Supporting Information

Mesoporous Octahedron-Shaped Tricobalt Tetraoxide Nanoparticles for Photocatalytic Degradation of Toxic Dyes

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Supplementary Data S1: Characterization of Co_3O_4 NPs

X-ray diffraction (XRD) analysis was performed using Bruker AXS D8 Advance diffractometer in the 2θ range of 2°-80° using Cu Kα radiation (λ = 0.154 nm). Fourier transform infrared (FT-IR) spectra were recorded in the range of 400–4000 cm^{-1} at 4.0 cm^{-1} resolution using Bruker (IFS 66v) spectrophotometer by the KBr pellets technique. UV–visible absorption spectra were recorded using Shimadzu-1800 UV–visible spectrophotometer (SL171 minispec). The qualitative elemental analysis was performed using energy dispersive spectroscopy (EDS) (Oxford Instrument, UK). The Brunauer–Emmett–Teller (BET) surface areas was obtained from nitrogen adsorption/desorption isotherms determined at liquid nitrogen temperature using Micromeritic (ASAP 2010) analyzer. The samples were out gassed for at 200 °C 2 hrs under vacuum prior to the adsorption/desorption measurements. Scanning electron microscopy (SEM) (JEOL, JSM-690LV) and transmission electron microscopy (TEM) (JEOL JEM 100SX) were used to analyze the morphology, size and shape of the spinel Co_3O_4. Electrochemical calculations were directed using a three-electrode electrochemical cell entailing of a platinum (Pt) as the counter electrode, Ag/AgCl electrode as reference electrode, and a prepared electrode as the working electrode filled with an aqueous solution of 0.1 M Na_2SO_4. The electrolyte was soaked with nitrogen gas prior to electrochemical measurements. The photo electrochemical measurements were performed using a Biologic single channel potentiostat under illumination conditions (λ = 400 nm). Irradiation was performed using a (400W) tungsten lamp as visible light source. The total organic carbon (TOC) analysis have been done via waste water method of this photo degradation methods. In this following total organic carbon study basically investigated the amount of organic carbon in the individual dye molecules have been done with Teledyne Tekmar TOC torch (USA). Standard solutions of dye molecule have been taken with potassium hydrogen phthalate (KHP) and distilled water. Prior sample analysis the instrument is calibrated. Liquid chromatography-mass spectrophotometer (LC-MS) (Shimadzu LCMS-8040) was used to investigate the structural elucidation and molecular fragmentation of toxic dyes with the following parameters: m/z 10 to 2000, scan speed 15000 u/sec, secondary electron multiplier.

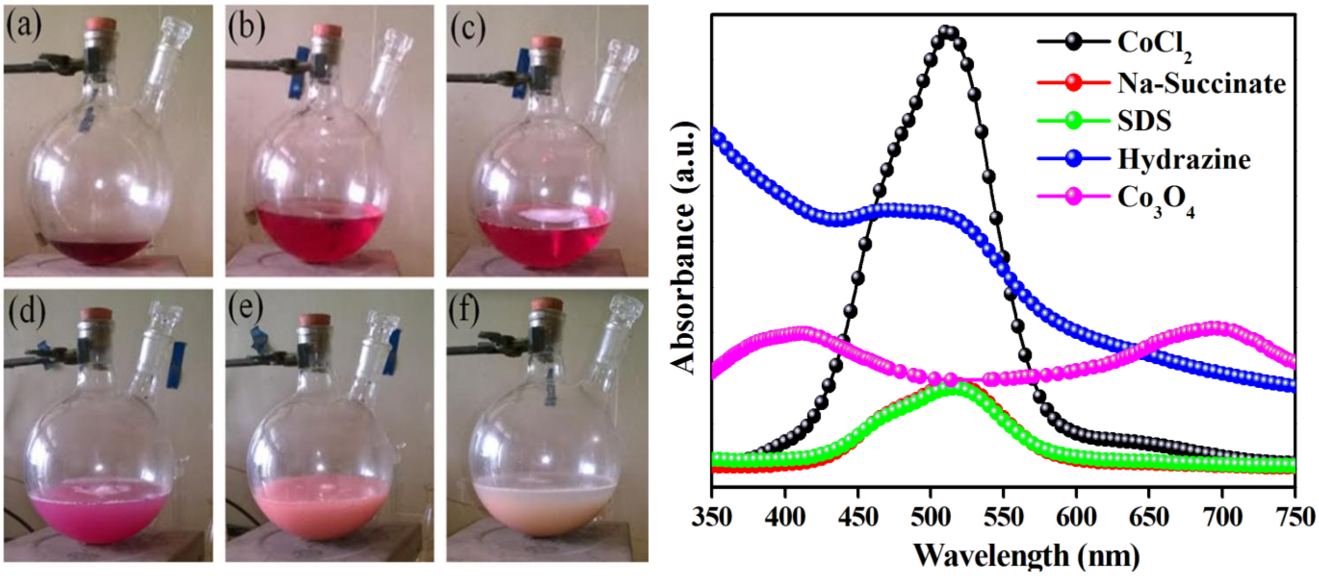


Figure S1. Different reaction step and their corresponding UV-Visible spectra follow the order such as (a) $CoCl_2$. xH_2O + SDS solution, (b) $CoCl_2.xH_2O$ +SDS solution + sodium succinate solution, (c) Co_3O_4, (d) $CoCl_2.xH_2O$ + sodium succinate solution + SDS + Hydrazine, and (e-f) $CoCl_2.xH_2O$.

