

Supporting Information

Catalytic Ozonation in Arrayed Zinc Oxide Nanotubes as Highly Efficient Mini-Column Catalyst Reactors (MCRs): Augmentation of Hydroxyl Radical Exposure

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Pages 23; Figures 16; Table 1

I. Supplemental Materials and Methods

Reagents. N-methyl-pyrrolidone ($\geq 99\%$, AR), zinc acetate dihydrate ($\geq 99\%$, AR), methanol ($\geq 99.5\%$, AR) and ethanol ($\geq 99.7\%$, AR) were purchased from Damao Chemical Reagent Co. Ltd. (Tianjin, China). Cetytrimethylammonium bromide (CTAB, $\geq 99\%$, AR) was supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Sodium benzenesulfonate (SBS, 97%), 5,5-dimethyl-pyrroline-oxide (DMPO, 97%), coumarin (AR) and 7-hydroxycoumarin (7-HC, 98%) were purchased from Aladdin Industrial Corporation (Shanghai, China).

All the powdered metal oxides were analytical reagent. Zinc oxide (ZnO), aluminum oxide (Al_2O_3), ferric oxide (Fe_2O_3), and titanium oxide (TiO_2) were supplied by Damao Reagent Co. Ltd. (Tianjin, China). Manganese black (MnO_2) and molybdenum trioxide (MoO_3) were purchased from Kermel Reagent Co. Ltd. (Tianjin, China). Vanadium pentoxide (V_2O_5) and cerium oxide (CeO_2) were purchased from Fuchen Chemical Reagent Co. Ltd. (Tianjin, China). Chromium oxide (Cr_2O_3), cobalt oxide (Co_2O_3), nickel monoxide (NiO) and palladium oxide (PdO) were respectively obtained from Bodi Chemical Reagent Co. Ltd. (Tianjin, China), Xilong Chemical Reagent Co. Ltd. (Shantou, China), Aladdin Industrial Corporation (Shanghai, China), and Macklin Biochemical Co. Ltd. (Shanghai, China). In pretreatment steps, the metal oxides were milled by an agate mortar, washed by ultrapure water, vacuum filtrated, dried overnight at $60\text{ }^\circ\text{C}$, and stored in a drying bottle for experiments.

Analytical Methods. A fluorescent photometer (PerkinElmer LS55, UK Liantrisant) was utilized to determine the abundance of 7-HC as $\text{HO}\cdot$ marker in metal oxide/ozone systems (Figure S1). An aliquot of sample was periodically withdrawn from a bubbling reactor, immediately mixed at volume ratio of 1:1 with prepared coumarin solution (1 mM), placed in a $70\text{ }^\circ\text{C}$ water bath for 30 min for a desorption of 7-HC (if any), filtered through a $0.45\text{ }\mu\text{m}$ membrane to remove the solid phase, and finally, the obtained liquid sample was sent for analysis. To quantify the 7-HC, the characteristic peak of emission was set at 458.5 nm with UV-excitation at 325 nm . Both the emission and excitation slits were set to 5.0 nm .

The concentrations of oxalic acid and atrazine were respectively detected by HPLC (Waters 2695 Separations Module). The stationary phase was SunFire[®] C18 $5\text{ }\mu\text{m}$ column ($250\text{ mm} \times 4.6\text{ mm} \times 5\text{ }\mu\text{m}$). Oxalic acid was quantified at wavelength of 197 nm with an eluent solution mixed by A (98% ammonium biphosphate solution) and B

(methanol) under flowrate of 0.7 mL/min ($V_A/V_B = 98/2$). Atrazine was detected at wavelength of 224 nm with an eluent solution mixed by ultrapure water (30%) and methanol (70%) at a flowrate of 1.0 mL/min.

Determination of Retention Time (t_R) in MCR. The time spent for catalytic ozonation in the arrayed nanotubes closely correlates with the pore size, arrangement, as well as the flux of target solution. First, we recorded the diameter for each of the pores (labeled as d_i) as presented in the selected region of SEM images shown in Figure S3. Then the total porous area for passage of mixture solution (s_p , m^2) can be determined according to Equation (S1),

$$s_p = \frac{A_0}{A_{SEM}} \cdot \sum_{i=1}^n d_i^2 \cdot \frac{\pi}{4} \quad (S1)$$

where A_0 is the actual exposed area of ZnO_{NT} -AAO composite fixed in the two-pass reaction module for passage of solution, m^2 ; A_{SEM} is the total area of selected SEM image for collection of d_i , m^2 ; n is the total number of pores recorded in the selected SEM image, dimensionless.

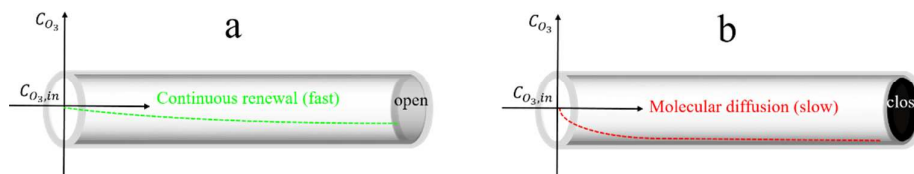
If the flux of solution is controlled at Q ($mL \min^{-1}$), the t_R (s) can be expressed as

$$t_R = \frac{s_p \cdot \delta \cdot 10^{-5}}{Q} \quad (S2)$$

where δ is the thickness of ZnO_{NT} array, m.

II. Supplemental Results and Discussion

Comparison of MCR with a dead-end mode on internal ozone consumption. With a continuous feeding of saturated ozone, the MCR working in double-pass mode allows a fast mass delivery and timely ozone renewal within the inner void (Scheme 1a). As for a dead-end nanotube, however, molecular diffusion is the driving force for aqueous ozone molecules to penetrate into a deeper inner void (Scheme 1b). The latter process would be very slow, and meanwhile, aqueous ozone would gradually decompose or be consumed via surface without a mass renewal.



Scheme 1. Schematic illustration for the evolution of ozone concentration alongside the wall of (a) MCR in double-pass mode and (b) a dead-end nanotube.

