Copper nanoparticles supported on diamond nanoparticles as cost-effective and efficient catalyst for natural Sunlight assisted Fenton reaction

Supplementary material

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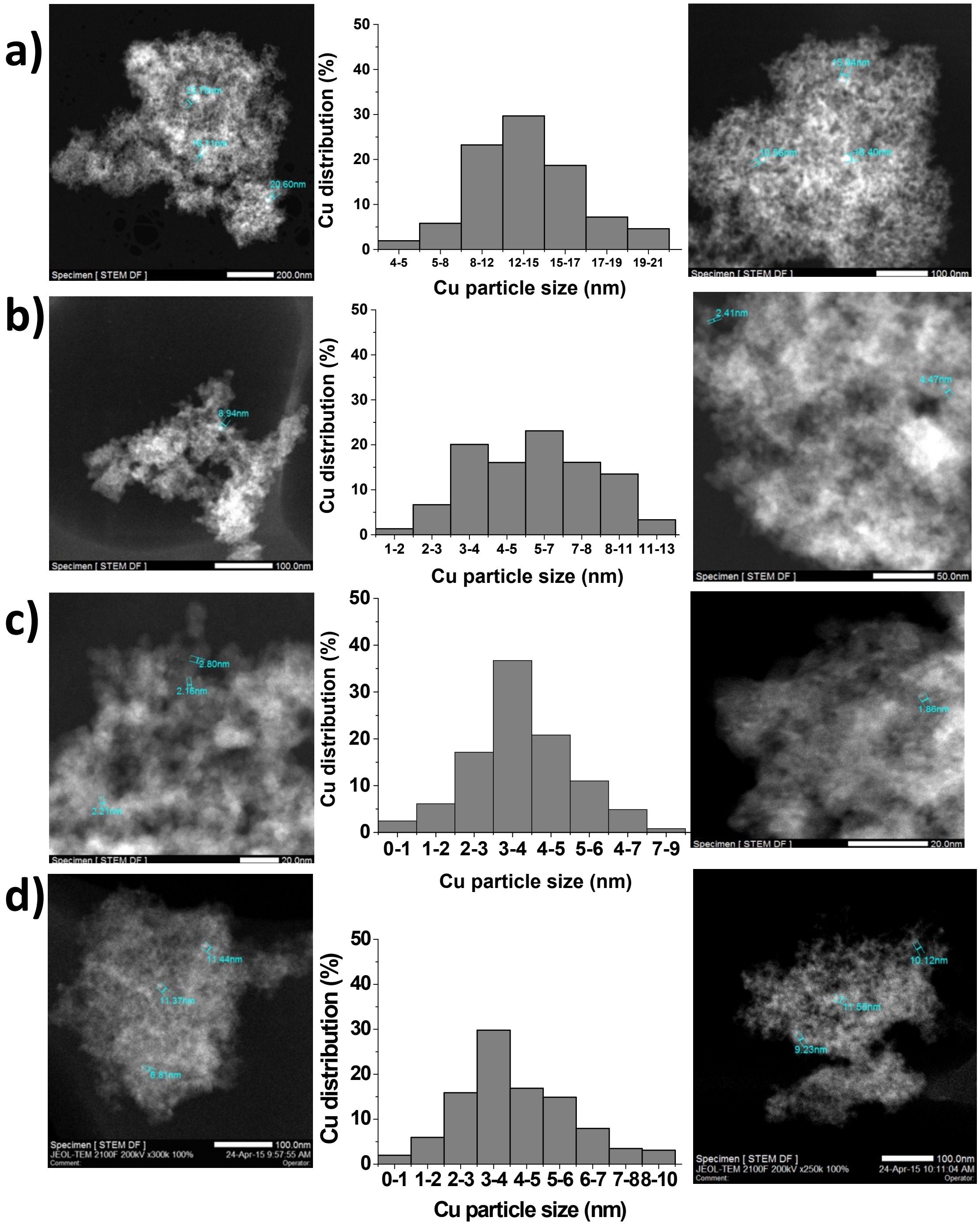

Figure S1. DF-STEM images and particle size distributions of Cu(0.2 wt%)/D1 (a), Cu(0.2 wt%)/D2 (b), Cu(0.2 wt%)/D3 (c) and Cu(1.0 wt%)/D3 (d). Cu average particle size for Cu(0.2 wt%)/D1 (a), Cu(0.2 wt%)/D2 (b), Cu(0.2 wt%)/D3 and Cu(1.0 wt%)/D3 (c) was 13.4 ± 5.3, 6.3 ± 4.2, 3.7 ± 2.7 and 11.1±5.6 nm, respectively.