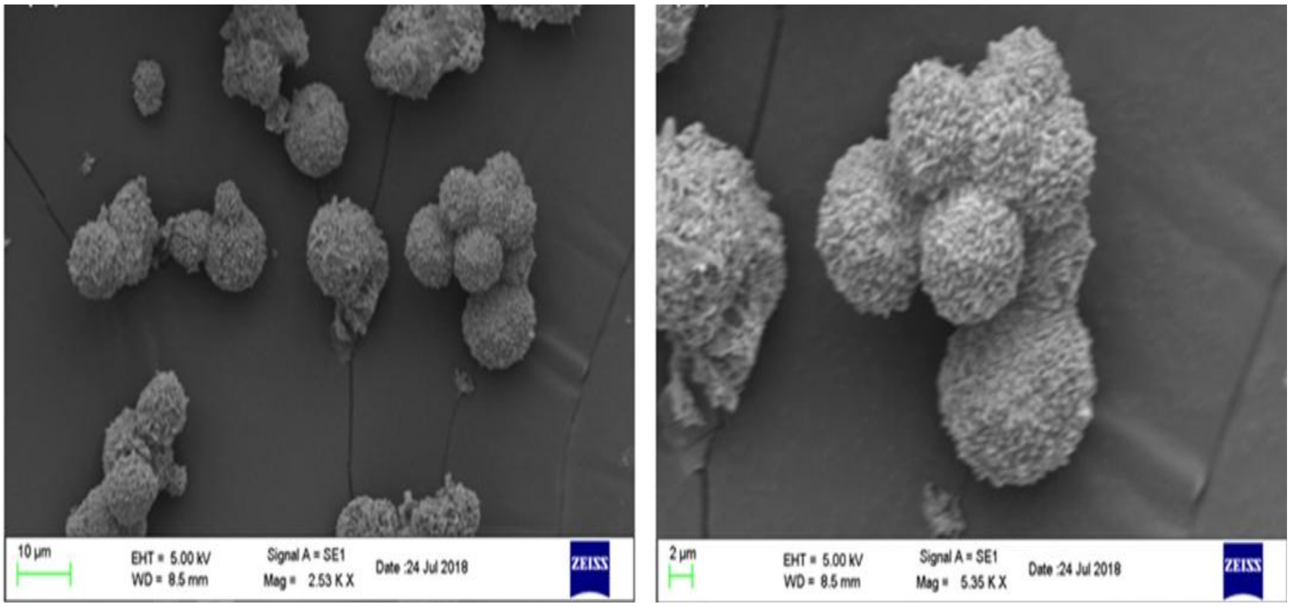


Figure S2. SEM images of before-calcined Co_3O_4 NPs.

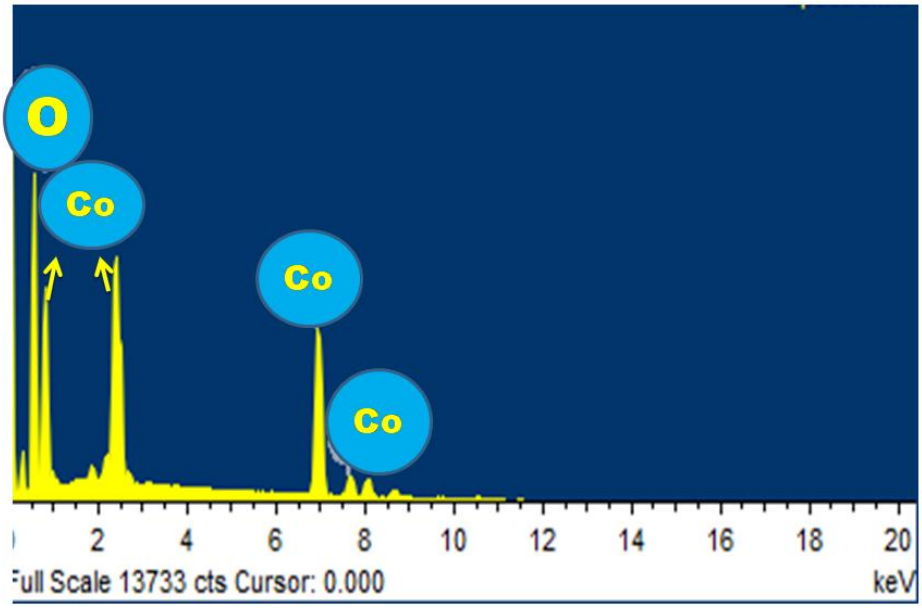
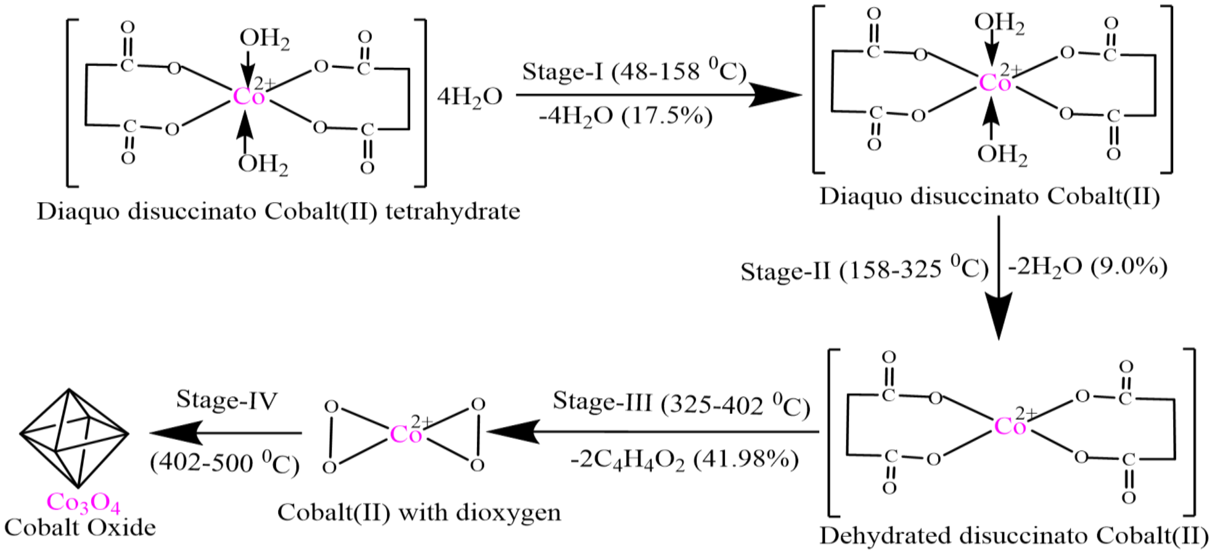


