-Supporting information-

Cobalt promoted TiO_2/GO for the photocatalytic degradation of oxytetracycline and Congo Red

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Materials and methods

Graphite powder (>20µm), Cobalt nitrate ($Co(NO_3)_2.6H_2O$)(98%), titanium (IV) isopropoxide (TIP)(97%), anatase titanium dioxide (99.7%), cobalt oxide, oxytetracyline (OCT, >95%), Congo Red (CR), terephthalic acid (98%), sodium sulfate (≥ 99%) and Indium tin oxide (ITO) coated glass slides were purchased from Sigma Aldrich. Table S1 shows the structure, chemical properties, and absorbance maximum (λ_{max}) of oxytetracyline (OTC), Congo Red (CR). Ethanol, sodium hydroxide (NaOH, 99%) and methanol (MeOH, analytical grade) were purchased from Merck Millipore, Germany. Hydrochloric acid (HCl) was purchased from PFP Matsunden Chemicals Ltd., South Korea. 500 W Xenon lamp was purchased from Woosung Electric Co. Ltd., South Korea.

Table S1. Surface (XPS) and bulk (XRF) Co content of composites.

Sample	Co loading / wt%	
	Surface	Bulk
0.5 wt% Co_3O_4/TiO_2	0	2.3
1 wt% Co_3O_4/TiO_2	0.61	6.1
2% Co_3O_4/TiO_2	0.75	10.3
2 wt% Co_3O_4/TiO_2/GO	0.8	8.5

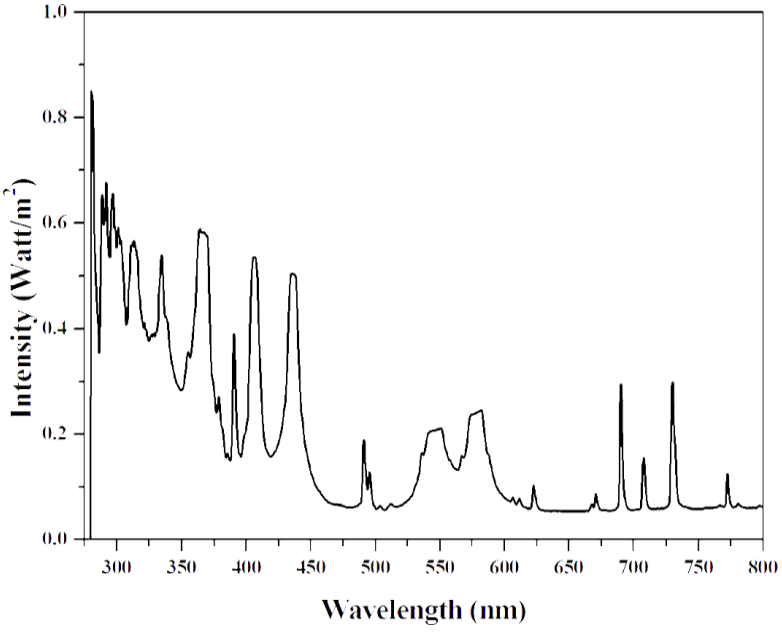


Figure S1. Spectral distribution of light.

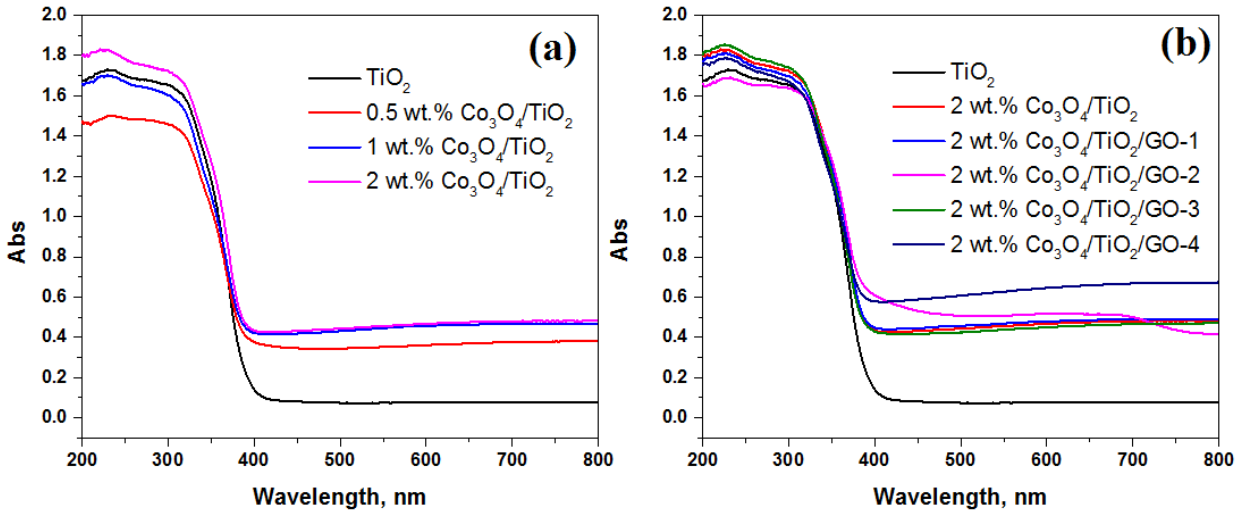


Figure S2. DRUV absorption spectra of (a) Co_3O_4/TiO_2 and (b) amine functionalized 2 wt% Co_3O_4/TiO_2/GO nanocomposites as a function of Co or GO loading. Reference anatase is shown for comparison.

