

# Supporting Information

## **Activation of Peroxymonosulfate by Oxygen Vacancy-enriched Cobalt-doped Black TiO<sub>2</sub> Nanotubes for Removal of Organic Pollutants**

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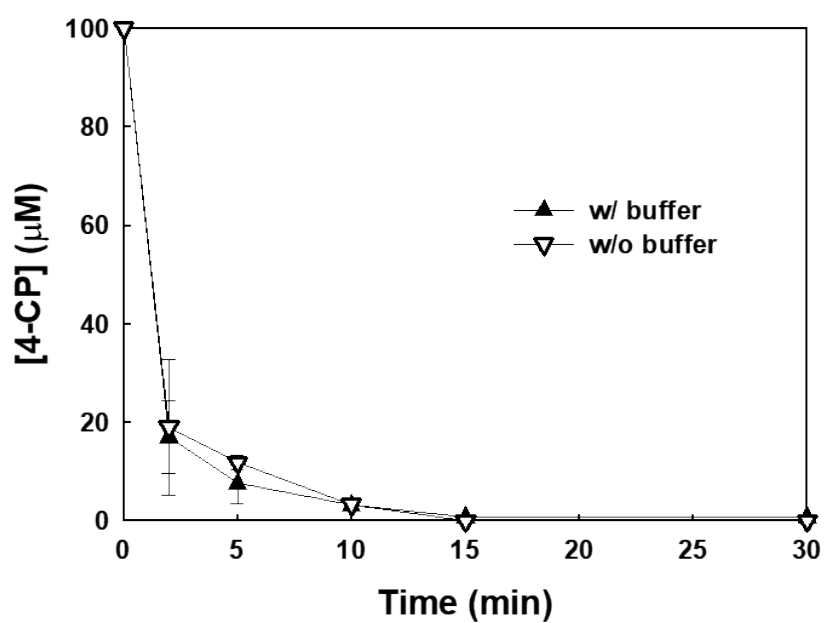
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Experimental details for preparation of four control samples, Discussions on Figure S2-S4 and S13, Figures S1-S14, Table S1, and References are included.