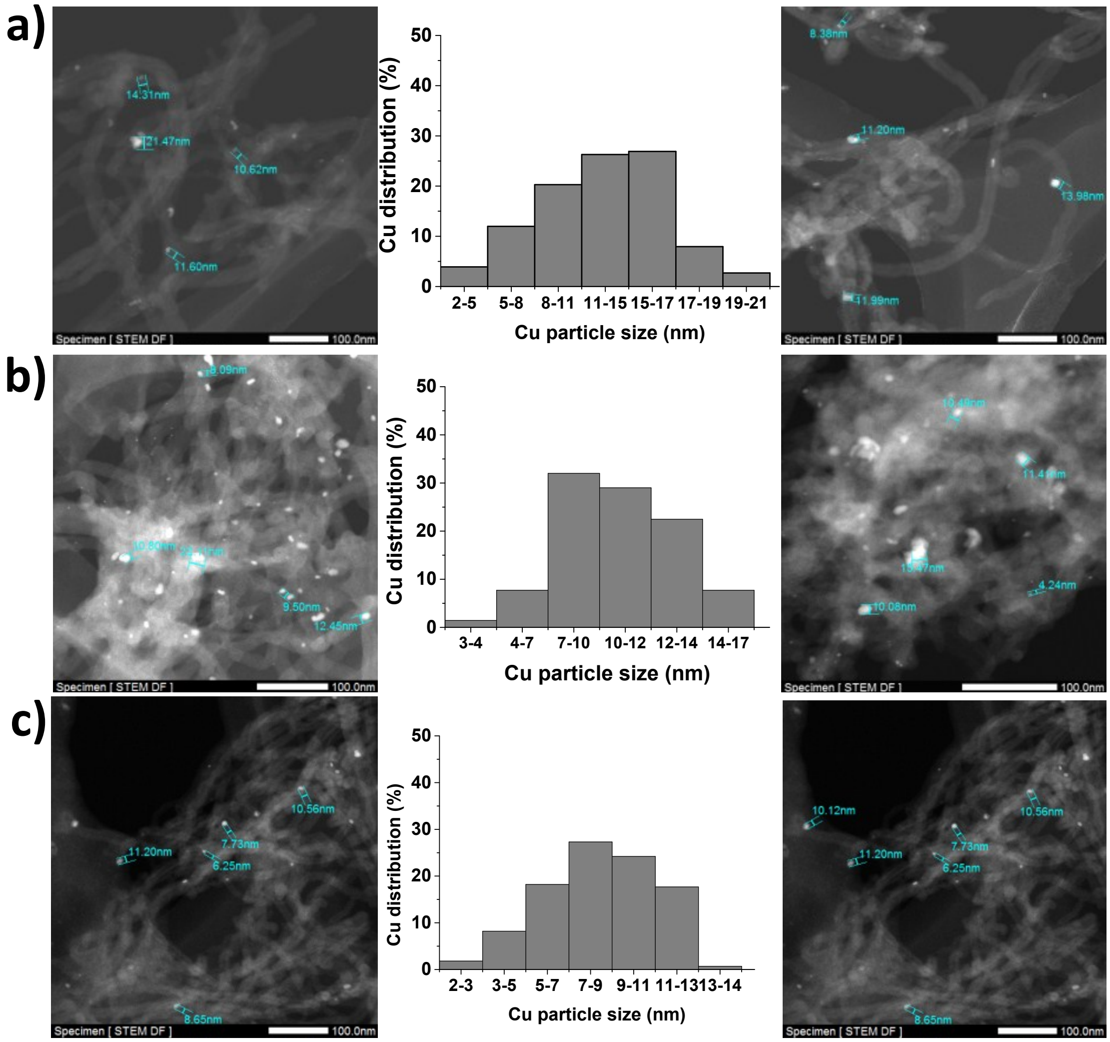

Figure S2. DF-STEM images and particle size distribution of Cu/NT1 (a), Cu/NT2 (b) and Cu/NT3 (c). Cu average particle size for Cu/NT1, Cu/NT2 and Cu/NT3 was 12.2 ±6.0, 9.9 ± 4.2 and 7.8 ± 3.6 nm, respectively. Note: Cu loading 0.2 wt %.

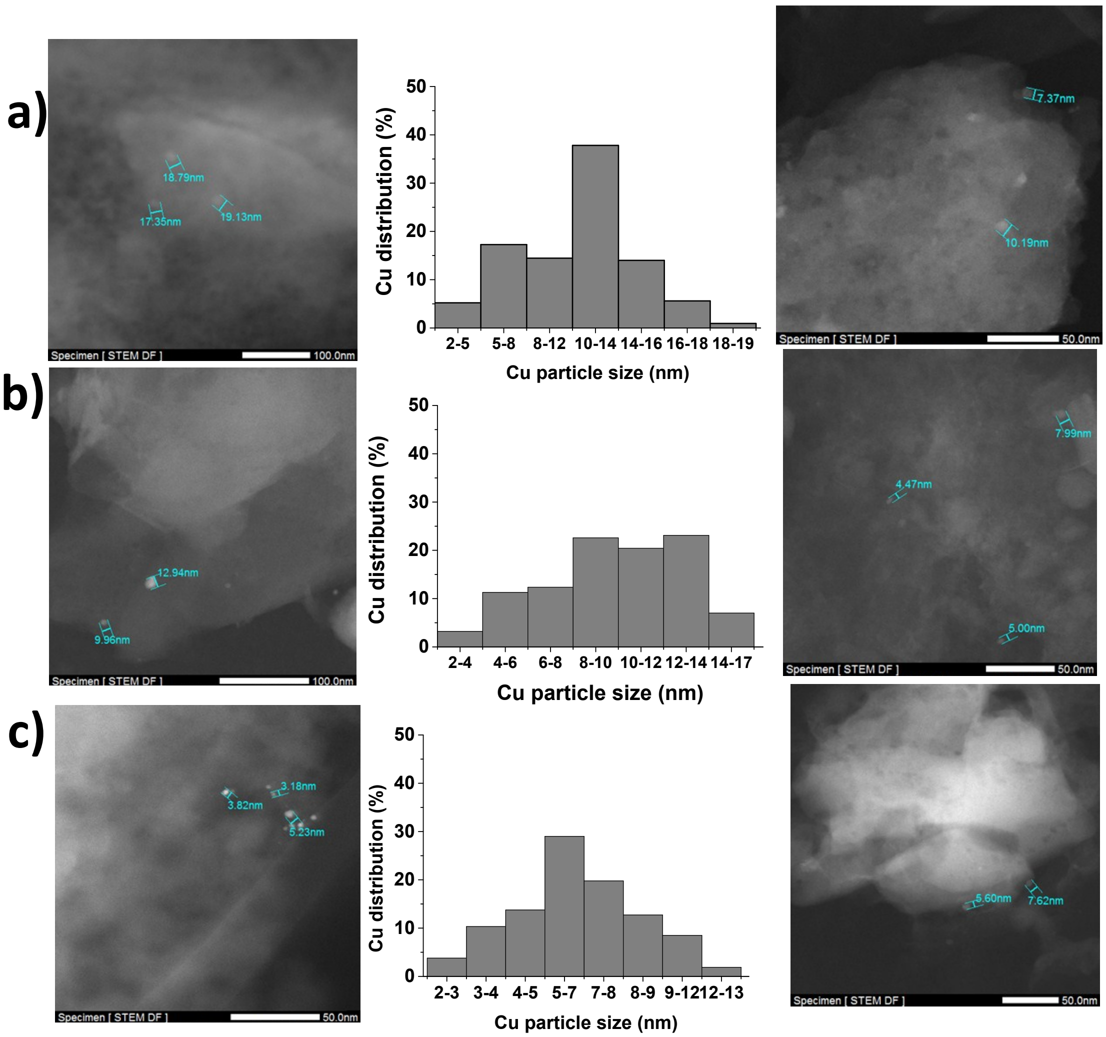

Figure S3. DF-STEM images and particle size distribution of Cu/AC1 (a), Cu/AC2 (b) and Cu/AC3 (c). Cu average particle size for Cu/AC1, Cu/AC2 and Cu/AC3 was 11.4 ±5.3, 9.4 ± 4.2 and 6.0 ± 3.6 nm, respectively. Note: Cu loading 0.2 wt %.