The evolution of aqueous ozone concentration (C_{O_3} , M) alongside the inner wall of a dead-end nanotube can be expressed by Equation (S3),

$$\frac{\pi d_s^2}{4} \cdot D_{O_3} \cdot \left(\frac{dC_{O_3}}{dx} \right)_x - \frac{\pi d_s^2}{4} \cdot D_{O_3} \cdot \left(\frac{dC_{O_3}}{dx} \right)_{x+dx} = -\pi \cdot d_s \cdot dx \cdot k_e \cdot C_{O_3} \quad (S3)$$

where d_x represents an axial displacement of liquid element, m.

Equation (S3) yields Equation (S4) as dx is close to zero,

$$\frac{d^2 C_{O_3}}{dx^2} = \lambda^2 \cdot C_{O_3} \quad (S4)$$

where λ is the term $\left(\frac{4k_e}{d_s \cdot D_{O_3}} \right)^{1/2}$, m^{-1} .

The boundary conditions for Equation (S3) are respectively $x = 0$, $C_{O_3} = C_{O_3,in}$ and $x = \sigma$, $\frac{dC_{O_3}}{dx} = 0$. The parameter σ (m) is the displacement of solution for a complete decay of ozone through an internal diffusion, which closely correlates with half-life of ozone decay during catalysis in nanotubes. Then Equation (S4) turns to Equation (S5),

$$C_{O_3}(x) = C_{O_3,in} \cdot \frac{e^{\lambda x} + e^{-\lambda x}}{e^{\lambda \sigma} + e^{-\lambda \sigma}} \quad (S5)$$

where $C_{O_3,in}$ is the entrance ozone concentration, M.

The rate for catalytic ozone consumption within the dead-end nanotube (σ'_{O_3} , $M s^{-1}$) and double-pass nanotube (σ_{O_3} , $M s^{-1}$) can be expressed respectively as,

$$\sigma'_{O_3} = \pi \cdot d_s \cdot \int_{x=0}^{\sigma} k_e \cdot C_{O_3}(x) \cdot d(x) \quad (S6)$$

$$\sigma_{O_3} = \pi \cdot d_s \cdot \delta \cdot k_e \cdot \frac{\int_0^{t_R} C_{O_3,t} dt}{t_R} \quad (S7)$$

Then, the relative ratio of σ_{O_3} to σ'_{O_3} can be expressed as,

$$\eta = \frac{\sigma_{O_3}}{\sigma'_{O_3}} = \frac{\delta \cdot \frac{\int_0^{t_R} C_{O_3,t} dt}{t_R}}{\int_{x=0}^{\sigma} C_{O_3}(x) \cdot d(x)} \quad (S8)$$

Integrate Equation (S11) yields Equation (S9),

$$\eta = \frac{1-e^{-(\theta \cdot t_R)}}{\theta \cdot t_R} \cdot \frac{\varphi}{\tanh \varphi} \cdot \frac{\delta}{\sigma} \quad (S9)$$

where θ is the term $\frac{4k_e}{d_s}$; φ is the term $\left(\frac{4k_e}{d_s \cdot D_{O_3}}\right)^{\frac{1}{2}} \cdot \delta$; σ can be calculated by

$$\frac{2 \cdot k_e}{d_s \cdot D_{O_3} \cdot \left(\frac{4}{\pi}\right)^{0.5} \cdot \ln(0.5)}.$$

According to Equation (S9), the ratio of ozone consumption by MCR compared to a dead-end nanotube (i.e. η) closely correlates with several parameters including the combined effect of ozone transfer and catalyst surface chemistry (k_e), nanotube scale (d_s and δ), retention time (t_R), as well as ozone diffusion in aqueous phase (D_{O_3}). Our simulated results of η for MCR-168, MCR-61 and MCR-10 were about 9.6×10^4 , 2.9×10^5 , and 9.5×10^5 , respectively. The results clearly indicate that the use of nanotube reactor, if not permeable, would suffer dramatic mass transfer resistance against a timely renewal of internal ozone for catalytic conversion. This is at least a considerable reason why the catalyst particles (Table 1 in the main text), even having good nanoscale porosity and enlarged specific surface area, did not work with an expected exposure of $HO\cdot$ during catalytic ozonation.

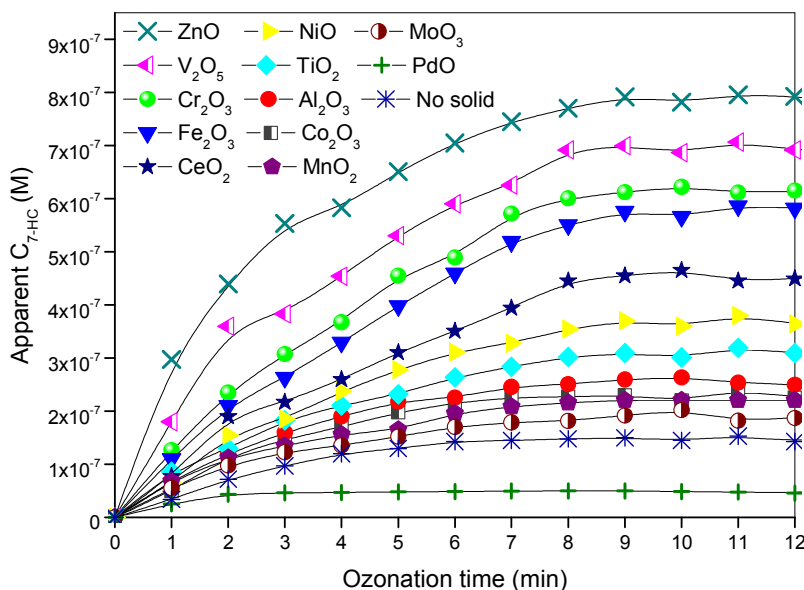


Figure S1. Evolution of 7-hydroxycoumarin concentration ($C_{7\text{-HC}}$) versus time during ozonation of metal oxide particles. Conditions: solid load, 0.5 g L^{-1} ; liquid volume, 0.25 L ; bubbling rate, 1 L min^{-1} ; temperature, $25 \text{ }^{\circ}\text{C}$.