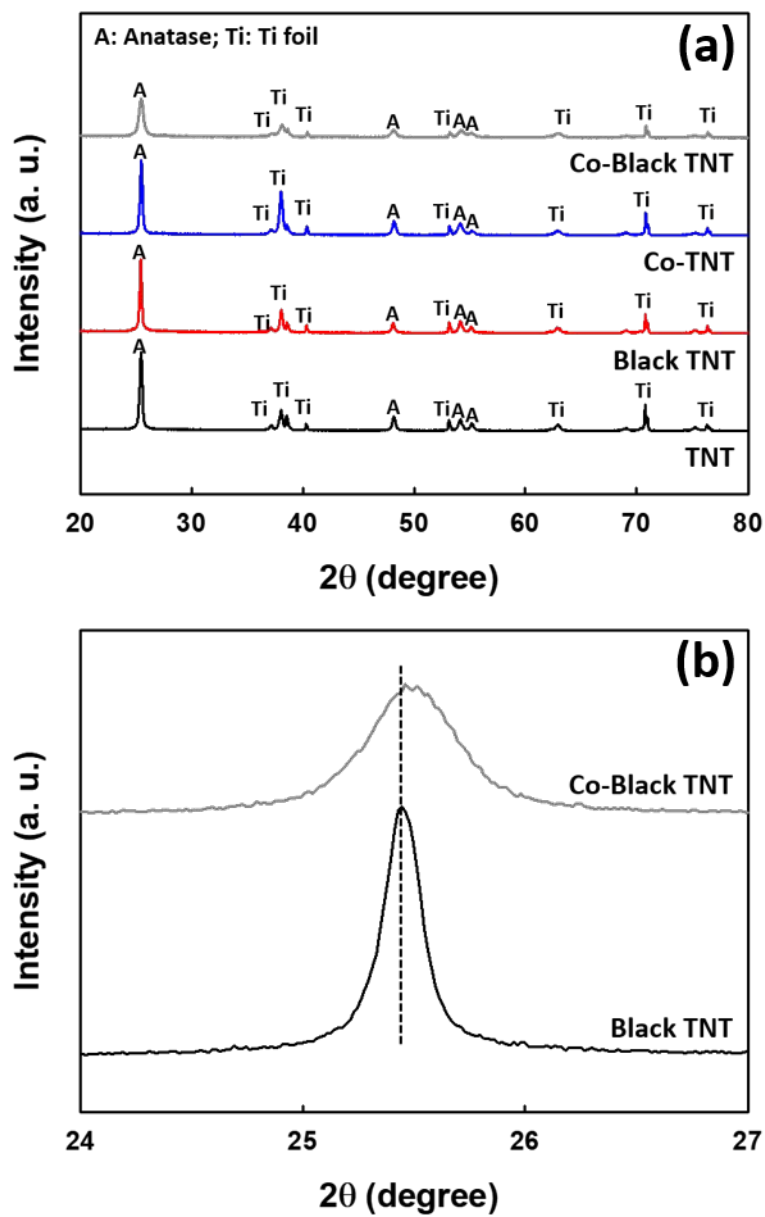
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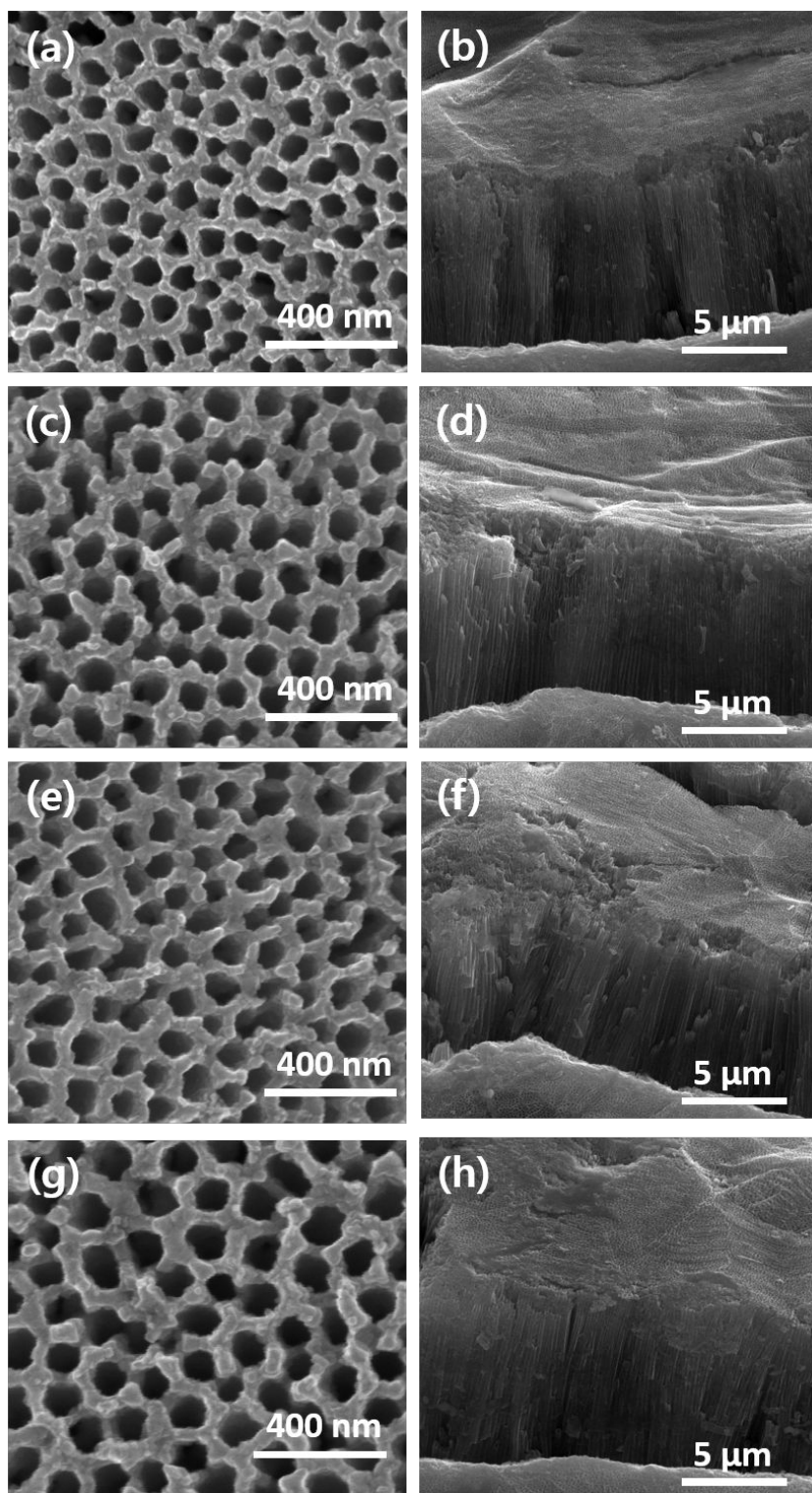
**Experimental details for preparation of four control samples.** Cobalt oxide ( $\text{Co}_3\text{O}_4$ ) was prepared on a Ti plate by a drop-casting method using 250 mM  $\text{Co}(\text{NO}_3)_2$  in ethanol solution. The prepared  $\text{Co}_3\text{O}_4/\text{Ti}$  electrode was dipped into reduced graphene oxide (rGO prepared by following a previous method)<sup>S1</sup> solution to make  $\text{Co}_3\text{O}_4/\text{rGO}$  composites. And, it was dried in air for 5 h and cleaned with DW. Cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) was synthesized on Ti plate by using a mixture of 250 mM  $\text{Co}(\text{NO}_3)_2$  and 500 mM  $\text{Fe}(\text{NO}_3)_3$  in ethanol. Cobalt-doped  $\text{TiO}_2$  (Co- $\text{TiO}_2$ ) was prepared by drop-casting method using a mixture of 250 mM titanium-glycolate complex and 25 mM  $\text{Co}(\text{NO}_3)_2$  on Ti plate. All samples except for  $\text{Co}_3\text{O}_4/\text{rGO}$  were annealed in air at 450 °C for 1 h.