Figure S3.EDS spectrum of calcined-Co_3O_4NPs.

Supplementary Data S2: TG of pre-calcined Co_3O_4 NPs

As observed in [Fig. 2(a)] sequence of degradation of pre-calcined material takes place *via* multiple stages starting with dehydration of adsorbed water molecules followed by succinate organic fragments as proposed in Scheme. A well-defined thermograph with three-stage thermal decomposition process between 48-555°C, which resembles a standard sigmoid shape at initial stage, a significant mass loss of about 17.5% (Calc.18.0%) between 48-158°C with T_{HDT} peak at 118 °C attributed to removal of four moles of lattice water. The second stage decomposition lies between 160 and 325 °C with mass loss 9.0% (Calc. 9.02%) and T_{HDT} peak at 258 °C associated with the loss of two moles of coordinated water. In the third stage, a mass loss of about 41.98% (Calc. 41.13) between 325 and 402 °C with T_{HDT} peak at 355 °C due to removal of coordinated succinate molecules was observed. This suggested pre-calcined material was complexing type. Eventually, stability achieved between 402-500 °C indicating formation of a stable Co_3O_4 (Scheme S1). The half decomposition temperature (HDT), temperature range, and degraded materials at each step are provided in Table S1.



Scheme S1. Thermal degradation mechanism of SDS mediated pre-calcined Co_3O_4 NPs.

Table S1. Thermal data of pre-calcined and calcined Co_3O_4.

Material	Step	HDT$_{max}$ T_{HDT} (°C)	Temperature range (°C)	Weight loss (%) Obs /Calc.	Assignment degraded materials
Pre-calcined Co_3O_4	1st	118	48-158	17.5/18.0	$-4H_2O$ (lattice water)
	2nd	258	160-325	9.02/9.02	$-2H_2O$ (Coordinate water)
	3rd	355	326-402	41.98/41.13	$-2C_4H_4O_2$ (Succinate ions)
	4th	----	402-500	No loss	Residue of Co_3O_4
Calcined Co_3O_4	1st	88	48-120	0.23/0.5	$-H_2O$ (lattice water)
	2nd	----	120-798	-----	Material is stable (Co_3O_4)
	3rd	878	798-902	7.0/7.1	$-O_2$ (Dioxygen)
	4th	----	902-1000	No loss	Residue $CoO.Co_3O_4$

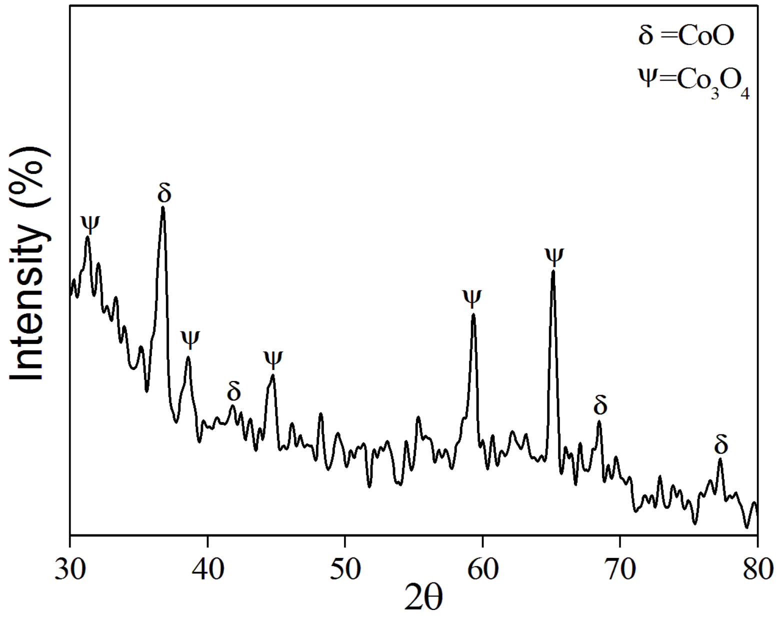


Figure S4. XRD profile of Mixed phase $CoO.Co_3O_4$ after calcined material at 900 °C