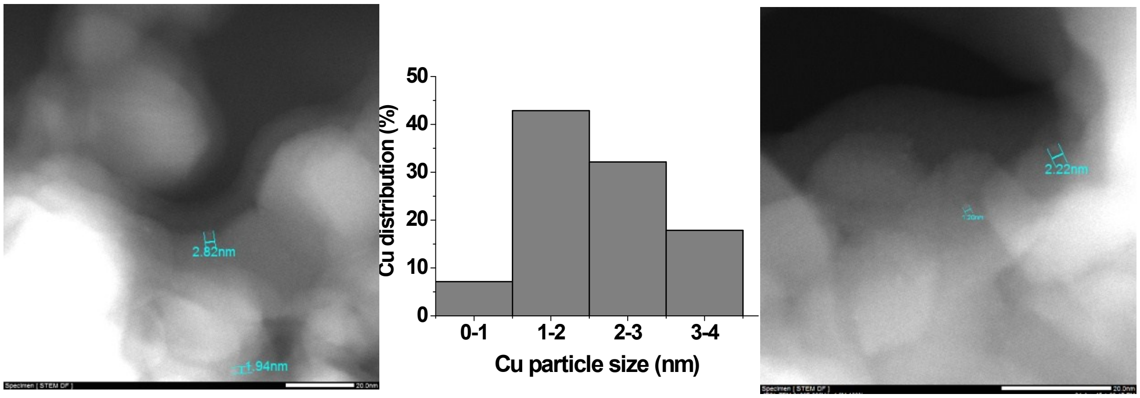

Figure S4. DF-STEM images and particle size distributions of Cu/TiO_2. Cu average particle size of 2.6 ± 1.6 nm. Note: Cu loading 0.2 wt %.

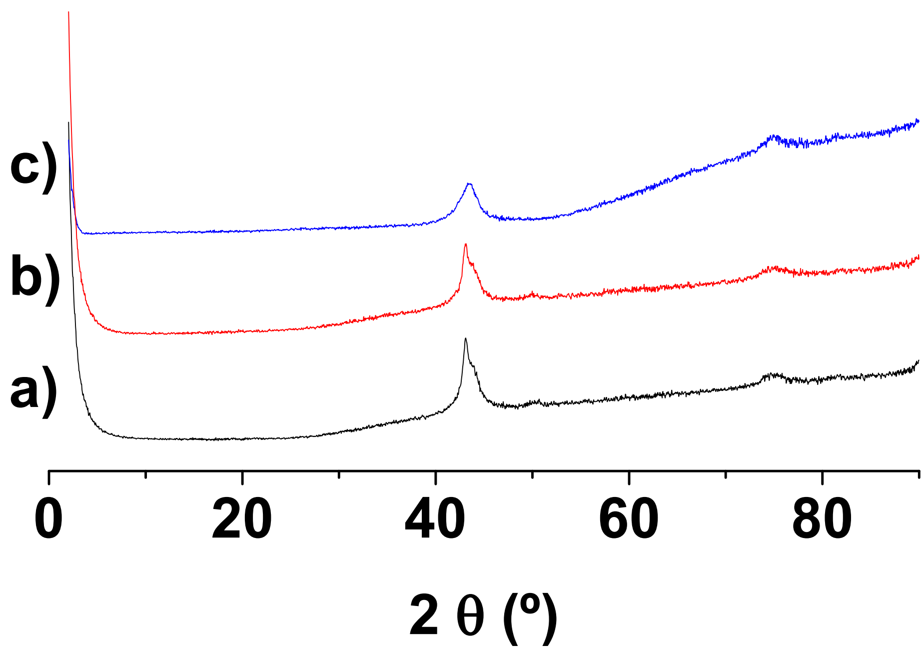

Figure S5. XRD diffractograms of Cu/D1 (a), Cu/D2 (b) and Cu/D3 (c). Note: Cu loading 0.2 wt %

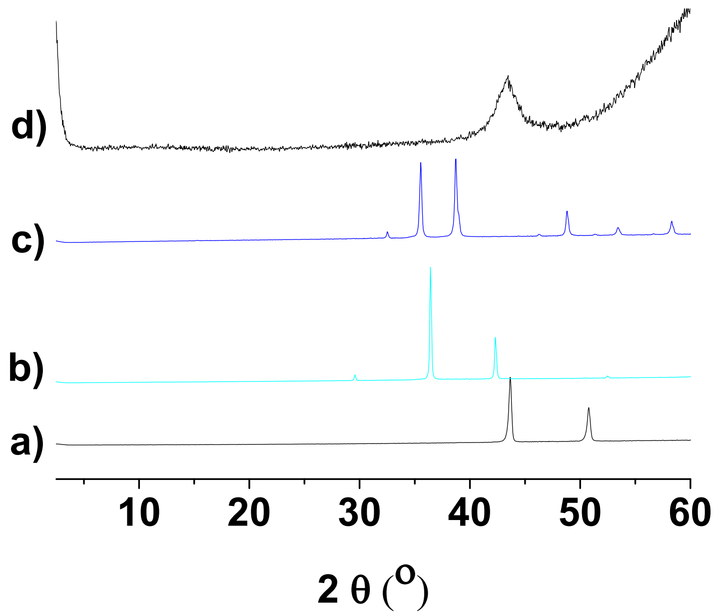

Figure S6. XRD diffractograms of Cu (a), Cu_2O (b), CuO (c) and Cu(1.0 wt%)/D3 (d). Note: a, b and c are commercial samples from Sigma-Aldrich.

