Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

-Supporting information-

Template free mild hydrothermal synthesis of core-shell $Cu_2O(Cu)@CuO$ visible light photocatalysts for N-acetyl-para-aminophenol degradation

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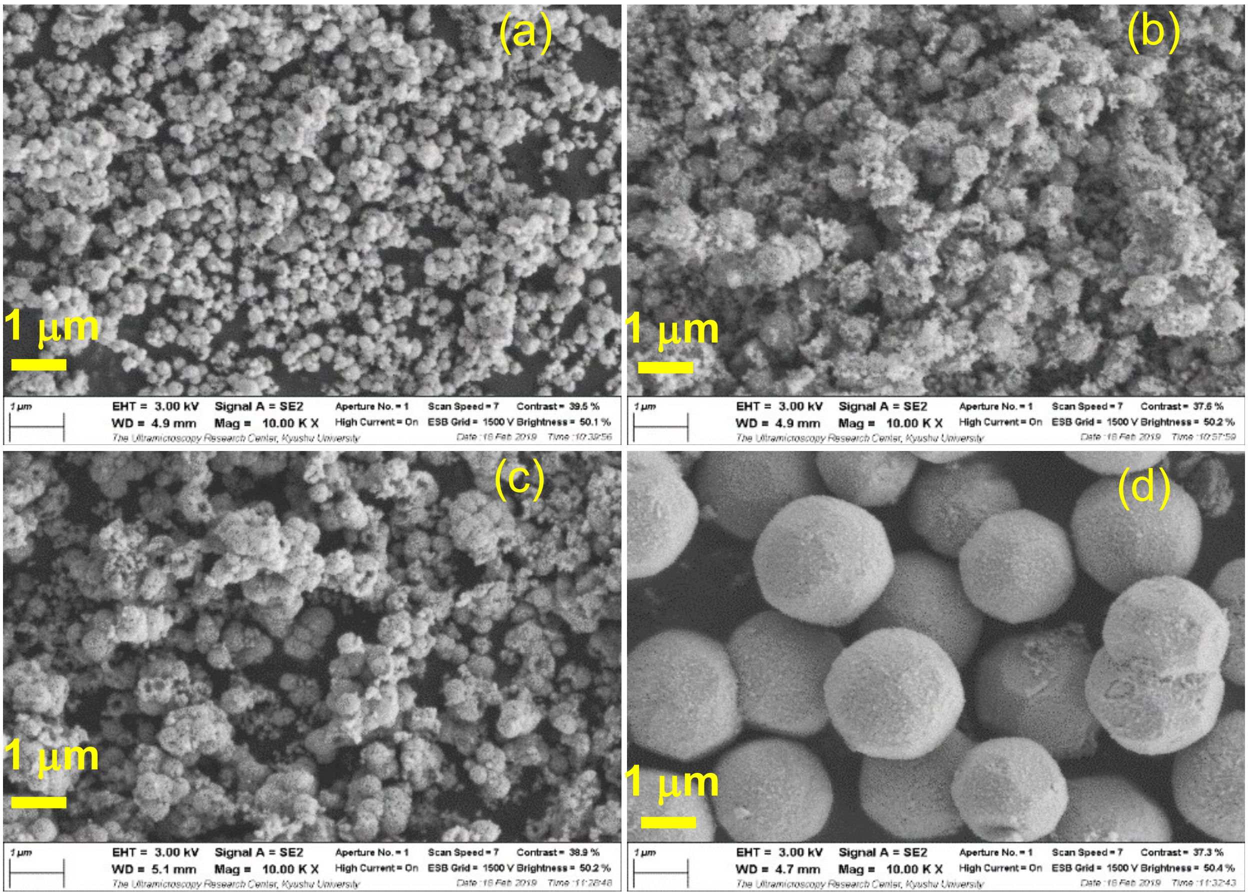


Fig. S1. Low magnification FE-SEM images of (a) $Cu_2O@CuO$-A, (b) $Cu_2O@CuO$-B, (c) $Cu_2O@CuO$-C, and (d) $Cu_2O@CuO$-D.