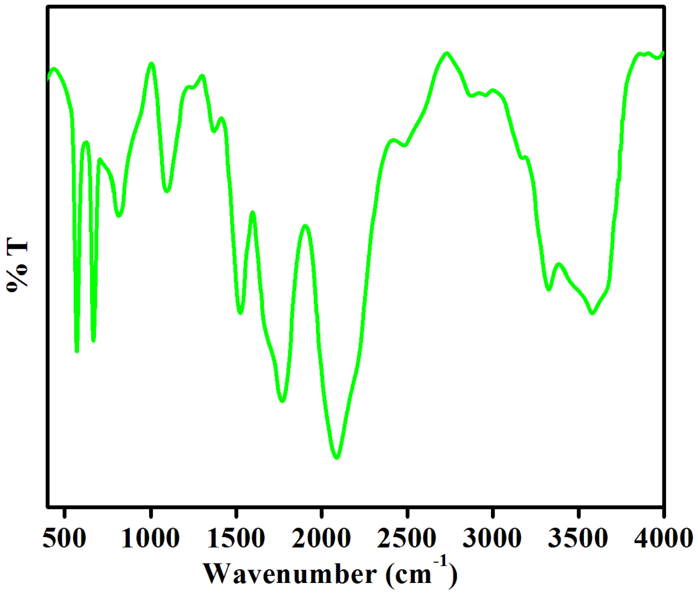


Figure S5. FT-IR spectra of Co_3O_4 NPs

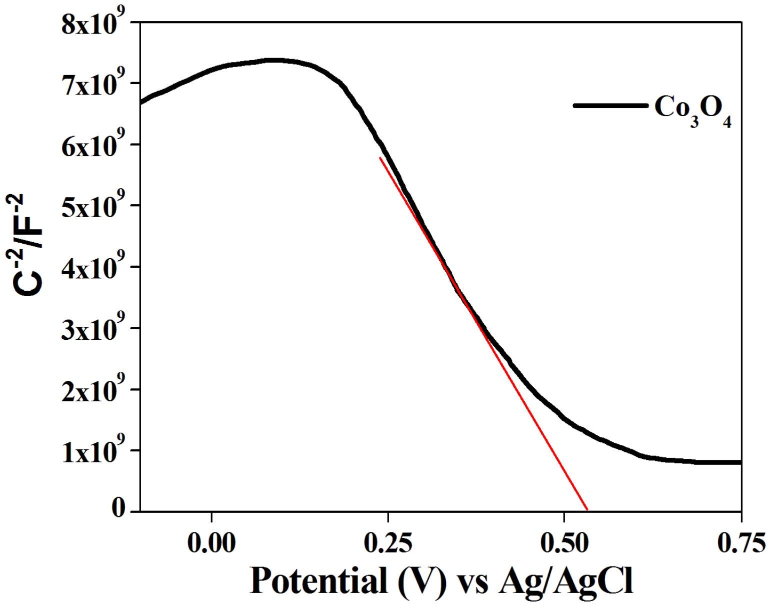


Figure S6. Mott−Schottky plot under light conditions of the synthesized Co_3O_4

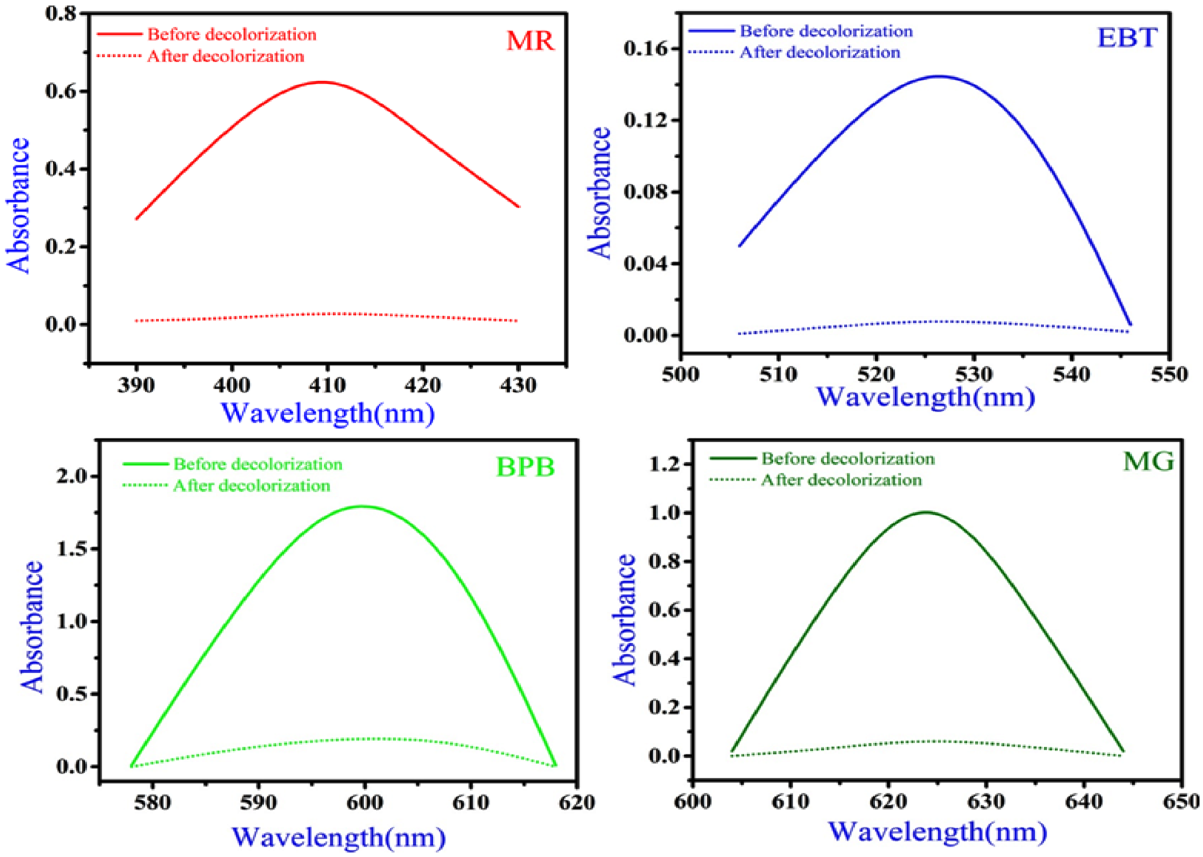