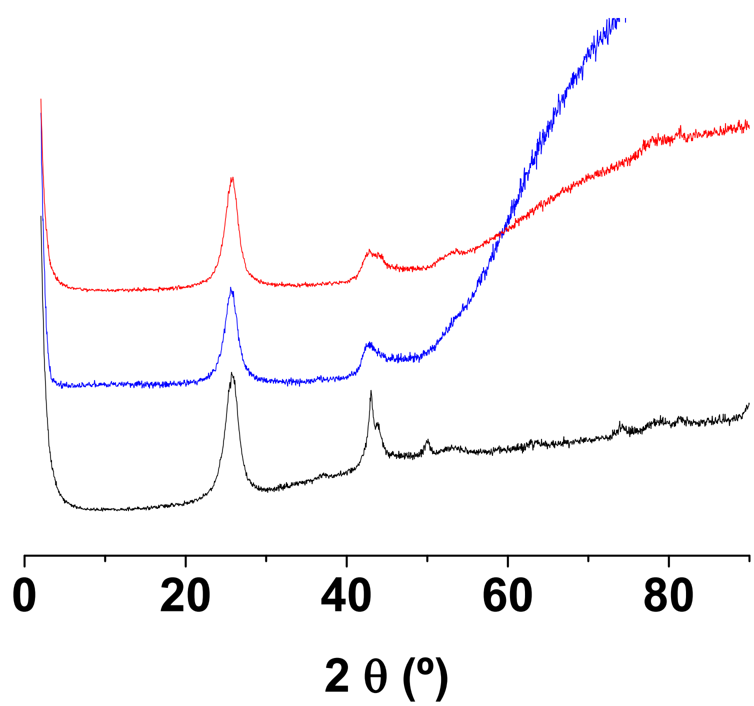

Figure S7. XRD diffractograms of Cu/NT1 (a), Cu/NT2 (b) and Cu/NT3 (c). Note: Cu loading 0.2 wt %.

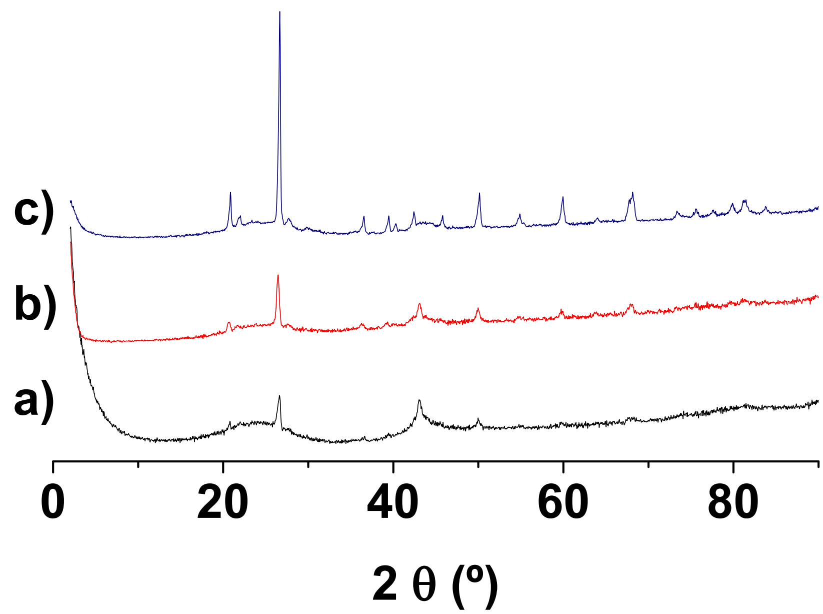

Figure S8. XRD diffractograms of Cu/AC1 (a), Cu/AC2 (b) and Cu/AC3 (c). Note: Cu loading 0.2 wt %.

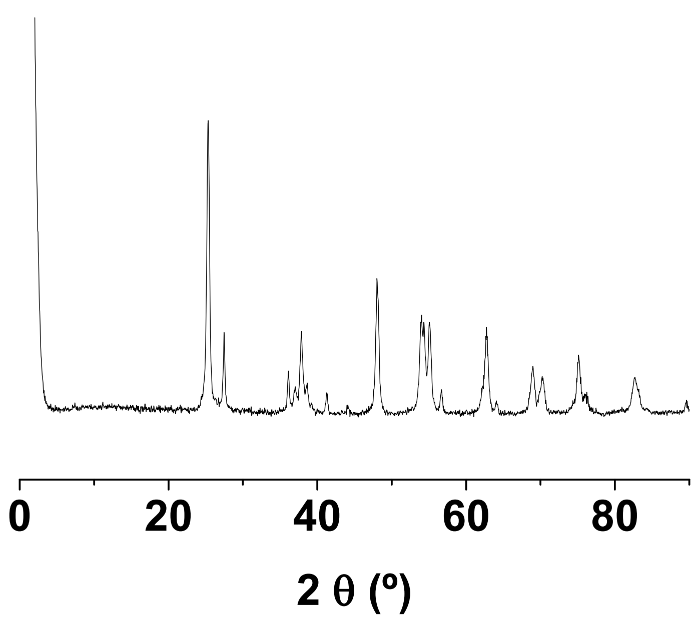

Figure S9. XRD diffractogram of Cu (0.2 wt%)/TiO_2.