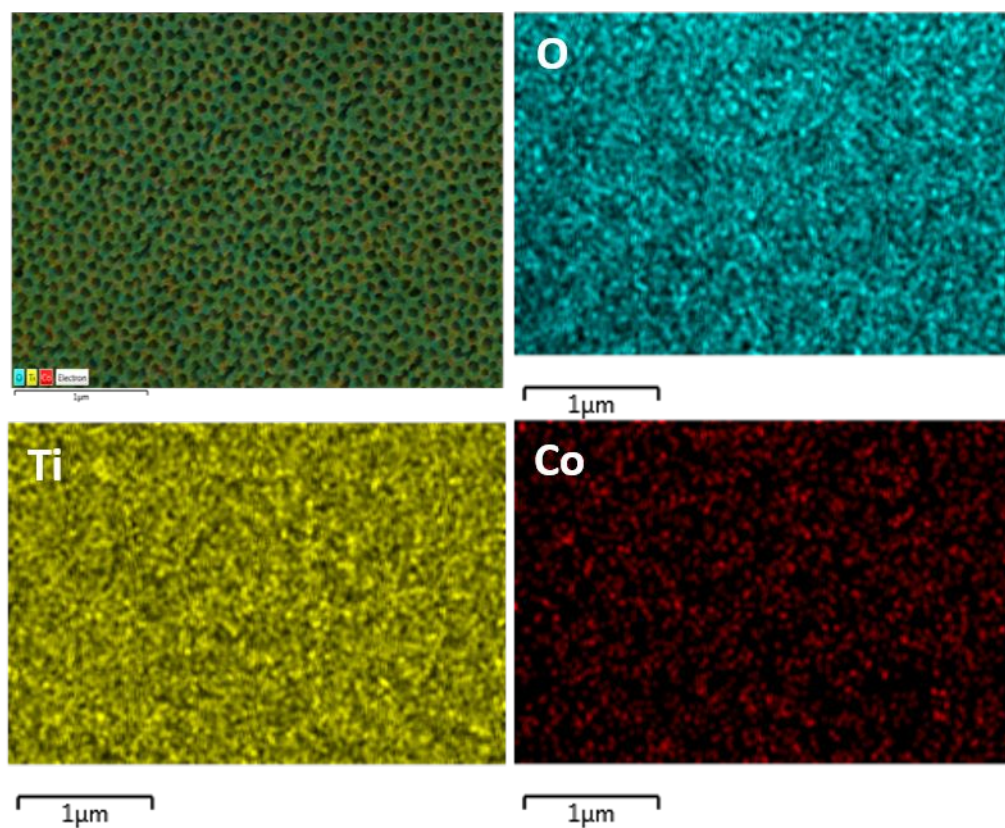
**Figure S1.** 4-CP removal by Co-Black TNT/PMS system with and without phosphate buffer solution ( $[4\text{-CP}]_0 = 100 \mu\text{M}$ ;  $[\text{PMS}]_0 = 1 \text{ mM}$ ;  $[\text{phosphate buffer}]_0 = 3 \text{ vol } \%$ ;  $\text{pH}_i = 7.0$ ).



**Figure S2.** (a) XRD patterns of bare TNT, Co-TNT, Black TNT, and Co-Black TNT. (b) Expanded XRD spectrum of (101) diffraction peaks of Black TNT and Co-Black TNT.

