/CuO NR sample (T = 240 °C) and a single phase CuO NR sample (T = 380 °C). Similarly, $T(\lambda)$ and $R(\lambda)$ spectra of other Cu_xO NR samples were used to estimate the absorption as shown in Fig. 3(a) in the main text.



Fig. S1 (a) *Transmittance* (%*T*) *and* (b) *Reflectance* (%*R*) *of some selected* Cu_xO NR *samples.*

S2. Tauc's plot for direct and indirect bandgap estimation for Cu_xO NR samples

Figures S2 (a) and (b) show the Tauc's plot for bandgap determination. Results show that all the single and mixed phases of Cu_xO NR samples exhibit a direct bandgap property while only Cu_2O and mixed phase Cu_2O/CuO NR samples exhibit an indirect bandgap.



Fig. S2 Tauc's plot for direct (a) and indirect (b) band gap calculation for Cu_xO NR samples.

S3. Self-degradation of MB and MO dyes under visible light irradiation

Figures S3 (a) and (b) show the time-dependent absorption spectra of MB (of initial conc. 31.3 μ M) and MO (of initial conc. 30.5 μ M) solution irradiated under visible light intensity of 65 mW/cm². As seen in the Fig. S3 (a), MB solution was observed to undergo a self-degradation, though the degradation rate was almost negligible compared to the photocatalytic degradation with Cu_xO NR samples. However, MO solution did not undergo the self-degradation even after 2-hour light illumination and under the same experimental conditions (see Fig. S3 (b)).



Fig. S3 Comparison of self-degradation of MB (a) and MO (b) dyes under the visible light irradiation (without the Cu_xO NR samples). Fig. insets (a) and (b) respectively represents the molecular structure of MB and MO.

S4. Photodegradation rates of MB and MO with Cu_xO NR samples

Figures S4 (a) and (b) show the semi-log plots of $\alpha(t)/\alpha(0)$ versus illumination time t for MB and MO degradation. The linear fitting by the equation $-Ln[\alpha(t)/\alpha(0)] = \kappa_c t$ is used to determine the photodecay rate k_c .



Fig. S4 Photocatalytic degradation kinetics of MB (a) and MO (b) with different Cu_xO NR samples, under visible light irradiation.

S5. H₂O₂ assisted photocatalytic activity of MB with Cu₂O/CuO NR sample ($T = 240 \degree$ C)

Figures S5 (a) to (d) show the enhanced photocatalytic activity of MB aqueous solution with H_2O_2 and Cu_2O/CuO NR sample. Fig. S5 (a) to (c) show the different kinetics of dye degradation.



Fig. S5 showing the enhanced photocatalytic activity with H_2O_2 and Cu_2O/CuO NR sample. UV-Vis absorbance spectra MB aq solution representing catalytic degradation: with (a) CuxO NR sample, (b) H_2O_2 , and (c) both Cu_xO and H_2O_2 . Fig. (d) shows the estimation of degradation rates using plots (a) to (c). Note that the degradation with only H_2O_2 (in dark) is added in order to compare the true photocatalytic activity with CuxO NR sample ($T = 240^{\circ}C$).

S6. H₂O₂ assisted photocatalytic activity of MO with Cu₂O/CuO NR samples ($T = 240 \ ^{\circ}C$)

Figures S6 (a) to (d) show the enhanced photocatalytic activity of MO aqueous solution with H_2O_2 and Cu_2O/CuO NR sample. Fig. S6 (a) to (c) show the different kinetics of dye degradation.



Fig. S6 showing the enhanced photocatalytic activity with H_2O_2 and Cu_2O/CuO NR sample. UV-Vis absorbance spectra MO aq solution representing catalytic degradation: with (a) CuxO NR sample, (b) H_2O_2 , and (c) both Cu_xO and H_2O_2 . Fig. (d) shows the estimation of degradation rates using plots (a) to (c). Note that the degradation with only H_2O_2 (in dark) is added in order to compare the true photocatalytic activity with CuxO NR sample ($T = 240^{\circ}C$).