Figure S7. UV-visible spectra of dyes before and after treatment using Co_3O_4 NPs

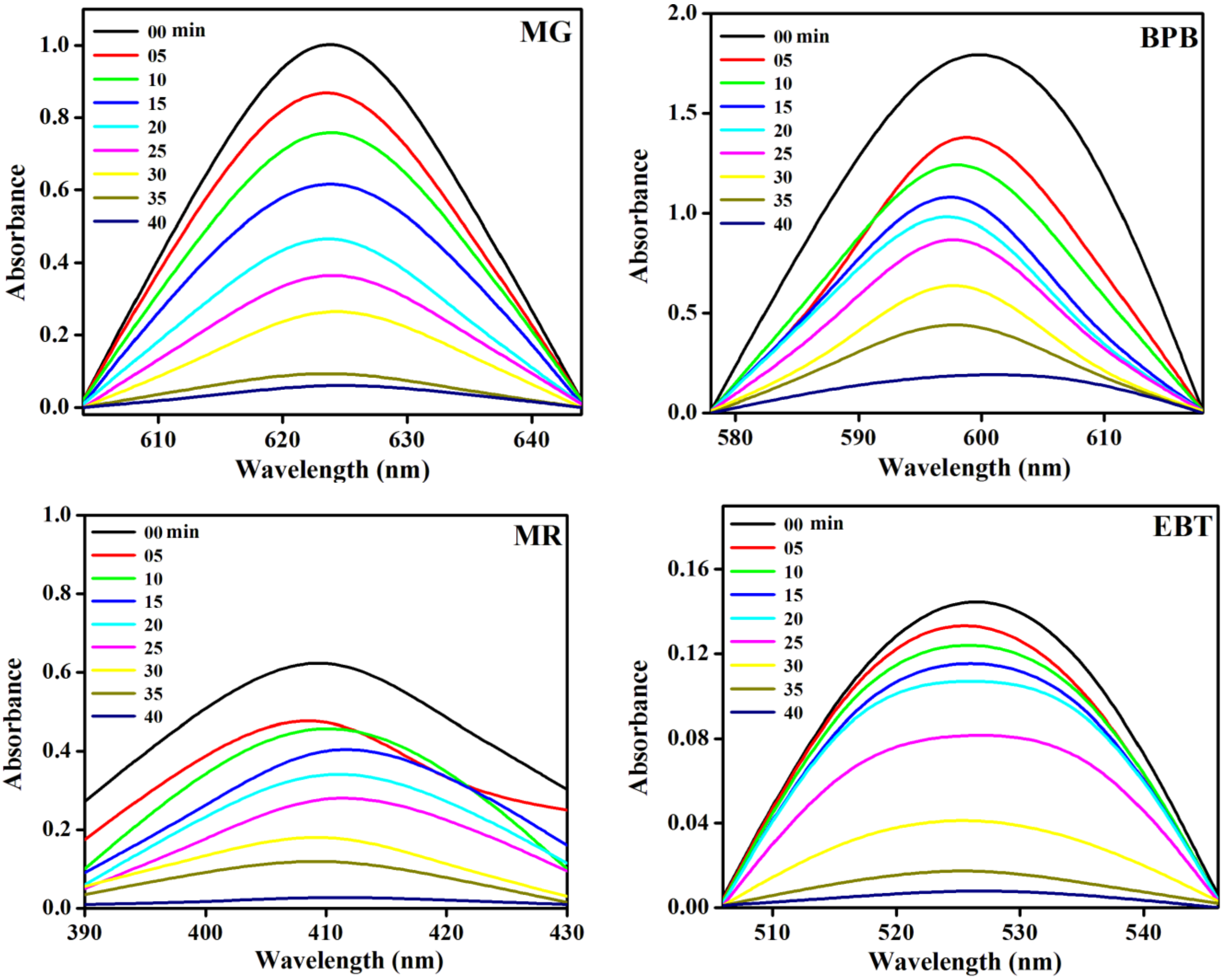


Figure S8. Changes in UV-Vis absorption pattern of degraded dyes with respect to irradiation time.