Discussion. Figure S1 presents the results of metal oxide enabled catalytic ozonation using 7-HC as the marker for $\text{HO}\cdot$ production ($\text{HO}\cdot$ attacks coumarin via hydroxylation forming the stable and fluorescence-sensitive 7-HC^1). All the tested metal oxides were reported as ozone catalyst according to the referenced works,²⁻⁹ and their relevant physical and chemical properties are listed in Table S1. The $C_{7\text{-HC}}$ generally climbs up versus time as catalytic ozonation commenced, since aqueous ozone was gradually enriched through gas-to-liquid mass transfer and thus was more kinetically available for the surface-mediated catalysis to generate $\text{HO}\cdot$. As shown in Figure S1, such time-dependent process lasted about 7 minutes for all the tested groups until ozone got saturated in the aqueous phase, and then the signal for $\text{HO}\cdot$ stopped increasing and stayed in almost steady-state level. The discriminatory profiles of resultant $C_{7\text{-HC}}$ can be used as a reflection of the catalytic ability of metal oxides tested here, following the order that $\text{ZnO} > \text{V}_2\text{O}_5 > \text{Cr}_2\text{O}_3 > \text{Fe}_2\text{O}_3 > \text{CeO}_2 > \text{NiO} > \text{TiO}_2 > \text{Al}_2\text{O}_3 > \text{Co}_2\text{O}_3 > \text{MnO}_2 > \text{MoO}_3 > \text{PdO}$. All the metal oxides tested were generally active in promoting the $\text{HO}\cdot$ production, whereas PdO was an exception with $\text{HO}\cdot$ signal much weaker than plain ozonation free from catalyst (this was in agreement with the reported work by Zhang et al.¹⁰).

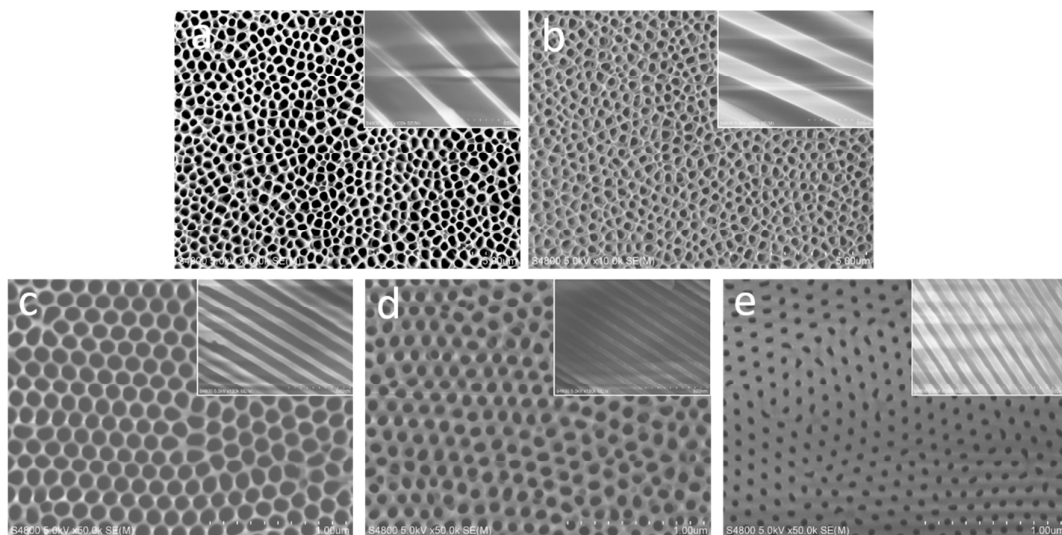


Figure S2. SEM images for the top-down view of AAO templates that were employed for solvothermal synthesis of ZnO_{NT} array (the inserted figures are the images for cross-section view). (a) 200-300 nm pore size for MCR-168. (b) 160-200 nm pore size for MCR-96. (c) 110-150 nm pore size for MCR-61. (d) 80-110 nm pore size for MCR-26. (e) 40-70 nm pore size for MCR-10.

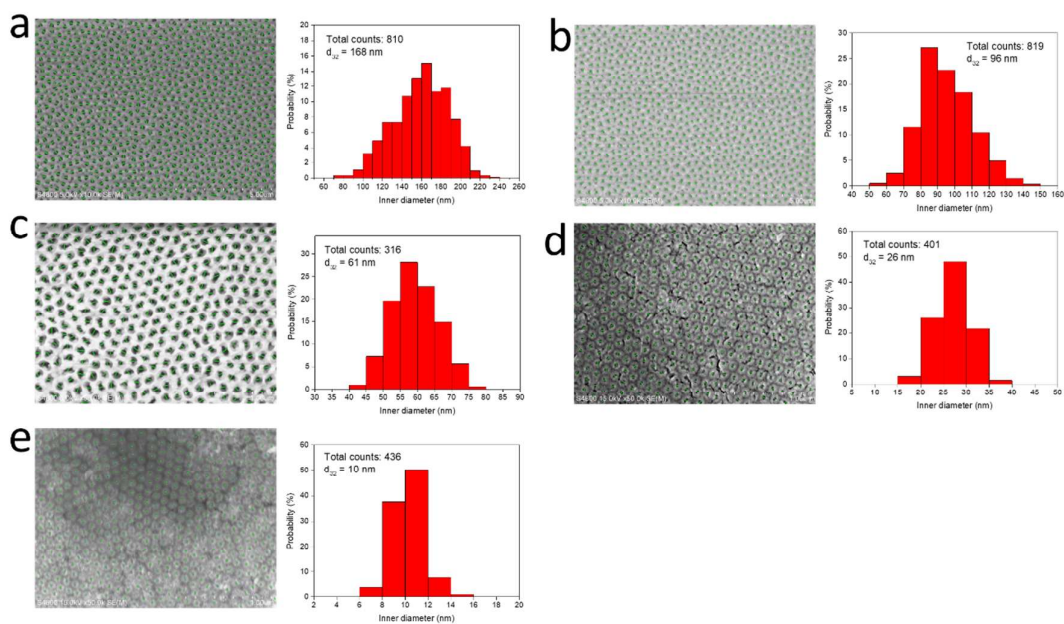


Figure S3. Plan-view SEM images of MCR groups with the beam parallel to the nanotube axis and relevant pore size distribution derived from the measurements of the inner diameters. (a) MCR-168. (b) MCR-96. (c) MCR-61. (d) MCR-26. (e) MCR-10.