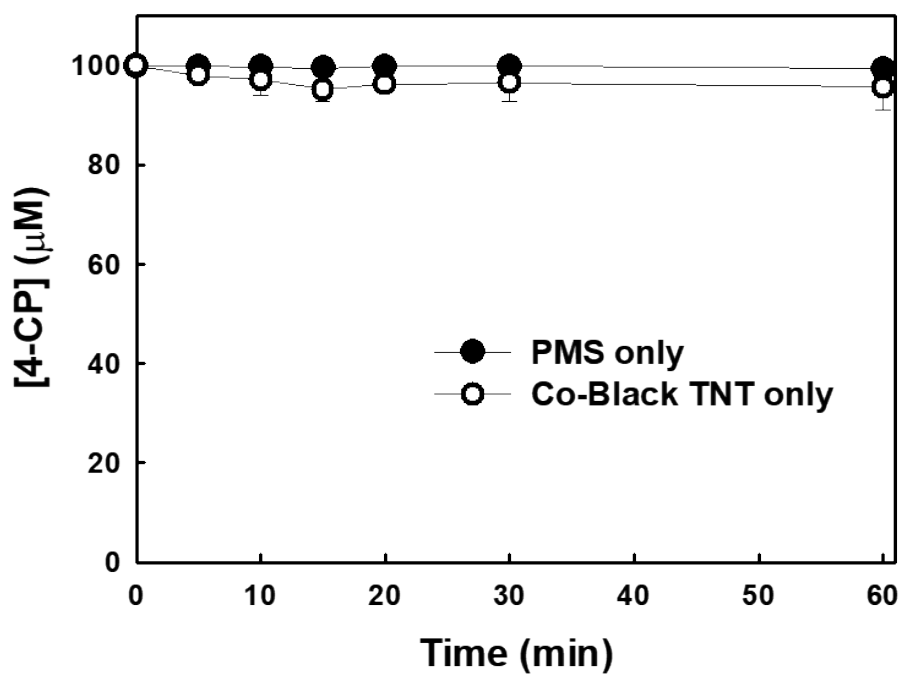


**Figure S3.** The horizontal and cross-sectional SEM images of (a and b) bare TNT, (c and d) Co-TNT, (e and f) Black TNT, and (g and h) Co-Black TNT.



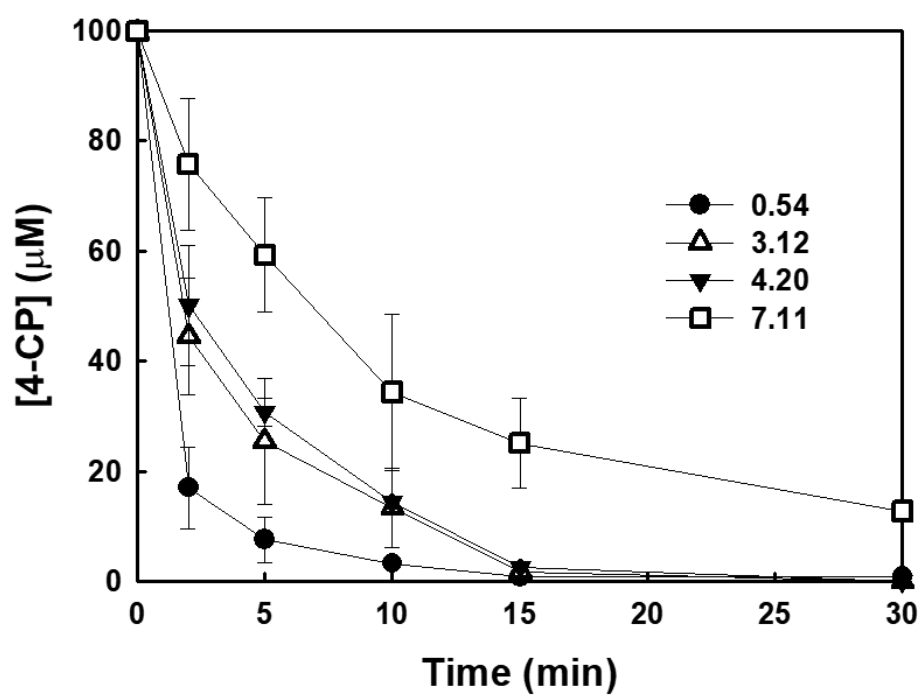
**Figure S4.** SEM-EDX image of O, Ti, and Co elements within Co-Black TNT sample.

**Discussion on Figure S2-S4.** The crystallographic phase of the synthesized materials was identified by XRD (Figure S2a). All samples were identified to be purely anatase phase, indicating that the doping of Co did not induce any phase transition. However, the peak position and the intensity of (101) plane was slightly shifted to a higher angle and reduced, respectively, after Co doping in Black TNT (Figure S2b). This result is ascribed to that the different ionic radius between  $\text{Co}^{2+}$  (0.65 Å) and  $\text{Ti}^{4+}$  (0.61 Å) change the lattice structure and crystallinity, and thus indicates Co doping in  $\text{TiO}_2$  lattice.<sup>S2</sup> The SEM images of all samples in Figure S3 show aligned nanotubes structure. The elemental energy-dispersive X-ray (EDX) images clearly display the uniform distribution of O, Ti, and Co elements within Co-Black TNT sample (Figure S4).

