

Electronic Supplementary Information

Fluorescence microscopic image-analysis (FMI) for characterization of interphase HO[•]-yielding originated by heterogeneous catalysis

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Experimental Section

Materials and reagents. Powdered manganese black (MnO₂) were purchased from Kermel Reagent Co. Ltd. (Tianjin, China). Fine aluminum oxide (Al₂O₃), ferric oxide (Fe₂O₃), copper oxide (CuO), and Titanium oxide (TiO₂) were supplied by Damao Reagent Co. Ltd. (Tianjin, China). Coumarin and 7-hydroxycoumarin were purchased from Shanghai Aladdin Co. Ltd. (Shanghai, China) and Bailingwei Co. Ltd. (Beijing, China), respectively. All the metal oxide particles were analytical reagent. Prior to use, they were milled by an agate mortar, washed by ultrapure water, vacuum filtrated, dried overnight at 60 °C, and then stored in a drying bottle. For each semi-batch test, the solid load were preset at 0.5 g L⁻¹ and ultrasonically dispersed in advance to reaction. The chemicals were analytical reagent and used as received without further purification.

Procedures of reactions. Catalytic ozonation was performed in a 500 mL wide-mouth bottle. Gaseous ozone was originated by an ozone-generator (5 g O₃ h⁻¹) using pure oxygen as the source gas, and bubbling introduced (1 L min⁻¹) from the bottom

of reactor through a ceramic sparger.

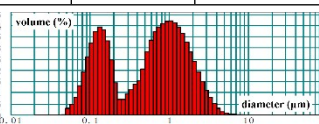
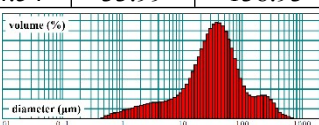
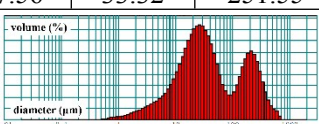
Photocatalysis tests were conducted in a cylindrical glass vessel containing 100 mL solid/liquid mixture. Magnetic agitation was exerted to ensure a well-dispersed state of metal oxide particles. A PCPA PLS-SXE300 Xe lamp (300 W, Beijing Perfect Light Co. Ltd., China) was used to serve as the light source with the output wavelength > 320 nm.

All the experiments were performed under atmospheric pressure with liquid temperatures controlled at 20±1 °C. The solution pH was initially adjusted to 7.0 and without further control during reactions.

Material characterization. Surface morphologies of metal oxides were observed using scanning electron microscopy (SEM) (S4800, Hitach, Japan). The profile of particle size distribution in water was obtained by Laser Particle Size Analyzer Mastersizer2000 (Lasentec, Redmond, Washington), and the Sauter mean

diameter (d_{32}) was automatically calculated according to
$$d_{32} = \frac{\sum_{i=1}^n d_i^3}{\sum_{i=1}^n d_i^2}$$
. Material texture properties were measured using Autosorb-1 (Quantachrome, USA), where the specific surface area (S_{BET}), total pore volume (V_{total}) and average pore diameter (D_{pore}) were determined by multi-point Brunauer-Emmett-Teller (BET) model following the adsorption-desorption isotherms of N_2 at -196.15 °C. The density of metal oxides (ρ_s) was determined by a pycnometer.

Table S1 The physical and chemical properties of metal oxide particles

Type	ρ_s (g cm ⁻³)	d ₃₂ (μm)	Size distribution (μm)			S _{BET} (m ² g ⁻¹)	V _{total} (cm ³ g ⁻¹)	D _{pore} (nm)
			d _{0.1}	d _{0.5}	d _{0.9}			
Fe ₂ O ₃	3.95	0.31	0.11	0.77	4.91	24.51	0.072	11.6 9
								