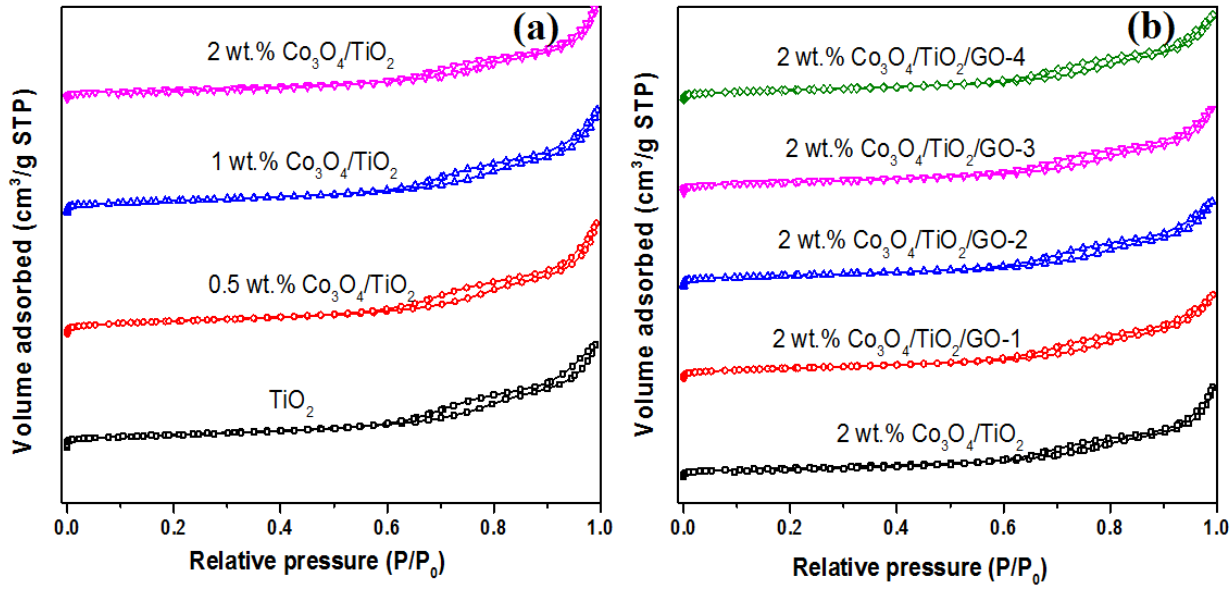


Figure S3. Adsorption-desorption isotherms of (a) Co_3O_4/TiO_2 and (b) amine functionalized 2 wt% Co_3O_4/TiO_2/GO nanocomposites as a function of Co or GO loading. Reference anatase is shown for comparison.

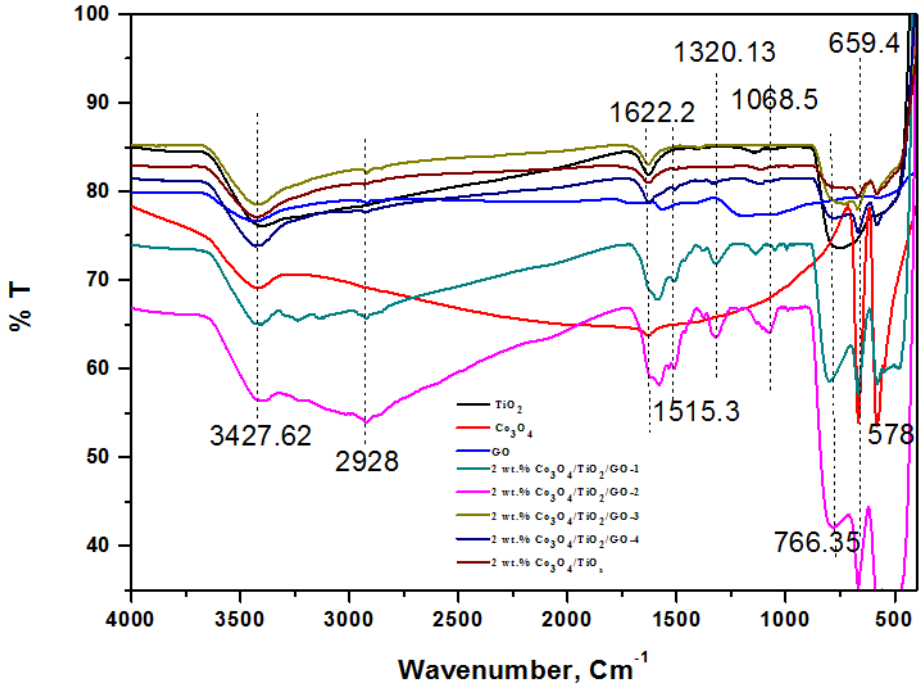


Figure S4. DRIFT spectra of Co_3O_4/TiO_2 and (b) amine functionalized 2 wt% Co_3O_4/TiO_2/GO nanocomposites.

