Electronic Supporting Information for

Visible light driven photo-reduction of Cu^{2+} to Cu_2O to Cu in water for photocatalytic hydrogen production

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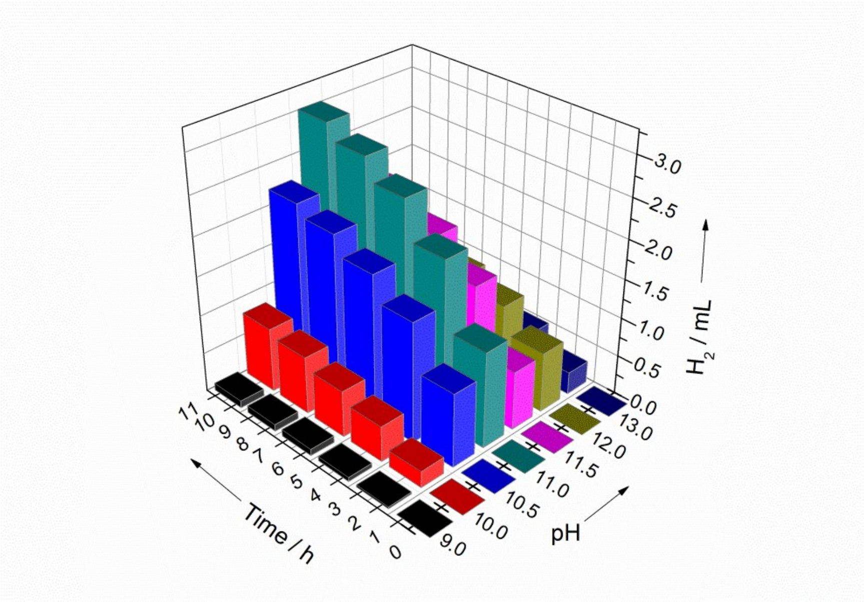
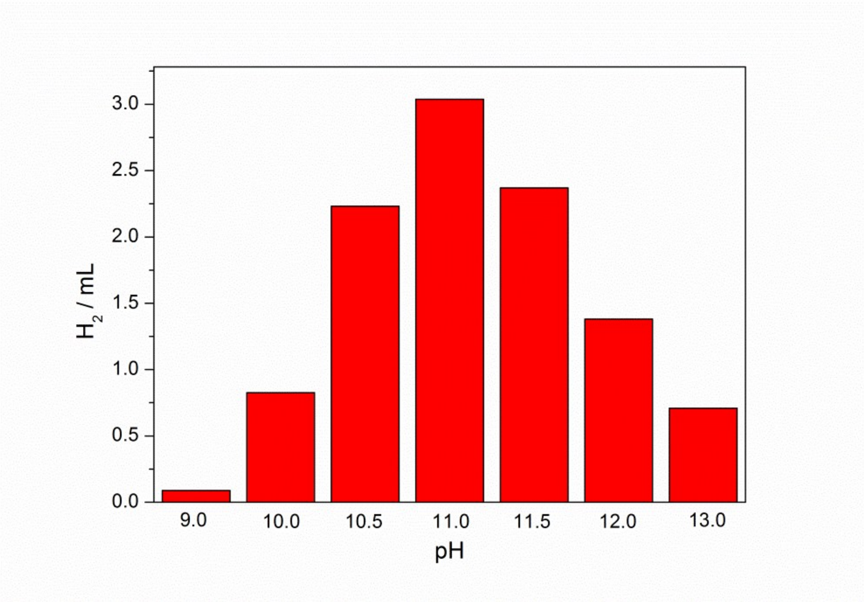
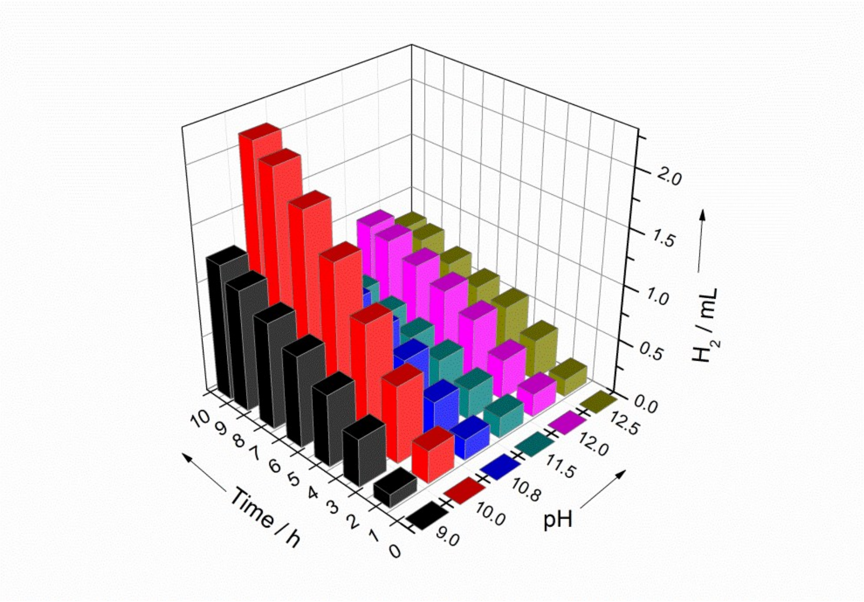