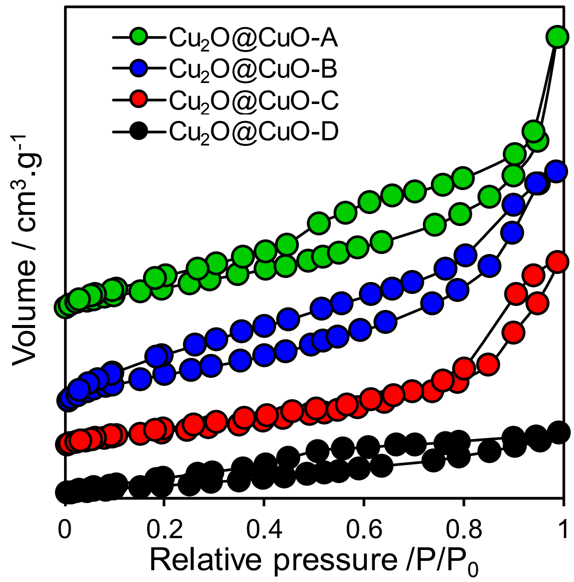


Fig. S2. N_2 adsorption-desorption isotherms of Cu_2O@CuO photocatalysts.

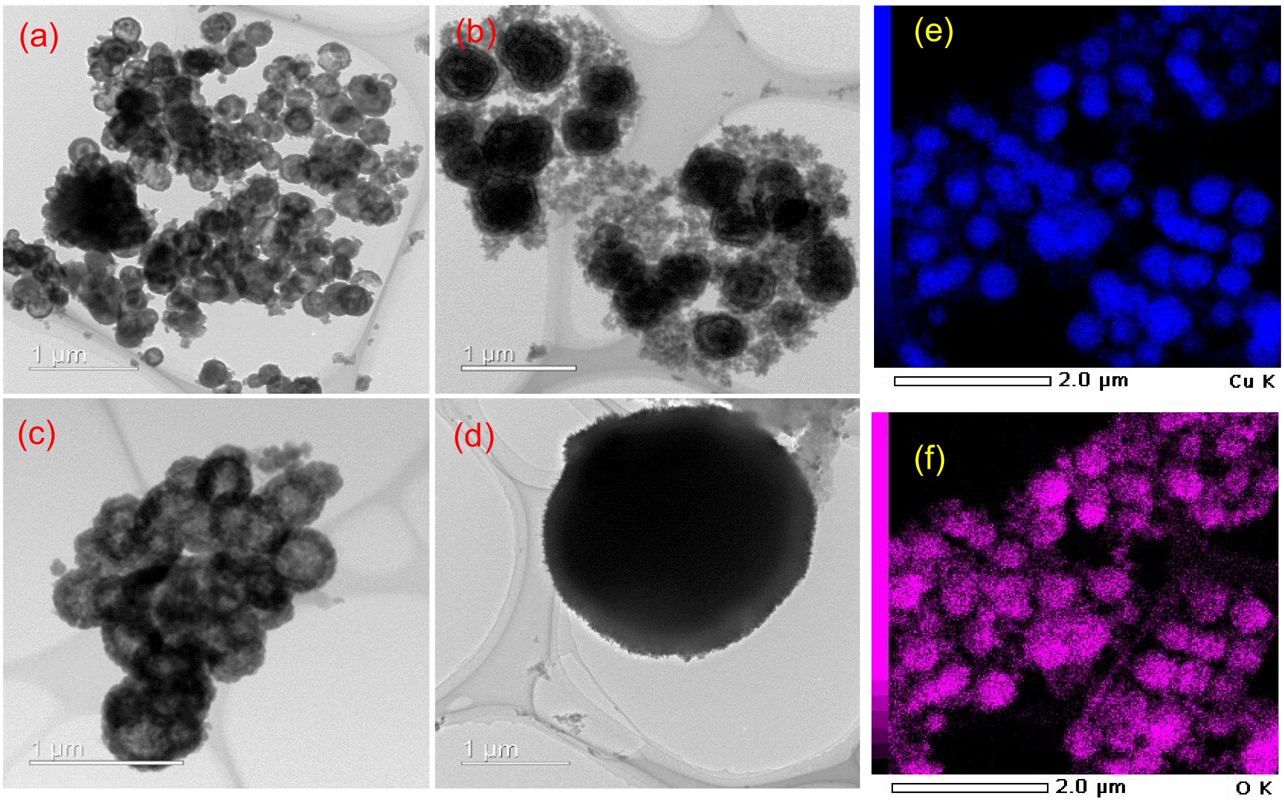
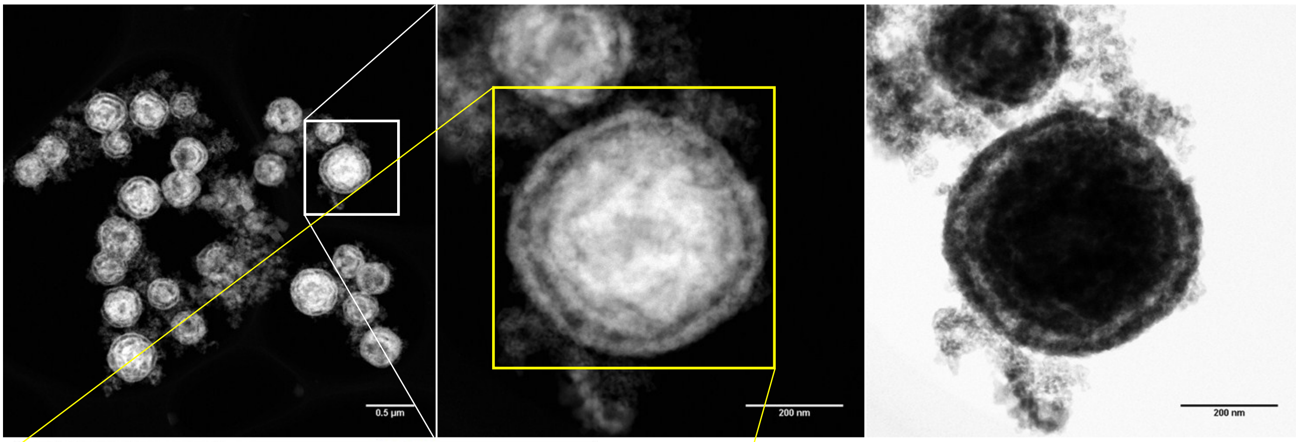
