

Supporting information

Activation of persulfate by Co₃O₄ nanoparticles for orange G degradation

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Text S1 The preparation of nano-Co₃O₄.

Nano-Co₃O₄ was prepared by precipitation method using cobalt nitrate as the precursor in the presence of CTAB. In a typical synthesis, 12.5 mmol of Co(NO₃)₂ • 6H₂O and 2.5 mmol of CTAB were dissolved in 750 mL deionized water, in a 1000 mL round bottom flask, giving a pink solution. After stirring for 20 min, 249.0 mmol of triethylamine (TEA) was rapidly added into the pink solution under vigorous agitation, giving a blue mixture. Then, the blue mixture was stirred at 348 K for 8 h, and the color of the mixture changed into black. The as-synthesized cobalt oxide was obtained by centrifugation and then dried at 353 K for 48 h. The dried material was treated by Soxhlet extraction over ethanol for 48 h to remove stabilizers. The obtained solid was calcined at 573 K under flowing air for 2 h after drying at 373 K for 8 h.

Text S2 Details of experiments to assess the leaching of nano-Co₃O₄ and the catalytic performance of dissolved Co ions.

To evaluate the leaching of Co from nano-Co₃O₄, 10 mL samples were withdrawn with plastic syringes at fixed time intervals during batch experiment and mixed immediately with appropriate amounts of methanol to quench any further oxidation reactions, and then the solution and nano-Co₃O₄ catalyst were separated by filtration. The concentrations of dissolved Co ions were determined by ICP-AES after microwave digestion in the mixture of nitric acid and hydrogen peroxide.

To evaluate the catalytic performance of dissolved Co ions, batch experiments were performed open to the air and in a series of 500-mL borosilicate glass jars that were placed in a water bath to keep temperature constant. The dosage of Co²⁺ was set according the maximum dissolved Co ions at the end of reactions in heterogeneous reaction. Before dosing catalyst, pH of the solution containing PS and OG was adjusted to the predetermined value with NaOH or HClO₄. At the given time intervals, the samples aliquots were collected with syringes and mixed immediately with appropriate amounts of methanol to quench any further oxidation reactions. The samples were filtered through a 0.22 μm membrane filter before measurement.

Text S3 Detailed parameters and procedure of EPR experiments

5, 5-dimethyl-1-pyrrolidine N-oxide (DMPO) was used as a spin-trapping agent. The mixture of DMPO and sample was mixed for 30 s and then sampled by a capillary tube, which was inserted into the EPR cavity. EPR experiments were performed on a Bruker A200 spectrometer. The condition was: a center field of 353.5 mT, a sweep width of 7 mT, a sweep time of 81.92 s, a modulation frequency of 100 kHz, a modulation amplitude of 0.05 mT, a microwave frequency of 9.85 GHz, and a microwave power of 6.1 mW.

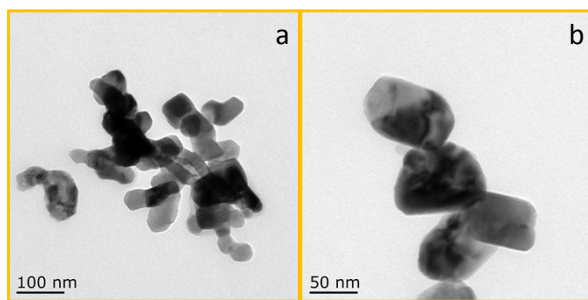


Fig. S1 TEM for virgin nano-Co₃O₄ (a) and spent nano-Co₃O₄ after five consecutive runs (b).