(a)

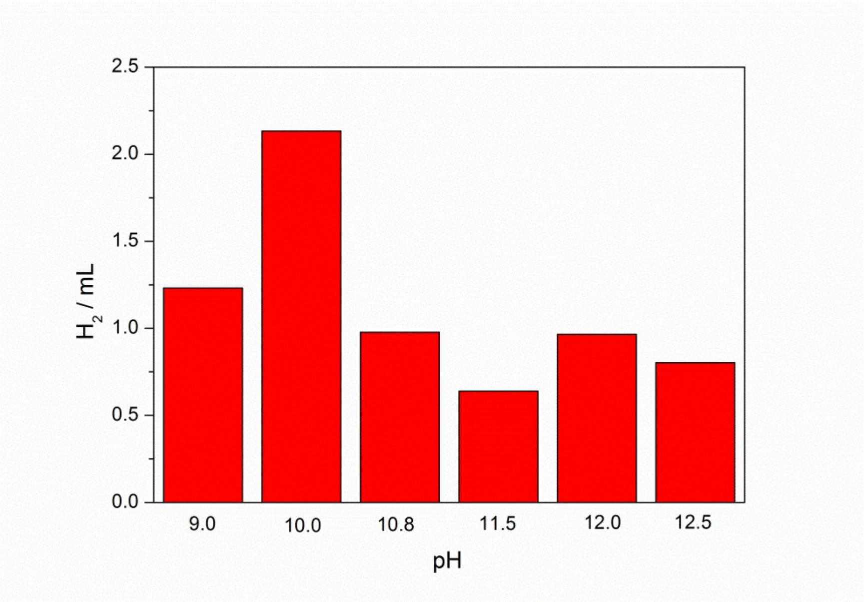


(b)

Figure S1. (a) and (b): Relationship between hydrogen production at various pH values and irradiation time from system containing $CuSO_4$ (1.0×10^{-5} M), TEA (1.5 mL) and Fl (1.0 × 10-3 M) in H_2O (28.5 mL) in a 60 mL volume quartz tube. The light source for irradiation is LED with λ > 420nm.



(a)



(b)

Figure S2. (a) and (b): Relationship between hydrogen production at various pH values and irradiation time from system containing $CuSO_4$ (1.0 × 10^{-5} M), TEOA (1.5 mL) and Fl (1.0 × 10-3 M) in H_2O (28.5 mL) in a 60 mL volume quartz tube. The light source for irradiation is LED with λ > 420nm.