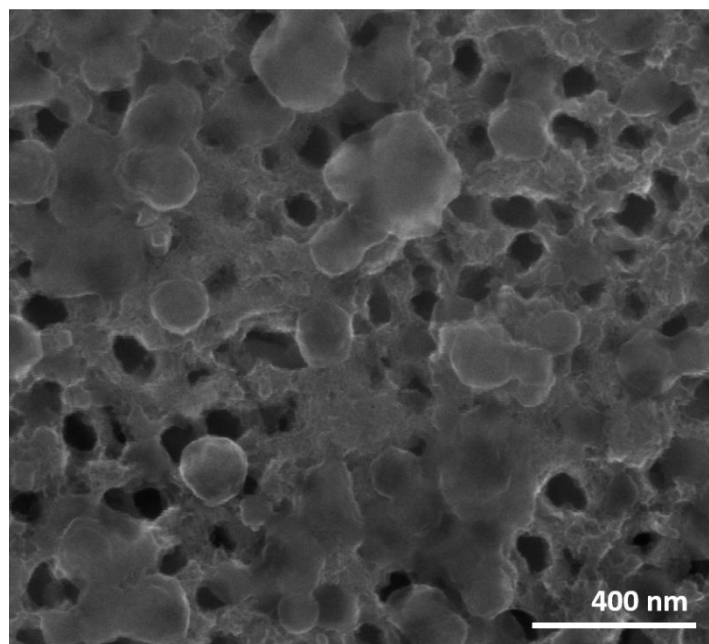


**Figure S5.** Degradation of 4-CP without Co-Black TNT or PMS ( $[4-CP]_0 = 100 \mu M$ ;  $[PMS]_0 = 1 \text{ mM}$ ;  $[\text{phosphate buffer}]_0 = 3 \text{ vol } \%$ ;  $pH_i = 7.0$ ).