S7. Decolorization/ Mineralization tests: towards oxidation of the dyes after photocatalytic reactions with Cu₂O/CuO NR sample (*T* = 240 °C)

Figures S7(a) to (d) show the confirmation of color change of the dyes, *i.e.*, after the photocatalytic reaction with or without the O₂ purging. Results showed that the decolorization of both dyes were not due to chromophore (for e.g. forming the leuco forms) but mineralization. The conclusion was made based on the fact that there were no new absorption peaks evolved and/or changed the absorption intensities with O₂ purging. Note that we tested the final products of dyes solution from the best Cu₂O/CuO NR (T = 240 °C) sample and we assume the same phenomenon will be occurred with other rest of the Cu_xO samples including each single phase.



Fig. S7 showing comparison of UV-Vis absorption spectra of the final products, i.e. after the photocatalytic reaction and without and with the O2 purging for 30 mins. Note that the overlapped spectra of each final product confirm the each decolorization was irreversible.

S8. Cycling photodecay test for Cu₂O NR samples

Fig. S8 shows the representative cycling test for MB degradation with the Cu₂O NR sample for three times in a row by air drying the sample for 24 hr after the each degradation experiment. Other experimental conditions including the light intensity, initial concentration of the dye, are kept the same. No significant reduction in the photocatalytic activity is observed as shown in Fig. S8.



Fig. S8 The cycling test of Cu₂O NR sample for MB degradation under visible light irradiation.

S9. Stability test for Cu_xO NR samples: XRD patterns

For stability tests of the samples, we recorded the XRD data of each samples before and after the dye degradation experiments that are performed for the cycling test, as mentioned above. Results showed that the samples were very stable and adherent to the glass substrates well, and no dissolution occurs during the test of total 21 hrs. Also no color change is observed by visual inspection and no phase change are noted by the XRD results as shown in Fig.S9.



Fig. S9 XRD patterns of the selected Cu_xO NR samples recorded before and after the dyes degradation experiments. T = 150 °C represents the Cu_2O phase while T = 380 °C represents CuO.

S10. Stability test for Cu_xO NR samples: UV-Vis spectra

For stability tests of the samples, we also recorded the UV-Vis transmittance (%*T*) spectra of the above mentioned three samples before and after the photocatalytic activity with MB and PEC characterization. Note that the samples were of five-month old and they were kept in petri dishes, which was exposed to the ambient laboratory air at room temperature. Results showed that the samples were relatively more stable for MB degradation (than PEC) as confirmed by the transmittance spectra as shown in Fig. S10 (a) and 10(b). In particular, after the PEC tests, we observed changes in the transmittance spectra of Cu_xO NR samples including the shift in absorption edges (see Fig. S10 (b)). Digital photos before and after the experiments, shown as insets in the figures, also supports this conclusion.



Fig. S10 UV-Vis transmittance spectra of the selected Cu_xO NR samples recorded before (solid curves) and after (dash-dotted curves) (a) MB degradation and (b) PEC characterization. Note that T =150 °C represents the single phase Cu_2O sample, T = 240 °C represents the mixed phase Cu_2O/CuO sample, and T = 380 °C represents the single phase CuO sample.

S11. Stability of photocurrent density of Cu_xO NR samples

Fig. S11 shows the net photocurrent density of Cu_xO NR samples as a function of cycling number. The net photocurrent density for all the Cu_xO NR samples were estimated by subtracting the average dark-current density from adjacent average light-current density. The cathodic photocurrent density of the mixed phase Cu_2O/CuO sample was estimated to 0.24 mA/cm² (red curve in Fig. S11). Similarly, the stable photocurrent with CuO NR sample was 0.18 mA/cm² and the least photocurrent with Cu_2O NR was 0.06 mA/cm² (blue and black curves respectively in Fig. S11).



Fig. 11 Net photocurrent density of the (a) Cu_2O ($T = 150^{\circ}C$), (b) Cu_2O/CuO ($T = 240^{\circ}C$), and (c) CuO ($T = 380^{\circ}C$) NR array samples in 0.5 M Na2SO4 solution at -0.5 V vs. Ag/AgCl. Note that the net photocurrent densities were estimated by subtracting the average dark-currents from the adjacent average light-currents and the % loss in photocurrent densities were estimated from the values at time zero to the test period (15 mins).