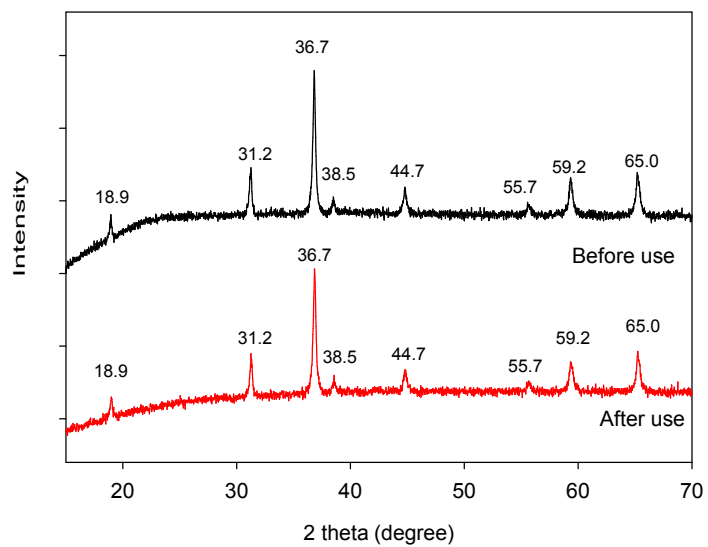


Fig. S2 XRD patterns for virgin nano-Co₃O₄ and spent nano-Co₃O₄ after five consecutive runs.

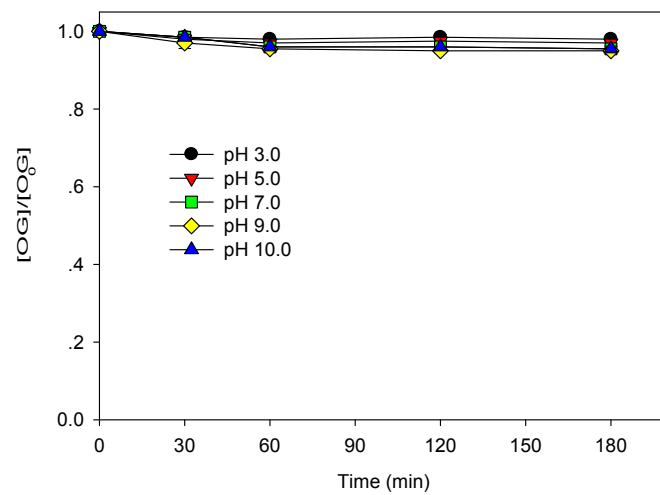


Fig. S3 Removal of OG by PS alone at various pH. Reaction conditions: $[OG]_0 = 0.1$ mM, $[PS]_0 = 2.0$ mM, $T=25$ °C.

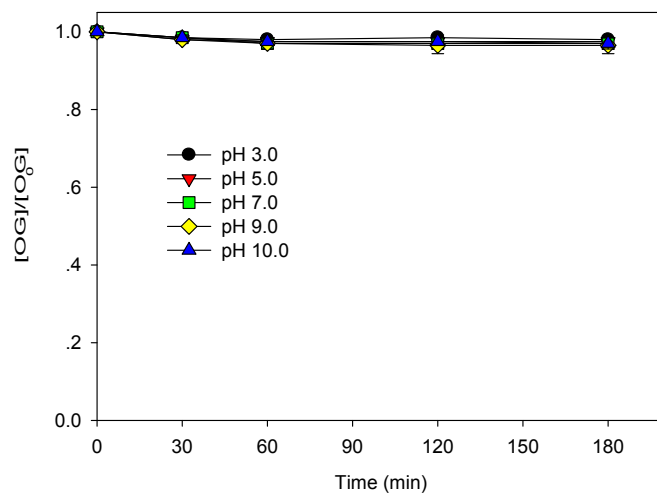


Fig. S4 Removal of OG by nano- Co_3O_4 adsorption at various pH. Reaction conditions:

$[\text{OG}]_0 = 0.1 \text{ mM}$, $[\text{nano-}\text{Co}_3\text{O}_4]_0 = 2.0 \text{ g L}^{-1}$, $T = 25 \text{ }^\circ\text{C}$.