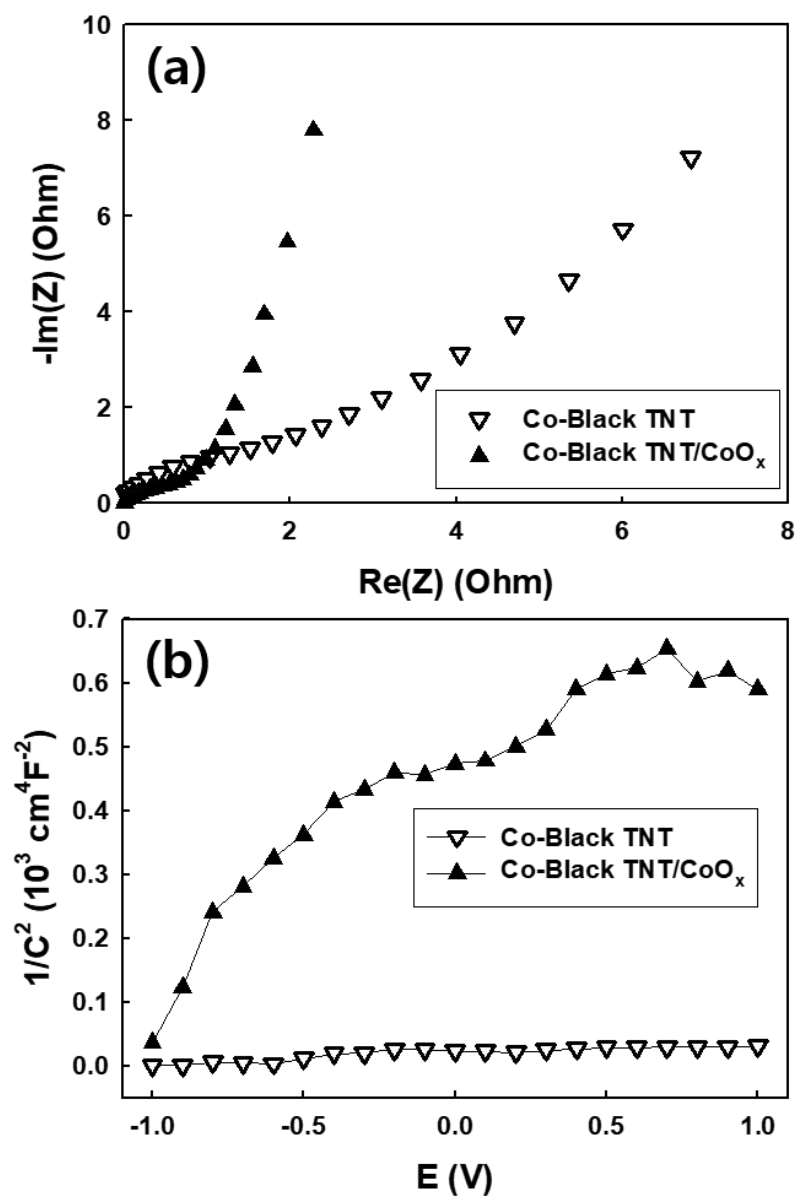




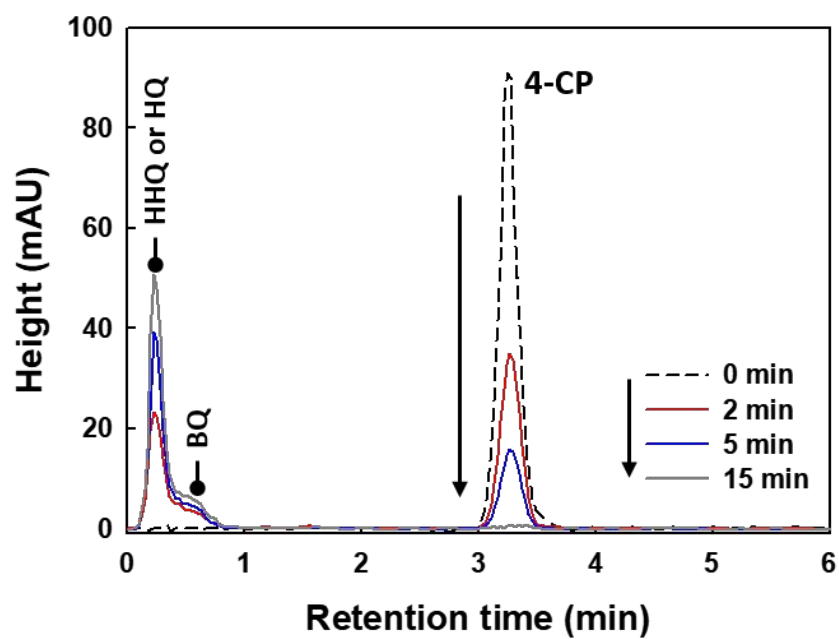
**Figure S6.** 4-CP removal by Co ( $\times \mu\text{mol}/\text{cm}^2$ )-Black TNT ( $[\text{4-CP}]_0 = 100 \mu\text{M}$ ;  $[\text{PMS}]_0 = 1 \text{ mM}$ ;  $[\text{phosphate buffer}]_0 = 3 \text{ vol } \%$ ;  $\text{pH}_i = 7.0$ ).



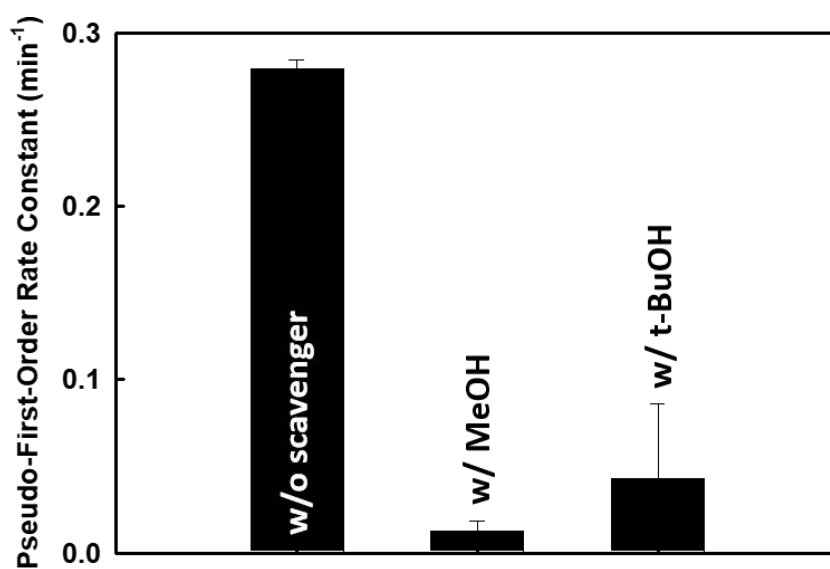
**Figure S7.** The horizontal SEM images of Co-Black TNT/CoO<sub>x</sub> (prepared with high concentration of Co precursor).



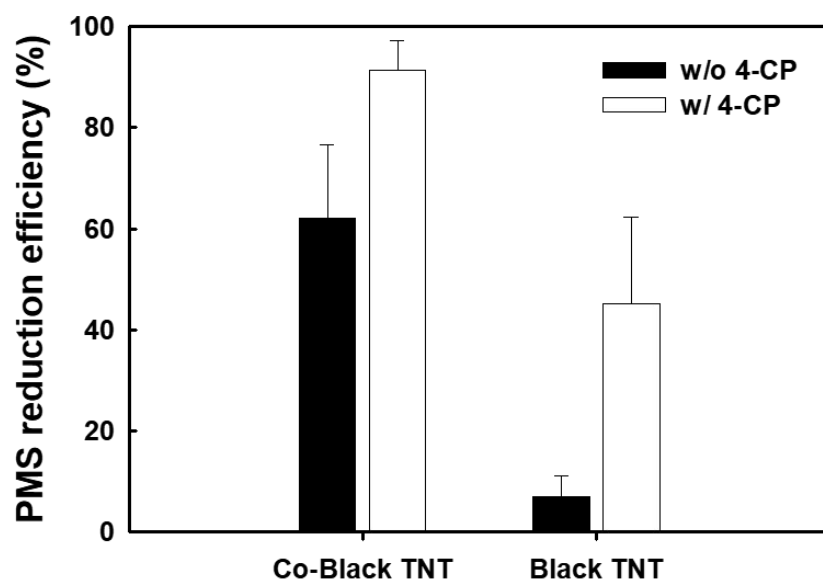
**Figure S8.** (a) Nyquist plots and (b) Mott-Schottky plots of Co-Black TNT and Co-Black TNT/CoO<sub>x</sub> prepared with low and high concentration of Co precursor, respectively. The experimental conditions were the same as those of Figure 2.