Al ₂ O ₃	3.33	10.57	4.54	33.99	138.93	93.61	0.225	9.61
								
CuO	5.32	15.96	7.56	33.32	251.55	4.52	0.013	11.8 2
								
MnO ₂	4.15	1.23	0.89	29.65	69.64	41.19	0.054	5.25

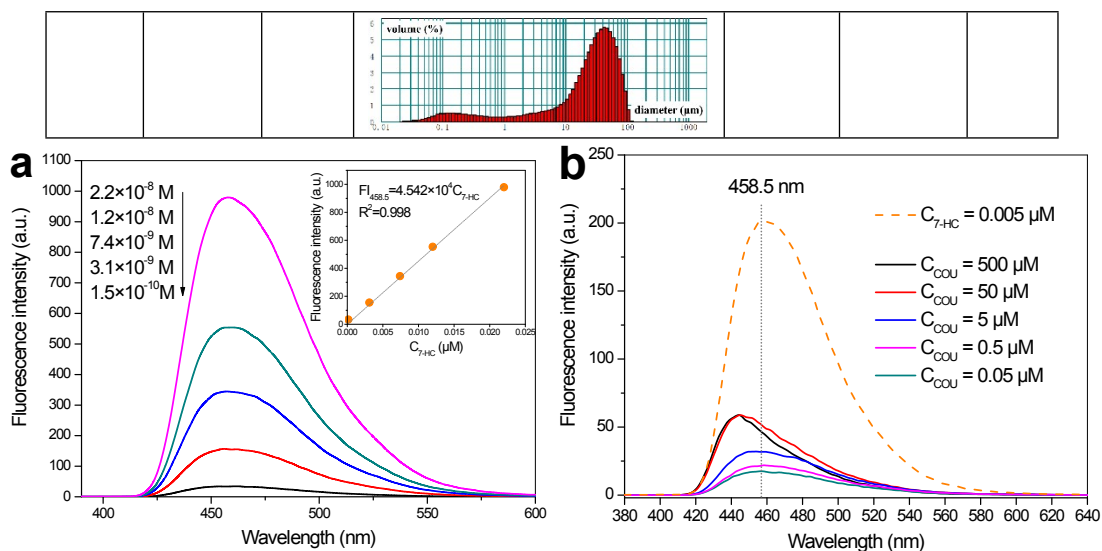


Fig. S1 (a) Calibration curve for aqueous 7-hydroxycoumarin at peak intensity of 458.5 nm using a fluorescence spectrophotometer. UV-excitation, 325 nm. (b) Fluorescence spectra for coumarin (0.05-500 μM) or 7-hydroxycoumarin (0.005 μM).