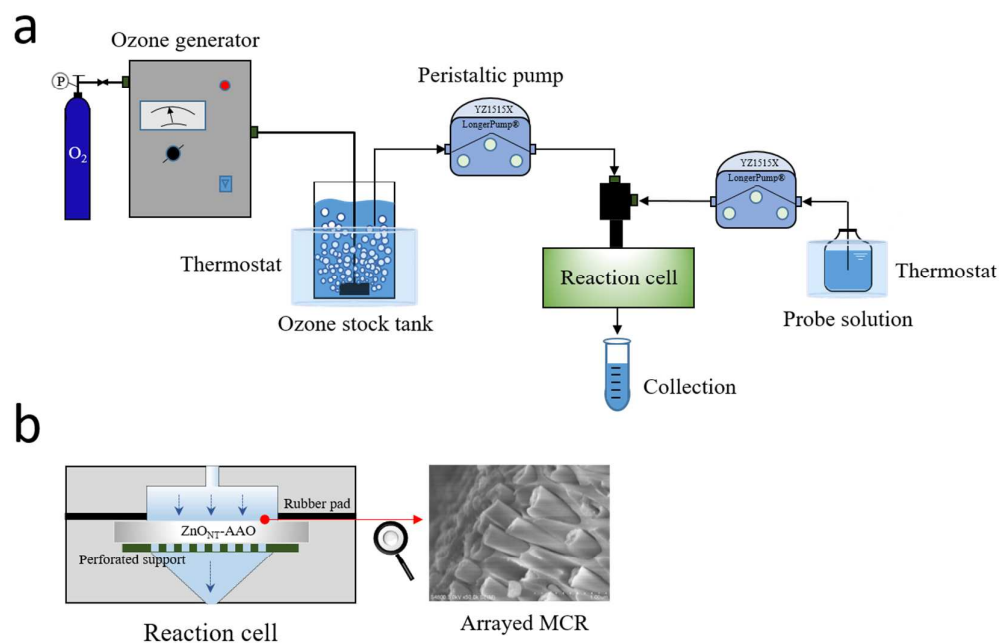


Figure S4. Schematic illustration of catalytic ozonation experiment. (a) Process flow diagram. (b) Cross-section view of the reaction cell.

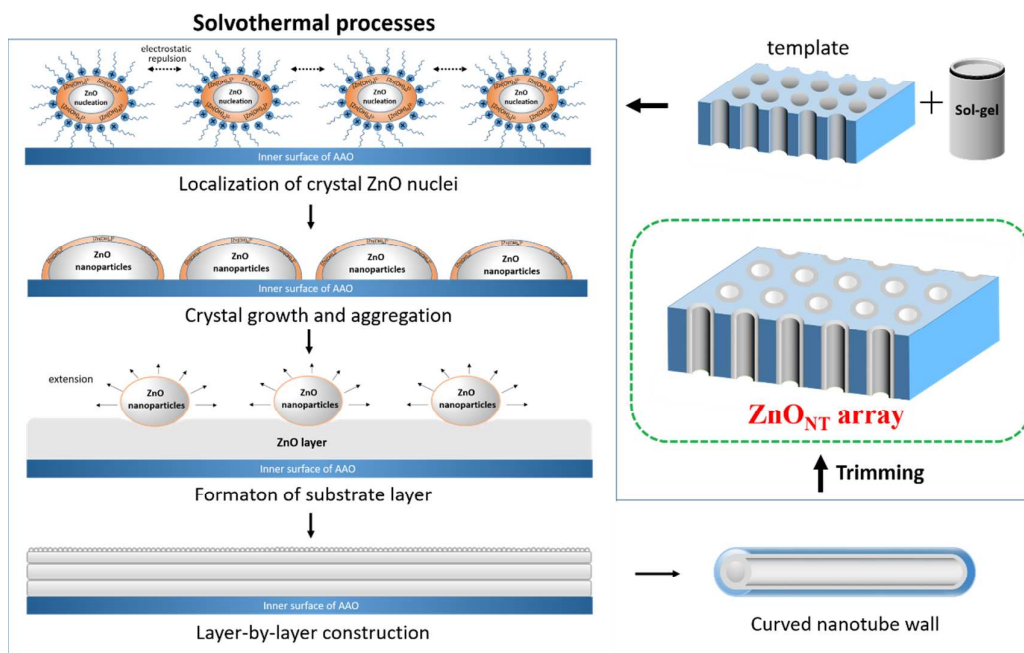


Figure S5. Illustrative description on the possible steps for template-synthesis of ZnO_{NT} array in the processes of combined sol-gel and solvothermal treatments.

Discussion. As illustrated in Figure S5, the ZnO_{NT} array may be formed stepwise with the following steps: nucleation, localization, growth/aggregation, and layer-by-layer construction. As evidence supporting the stepwise process, Figure S6 shows the gradual inward growth of zinc oxide from localized particles to nanorods as a function of an increasing precursor load, and Figure S7 further implies the connected interlayer growth of zinc oxide after solvothermal treatment.

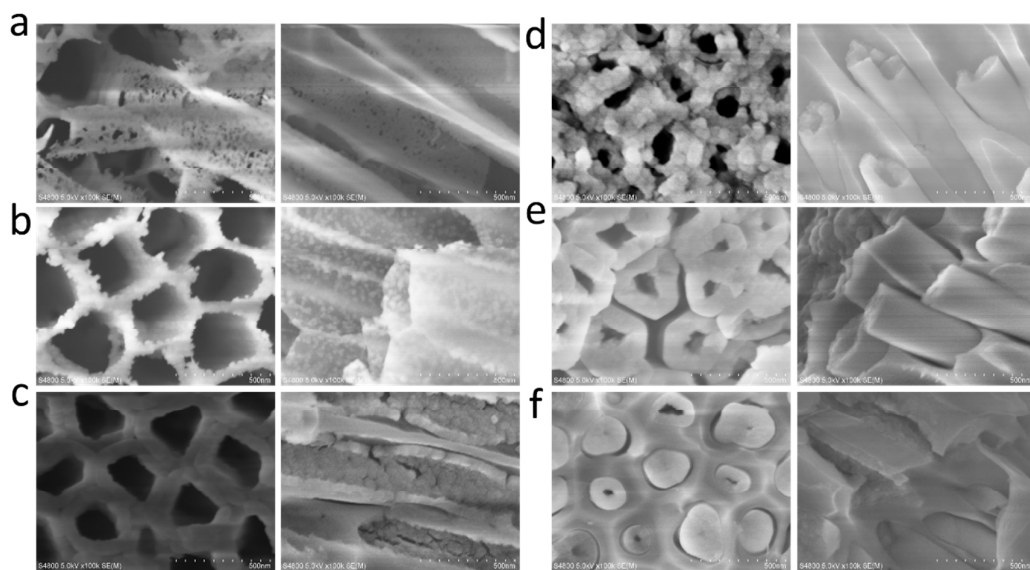


Figure S6. The morphologies of inward ZnO from localized particles to nanorods resulting from N-methyl-pyrrolidone based solvothermal treatments in the presence of 0.016 M CTAB and zinc acetate at concentrations of (a) 0.12 M, (b) 0.24 M, (c) 0.36 M, (d) 0.48 M, (e) 0.9 M and (f) 1.4 M, respectively.