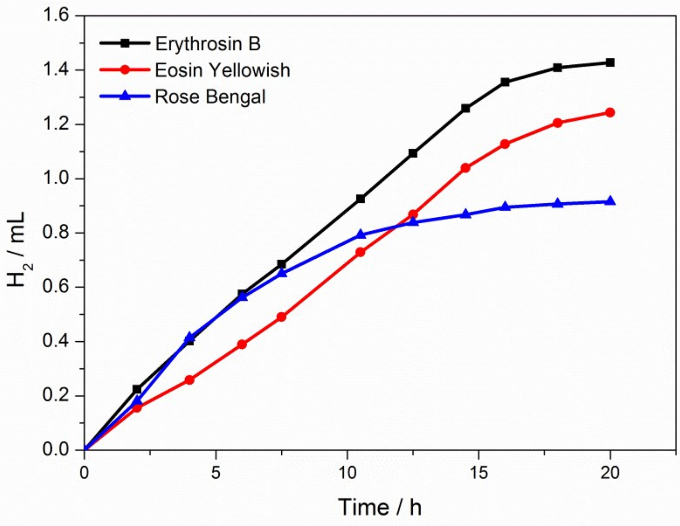


Figure S3. Time course of hydrogen production using various photosensitizers (10^{-3}M) with $CuSO_4 \cdot 5H_2O$ (1.0×10^{-5} M) and TEA (1.5 mL, 5% v/v) at pH 11 (adjusted with 0.1 M HCl) in H_2O (28.5 mL) under $\lambda > 420$nm LED visible-light irradiation.

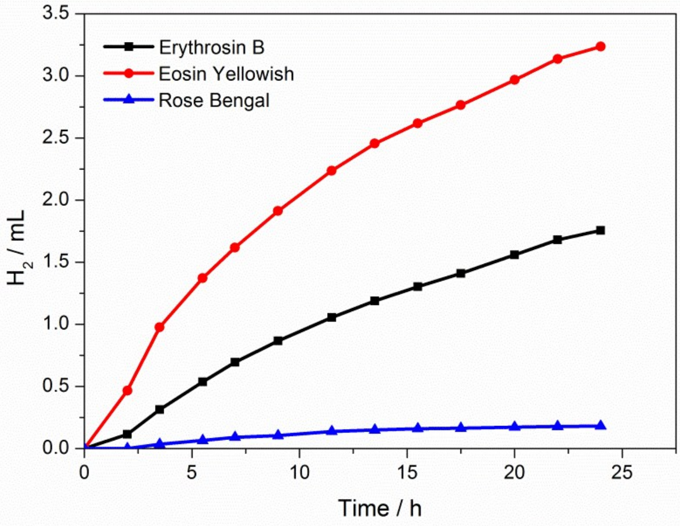


Figure S4. Time course of hydrogen production using various photosensitizers (10^{-3}M) with $CuSO_4 \cdot 5H_2O$ (1.0×10^{-5} M) and TEOA (1.5 mL, 5% v/v) at pH 10 (adjusted with 0.1 M HCl) in H_2O (28.5 mL) under $\lambda > 420$nm LED visible-light irradiation.

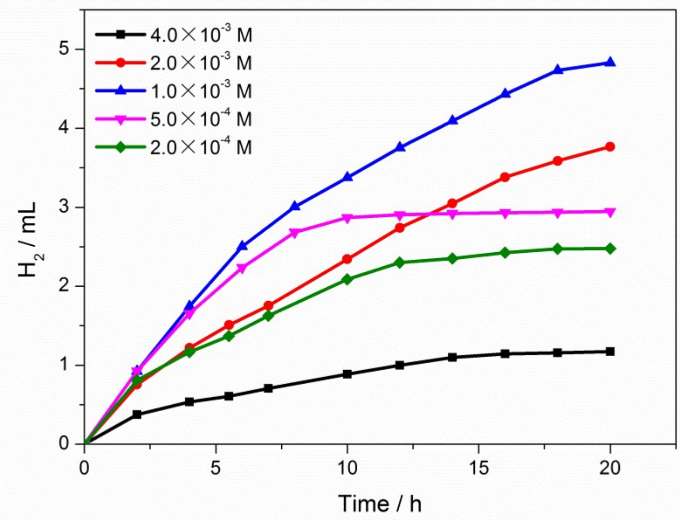


Figure S5. Time courses of photocatalytic H_2 evolution systems containing $CuSO_4$•$5H_2O$ (1.0 × 10^{-5} M) and TEA (1.5 mL, 5% v/v) at pH 11 (adjusted with 0.1M HCl) and various concentrations of Fl (0.2, 0.5, 1.0, 2.0 and 4.0 mM) in H_2O (28.5 mL) under visible-light irradiation.