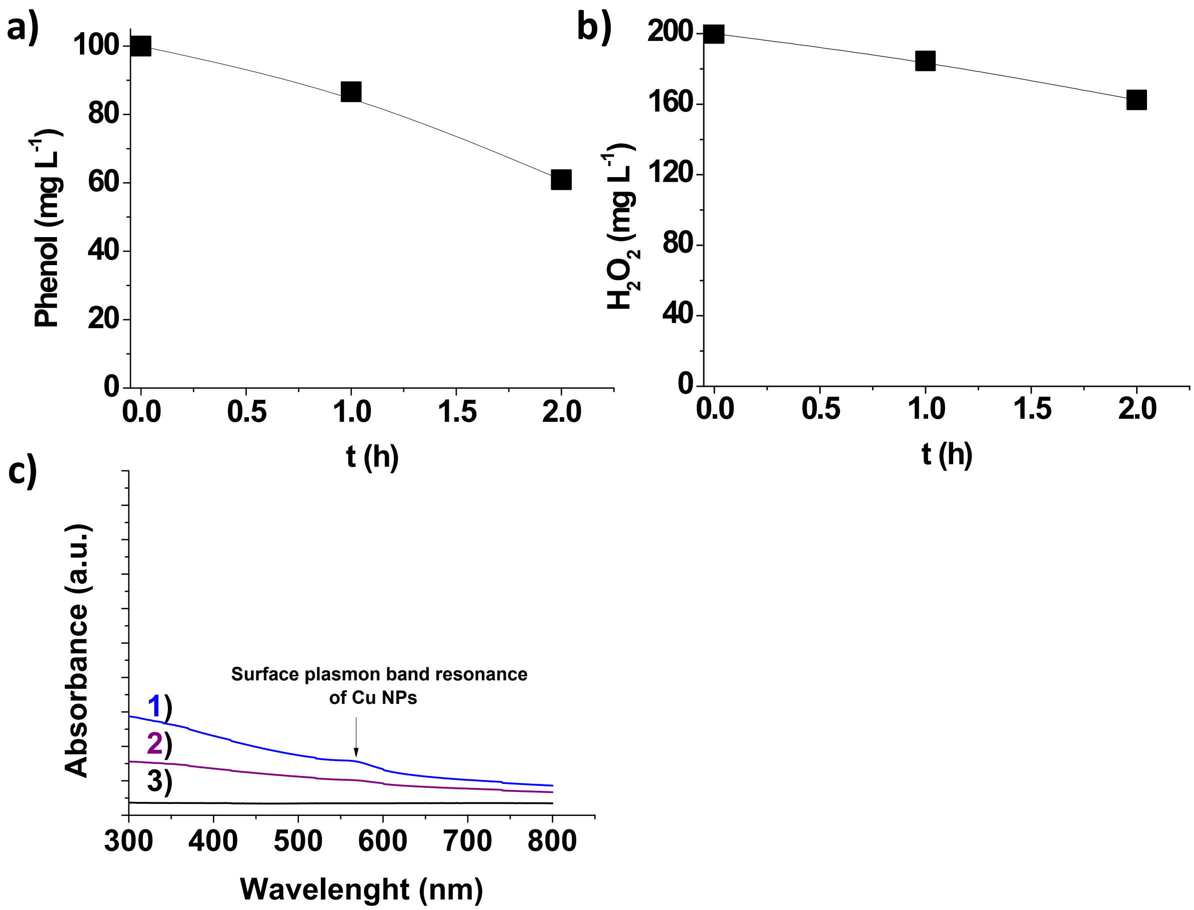

Figure S10. Phenol degradation (a) and H_2O_2 decomposition (b) using unsupported Cu NPs as catalyst. c) UV-Vis spectra of unsupported Cu NPs synthetized using Cu^{2+} at concentrations of 125 (1), 62 (2) and 0.4 mg L^{-1} (3). Catalyst (0.4 mg L^{-1}, 0.0063 mM of unsupported Cu NPs), phenol (100 mg L^{-1}; 1.06 mM), H_2O_2 (200 mg L^{-1}; 5.88 mM), initial pH 4.

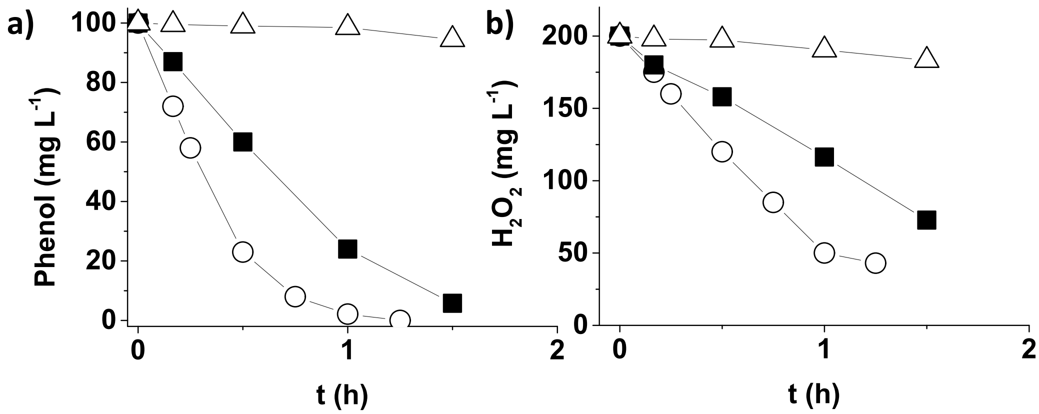

Figure S11. Phenol degradation (a) and H_2O_2 decomposition (b) using Cu NPs supported on D-based materials under natural Sunlight irradiation. Legend: Cu/D3 (○), Cu/D2 (■) and Cu/D1 (Δ).Catalyst (200 mg L^{-1}; 0.0063 mM of supported Cu NPs), phenol (100 mg L^{-1}; 1.06 mM), H_2O_2 (200 mg L^{-1}; 5.88 mM), initial pH 4.

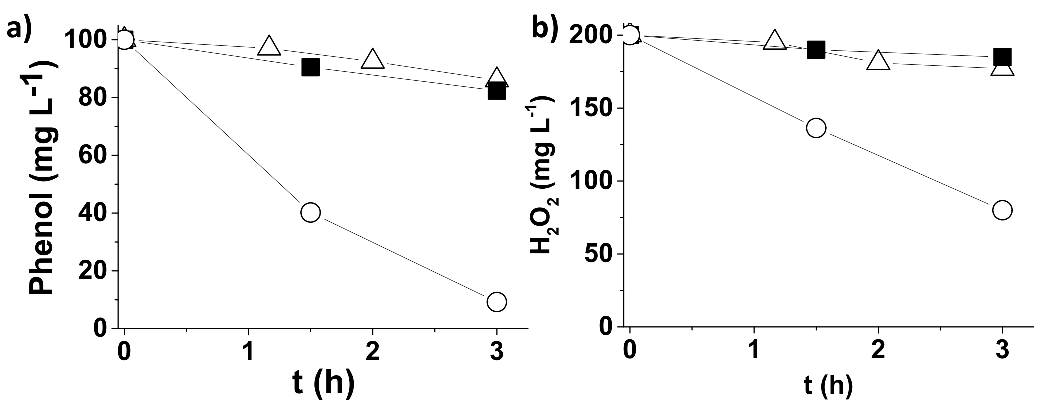

Figure S12. Phenol degradation (a) and H_2O_2 decomposition (b) using Cu NPs supported on AC-based materials under natural Sunlight irradiation. Legend: Cu/AC3 (○), Cu/AC2 (■) and Cu/AC1 (Δ). Catalyst (200 mg L^{-1}; 0.0063 mM of supported Cu NPs), phenol (100 mg L^{-1}; 1.06 mM), H_2O_2 (200 mg L^{-1}; 5.88 mM), initial pH 4.

