

Supporting Information

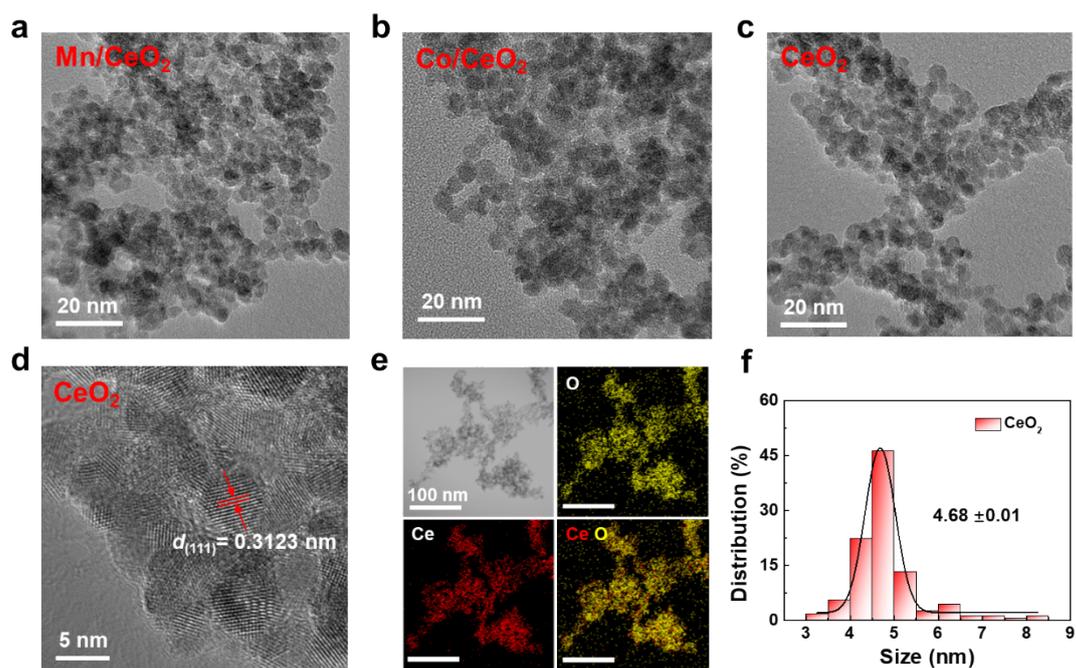
# Modulation of Biocatalytic Activity and Selectivity of CeO<sub>2</sub> Nanozyme via Atomic Doping Engineering

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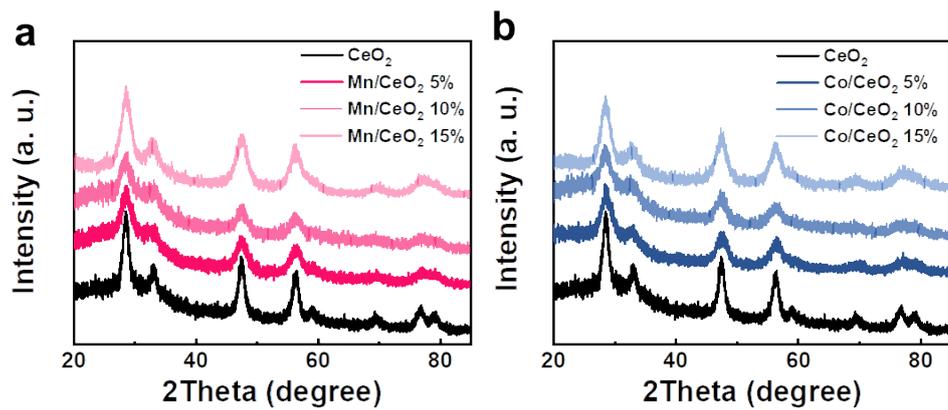
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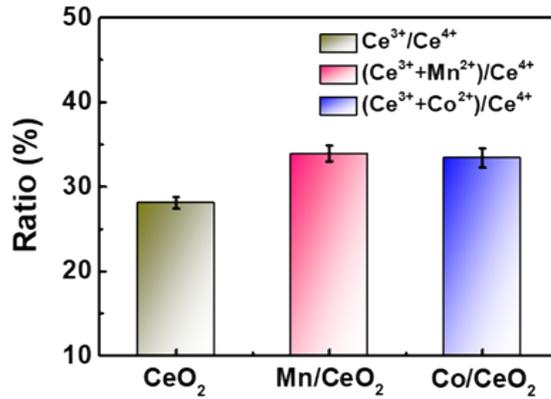
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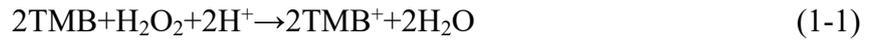
**Figure S1.** TEM images of (a) Mn/CeO<sub>2</sub>, (b) Co/CeO<sub>2</sub>, and (c) CeO<sub>2</sub>. (d) The high-resolution TEM and (e) corresponding EDS mapping images of CeO<sub>2</sub>. (f) The size of CeO<sub>2</sub>.