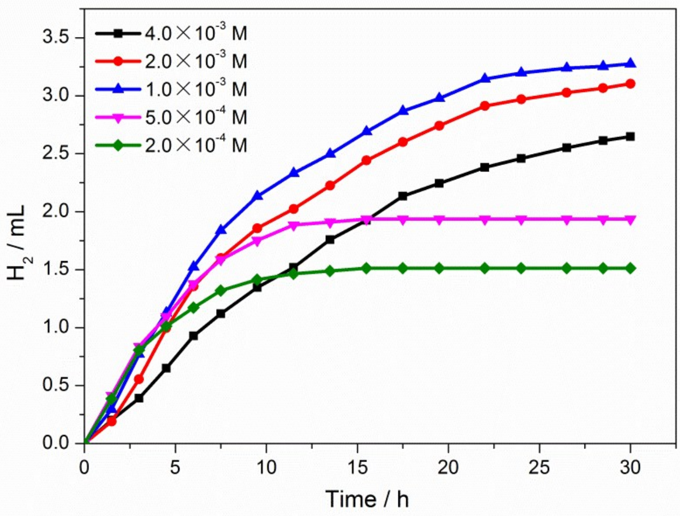


Figure S6. Time courses of photocatalytic H_2 evolution systems containing $CuSO_4$•$5H_2O$ (1.0 × 10^{-5} M) and TEOA (1.5 mL, 5% v/v) at pH 10 (adjusted with 0.1M HCl) and various concentrations of Fl (0.2, 0.5, 1.0, 2.0 and 4.0 mM) in H_2O (28.5 mL) under visible-light irradiation.

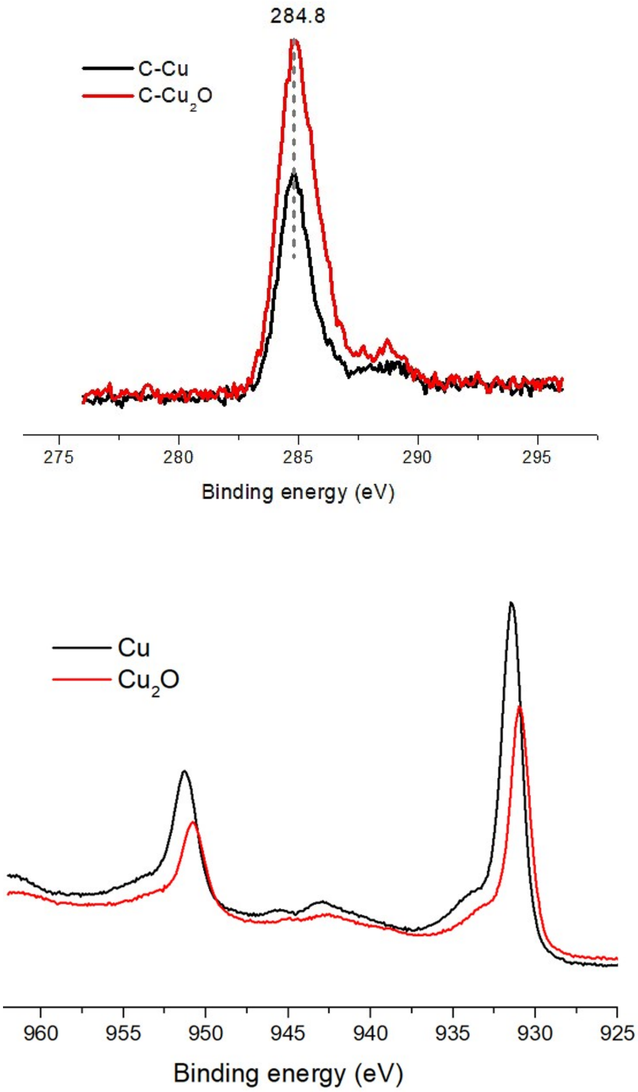


Figure S7. XPS results with on C and Cu with collected Cu and Cu_2O.