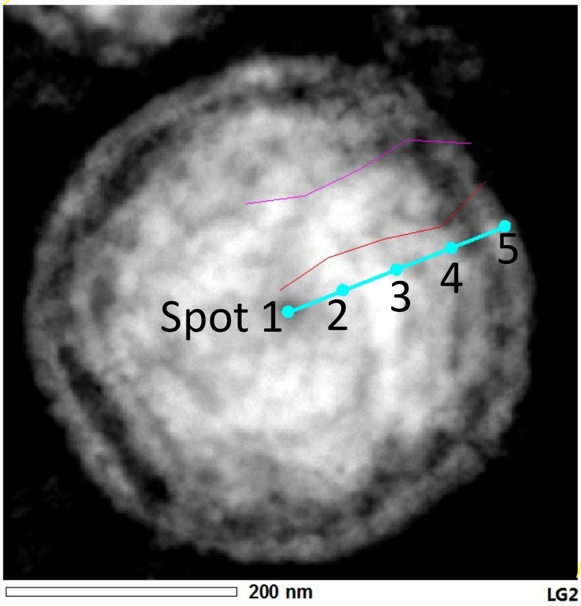


Fig. S3. Low magnification TEM images of (a) Cu_2O@CuO-A, (b) Cu_2O@CuO-B, (c) Cu_2O@CuO-C, and (d) Cu_2O@CuO-D, and (e-f) EDX elemental maps of Cu_2O@CuO-B.