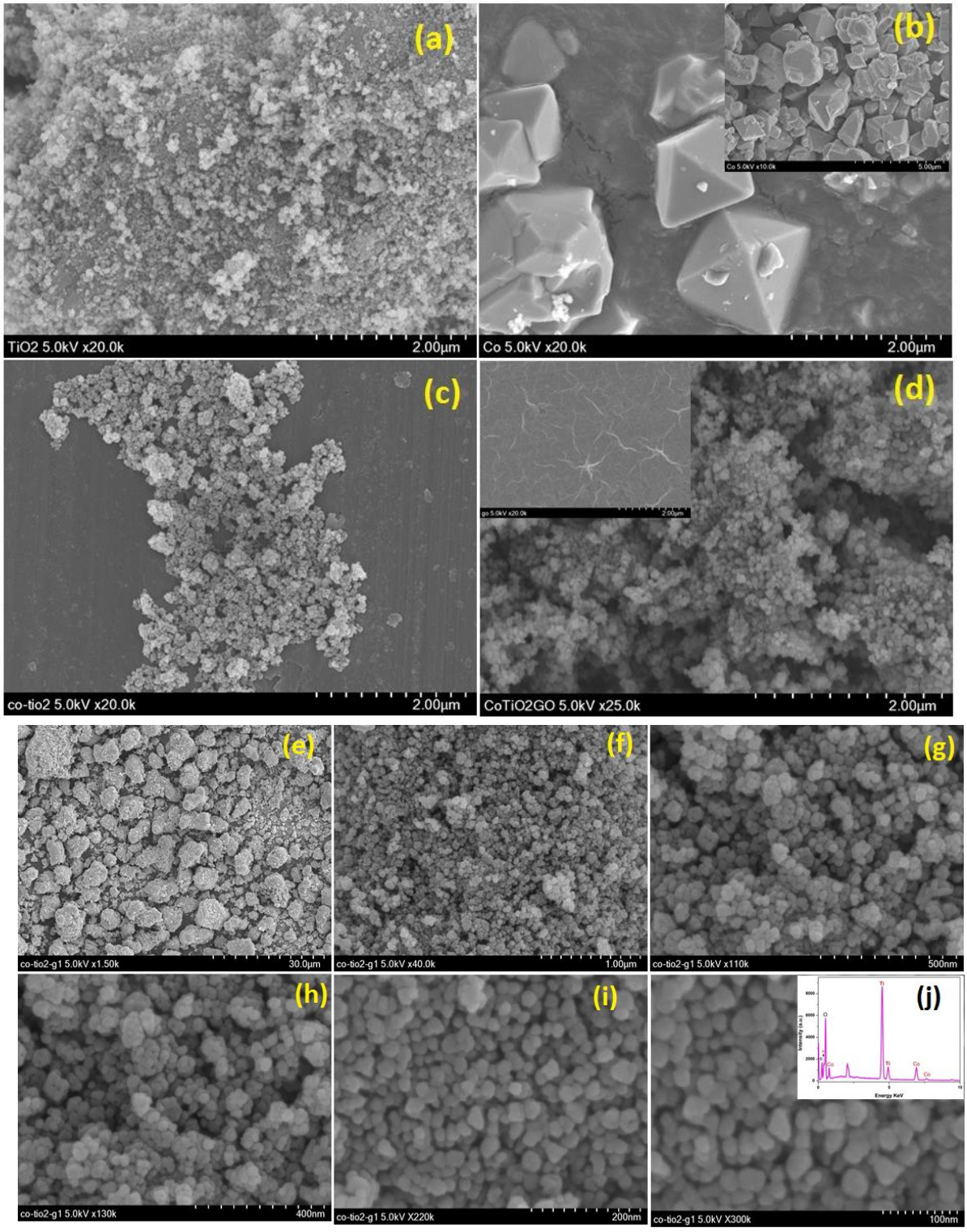


Figure S5. SEM micrographs (a) TiO_2 reference, (b) Co_3O_4 reference, (c) 2 wt% Co_3O_4/TiO_2, (d) 2 wt% Co_3O_4/TiO_2/GO-1(GO reference inset), (e-j) 2 wt% Co_3O_4/TiO_2/GO-1 (EDX spectra inset).

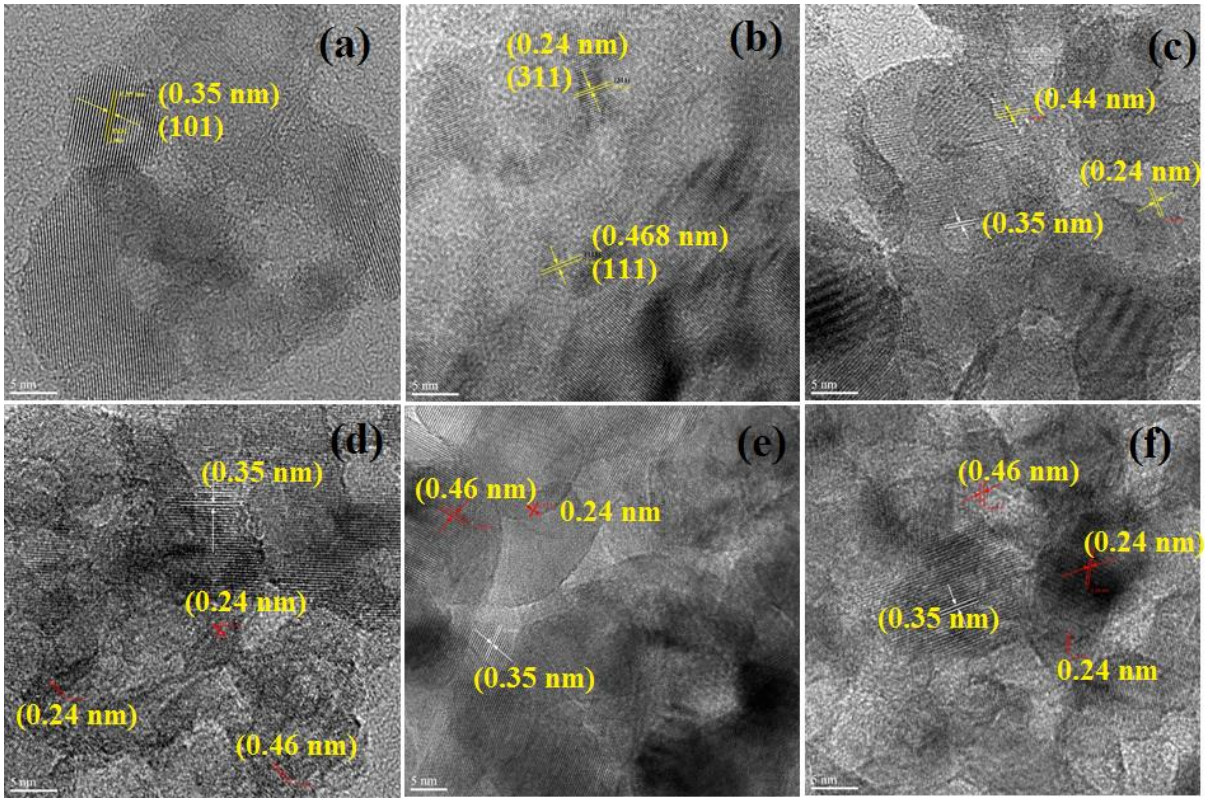


Figure S6. (a-f) HR-TEM d-space analysis of pure and doped TiO_2 photocatalysts (scale bar 5nm), (a) pure TiO_2, (b) Co_3O_4, (c,d) 2 wt % Co_3O_4/TiO_2, and (e,f) 2 wt% Co_3O_4/TiO_2/GO-1