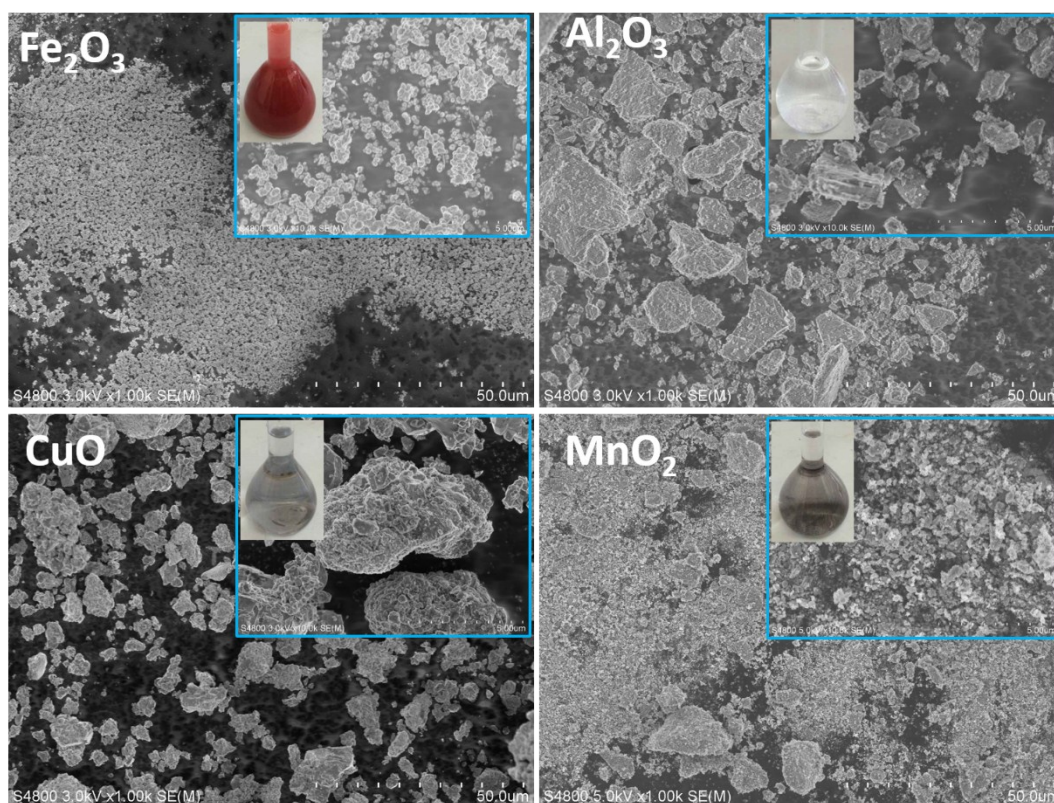


Fig. S2 SEM images of the tested four metal oxides. The insets show the images with further magnification of 10 times, and photographs of the suspended state in water with solid load of 0.5 g L^{-1} .

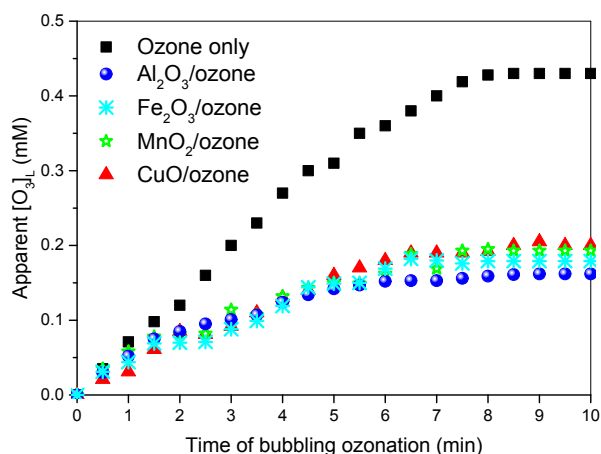


Fig. S3 Evolution of apparent aqueous ozone concentration ($[O_3]_L$) versus time for the counteraction of gas-to-liquid ozone transfer with surface-mediated ozone consumption. The $[O_3]_L$ was determined by indigo method.

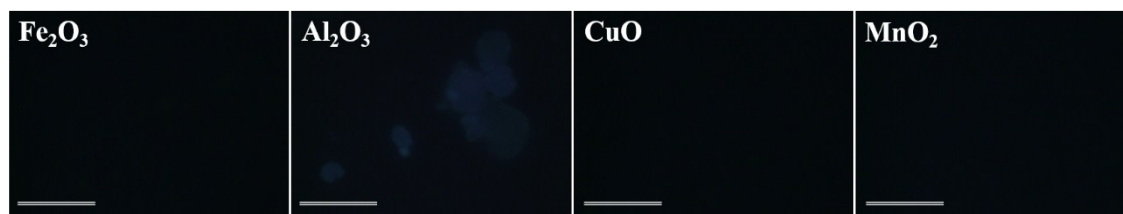


Fig. S4 Fluorescence microscopic images for the mixture of coumarin solution (1 mM) with the sample containing dispersed metal oxide particles (0.5 g L^{-1}). Conditions: magnification, 400 \times ; exposure time, 20 s; scale bar, 10 μm .

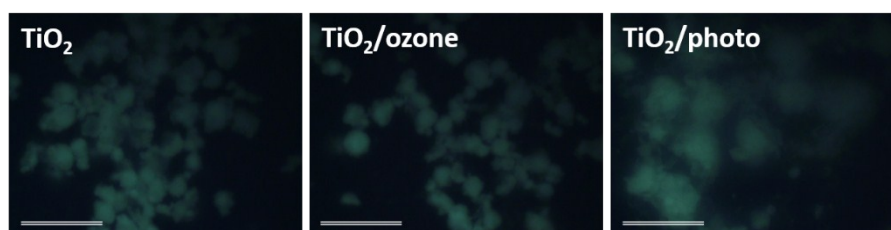


Fig. S5 Fluorescence microscopic images for the mixture of coumarin solution (1 mM) with the sample containing dispersed TiO_2 particles (0.5 g L^{-1}) from different systems. Conditions: magnification, 400 \times ; exposure time, 20 s; scale bar, 10 μm .