Supporting Information

Catalytic oxidation of alcohols and alkyl benzenes to carbonyls by Fe_3O_4@SiO_2/(TEMPO)-co-(Chlorophyll-Co^{III}) as a bi-functional, self co-oxidant nanocatalyst

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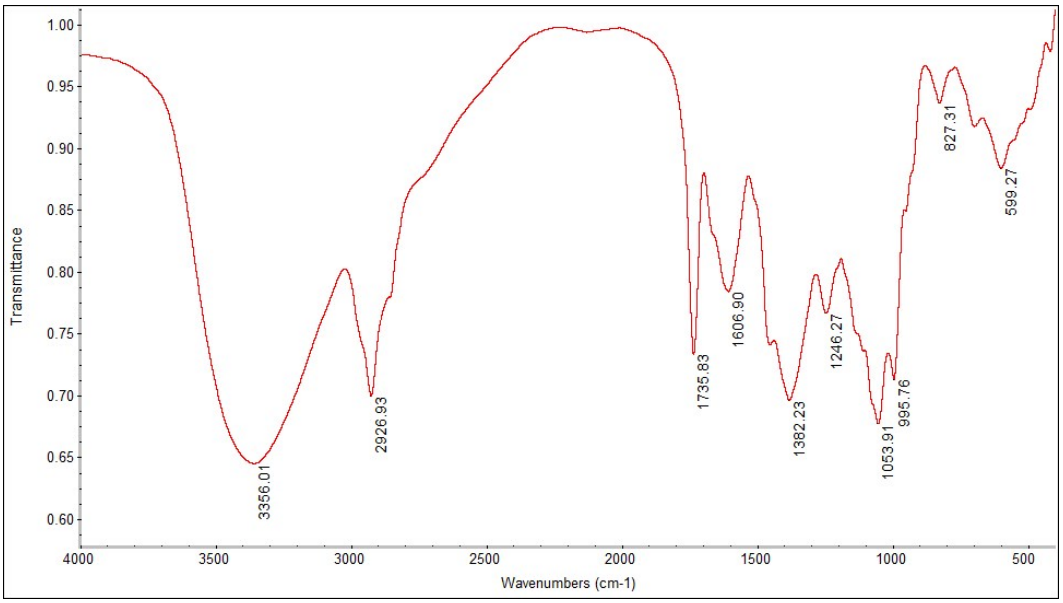

Fig. S1 FTIR spectrum of chlorophyll *b* extracted from *heliotropium europaeum*

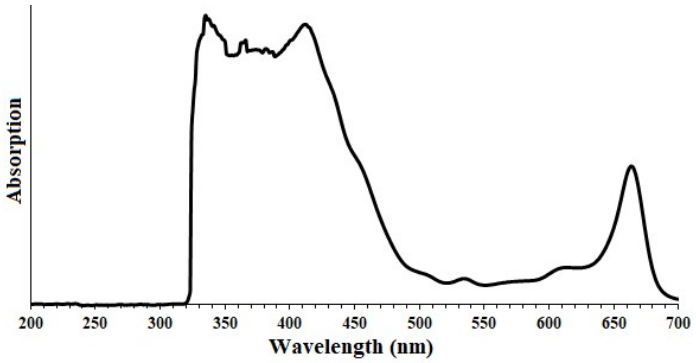

Fig. S2 UV-Vis spectrum of chlorophyll *b* extracted from *heliotropium europaeum* in EtOH