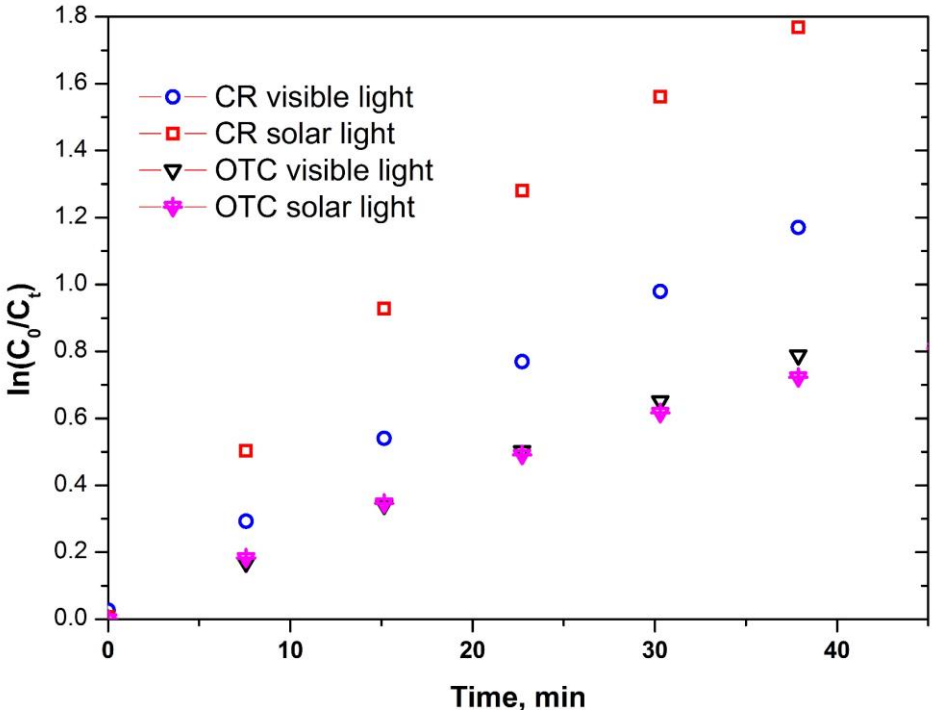


Figure S7. Photodegradation of CR and OTC under simulated solar and visible irradiation over amine functionalized 2 wt% Co_3O_4/TiO_2/GO nanocomposite determined by UV-Vis.