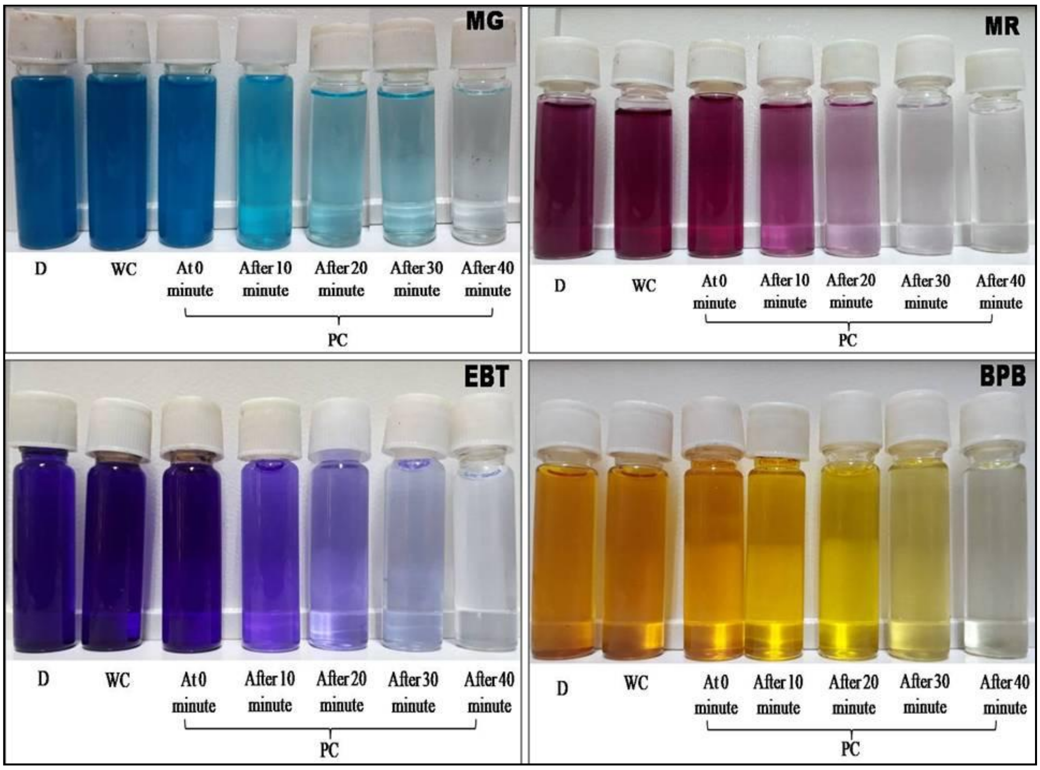


Figure S9. Photos of the corresponding dyes after degradation within 40 min using Co_3O_4NPs.

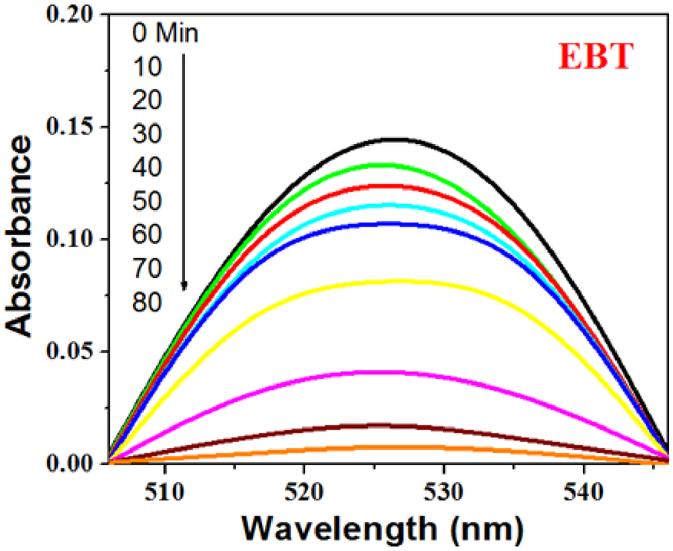


Figure S10. Photocatalytic degradation pattern of the industrially effluent waste product of the EBT

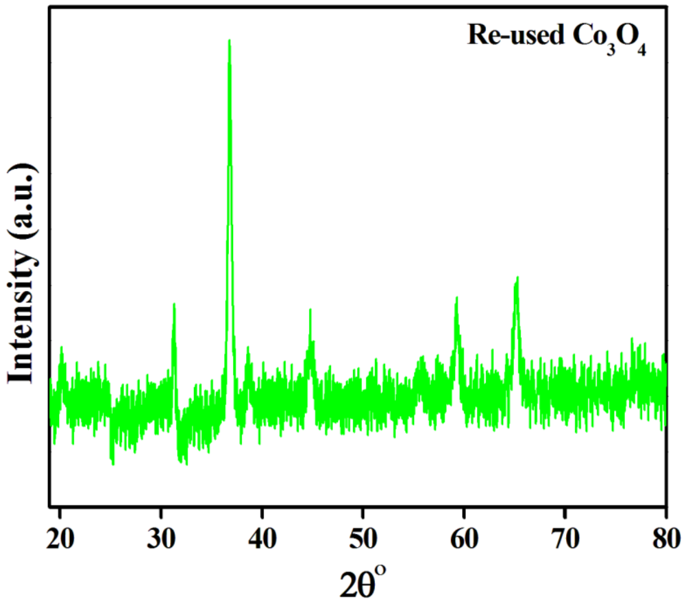


Figure S11. XRD pattern of re-used Co_3O_4 after 4 cycle photo-catalysis reaction.