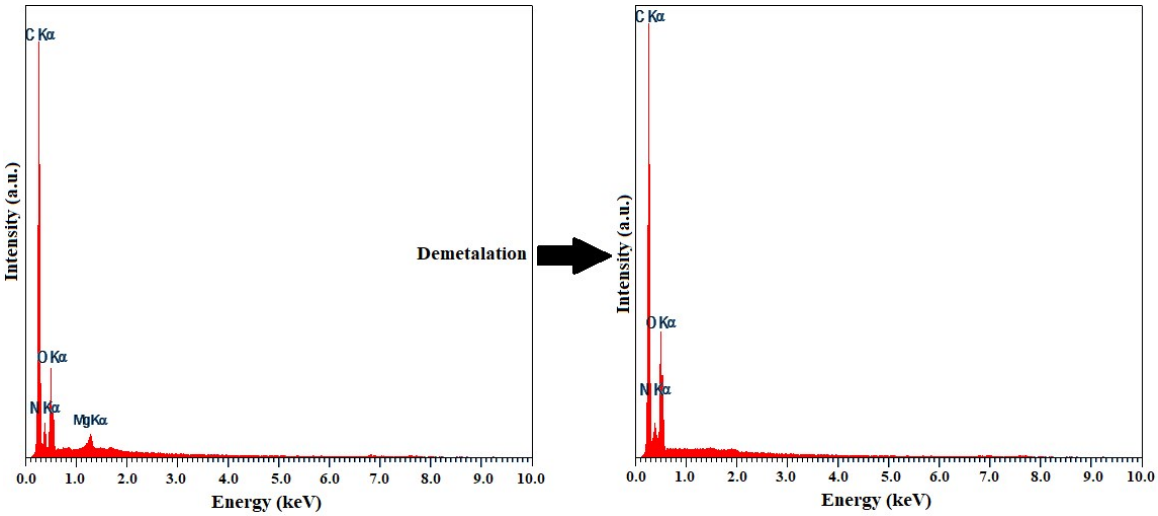

Fig. S3. EDX analysis of (a) chlorophyll *b* (**1**) and (b) demetalated chlorophyll *b* (**2**)

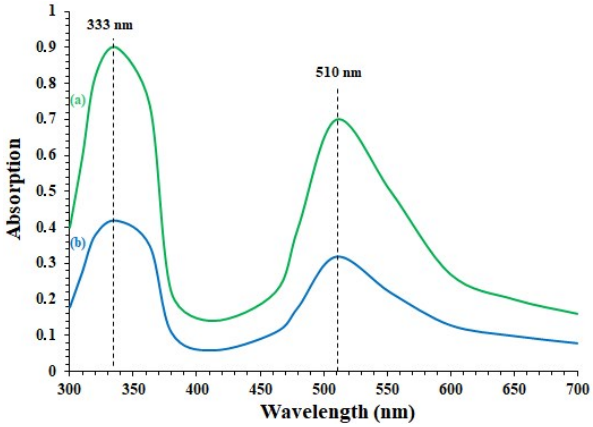

Fig. S4 The DPPH assay for determination of TEMPO content in compound **4**. (a) DPPH methanol solution, (b) for compound **4**