Spot position	Atom %	
	Cu	O
1 (core)	58.88	41.12
2	56.38	43.62
3	56.95	43.05
4	58.82	41.18
5	53.78	46.22
6 (corona)	49.94	50.06

Fig. S4. (a-c) Dark field (S)TEM and (b) bright field TEM images of Cu_2O@CuO-B, and (d) variation in EDX elemental compositions determined across a single rattle-like core-shell nanoparticle.

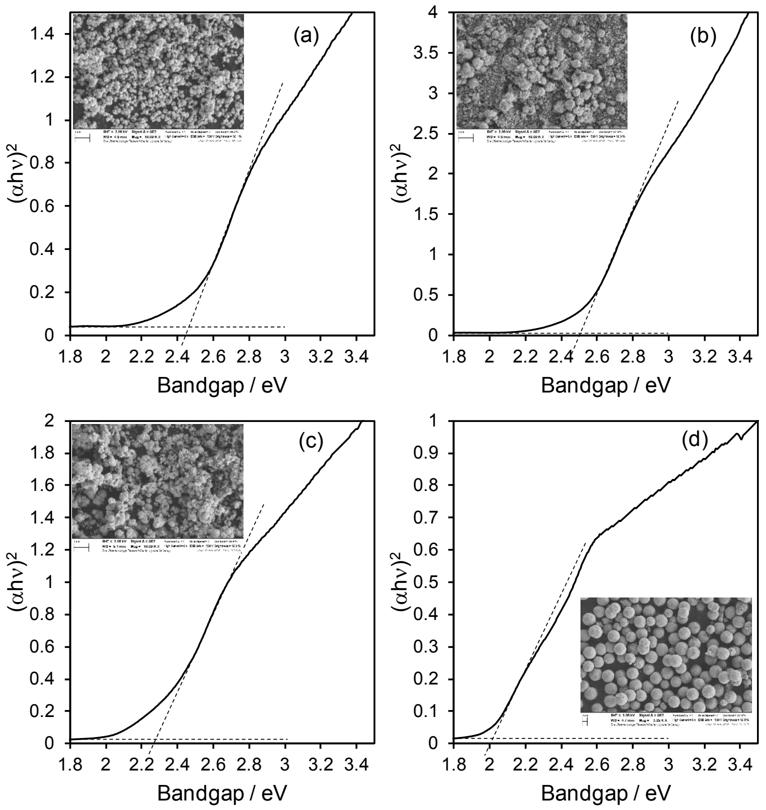


Fig. S5. Tauc plot for (a) Cu_2O@CuO-A, (b) Cu_2O@CuO-B, (c) Cu_2O@CuO-C, and (d) Cu_2O@CuO-D.

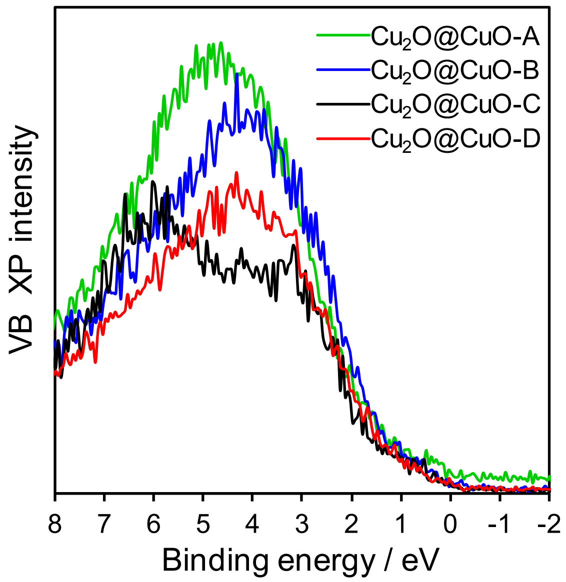


Fig. S6. Valence band XP spectra of Cu_2O@CuO photocatalysts.