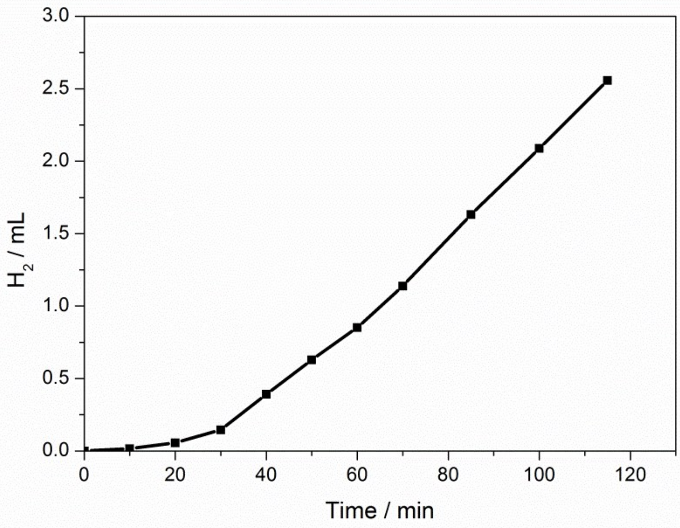


Figure S8. Hydrogen production induction period measurement from systems containing Cu_2O nanoparticles (30 μ M, 4.4 mg), Fl (2.0 mM) and TEA (5% v/v) at pH 11 in 30ml aqueous solution.

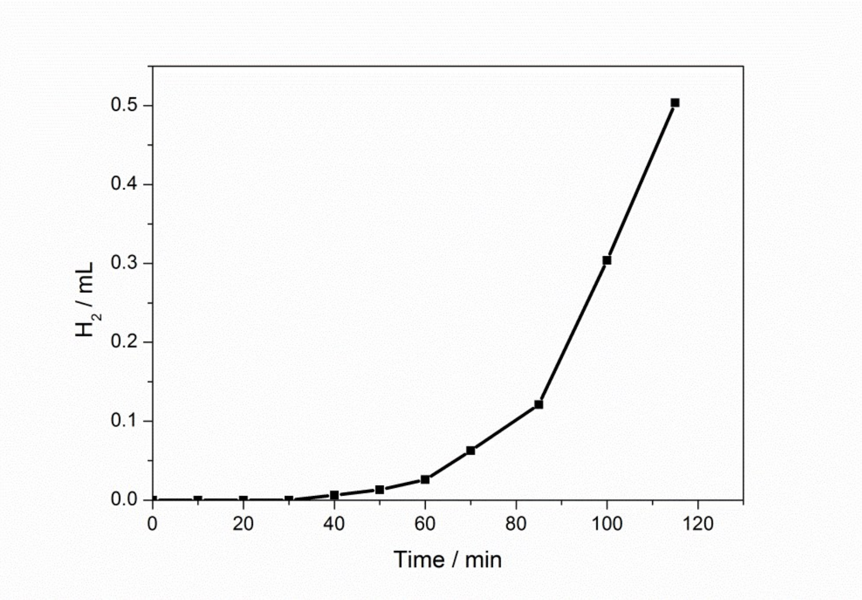


Figure S9. Hydrogen production induction period measurement from systems containing Cu_2O nanoparticles (30 μ M, 4.4 mg), Fl (2.0 mM) and TEOA (5% v/v) at pH 10 in 30ml aqueous solution.

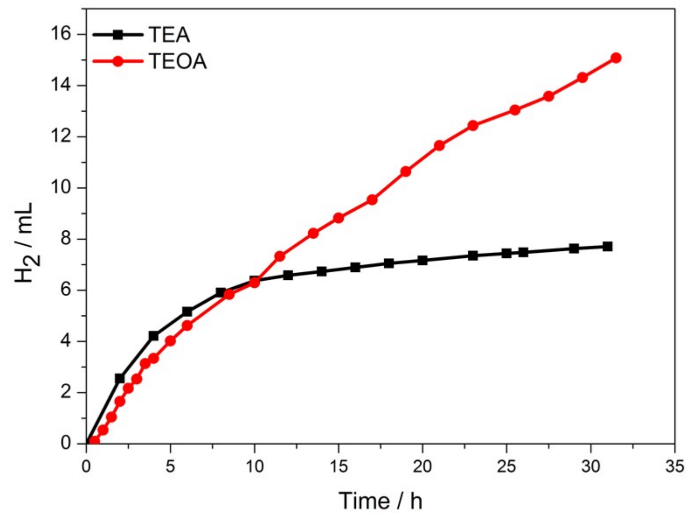


Figure S10. Hydrogen production from systems containing Cu nanoparticles (30 μ M, 2 mg), Fl (2.0 mM) in TEOA (5% v/v) or TEA (5% v/v) at pH 10 or pH 11 in 30ml aqueous solution.