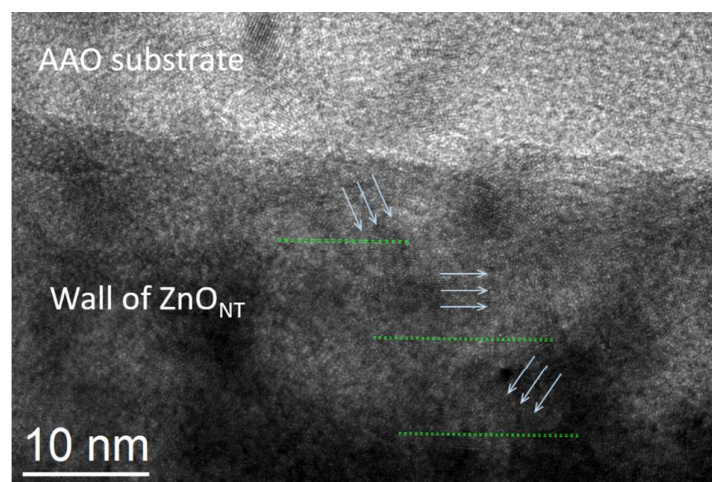


Figure S7. High-resolution TEM image of a template-tube interface region indicating the layer-by-layer growth of ZnO_{NT}.

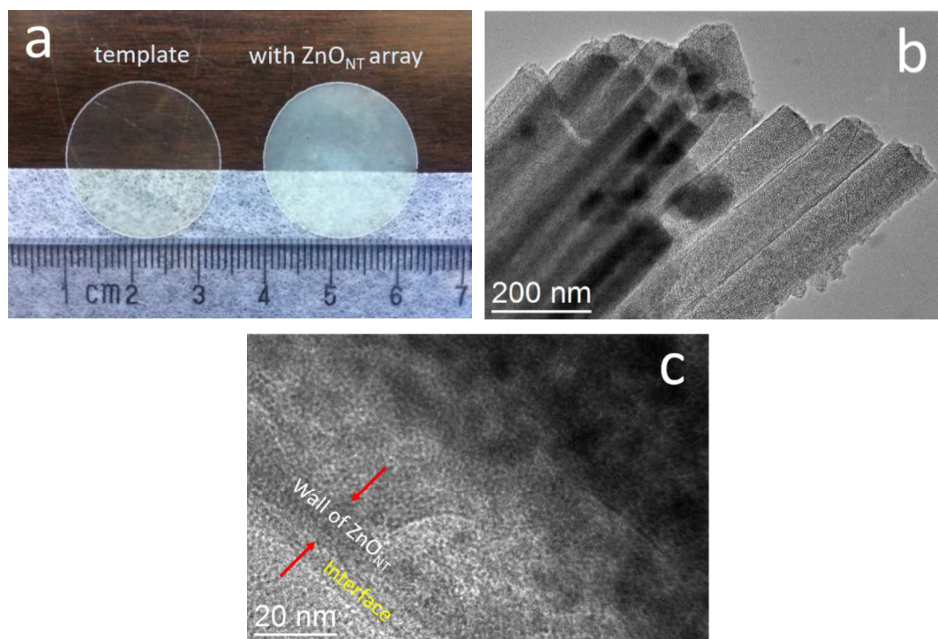


Figure S8. Characterizations on the 10-nm scale ZnO_{NT} grown in AAO template. (a) Photographs of AAO template and the ZnO_{NT}-AAO composite. (b) TEM image of ZnO_{NT}-AAO composite. (c) High-resolution TEM image of the template-tube interface region.

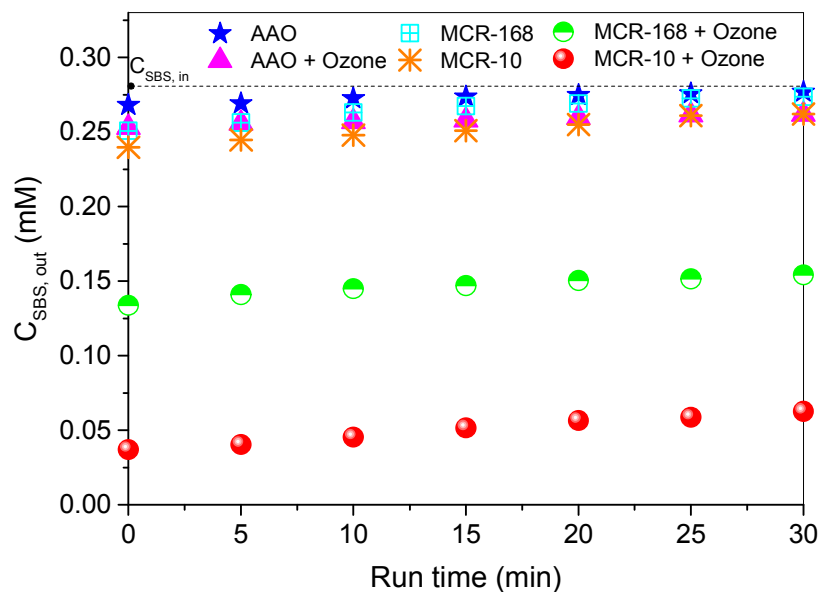


Figure S9. The outlet SBS concentration ($C_{\text{SBS, out}}$) versus the run time of reaction cell. Conditions: injection concentration of SBS, 0.28 mM; initial pH, 7.5; influent ozone concentration, 225 μM ; temperature, 20-22 $^{\circ}\text{C}$; flowrate, $1.0 \times 10^{-4} \text{ L min}^{-1}$.