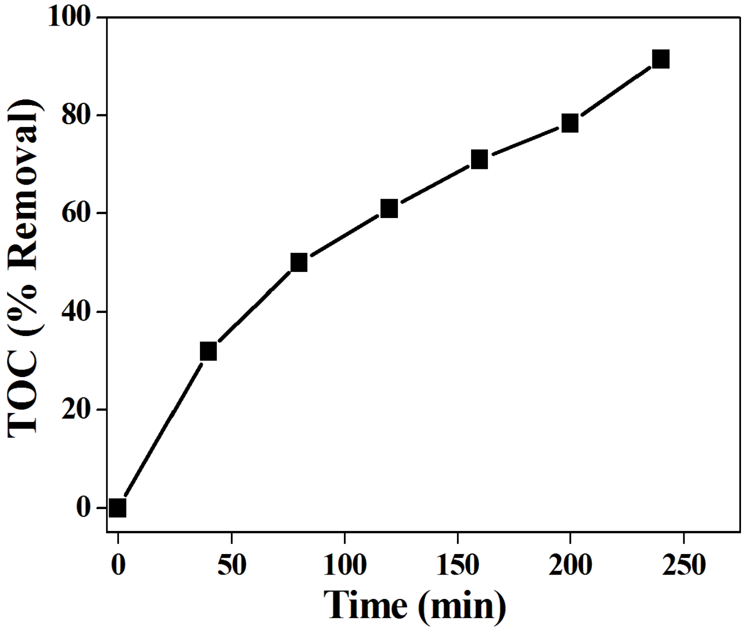


Figure S12. The TOC removal after 240 min

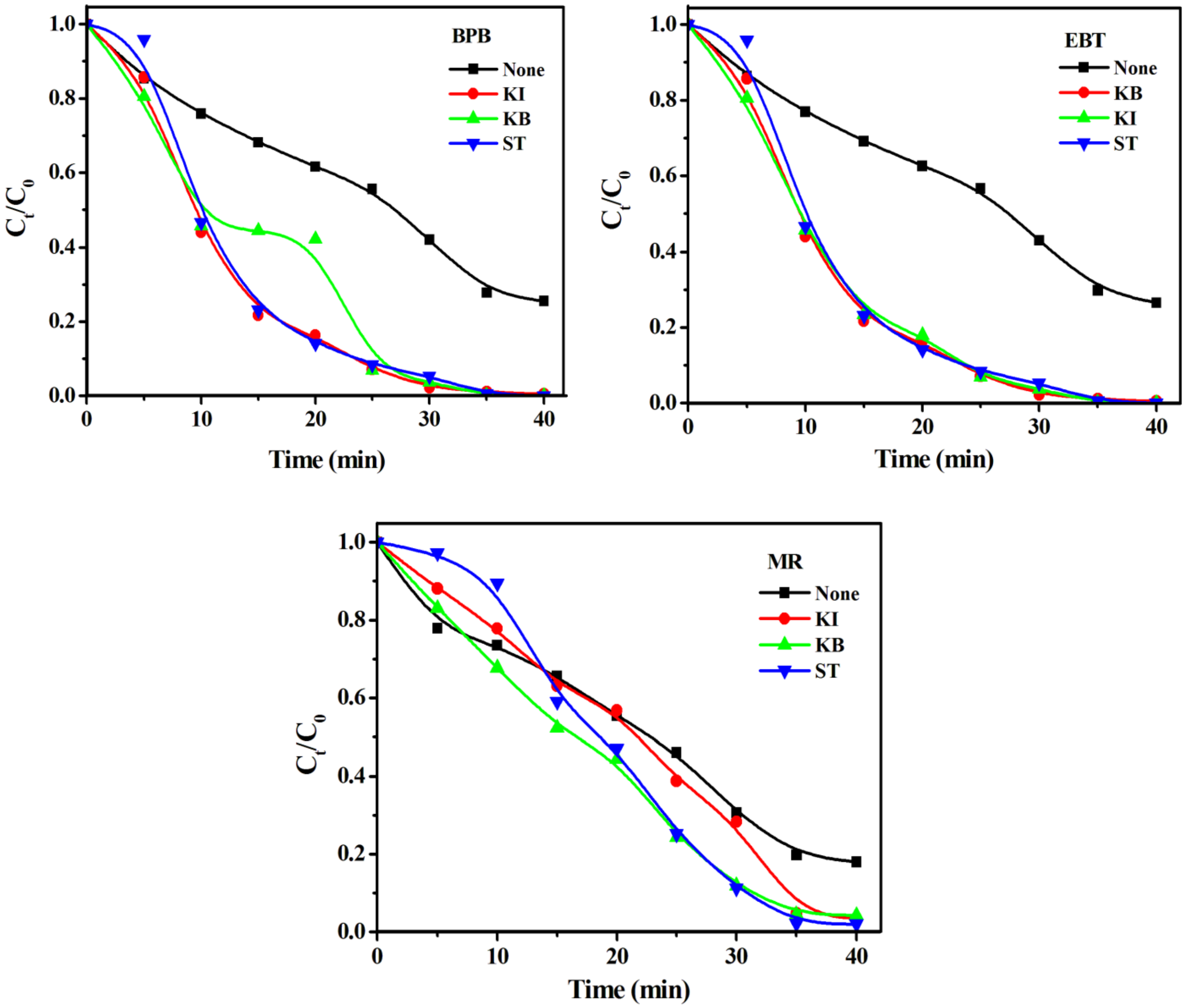


Figure S13. Scavenging test for BPB, EBT and MR using KB, KI and ST

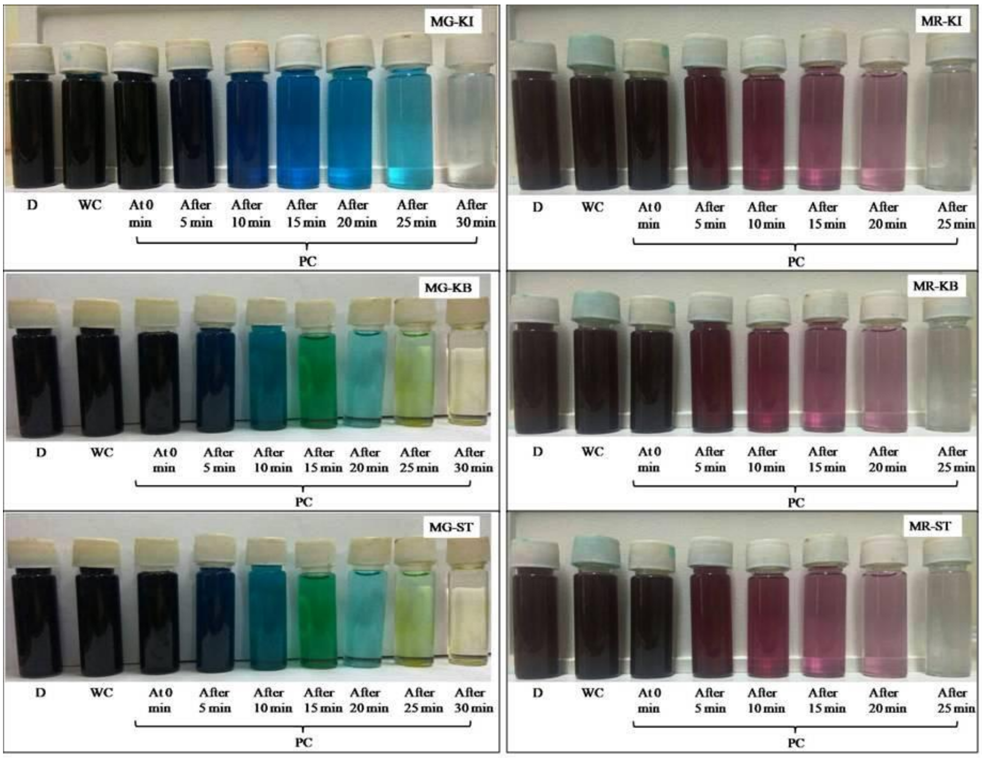