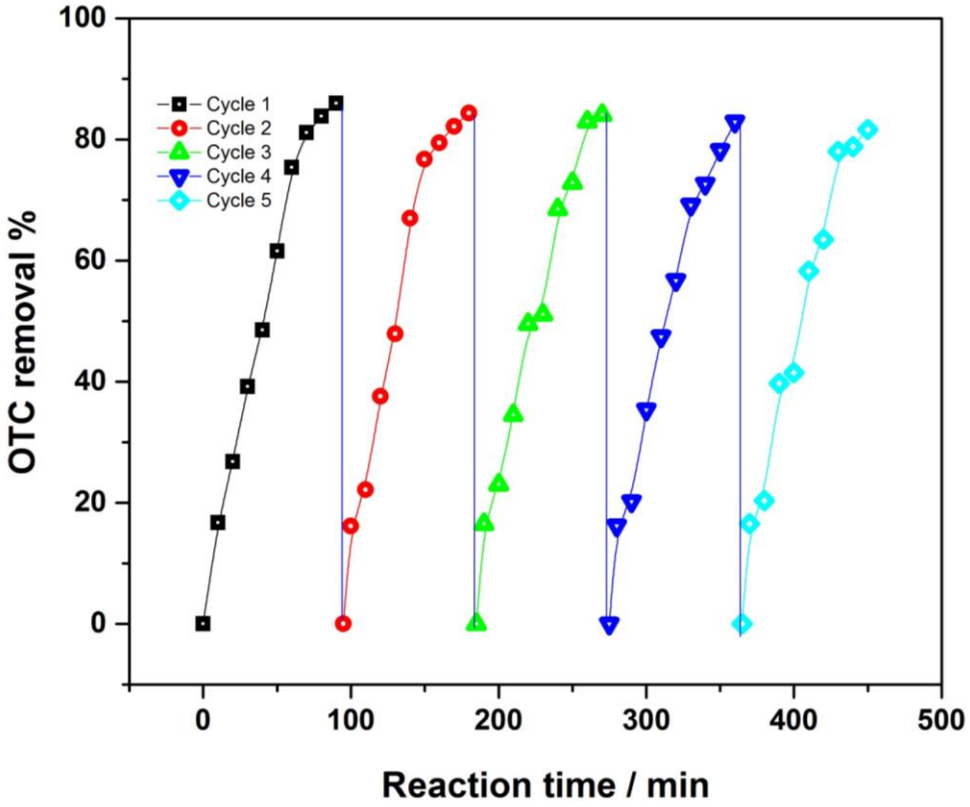
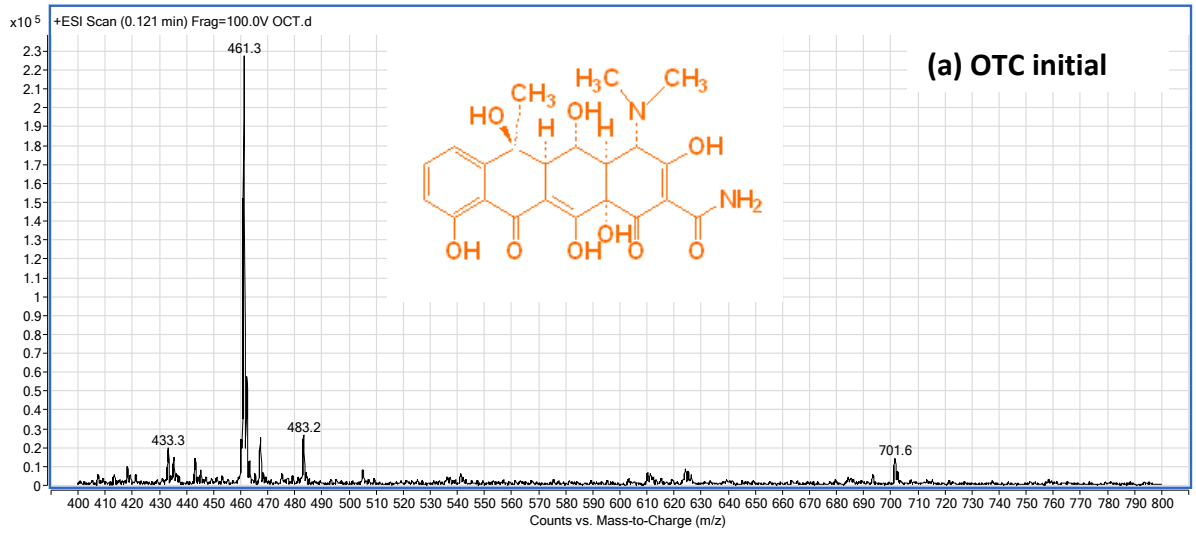
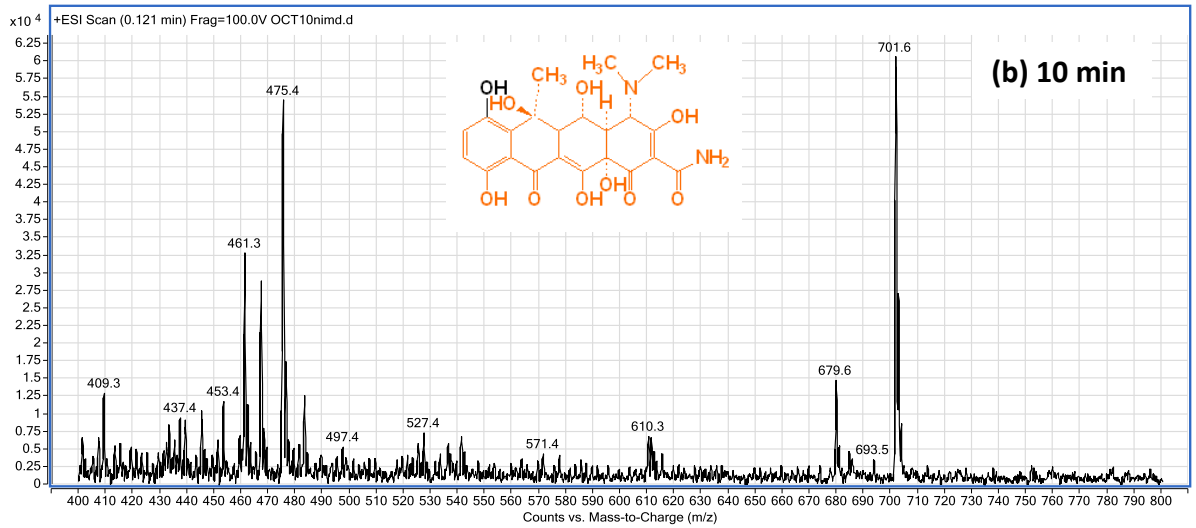
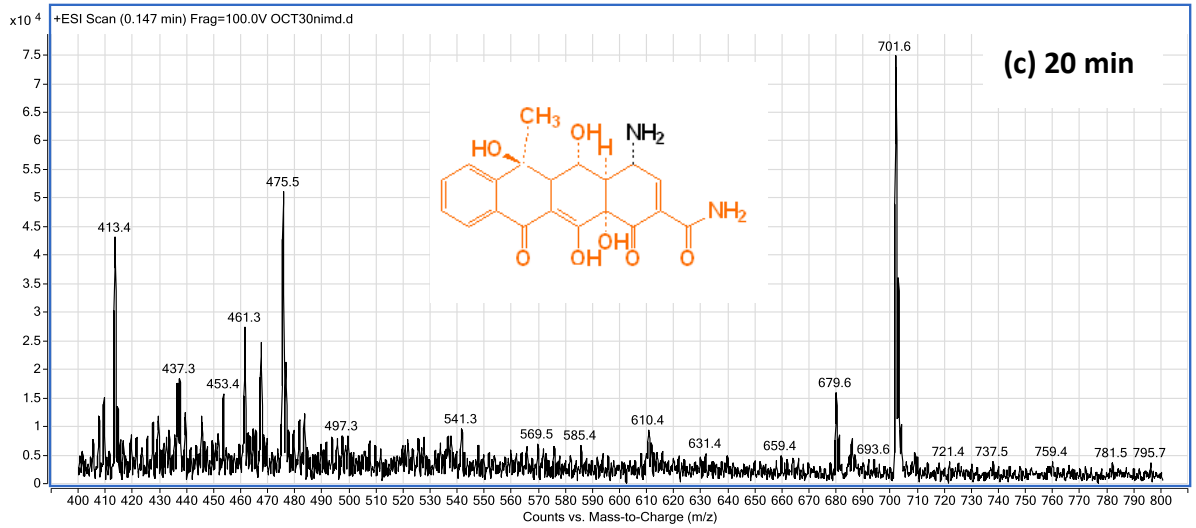
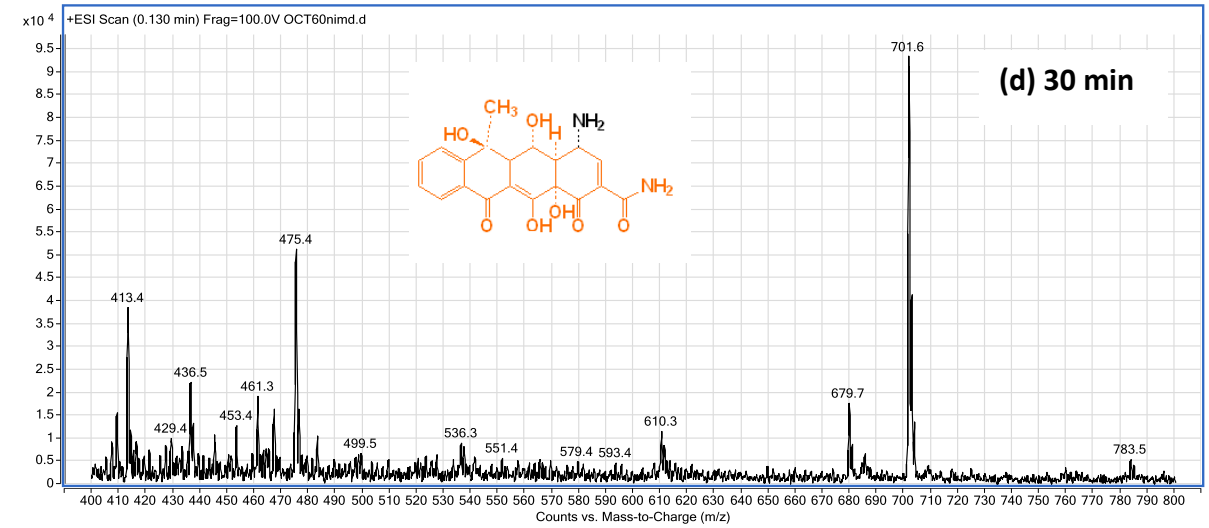


Figure S8. Recyclability of 2 wt% Co_3O_4/TiO_2/GO-1 for OTC depollution under simulated solar light.