Table S1. Photocatalytic APAP degradation comparison.

Catalyst	Rate constant / min^{-1}	Catalyst mass and APAP concentration	Flux of light source	Reference
TiO_2	0.0105	0.4 $g.L^{-1}$ catalyst, 4 μM APAP	15 W UV-C lamp (254 nm), 12.6 mW/cm^{-2}	1
Cu/TiO_2	0.0243	4.0 $g.L^{-1}$ catalyst APAP 25 mL	Rayonet RPR-100 photoreactor equipped with 16 visible light lamps	2
Pt/TiO_2	0.030	5 $mg.L^{-1}$ catalyst, 40 μM APAP	UV-C low-pressure Hg lamp (254 nm) 107.4 W/cm^{-2}	3
ZnO nanorod	0.0125	100 mg catalyst, 50 $mg.L^{-1}$ APAP	300 W Xe lamp (UV) with external applied bias	4
ZnFe-LDH/rGO	0.0074	25 mg catalyst, 5 $mg.L^{-1}$ APAP	500 W Xe lamp (300 nm cut-off filter)	5
Hollow TiO_2 microspheres	0.0448	50 $mg.L^{-1}$ APAP	500W Hg-lamp (UV)	6
Cu_2O@CuO-B	0.0679	20 mg catalyst, 0.06 mM APAP	500 W Xe lamp with 400 nm cut-off filter, 1.82 mW/cm^2	Present work

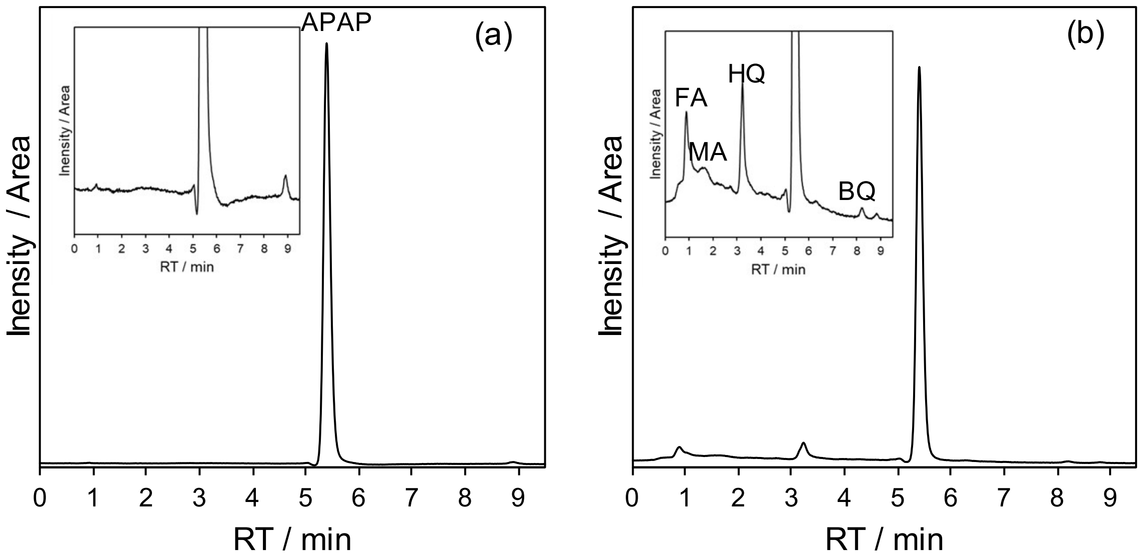


Fig. S7. HPLC of reaction mixture (a) before and (b) after photocatalytic APAP degradation presence of Cu_2O@CuO-B.