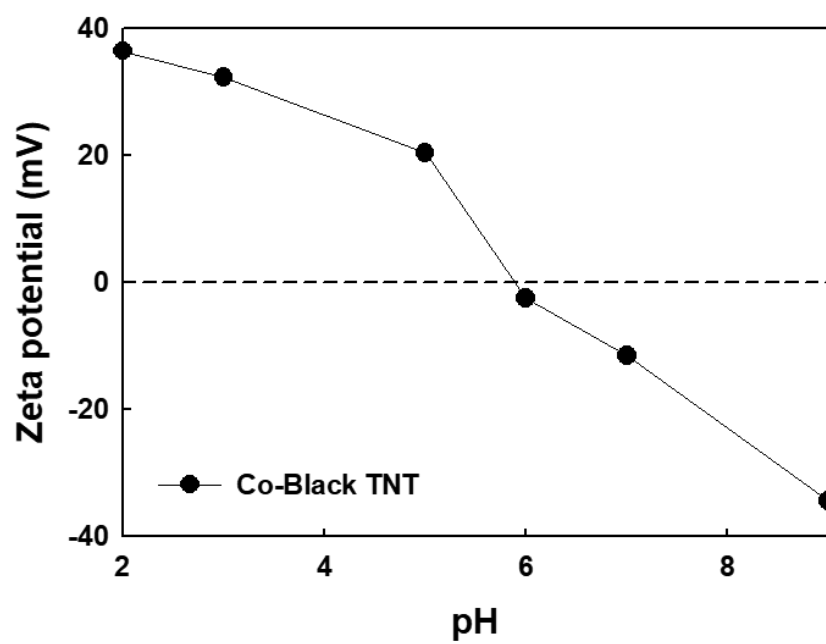
**Figure S9.** HPLC chromatograms of intermediates generated after 15 min PMS-activated 4-CP degradation in Co-Black TNT.



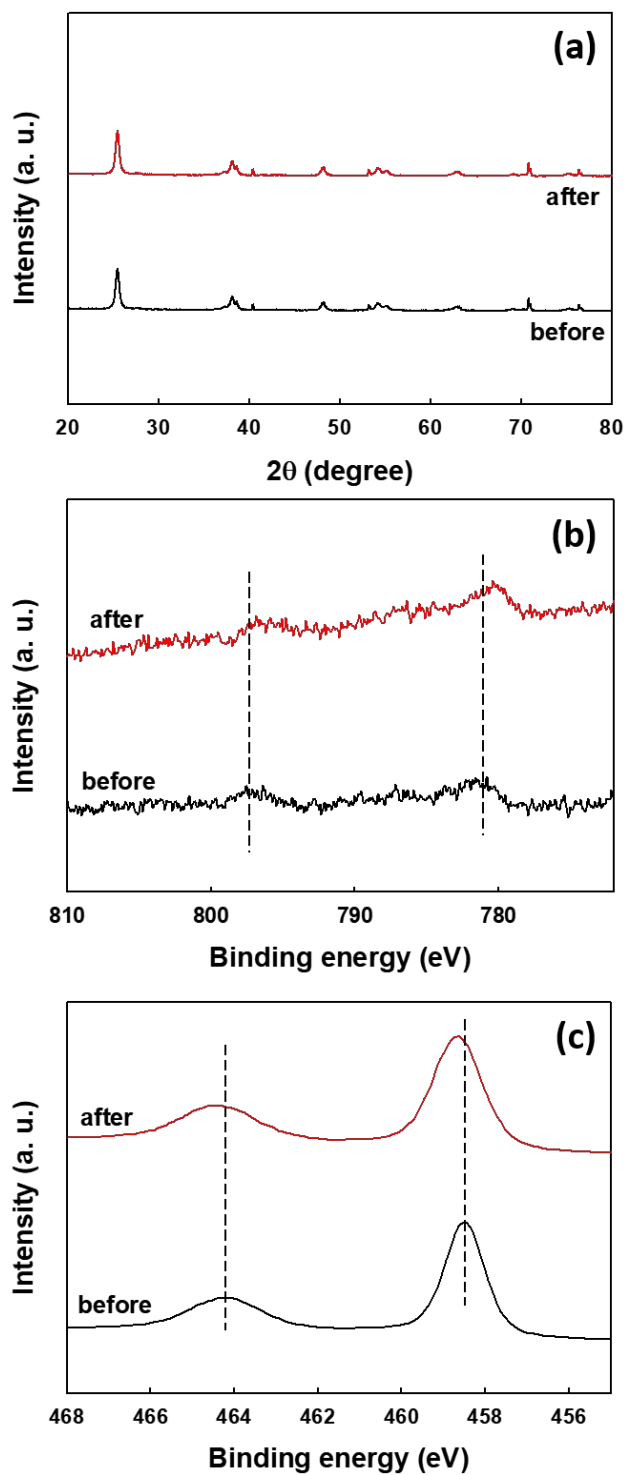
**Figure S10.** Effect of MeOH and t-BuOH on the rate of 4-CP degradation in Co-Black TNT/PMS system ( $[4\text{-CP}]_0 = 100 \mu\text{M}$ ;  $[\text{MeOH}]_0 = [\text{t-BuOH}]_0 = 100 \text{ mM}$  (for a);  $[\text{PMS}]_0 = 1 \text{ mM}$ ;  $[\text{phosphate buffer}]_0 = 3 \text{ vol } \%$ ;  $\text{pH}_i = 7.0$ ).