Discussion. Figure S9 illustrates the reduction of SBS in different reaction systems. Either the AAO template or that with inserted ZnO_{NTs} did not cause much adsorption of SBS, and a combined AAO/Ozone system seldom contribute to the SBS removal. In contrast, the MCR/Ozone systems induced substantial reduction of SBS, implying that catalytic ozonation truly occurred in the nanotube reactors giving rise to $\text{HO}\cdot$ radicals for the probe reaction.

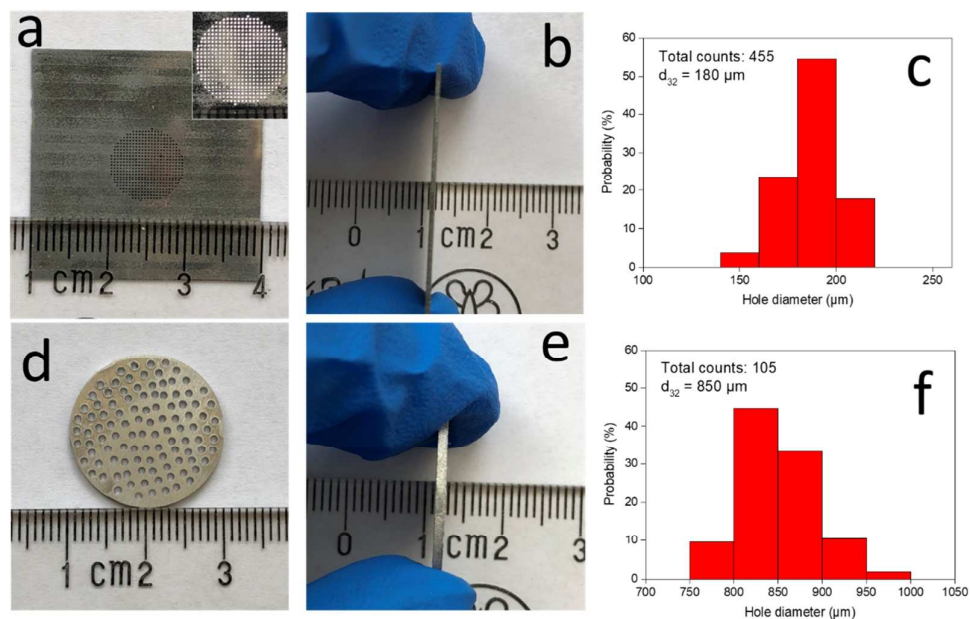


Figure S10. Characterization of the microscale zinc oxide holes used for catalytic ozonation. For MH-180, pictures (a) and (b) are respectively the top-down and lateral view, the inset of (a) is a magnified view without background object, and figure (c) is the pore size distribution; For MH-850, pictures (d) and (e) are respectively the top-down and lateral view, and figure (f) is the pore size distribution.

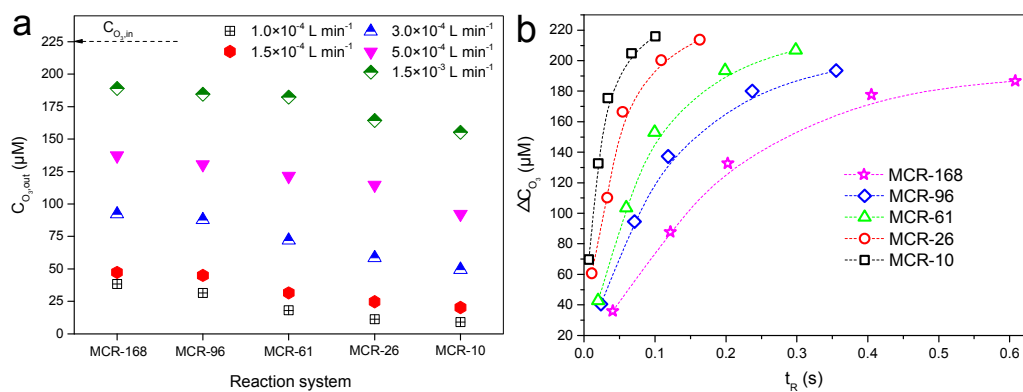


Figure S11. Variation of ozone concentration in different MCR systems under different flowrates. (a) Comparative exhibition of outlet ozone concentration ($C_{O_3,out}$) after reaction. (b) Reduction of ozone concentration versus retention time after internal HCO. Conditions: injection concentration of SBS, 0.28 mM; initial pH, 7.5; influent ozone concentration, 225 μM ; temperature, 20-22 $^{\circ}\text{C}$; flowrates were respectively 1.0×10^{-4} , 1.5×10^{-4} , 3.0×10^{-4} , 5.0×10^{-4} , and $1.5 \times 10^{-3} \text{ L min}^{-1}$.

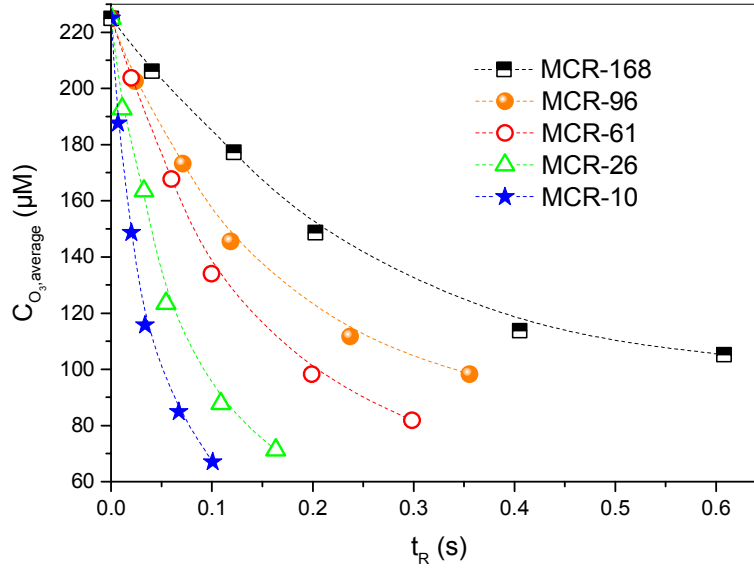


Figure S12. Variation of average internal ozone concentration ($C_{O_3,average}$) for different MCR systems under different flowrates. Conditions: injection concentration of SBS, 0.28 mM; initial pH, 7.5; influent ozone concentration, 225 μM ; temperature, 20-22 $^{\circ}\text{C}$; flowrates were respectively 1.0×10^{-4} , 1.5×10^{-4} , 3.0×10^{-4} , 5.0×10^{-4} , and 1.5×10^{-3} L min^{-1} .