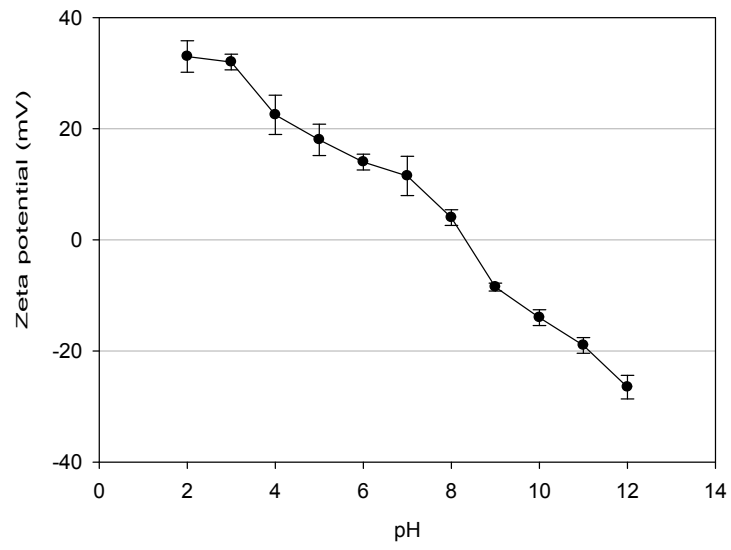


Fig. S5 Zeta potential versus pH for nano-Co₃O₄ in deionized water.

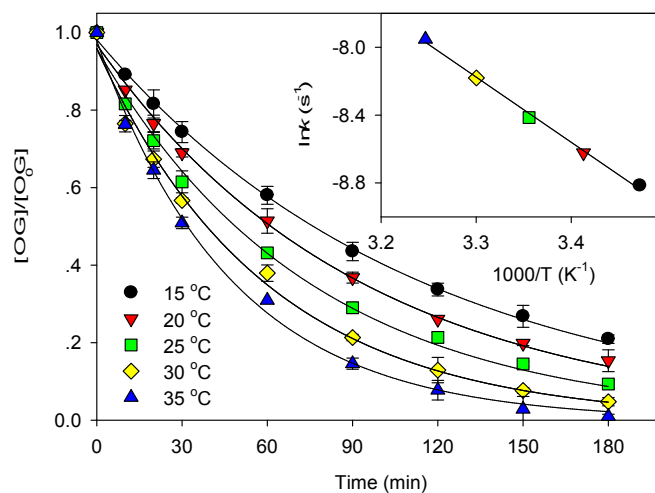


Fig. S6 Degradation of OG in nano-Co₃O₄/PS system at different temperatures. Inset indicates the Arrhenius plot for the OG degradation rate constants at 10, 15, 20, 25 and 30 °C. (Reaction conditions: [OG]=0.1 mM, [PS]=2 mM, [nano-Co₃O₄]=0.5 g L⁻¹, pH=7.0±0.1, T=15-35 °C).

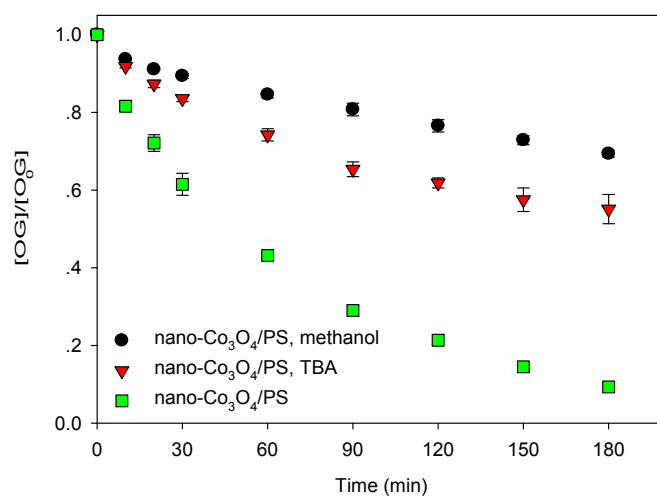


Fig. S7 Oxidation of OG in nano-Co₃O₄/PS system in the presence of TBA or methanol (Reaction conditions: [OG]=0.1 mM, [PS]=2 mM, [nano-Co₃O₄]=0.5 g L⁻¹, [TBA]=10 mM, [methanol]=10 mM, pH=7.0±0.1, T=25 °C).