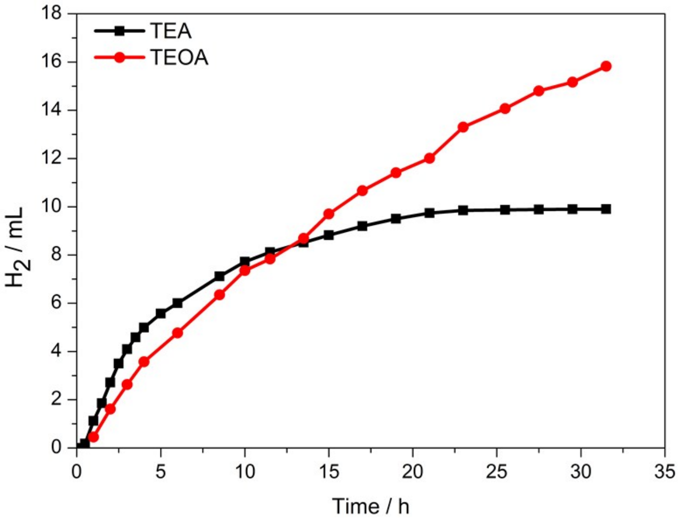


Figure S11. Hydrogen production from systems containing Cu_2O nanoparticles (30 μM, 4.4 mg), Fl (2.0 mM) in TEOA (5% v/v) or TEA (5% v/v) at pH 10 or pH 11 in 30ml aqueous solution.

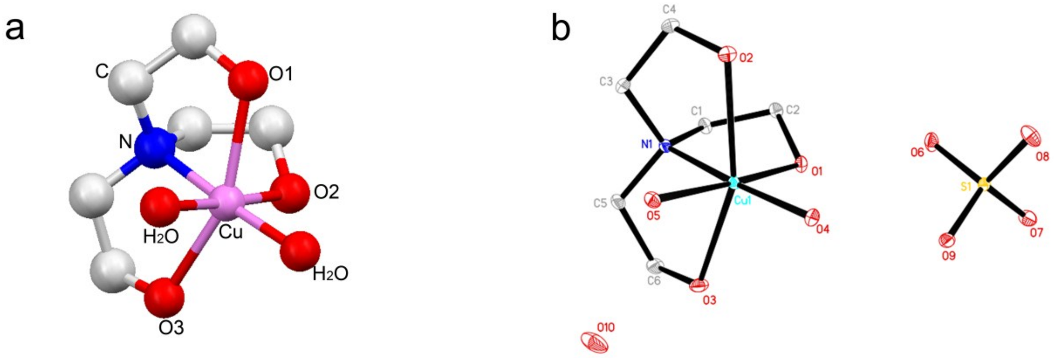
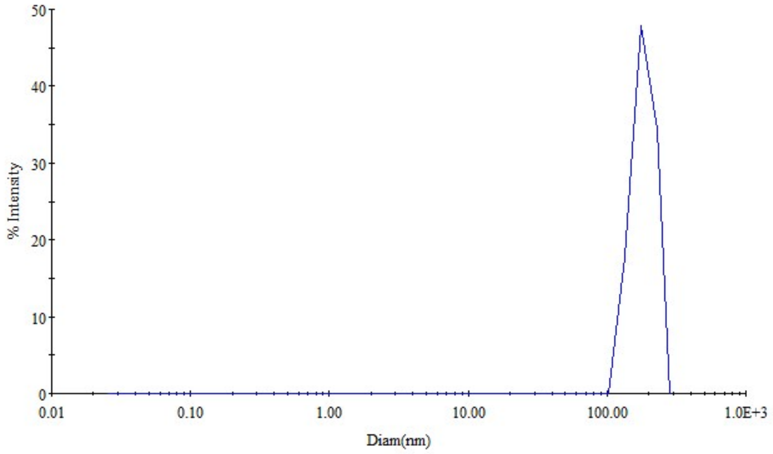
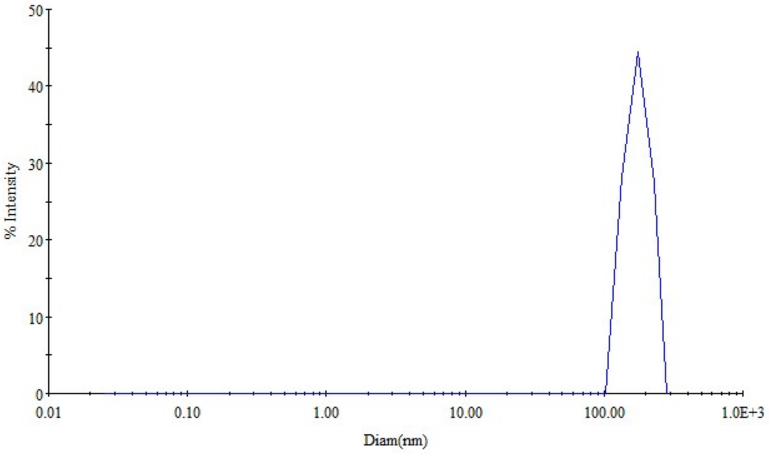