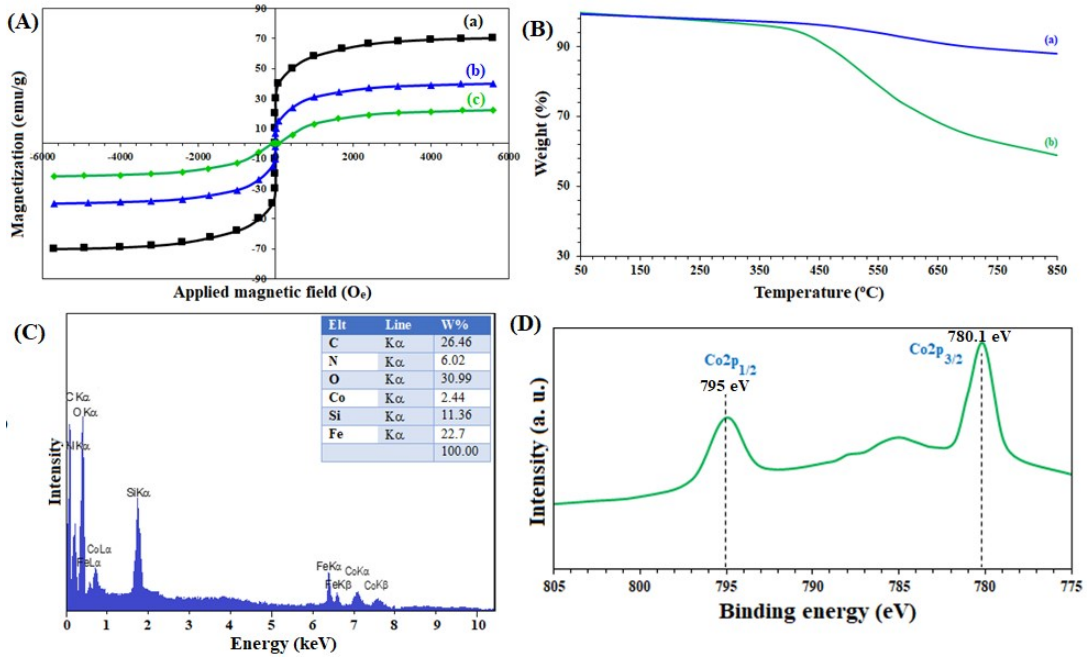

Fig. S5 (A) VSM curves of (a) Fe_3O_4, (b) Fe_3O_4@SiO_2-NH_2, and (c) catalyst **10**. (B) TGA spectra of (a) Fe_3O_4@SiO_2-NH_2 and (b) catalyst **10**. (C) EDX and (D) high resolution Co2p XPS analysis (energy corrected) of the catalyst **10**.

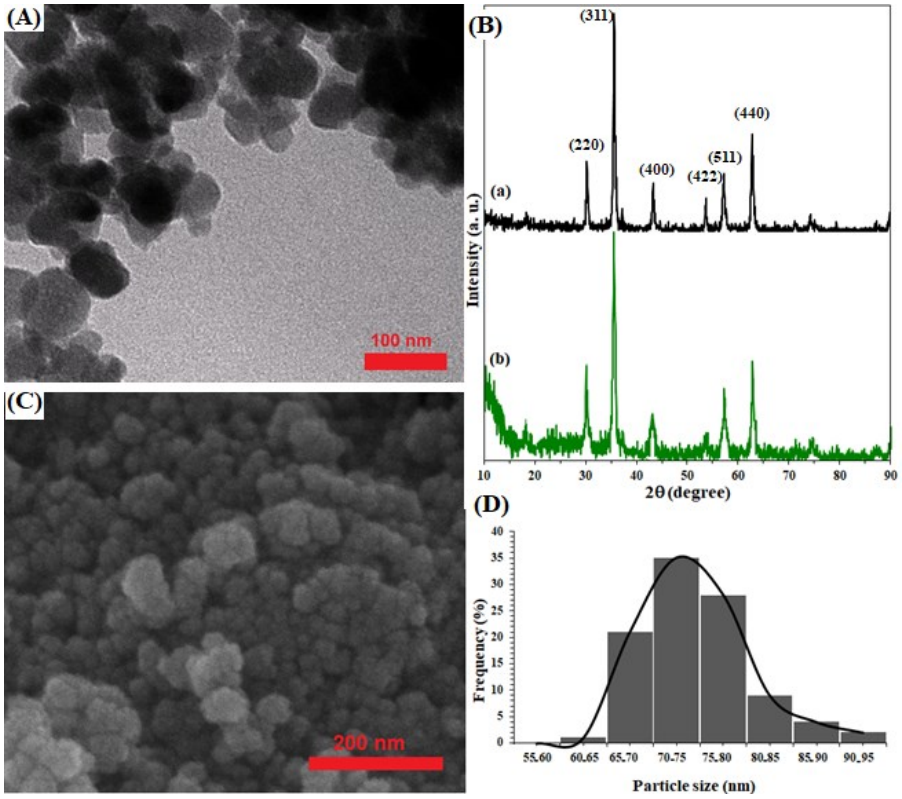

Fig. S6 (A) TEM, (B) XRD spectra (a) Fe_3O_4, (b) catalyst **10**, (C) FE-SEM, and (D) DLS analysis of catalyst **10**