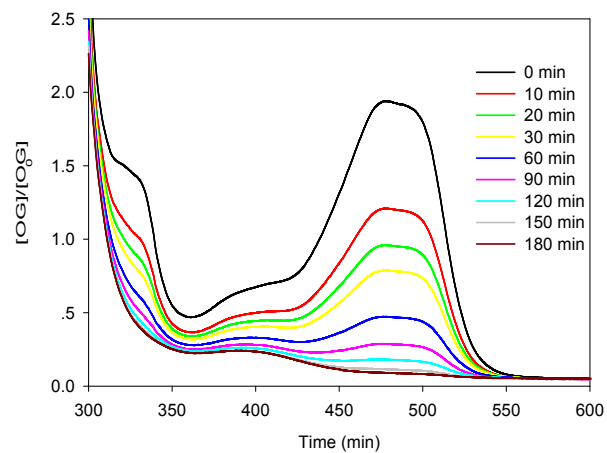


Fig. S8 Variation of the UV-Vis spectra of OG with time in the nano- $\text{Co}_3\text{O}_4/\text{PS}$ system (Reaction conditions: $[\text{OG}]_0=0.1 \text{ mM}$, $[\text{PS}]_0=2.0 \text{ mM}$, $[\text{nano-}\text{Co}_3\text{O}_4]_0=0.5 \text{ g L}^{-1}$, $\text{pH}=7.0\pm 0.1$, $T=25 \text{ }^\circ\text{C}$).

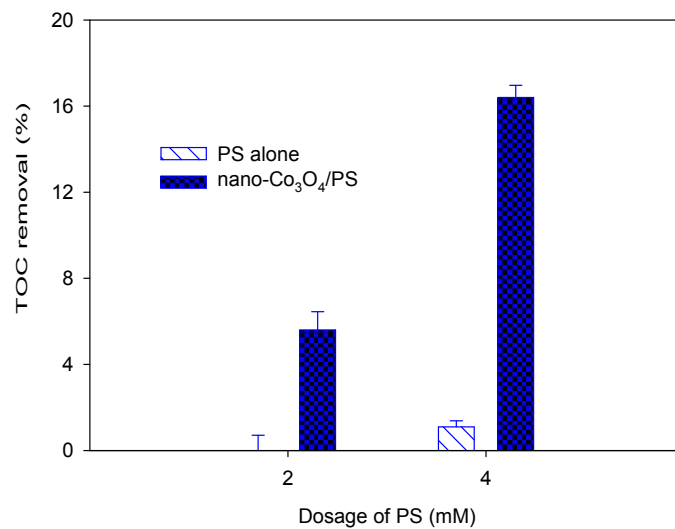


Fig. S9 Influence of nano-Co₃O₄ on mineralization of OG by PS at different PS dosages (Reaction conditions: [OG]₀=0.1 mM, [nano-Co₃O₄]₀=0.5 g L⁻¹, pH=7.0±0.1, T=25 °C, reaction time=3 h).