Discussion. The data shown in Figure S12 were calculated by $\frac{\int_0^{t_R} C_{O_3,t} dt}{t}$ in which the term $C_{O_3,t}$ was replaced by Equation (6) in the manuscript (this equation indicates that the internal ozone concentration was time-dependent and decreased following an exponential profile when the solution pass through MCR). In the same reaction conditions, the obtained values of $C_{O_3,average}$ were generally higher than the corresponding outlet ozone concentration ($C_{O_3,out}$, Figure S11a), while the profiles for variation of $C_{O_3,average}$ was in accordance with $C_{O_3,out}$ (Figure S11b).

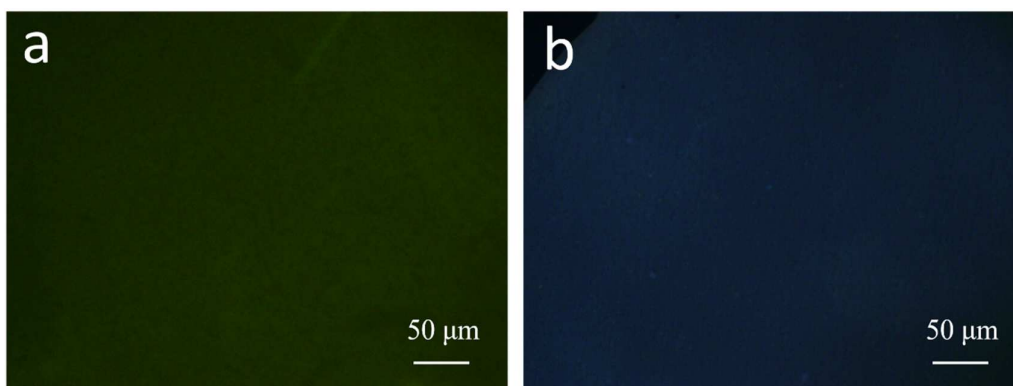


Figure S13. Fluorescence microscopy images for the top-down view of MCR-168 immersed in coumarin solution (a) without ozone and (b) with addition of saturated ozone solution. Conditions: concentration of coumarin, 500 μM ; magnification, 200 $\times$; exposure time, 20 s; scale bar, 50 μm .

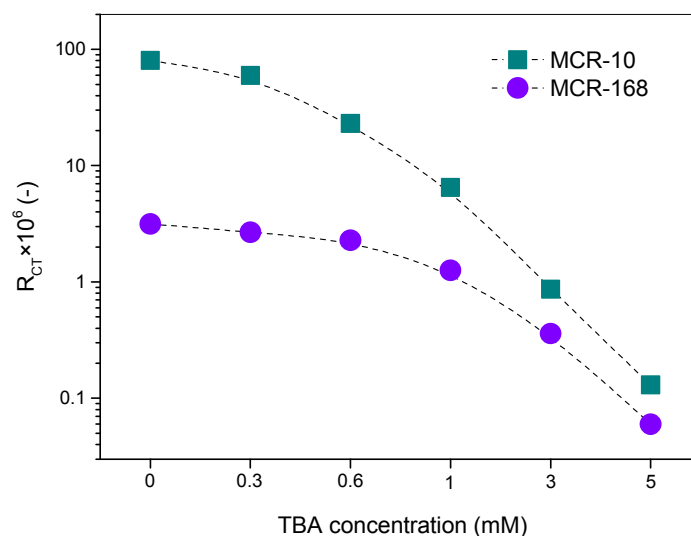


Figure S14. Evolution of R_{CT} value as a function of TBA concentration for MCR-168 and MCR-10, respectively. Conditions: injection concentration of SBS, 0.28 mM; initial pH, 7.5; influent ozone concentration, 225 μM ; temperature, 20-22 $^{\circ}\text{C}$; liquid flux, $1.0 \times 10^{-4} \text{ L min}^{-1}$.

Discussion. As shown in Figure S13, the exposure of $\text{HO}^{\cdot}$ in the tested MCR systems with an added TBA in μM level did not decrease by much relative to those without TBA, although merely 0.3 mM TBA is kinetically considerable to quench $\text{HO}^{\cdot}$ in the aqueous bulk phase according to our preliminary test as well as the reported work¹¹. Only when the concentration of TBA extended up to 5 mM will cause a kinetically considerable quenching of $\text{HO}^{\cdot}$. This may serve as an evidence supporting the speculated interphase effect on the $\text{HO}^{\cdot}$ exposure in MCR. The results of TBA test also indicates that the zinc oxide based MCR system could to some extent resist undesired radical scavenging that would otherwise take place if there were coexisting organic scavengers like TBA.