Table S1 Surface characteristics of Fe_3O_4, Fe_3O_4@SiO_2 Fe_3O_4@SiO_2-NH_2, and Fe_3O_4@SiO_2/ (TEMPO)-copolymer-(Chlorophyll *b*)-Co(III) (**10**)

Entry	Sample	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Average pore radius (nm)
1	Fe_3O_4	484	0.813	1.259
2	Fe_3O_4@SiO_2	450	0.790	1.810
3	Fe_3O_4@SiO_2-NH_2	410	0.758	1.902
4	Catalyst **10**	362	0.714	1.980

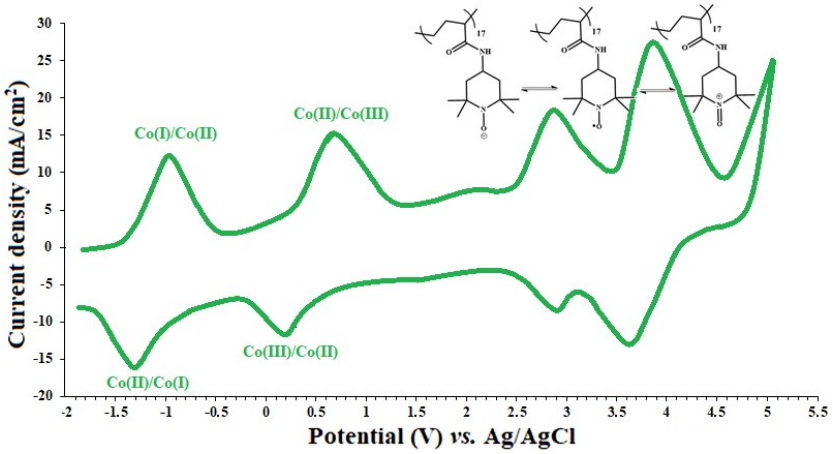

Fig. S7 The cyclic voltammetry curve of catalyst **10** in 0.1 mol/L Britton–Robinson (BR) buffer solution (pH 7.0) with a scan rate of 100 mV/s at room temperature

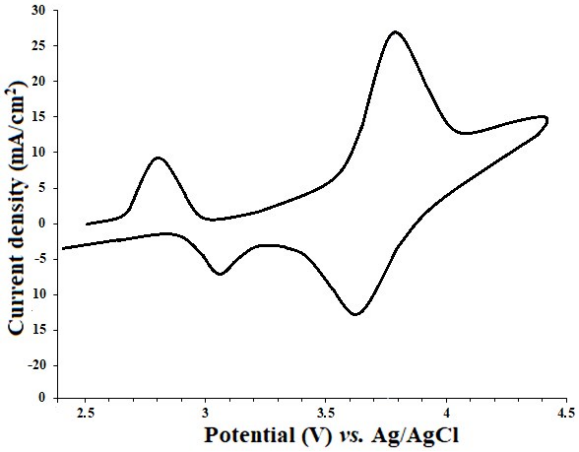

Fig. S8 The cyclic voltammetry curve of polyvinyl chlorophyll-Co(III) complex (**12**) in 0.1 mol/L Britton–Robinson (BR) buffer solution (pH 7.0) with a scan rate of 100 mV/s at room temperature