x10 5
+ESI Scan (0.121 min) Frag=100.0V OCT.d
(a) OTC initial
461.3
483.2
433.3
701.6
Counts vs. Mass-to-Charge (m/z)


x10 4
+ESI Scan (0.121 min) Frag=100.0V OCT10nimd.d
(b) 10 min
701.6
475.4
461.3
409.3
453.4
437.4
497.4
527.4
571.4
610.3
679.6
693.5
Counts vs. Mass-to-Charge (m/z)


x10 4
+ESI Scan (0.147 min) Frag=100.0V OCT30nimd.d
(c) 20 min
701.6
475.5
413.4
461.3
437.3
453.4
497.3
541.3
569.5
585.4
610.4
631.4
659.4
679.6
693.6
721.4
737.5
759.4
781.5
795.7
Counts vs. Mass-to-Charge (m/z)



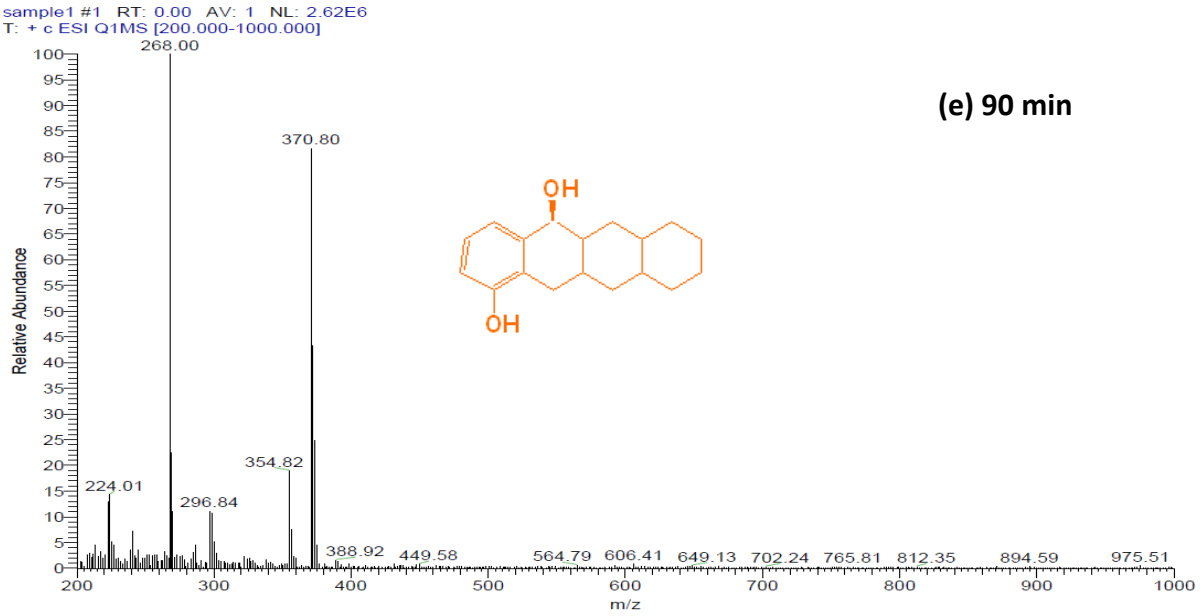
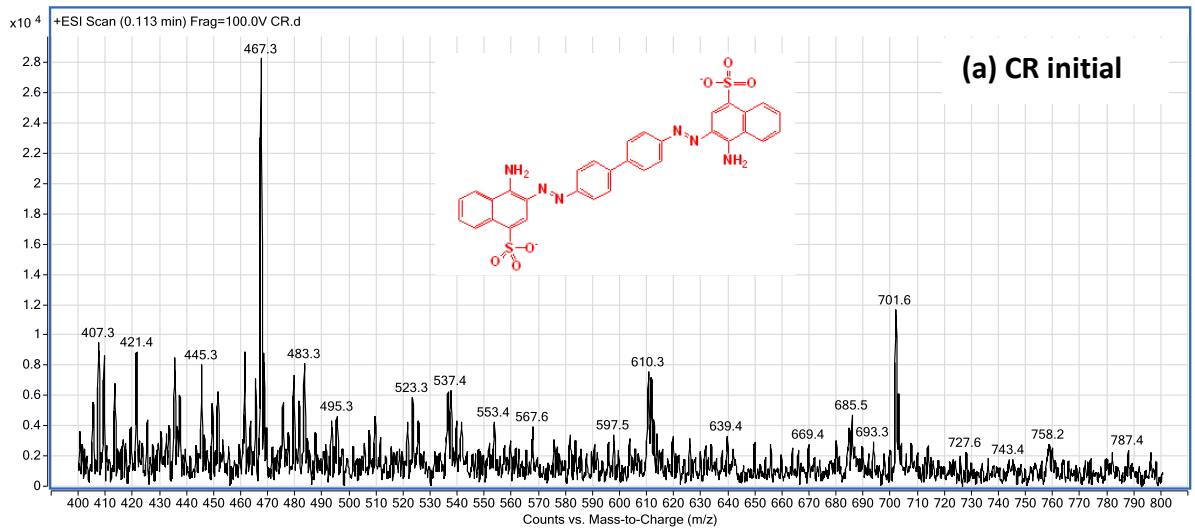
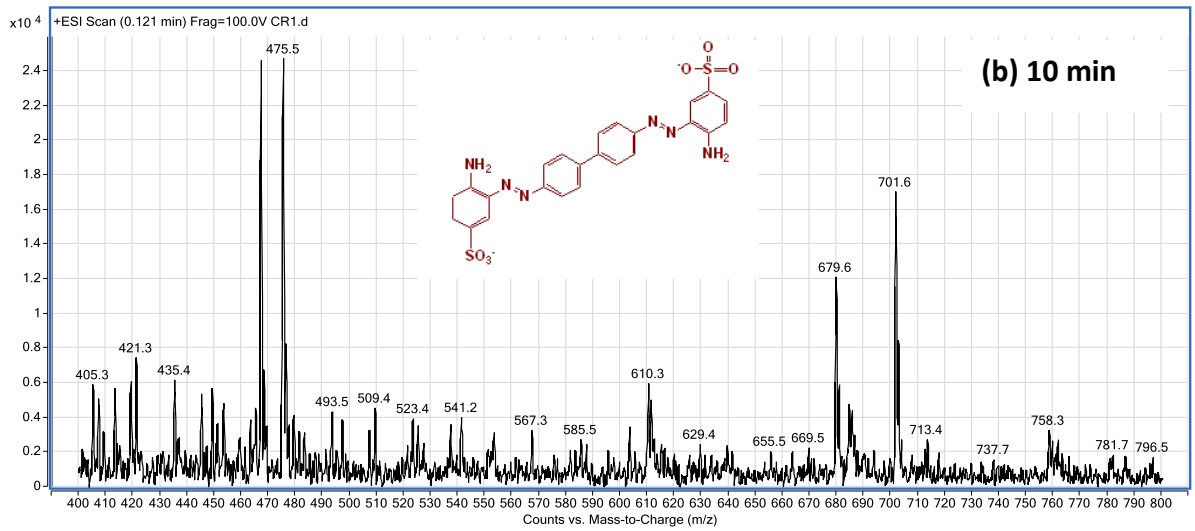
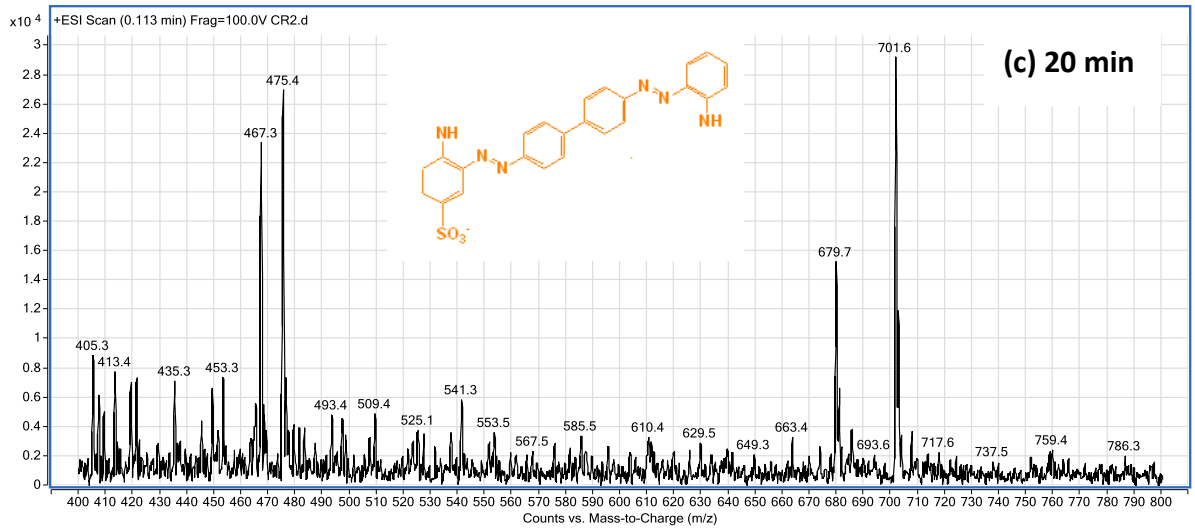