**Figure S11.** Effect of 4-CP on PMS reduction in Co-Black TNT and Black TNT ( $[4\text{-CP}]_0 = 100\ \mu\text{M}$ ;  $[\text{PMS}]_0 = 1\ \text{mM}$ ;  $[\text{phosphate buffer}]_0 = 3\ \text{vol}\%$ ;  $\text{pH}_i = 7.0$ ).



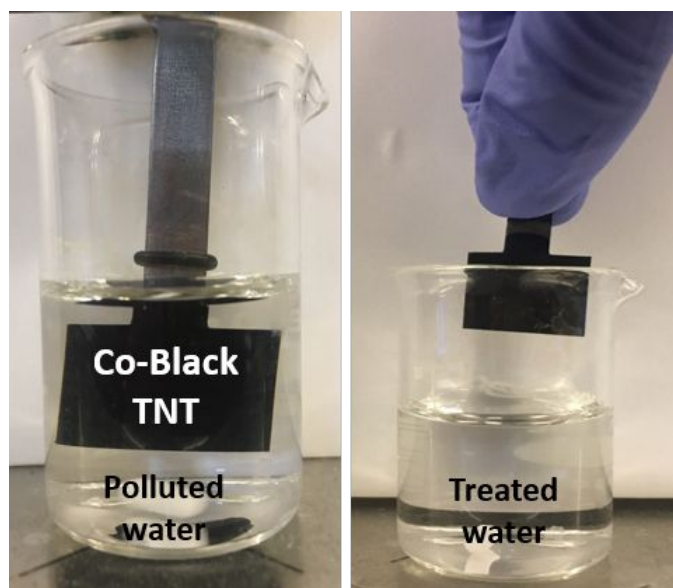
**Figure S12.** Zeta-potentials of Co-Black TNT as a function of pH.



**Figure S13.** (a) XRD patterns and (b) Co 2p and (b) Ti 2p XPS spectra of Co-Black TNT before and after reaction.



**Discussion of the data of Figure S13.** No difference in XRD patterns of Co-Black TNT were observed before and after reaction (10 cycles) (Figure S13a). On the other hand, the Co 2p and Ti 2p XPS spectra of Co-Black TNT were slightly shifted to lower and higher binding energies (Figure S13b and c), respectively, which is attributed to the partial oxidation of  $\text{Co}^{2+}$  and  $\text{Ti}^{3+}$  in Co-Black TNT during the reaction. However, this partial oxidation does not affect the stability and reusability of Co-Black TNT. Black TNT showed a slight deactivation during repeated PMS activation, which may be due to the accumulation of intermediates generated from 4-CP degradation by low mineralization activity (*see* Figure 3c).



**Figure S14.** A digital photo for demonstration of catalyst recovery from treated water: Co-Black TNT dipped in PMS solution for treatment of polluted water (left) and easily separated Co-Black TNT from treated water without Co leaching (right).

Activator	Initial pH	Dissolved Co concentration in the solution (mg/L)
Co-Black TNT	pH 3	0.003
	pH 7	0.001
	pH 9	0.002
Co-TNT	pH 3	0.003
	pH 7	0.004
	pH 9	0.002

**Table S1.** The effect of initial pH on loss of cobalt during PMS activation on Co-doped TNTs.

## References

- S1. Moon, G.-h.; Kim, W.; Bokare, A. D.; Sung, N.-e.; Choi, W. Solar production of H<sub>2</sub>O<sub>2</sub> on reduced graphene oxide-TiO<sub>2</sub> hybrid photocatalysts consisting of earth-abundant elements only. *Energy Environ. Sci.* **2014**, 7, 4023-4028.
- S2. Chanda, A.; Rout, K.; Vasundhara, M.; Joshi, S. R.; Singh, J. Structural and magnetic study of undoped and cobalt doped TiO<sub>2</sub> nanoparticles. *RSC Adv.* **2018**, 8, 10939-10947.