Figure S14. Photos of the corresponding dyes (MG and MR) in scavenging test using Co_3O_4 NPs and scavenger

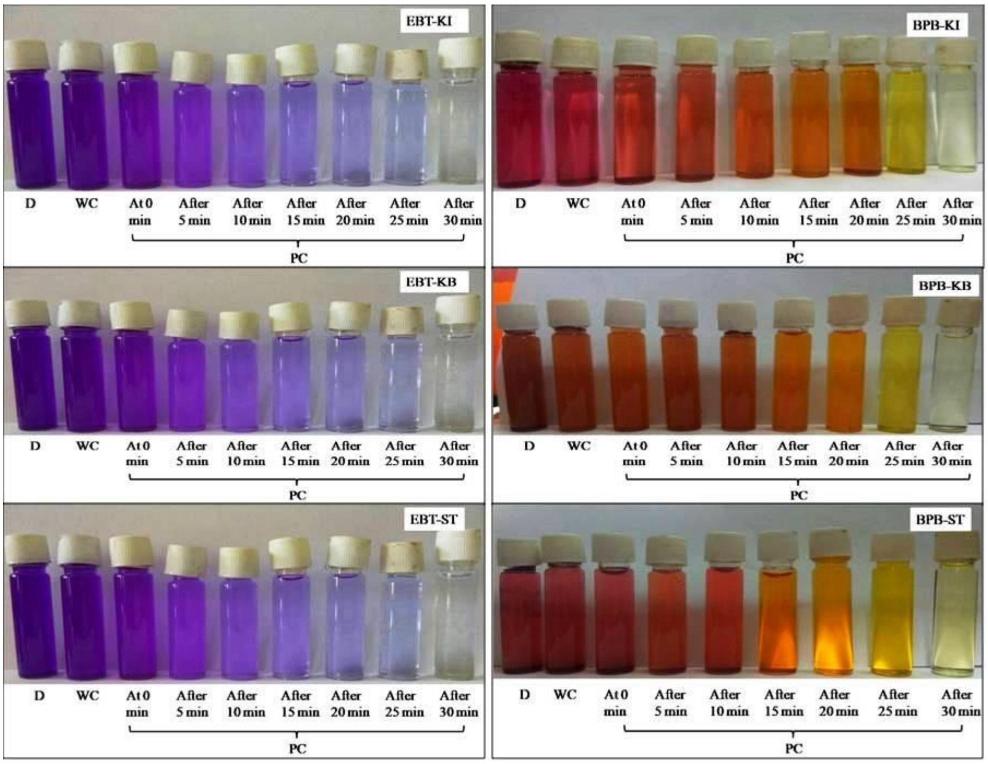


Figure S15. Photos of scavenging test for EBT and BPB using Co_3O_4 NPs.