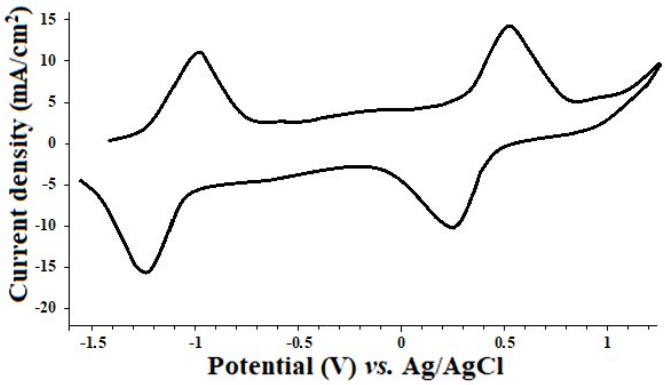

Fig. S9 The cyclic voltammetry curve of polyvinyl TEMPO (**13**) in 0.1 mol/L Britton–Robinson (BR) buffer solution (pH 7.0) with a scan rate of 100 mV

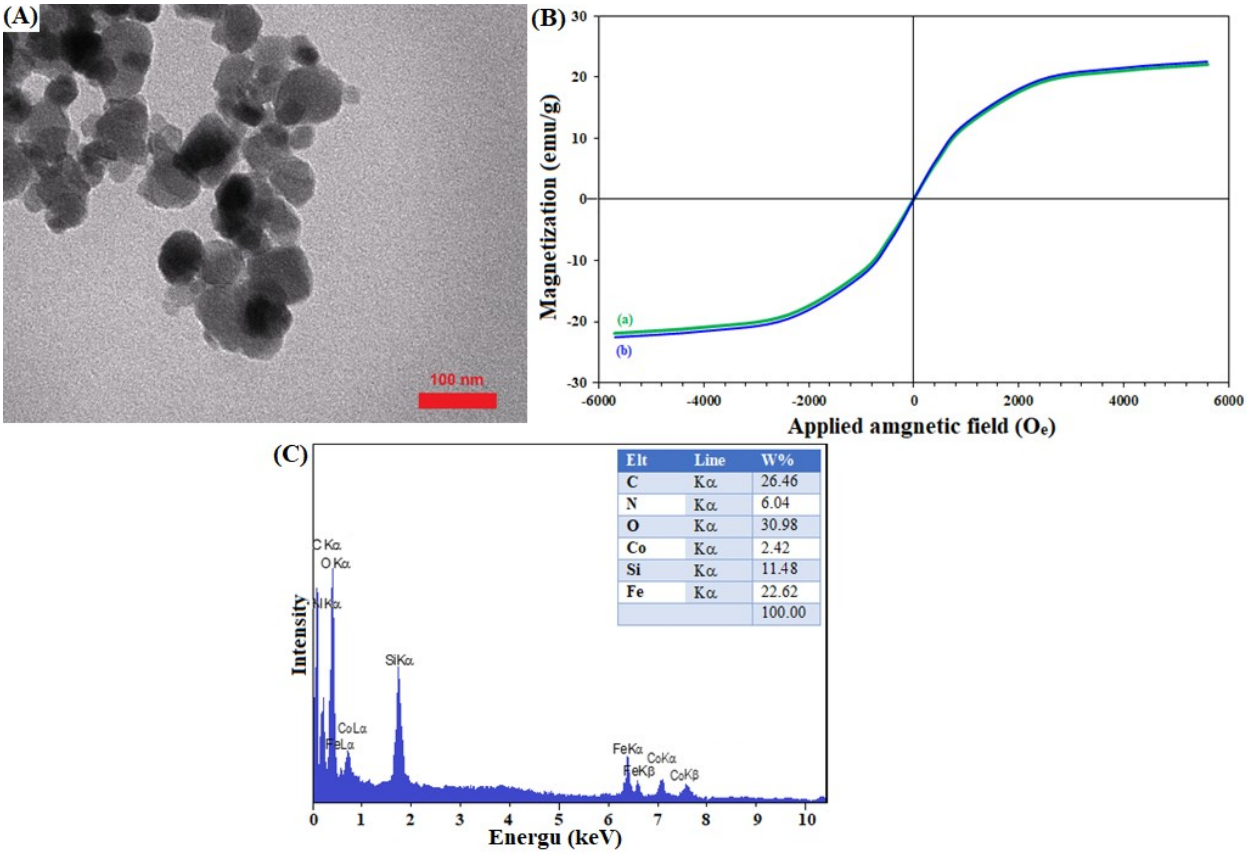

Fig. S10 (A) TEM image, (B) TGA spectra of (a) the fresh catalyst and (b) the recovered catalyst after the 7th cycle, and (C) EDX analysis of the recovered catalyst after 7th cycles at room temperature