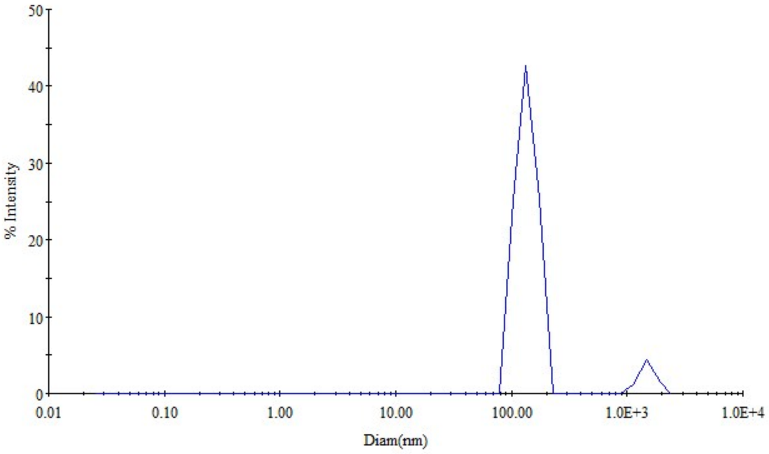
Figure S12. X-ray crystal structure (a) and ORTEP view (b) of $Cu(TEOA)(H_2O)_2$ complex with thermal ellipsoids at the 50% probability level. H atoms are omitted for clarity.



(a)


50
40
30
20
10
0
% Intensity
0.01
0.10
1.00
10.00
100.00
1.0E+3
Diam(nm)

(b)


50
40
30
20
10
0
% Intensity
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0.10
1.00
10.00
100.00
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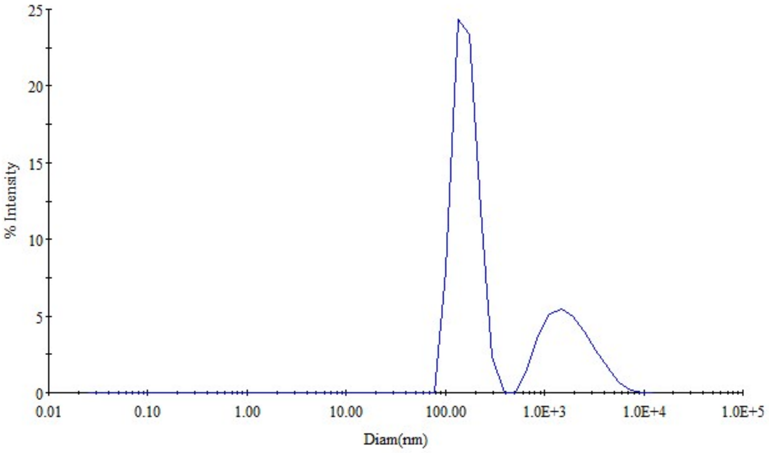
Diam(nm)

(c)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20
15
10
5
0
% Intensity
0.01
0.10
1.00
10.00
100.00
1.0E+3
1.0E+4
1.0E+5
Diam(nm)

(d)

Figure S13. (a) Particle size distribution at irradiation time of 0 min (a), 2 min (b), 4 min (c), 7 min (d) determined by DLS measurements with CuSO4 (1.0 mM), TEOA (5％ v/v) and Fl (1.0 mM).