**Figure S2.** XRD spectra of (a) Mn/CeO<sub>2</sub> and (b) Co/CeO<sub>2</sub> with different doping ratios.



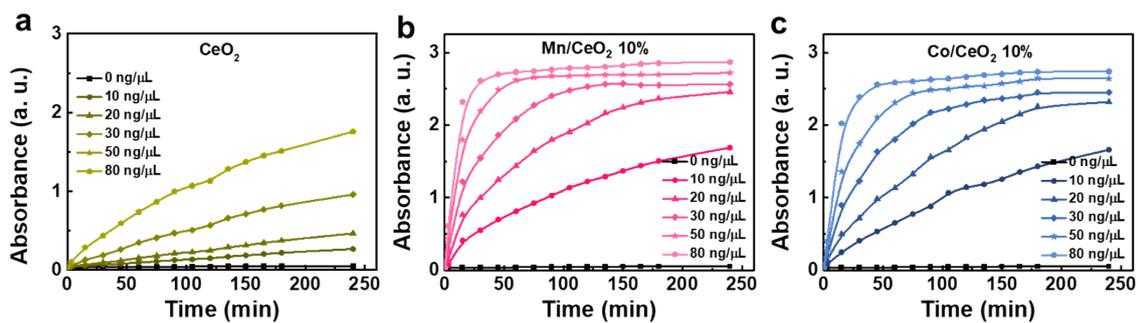
**Figure S3.** Ratio of Ce<sup>3+</sup>/Ce<sup>4+</sup> or (Ce<sup>3+</sup>+M<sup>2+</sup>)/Ce<sup>4+</sup> in CeO<sub>2</sub> and M/CeO<sub>2</sub> nanozymes. The results confirmed that the ratios of (Mn<sup>2+</sup>+Ce<sup>3+</sup>)/Ce<sup>4+</sup> and (Co<sup>2+</sup>+Ce<sup>3+</sup>)/Ce<sup>4+</sup> in M/CeO<sub>2</sub> nanozymes were higher than the Ce<sup>3+</sup>/Ce<sup>4+</sup> in undoped CeO<sub>2</sub> nanozymes. The Mn<sup>2+</sup> or Co<sup>2+</sup> may accelerate the catalytic rate by participating in catalytic reactions similar to Ce<sup>3+</sup>, while also promoting the conversion of more Ce<sup>4+</sup> to Ce<sup>3+</sup>, which is energetically favorable. For the POD-like activity of CeO<sub>2</sub>, the reaction path is as follows:



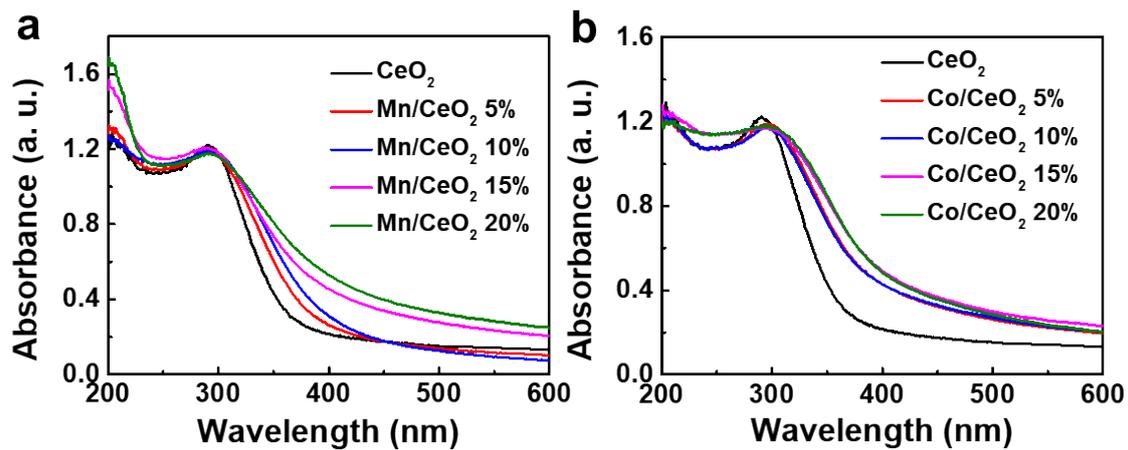
The specific reactions in which Mn<sup>2+</sup> or Co<sup>2+</sup> may be involved are speculated as follows:



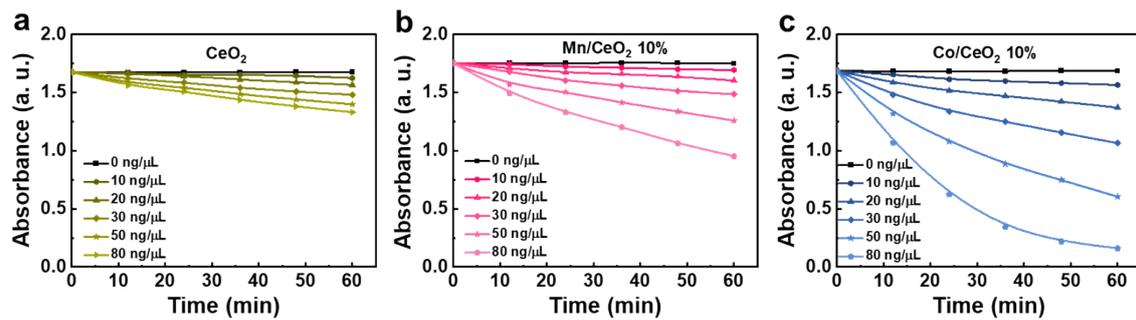
Thus, the doping of Mn<sup>2+</sup> or Co<sup>2+</sup> may enhanced the catalytic activity by forming new active sites and participating in catalytic reactions.