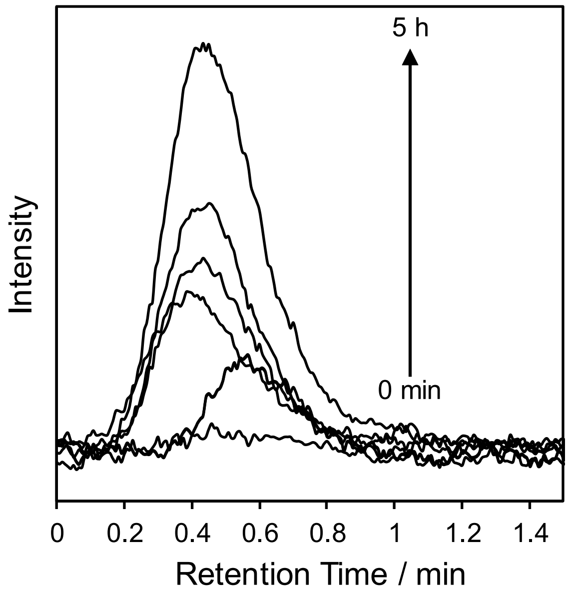


Fig. S8. HPLC of reactively-formed DNPH-HCHO resulting from DMSO oxidation to formaldehyde in the presence of Cu_2O@CuO-B under visible light. Conditions: 20 mg Cu_2O@CuO-B; 50 mL of 250 µM DMSO; 1 mL samples derivatized using 20 µL H_3PO_4-NaH_2PO_4 buffer and 200 µL of 240 µmol/L DNPH. JASCO LC-netII/ADC HPLC with UV-2075 (355 nm) detector and a Shodex C18M4E analytical column (4.6 mm I.D × 250 mm) held at 32.2 °C and 17.4 MPa; mobile phase of 60:40 (v/v) methanol:water; flow rate of 0.8 mL/min.

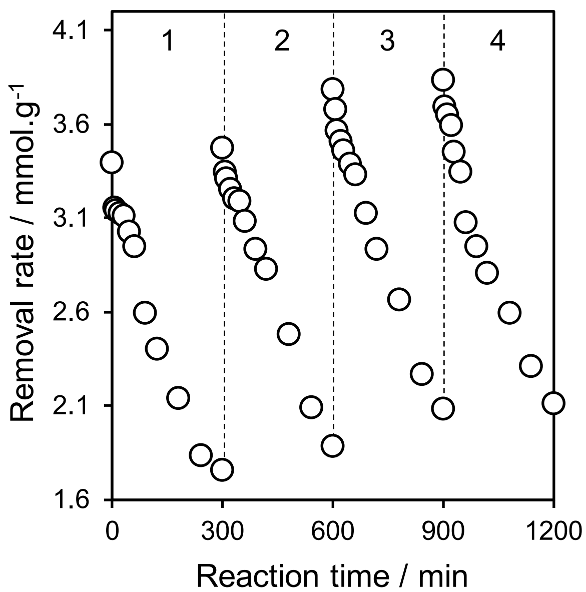


Fig. S9. Recycling of APAP photocatalytic degradation over Cu_2O@CuO under visible light.

Apparent quantum efficiency (AQE) determination

The apparent quantum efficiency under visible light irradiation was measured at 420 nm with a band-pass filter according to the following equations:

$$Apparent\ quantum\ efficiency\ (\%) = \frac{Mols\ of\ reacted\ electrons\ per\ unit\ time}{Mols\ of\ incident\ photons\ per\ unit\ time} \times 100 \quad \text{(S1)}$$

Mols incident photons per unit time ($N_{Einstein}$) = Number incident photons per unit time / N_A