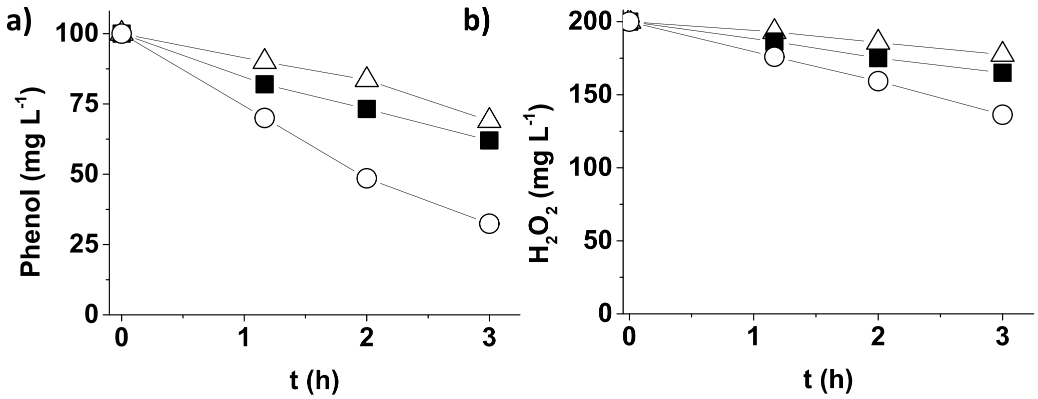

Figure S13. Phenol degradation (a) and H_2O_2 decomposition (b) using Cu NPs supported on NTs-based materials under natural Sunlight irradiation. Legend: Cu/NT1 (Δ), Cu/NT2 (■) and Cu/NT3 (○). Catalyst (200 mg L^{-1}; 0.0063 mM of supported Cu NPs), phenol (100 mg L^{-1}; 1.06 mM), H_2O_2 (200 mg L^{-1}; 5.88 mM), initial pH 4.

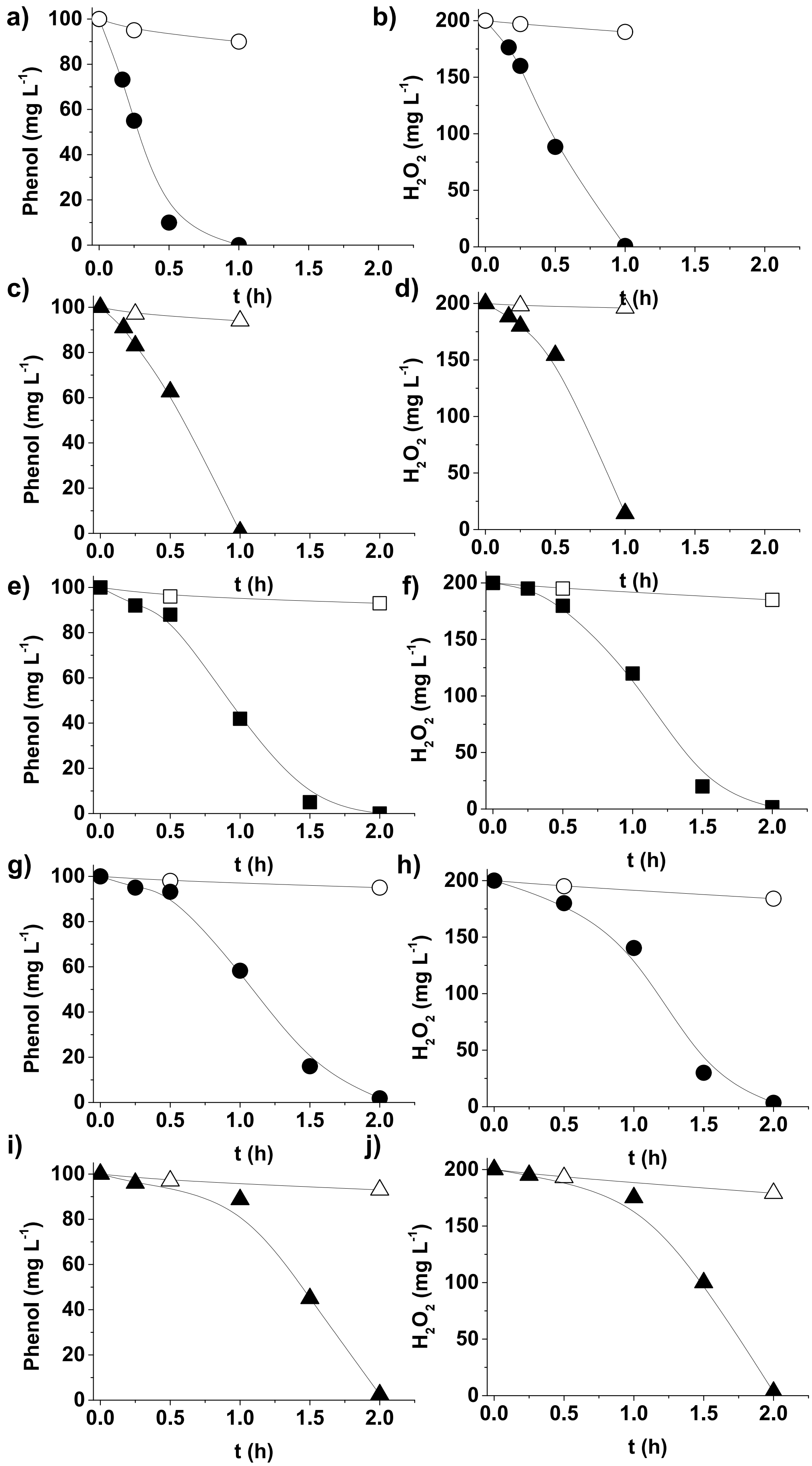
a)
b)
c)
d)
e)
f)
g)
h)
i)
j)
Phenol (mg L-1)
H2O2 (mg L-1)
t (h)
0.0
0.5
1.0
1.5
2.0
0
20
40
60
80
100
50
150
200

Figure S14. Phenol degradation (a, c, e, g, i) and H_2O_2 decomposition (b, d, f, h, j) as a function of the initial pH value under dark (empty symbols) and natural Sunlight (full symbols) irradiation using Cu/D3. Legend: pH 4 (a, b), 4.5 (c, d), 5.5 (e, f), 6.5 (g, h) and 7.5 (i, j). Reaction conditions: Catalyst (200 mg L^{-1}; 0.0063 mM of supported Cu NPs), phenol (100 mg L^{-1}; 1.06 mM), H_2O_2 (200 mg L^{-1}; 5.88 mM), pH 4, natural Sunlight irradiation intensity (1.2 $mWcm^{-2}$), temperature (42 ºC).