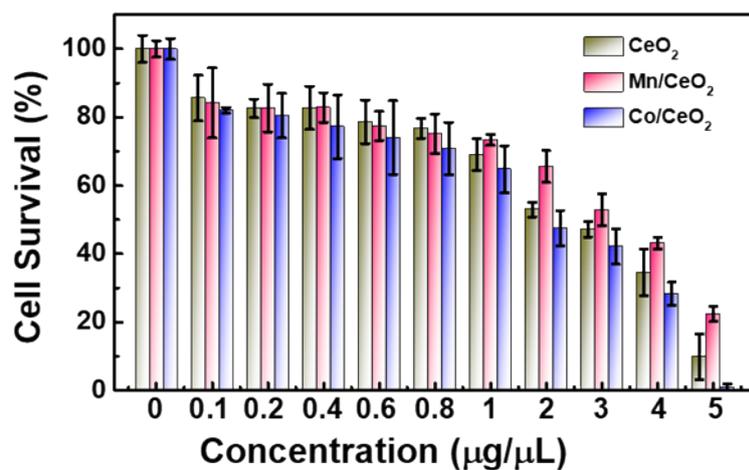
**Figure S4.** Reaction-time curves of the TMB color development reaction catalyzed by (a) CeO<sub>2</sub>, (b) Mn/CeO<sub>2</sub> and (c) Co/CeO<sub>2</sub> with different concentrations.



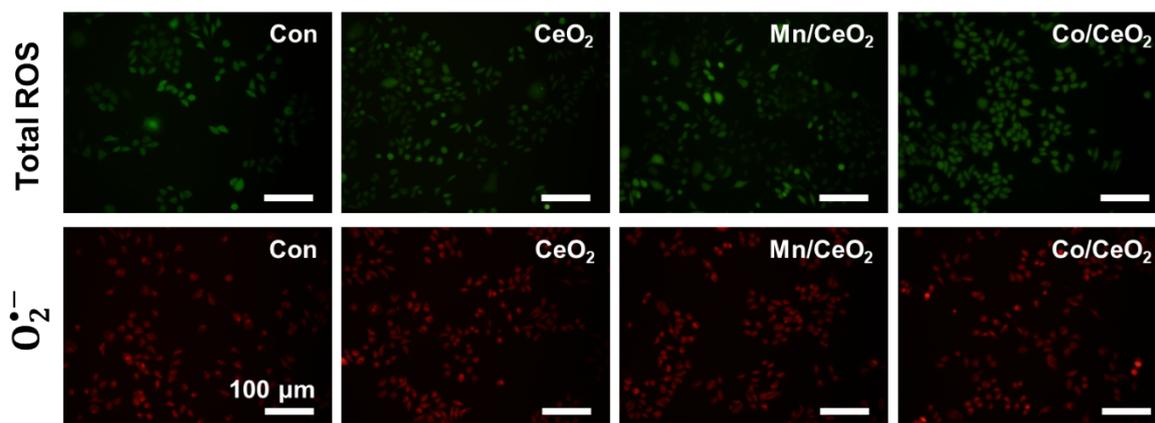
**Figure S5.** UV-vis absorption spectra of (a) Mn/CeO<sub>2</sub> and (b) Co/CeO<sub>2</sub> with different doping ratios.



**Figure S6.** Reaction-time curves of the decomposition of  $\text{H}_2\text{O}_2$  catalyzed by (a)  $\text{CeO}_2$ , (b)  $\text{Mn/CeO}_2$  and (c)  $\text{Co/CeO}_2$  with different concentrations.



**Figure S7.** Cytotoxicity of HT22 cells treated with CeO<sub>2</sub> and M/CeO<sub>2</sub> at 0.1-10 µg/µL determined by MTT assays.



**Figure S8.** Fluorescence microscopic images of intracellular total ROS and  $O_2^{\bullet-}$  levels treated with or without nanozymes using DCFH-DA and DHE fluorescent probes, respectively.

**Table S1.** Quantification of elemental contents of CeO<sub>2</sub> and M/CeO<sub>2</sub> nanozymes by EDS element mapping.

Samples	Ce		O		Mn		Co	
	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%
CeO <sub>2</sub>	20.8	69.67	79.2	30.33				
Mn/CeO <sub>2</sub>	19.1	65.91	78.4	31.39	2.5	2.8		
Co/CeO <sub>2</sub>	24.1	70.3	70.9	23.6			5.0	6.1