Number of incident photons N_p per unit time can be calculated by:

$$N_P = \frac{Intensity\ (E)}{Photon\ energy\ (E_p)} \text{ ; and } photon\ energy\ (E_p) = \frac{hc}{\lambda} \quad \text{(S2)}$$

E = Irradiance × reactor area illuminated

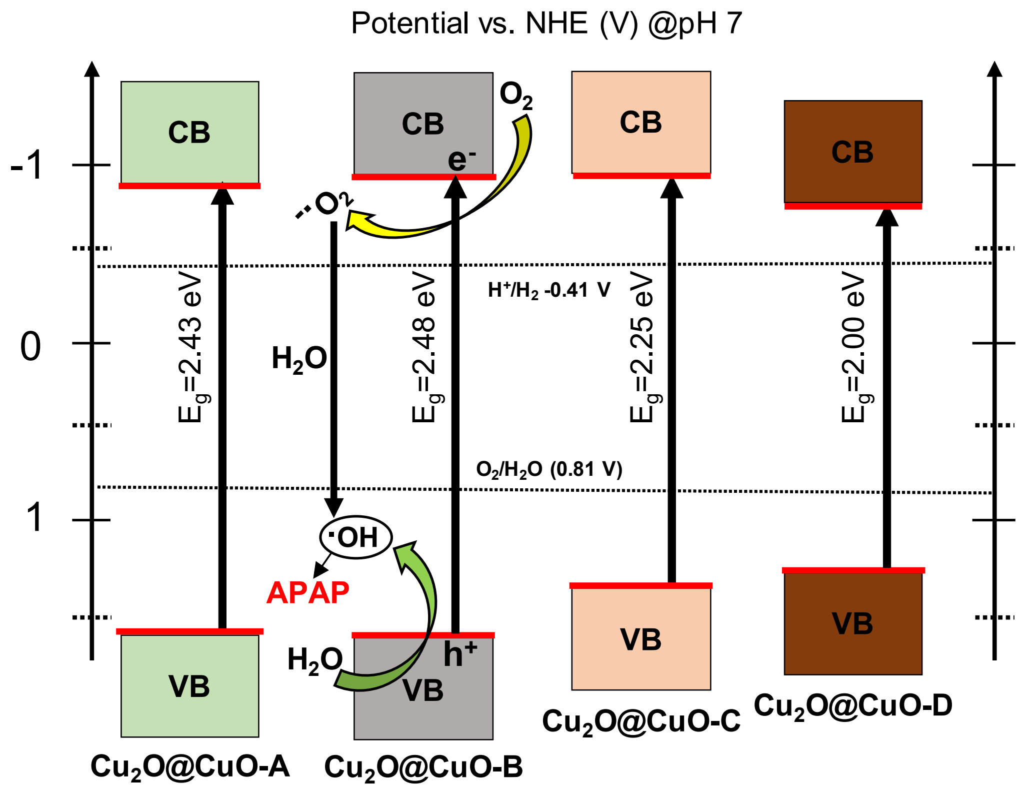
$$E_p = \frac{(6.625 \times 10^{-34}\ J.s)\ (3 \times 10^{17}\ nm.s^{-1})}{\lambda\ (nm)} = \frac{19.88 \times 10^{-17}}{\lambda\ (nm)} = 4.73\text{x}10^{-19}\ \text{J} \quad \text{(S3)}$$

$$N_p = \frac{E}{E_p} = 0.00819 / 4.73\text{x}10^{-19} = 1.73\text{x}10^{16}\ \text{s}^{-1} \quad \text{(S4)}$$

$$N_{Einstein} = \frac{N_P}{N_A} = 2.87\text{E-}06\ \text{mols.s}^{-1} \quad \text{(S5)}$$

For APAP photodegradation:

$$Quantum\ efficiency\ (\%) = \frac{APAP\ removal\ rate\ (mol.s-1)}{Neins} \times 100 \quad \text{(S6)}$$



Scheme S1. Band positions of $Cu_2O@CuO$.

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