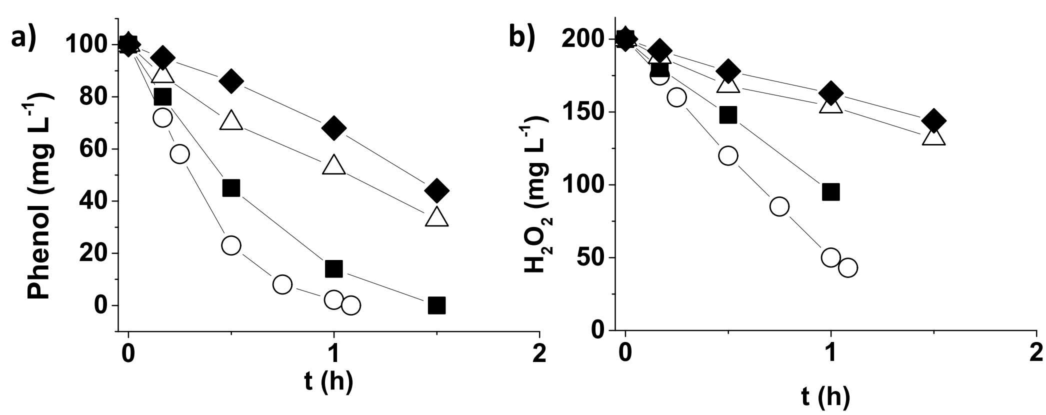

Figure S15. Reusability test for phenol degradation (a) and H_2O_2 decompositon (b) using Cu/D3 as catalyst under natural Sunlight irradiation. Legend: run 1 (○), run 2 (■), run 3 (Δ) and run 4 (♦). Note: After every use the catalyst was recovered by filtration, washed using basic water (pH 10) and distilled H_2O and, then, used for the subsequent run without any additional treatment to the catalyst. Catalyst (200 mg L^{-1}; 0.0063 mM of supported Cu NPs), phenol (100 mg L^{-1}; 1.06 mM), H_2O_2 (200 mg L^{-1}; 5.88 mM), initial pH 4.

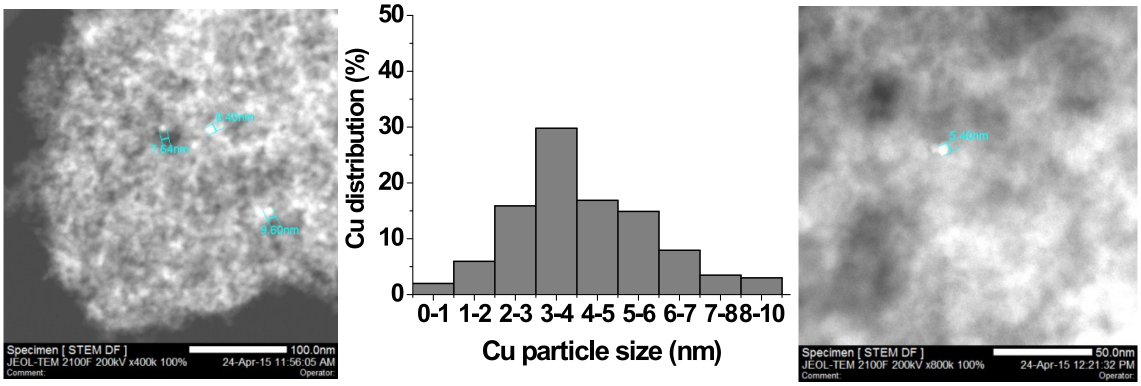

Figure S16. DF-STEM images and particle size distribution of Cu (0.2 wt%)/D3 after eight uses.

Copper average particle size of 4.2 ± 2.9 nm.