Figure S9. (a-e) LC-MS/MS spectra of OTC products over 2 wt% Co_3O_4/TiO_2/GO-1 catalyst under simulated solar irradiation as a function of time.


x10 4
+ESI Scan (0.113 min) Frag=100.0V CR.d
(a) CR initial
467.3
407.3
421.4
445.3
483.3
495.3
523.3
537.4
553.4
567.6
597.5
610.3
639.4
669.4
685.5
693.3
701.6
727.6
743.4
758.2
787.4
Counts vs. Mass-to-Charge (m/z)


x10 4
+ESI Scan (0.121 min) Frag=100.0V CR1.d
(b) 10 min
475.5
405.3
421.3
435.4
493.5
509.4
523.4
541.2
567.3
585.5
610.3
629.4
655.5
669.5
679.6
701.6
713.4
737.7
758.3
781.7
796.5
Counts vs. Mass-to-Charge (m/z)


x10 4
+ESI Scan (0.113 min) Frag=100.0V CR2.d
(c) 20 min
475.4
467.3
405.3
413.4
435.3
453.3
493.4
509.4
525.1
541.3
553.5
567.5
585.5
610.4
629.5
649.3
663.4
679.7
693.6
701.6
717.6
737.5
759.4
786.3
Counts vs. Mass-to-Charge (m/z)