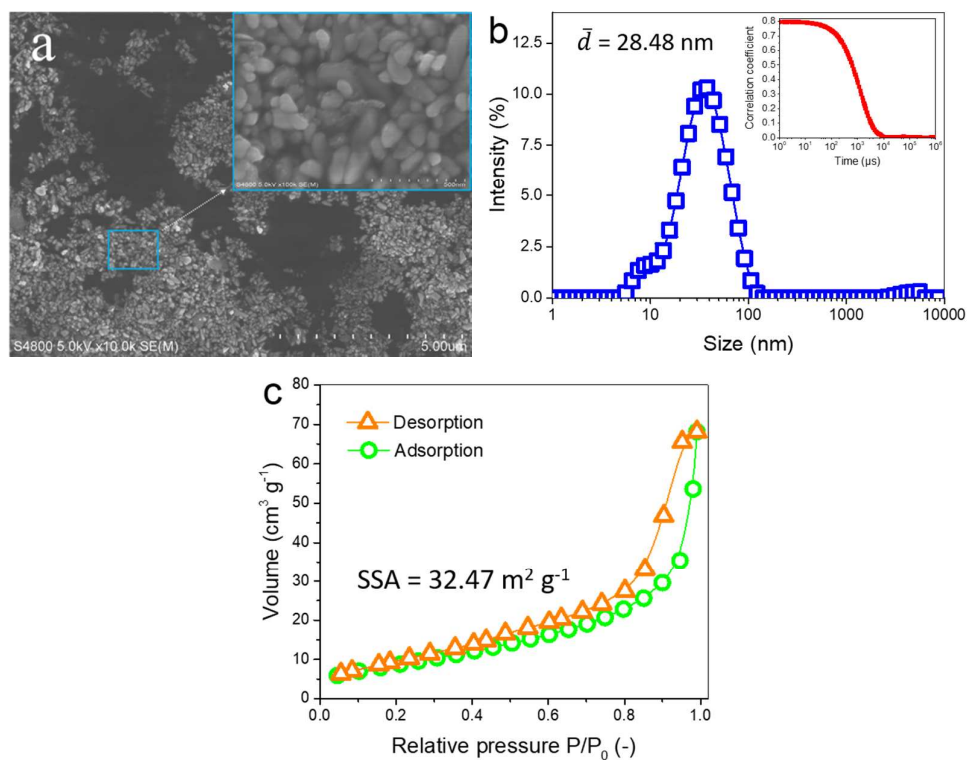


Figure S15. Characterizations on the ZnO nanoparticles produced in a same condition as was depicted for the production of ZnO_{NTs} but without a template. (a) SEM images. (b) Size distribution. (c) Nitrogen adsorption/desorption isotherms.

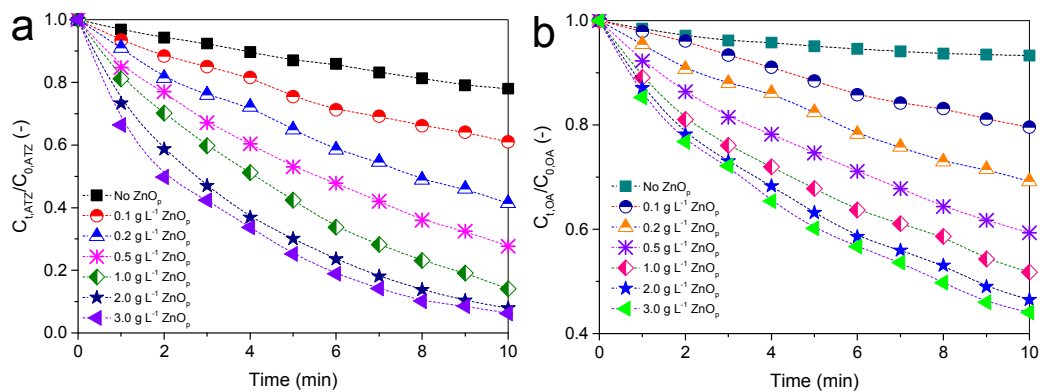
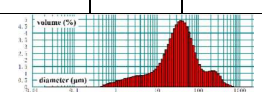
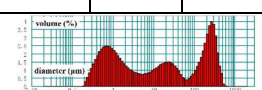
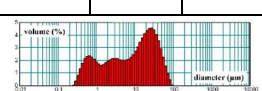
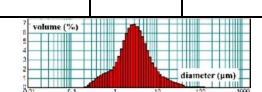
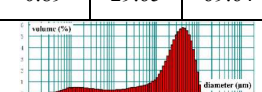
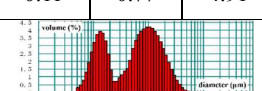
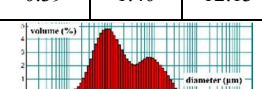
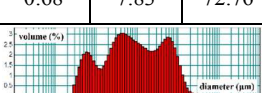
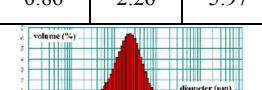
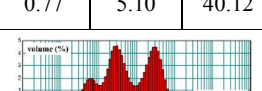
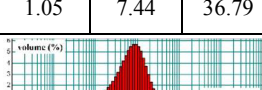
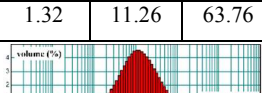


Figure S16. Normalized concentration of (a) ATZ and (b) OA versus time during HCO in the presence of ZnO nanoparticles as catalyst. Conditions: initial concentrations of model organics, 50 mg L⁻¹; initial pHs for ATZ and OA are 7.9 and 4.2, respectively; liquid volume, 0.5 L; flux of ozone gas, 1 L min⁻¹; temperature, 20 °C.

Table S1. Relevant physical and chemical properties of the metal oxide particles tested for HCO.

Type	ρ_s (g cm ⁻³)	d_{32} (μ m)	d_{43} (μ m)	Size distribution (μ m)			S_{BET} (m ² g ⁻¹)	V_{total} (cm ³ g ⁻¹)	d_{pore} (nm)
				$d_{0.1}$	$d_{0.5}$	$d_{0.9}$			
Al ₂ O ₃	3.33	10.57	58.23	4.54	33.99	138.93	93.61	0.225	9.61
									
TiO ₂	4.45	1.65	88.63	0.51	13.33	291.87	14.972	0.058	15.46
									
V ₂ O ₅	4.71	2.36	16.95	0.69	10.62	43.12	10.21	0.035	13.70
									
Cr ₂ O ₃	5.35	1.91	4.82	0.86	2.98	9.54	2.52	0.0081	12.68
									
MnO ₂	4.15	1.23	33.21	0.89	29.65	69.64	41.19	0.054	5.25
									
Fe ₂ O ₃	3.95	0.31	23.57	0.11	0.77	4.91	24.51	0.072	11.69
									
Co ₂ O ₃	5.38	0.93	4.14	0.39	1.40	12.13	9.48	0.026	11.05
									
NiO	6.32	2.33	24.40	0.68	7.83	72.76	3.07	0.0086	11.25
									
ZnO	5.57	1.74	3.18	0.86	2.26	5.97	4.28	0.018	16.43
									
MoO ₃	4.29	2.40	15.00	0.77	5.10	40.12	6.42	0.025	15.43
									
PdO	7.67	2.90	20.31	1.05	7.44	36.79	37.78	0.067	7.08
									
CeO ₂	6.54	3.64	29.81	1.32	11.26	63.76	8.13	0.043	21.01
									

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