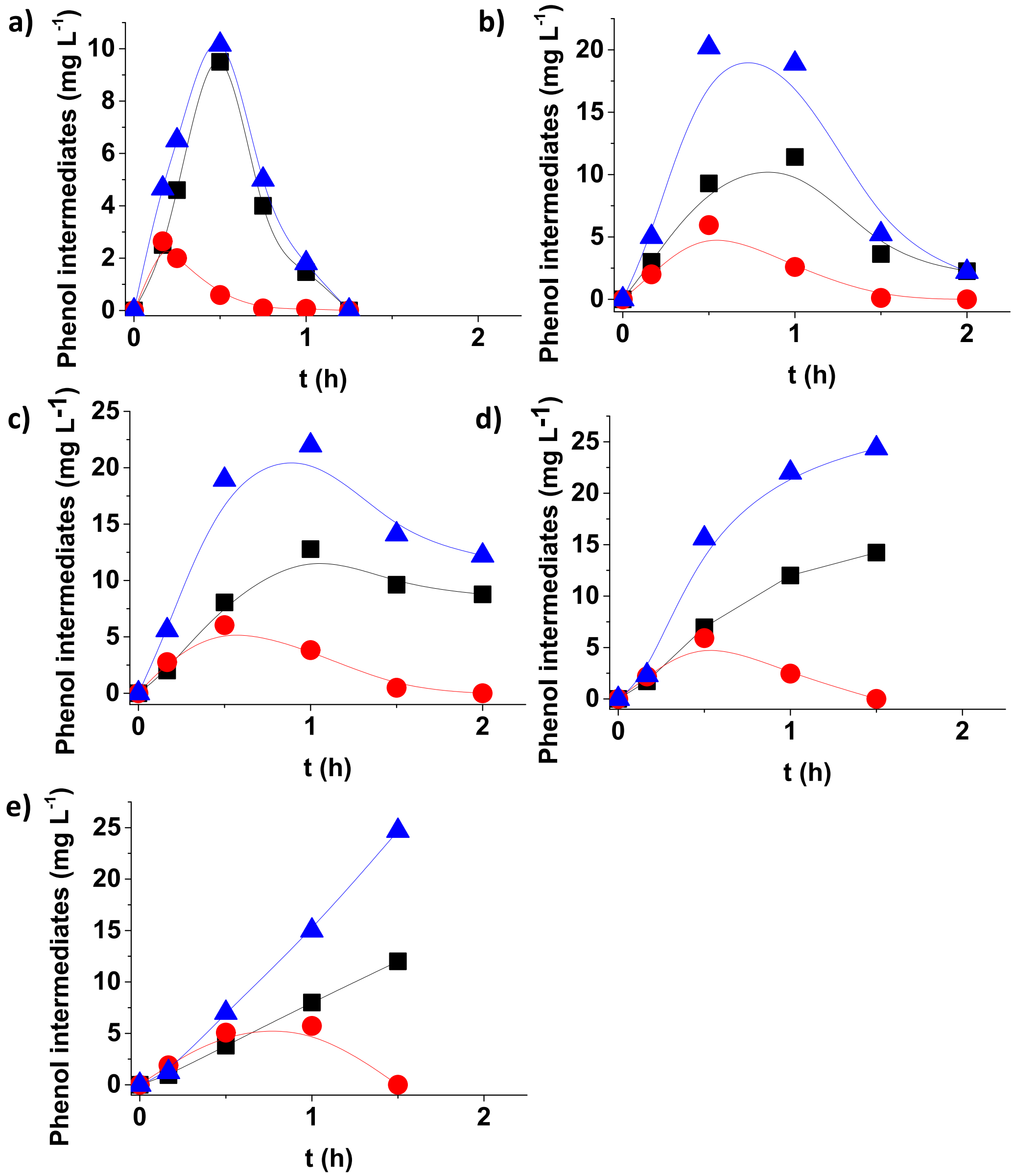

Figure S17. Influence of H_2O_2 to phenol molar ratio for the degradation of phenol and its reaction intermediates (catechol, hydroquinone and *p*-benzoquinone) using Cu/D3 as catalyst under natural Sunlight irradiation. 5.5 (a), 4 (b), 3 (c), 2 (d) and 1 (e) equivalent. Catalyst (200 mg L^{-1}; 0.0063 mM of supported Cu NPs), phenol (100 mg L^{-1}; 1.06 mM), H_2O_2 as indicated, pH 4. Legend: Catechol (blue triangle), hydroquinone (black square) and *p*-benzoquinone (red circle).

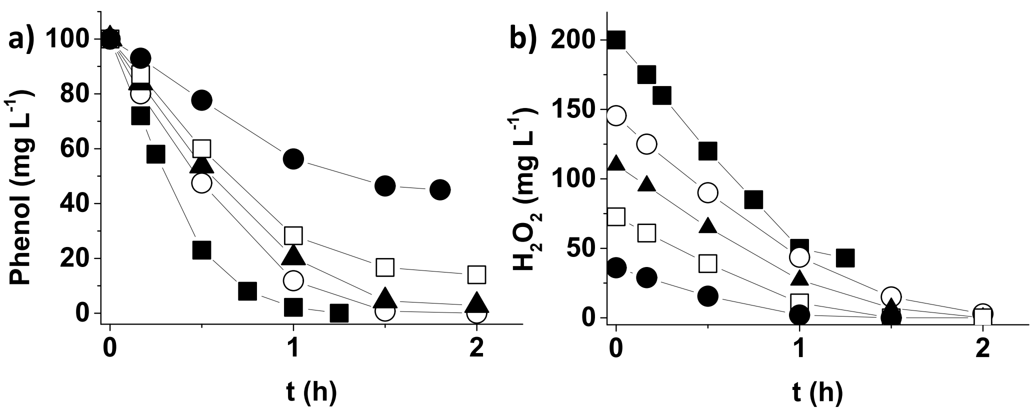

Figure S18. Influence of H_2O_2 to phenol molar ratio for phenol degradation (a) and H_2O_2 decomposition (b) using Cu/D3 as catalyst under natural Sunlight irradiation. Legend: 5.5 (■), 4.0 (○), 3.0 (▲), 2.0 (□) and 1.0 (●) H_2O_2 to phenol molar ratio. Catalyst (200 mg L^{-1}), phenol (100 mg L^{-1}; 1.06 mM), H_2O_2 (as indicated), initial pH 4.

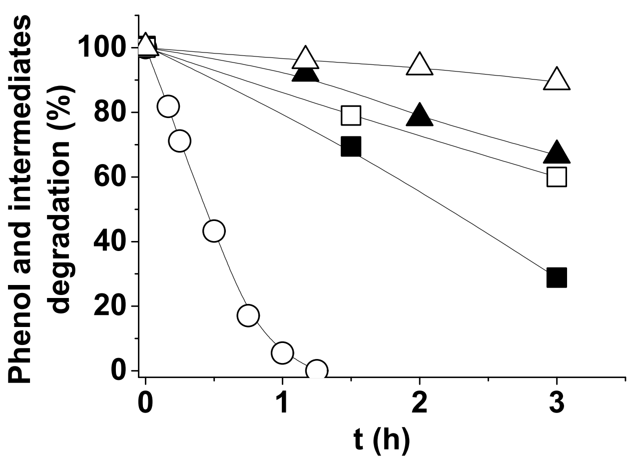

Figure S19. Phenol and reaction intermediates (catechol, hydroquinone and *p*-benzoquinone) degradation using Cu/D3 (○), Cu/AC3 (■), Cu/NT3 (▲), Cu/TiO_2 (□) and Cu/TiO_2 without H_2O_2 (Δ) as catalysts under natural Sunlight irradiation. Catalyst (200 mg L^{-1} and 0.0063 mM of supported Cu NPs), phenol (100 mg L^{-1}; 1.06 mM), H_2O_2 (200 mg L^{-1}; 5.88 mM), initial pH 4.