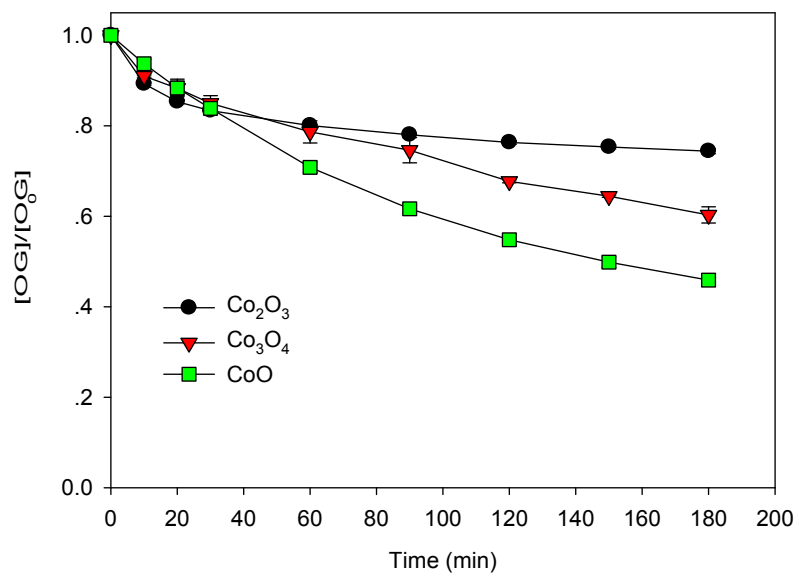
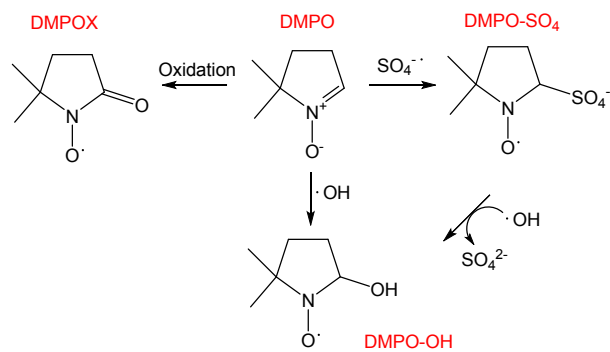


Fig. S10 Oxidation of OG by PS with Co_2O_3 , Co_3O_4 and CoO (Reaction conditions: $[OG]=0.1$ mM, $[PS]=2$ mM, $[Co_2O_3]=[Co_3O_4]=[CoO]=2.08$ mM (the mass of Co_3O_4 was 0.5 g L^{-1} with the dosage of 2.08 mM), $pH=7.0\pm 0.1$, $T=25$ °C).



Scheme S1. Formation of DMPO-SO₄ and DMPO-OH adducts, and DMPOX radicals.

Table S1 BET, the first order reaction rate constant (k) and the specific rate constant

(k_{SA}) normalized by BET surface area for Co_3O_4 and nano- Co_3O_4 .

	BET surface area ($\text{m}^2 \text{g}^{-1}$)	k (s^{-1})	k_{SA} ($\text{g m}^{-2} \text{s}^{-1}$)
	1)		
Co_3O_4	4.9	4.50×10^{-5}	9.18×10^{-6}
Nano- Co_3O_4	18.1	2.22×10^{-4}	1.23×10^{-5}

Table S2 The information of OG and the identified OG degradation products.

Peak number	Retention time (min)	Proposed molecular formula	Molecular weight
Orange G	6.71	$C_{16}H_{12}N_2O_7S_2$	408
A	6.44	$C_{16}H_{12}N_2O_4S$	328
B	7.05	$C_{16}H_{12}N_2O_3S$	312
C	4.73	$C_{16}H_{10}N_2O_4S$	326
D	7.64	$C_{16}H_{10}N_2O_5S$	342
E	5.51	$C_{10}H_{10}O_7S_2$	304
F	6.32	$C_{10}H_8O_8S_2$	320
G	8.04	$C_{10}H_8O_9S_2$	336
H	5.86	$C_{10}H_6O_9S_2$	334
I	6.49	$C_{10}H_8N_2O_7S_2$	332
J	6.54	$C_{10}H_8N_2O_6S_2$	316
K	7.14	$C_{10}H_6N_2O_7S_2$	330
L	6.02	$C_{10}H_8N_2O_8S_2$	348
M	1.64	$C_{10}H_8N_2O_9S_2$	364
N	7.18	$C_{10}H_8N_2O_{10}S_2$	380
O	6.52	$C_{16}H_{12}N_2O_6S_2$	392