General procedure for the preparation of Polyvinyl chlorophyll-Co(III) complex (12)

Radical polymerization of chlorophyll-allyl was performed according to a previously reported procedure [1]. Typically, chlorophyll-allyl (0.15 g) was added to a dried bottom flask. The flask was nitrogen-purged for 2.0 min, then 6.0 mL dioxane, 6.0 mg AIBN (as an initiator) was added to the flask. The system was sealed and equipped with a N_2 inlet and then immersed in an oil bath. The mixture was stirred at 85 °C for 24 h. Then, the solution was allowed to cool to room temperature and added to excess MeOH as a precipitating solvent in one step. The product was obtained after removal of solvents under reduced pressure. The product (polyvinyl chlorophyll) was purified with treatment with diethyl ether (25 mL), then it was dried under vacuum at room temperature for a day. Average molecular weight= 13821, polydispersity index = 1.212, DP according to GPC analysis= 15.
Coordination of Co ions to polyvinyl chlorophyll (as a ligand) was performed as follows: Polyvinyl chlorophyll (0.5 g) was added to 25 mL EtOH at 50 °C, then $Co(OAc)_2.4H_2O$ (0.05 g, 0.2 mmol) was added to the mixture. The mixture was stirred for 2 h, then it was filtered, washed with dry toluene (2 × 10 mL), and dried into oven (60 °C). ICP = 1.93 %wt Co.

DPPH assay for determination of TEMPO functional groups in the catalyst (11)

To determine the TEMPO groups in the catalyst, DPPH assay was served. The ability of the catalyst towards quenching of DPPH, the catalyst was treated with the DPPH methanol solution as a reagent, then the reduction of the peak related to DPPH absorption was measured by a spectrophotometric assay [2]. A calibration curve was obtained by recording of absorption of different concentrations of the DPPH ethanolic solutions. The DPPH test was performed with addition of 1.5 g compound 4 in 0.7M DPPH ethanolic solution (contain 5.0 mmol DPPH). The final solution was protected with an aluminum foil to prevent from light. After vigorous shaking the solution, it lefts for 90 min (incubation period) at ambient temperature. The catalyst was filtered and absorption of the residue was read at 517 nm. The percent of the remaining radicals at 90 min was calculated using the following equation:

$$\text{Remaining DPPH}(\%) = \frac{A_c - A_s}{A_c} \times 100$$

where A_c and A_s, are the absorbance of the control (consist of solvent and DPPH) and the residue, respectively. Methanol and ascorbic acid was used as blank and positive control respectively. All of the experiments were repeated for three times and their average were reported.

General procedure for the preparation of Polyvinyl TEMPO (13)

Radical polymerization of acrylated-TEMPO was performed as same procedure as described for polyvinyl chlorophyll. Average molecular weight= 4579, polydispersity index = 1.212, DP according to GPC analysis= 19.

References

[1] Zhuang, X., Zhang, H., Chikushi, N., Zhao, C., Oyaizu, K., Chen, X., & Nishide, H. (2010). Biodegradable and Electroactive TEMPO-Substituted Acrylamide/Lactide Copolymers. *Macromolecular bioscience*, *10*(10), 1203-1209.

[2] Williams, L. A. D., Vasques, E., Reid, W., Porter, R., Kraus, W., 2003. Biological activities of an extract from Cleome viscosa L. (Capparaceae). Naturwissenschaften, 90, 468-472.