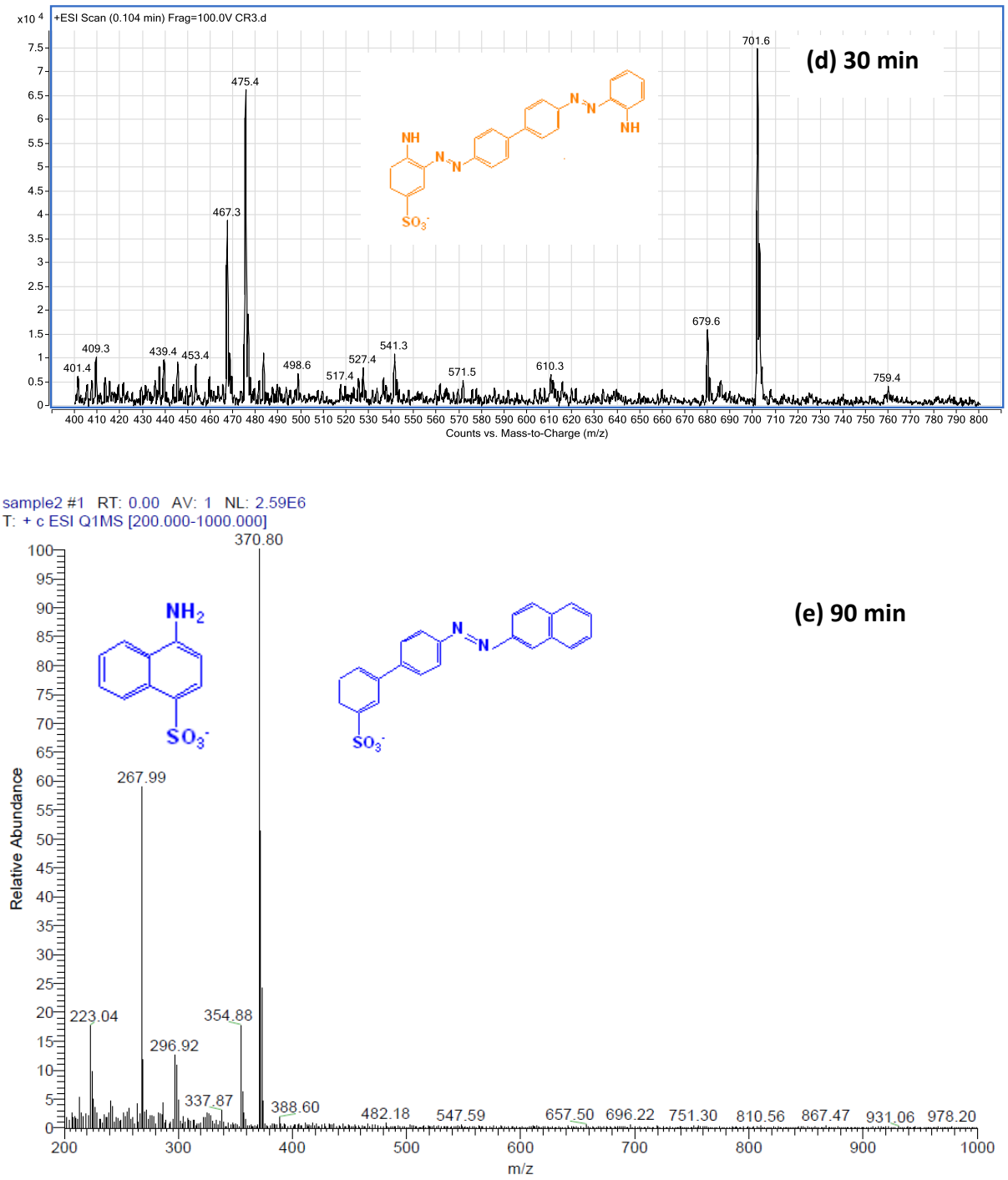


Figure S10. (a-e) LC-MS/MS spectra of OTC products over 2 wt% Co_3O_4/TiO_2/GO-1 catalyst under simulated solar irradiation as a function of time.

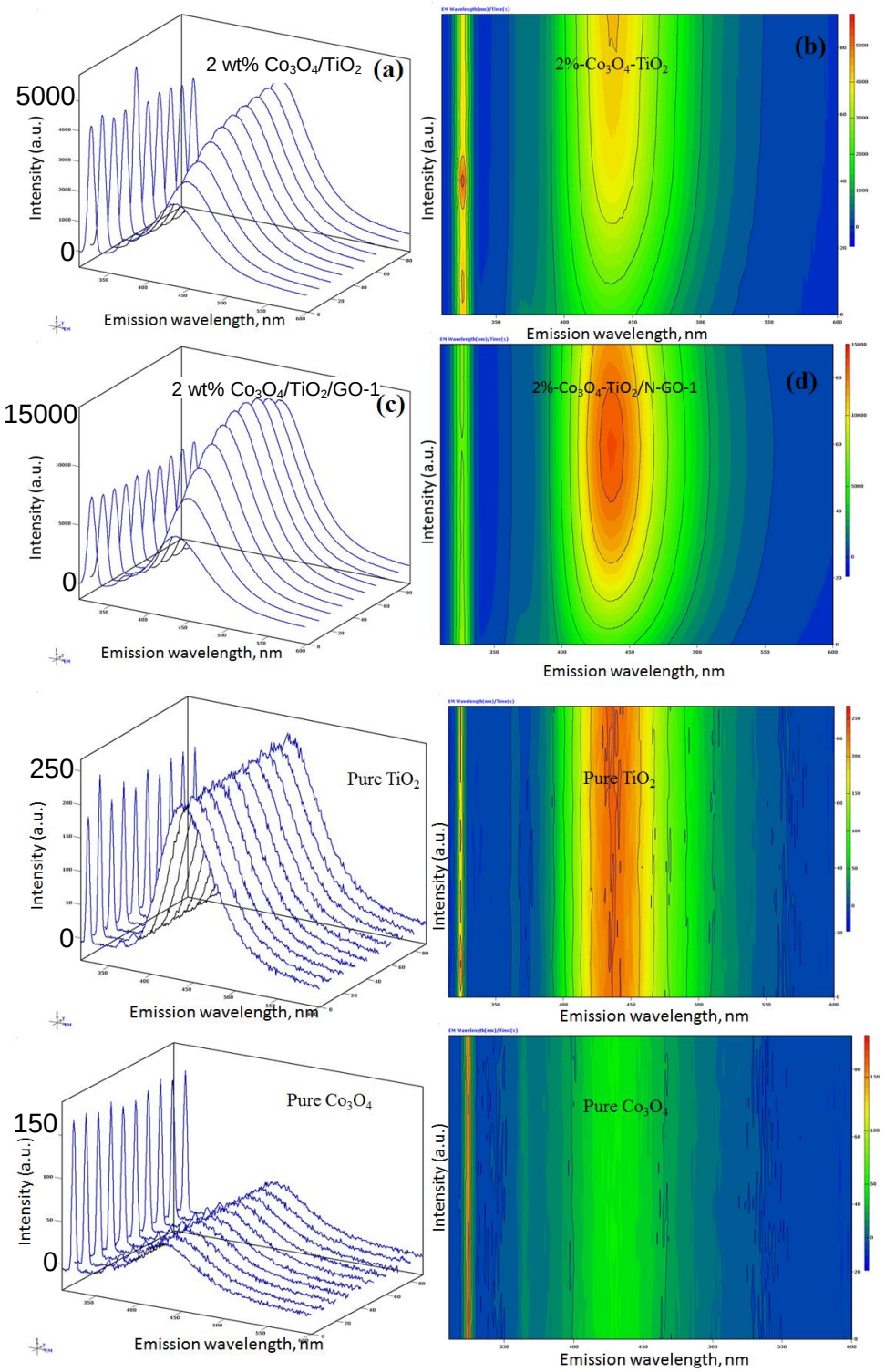


Figure S11. Emission spectra following terephthalic acid trapping by 2 wt% Co_3O_4/TiO_2 and 2 wt% Co_3O_4/TiO_2/GO-1 nanocomposites, and TiO_2 and Co_3O_4 references.