Supplementary Information (SI) for Inorganic Chemistry Frontiers.

# Homogeneous Bismuth Dopants Regulate Cerium Oxide Structure to Boost Hydrogen Peroxide Electrosynthesis via Two-Electron Oxygen Reduction

Qiying Yang<sup>a</sup>, Changhui Sun<sup>a</sup>, Lanju Sun<sup>a</sup>, Hangning Liu<sup>a</sup>, Linghao Su<sup>a</sup>, Chuanli Ma<sup>a</sup>, Jie Wang<sup>a,\*</sup>, Liangyu Gong<sup>a,\*</sup>, Zhenhua Yan<sup>b</sup>

a College of Chemistry and Pharmaceutical Sciences, Qingdao Agricultural University, Qingdao 266109, China

b Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China

#### **1. EXPERIMENTAL SECTION**

#### 1.1 Synthesis of Bi-CeO<sub>2</sub>

Bi-CeO<sub>2</sub> catalysts were prepared as follows: Firstly, 937.5 mg of ceric ammonium nitrate (Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>) and an appropriate amount of bismuth nitrate  $(Bi(NO_3)_3 \cdot 5H_2O)$  were ultrasonically dissolved in 37.5 mL of ethylene glycol for 30 min, by controlling the atomic percentage of  $Bi(NO_3)_3 \cdot 5H_2O$  in  $Ce(NH_4)_2(NO_3)_6$  in the range from 0.5% to 5.0%. Subsequently, a mixture containing 1.875 mL of ultrapure water and 1.875 mL of acetic acid were dropped in the preceding mixture and vigorously stirred for 30 min. The solution was then transferred to a 50 mL volume Teflon-lined autoclave, and hydrothermally treated at 180 °C for 18 h in an oven. After cooling down to room temperature, the resulting precipitate was collected by centrifugation at 7000 rpm and washed to near-neutral pH with deionized water, and then further washed with 2-propanol to remove organic impurities. Finally, the obtained precursor was dried and then annealed in a tubular oven with saturated nitrogen atmosphere at a heating rate of 5 °C min<sup>-1</sup> from room temperature to 500 °C for 2 h, then the resulting product was obtained by naturally cooling to room temperature. The obtained products with a gradual increase in Bi/Ce percentage were labeled as 0.5%-Bi-CeO<sub>2</sub>, 1%-Bi-CeO<sub>2</sub>, 2%-Bi-CeO<sub>2</sub> and 5%-Bi-CeO<sub>2</sub>, respectively. For comparison, pristine CeO<sub>2</sub> was prepared according to the above procedure without introduction the  $Bi(NO_3)_3 \cdot 5H_2O$ .

### **1.2 Physical Characterizations**

The morphology and the surface elemental distribution of the catalysts were

characterized by scanning electron microscopy (FE-SEM, JSM-IT500) and Fieldemission transmission electron microscopy (FE-TEM, JSM F200) coupled with Oxford energy-dispersive X-ray spectroscopy (EDX). The crystallographic phases were investigated by powder X-ray diffraction (XRD) via an X-ray diffractometer (Bruker D8 ADVANCE, Cu K $\alpha$  radiation,  $\lambda = 0.15418$  nm) in the  $2\theta$  range of 5- 80°. The Xray photoelectron spectroscopy (XPS) measurements were carried out with a PHI-5000 VersaProbe III spectrophotometer (Thermo Scientific, Thermo Kalpha, America) using an Al K $\alpha$  X-ray source. The Raman spectra measurement was characterized on a Raman spectrometer (DXR 2xi Raman microscope with excitation laser beam wavelength of 532.17 nm). Electron spin resonance (EPR) spectra were detected using a JES-FA200 spectrometer (JEOL, Tokyo, Japan) with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as spin-trapping reagents (center field 337 mT, microwave power 2 mW, microwave frequency 9.455 GHz, modulation frequency 100 kHz).

#### **1.3 Electrochemical measurements**

The electrochemical measurements were performed by an electrochemical workstation (CHI 760E, Shanghai CH Instruments Co., Ltd.) using a conventional three-electrode system with a catalyst-modified rotating ring disk electrode (RRDE) as the working electrode, a reversible hydrogen electrode (RHE) as reference electrode, and a Pt wire as counter electrode. To prepare the catalyst-modified working electrode, 5.0 mg of the as-synthesized x%-Bi-CeO<sub>2</sub> catalyst (x represents the atomic percentage of Bi) was dispersed into 1.0 mL of solution containing 980  $\mu$ L of 2-propanol and 20  $\mu$ L of 5 wt. % Nafion solution followed by ultrasonication for 30 min to obtain a homogeneous suspension solution. 10  $\mu$ L of the catalyst ink was drop-cast on the RRDE and dried naturally. The cyclic voltammetry (CV) was recorded at a scan rate of 5 mV s<sup>-1</sup> with a potential window of 0.05 ~1.0 V versus RHE in N<sub>2</sub>- or O<sub>2</sub>-saturated 1.0 M KOH electrolyte. Linear sweep voltammetry (LSV) was investigated in O<sub>2</sub>-saturated 1.0 M KOH electrolyte using catalyst-modified RRDE at various rotation speeds ranging from 400 to 2500 rpm.

The Faraday efficiency of the catalyst towards can be determined using Eq. S1

$$(\%) = \frac{I_R/N}{I_D}$$
(1)

The selectivity of the catalyst towards H<sub>2</sub>O<sub>2</sub> can be determined using Eq. S2

$$(\%) = 200 \times \frac{I_R/N}{\frac{I_R}{N} + I_D}$$

$$(2)$$

Catalysts Selectivity of H<sub>2</sub>O<sub>2</sub>

The number of electron transfers involved in the catalytic process can be calculated utilizing Eq. S3.

$$n = \frac{4 \times I_D}{\frac{I_R}{N} + I_D}$$
Catalysis Electron-Transfer number (3)

The number of electron transfers (*n*) per  $O_2$  molecule for the ORR of the catalyst was estimated from the Koutecky-Levich (K-L) (Eq. S4) and Levich equations (Eq. S5)<sup>1</sup>

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{J_J} + \frac{1}{B\omega^{0.5}}$$
(4)  
$$B = 0.2nFC_{0_2} D_{0_2}^{\frac{2}{3}} V^{-\frac{1}{6}}$$
(5)

where J is the current density,  $J_k$  is the kinetic current density,  $J_L$  is the diffusionlimiting current density,  $\omega$  is the rotation speed of the electrode in rpm, n is the number of electron transfers during the ORR reaction, F is the Faraday's constant (96,485 C mol<sup>-1</sup>),  ${}^C O_2$  represents the saturation concentration of O<sub>2</sub> in 1 M KOH at 1 atm., v is kinematic viscosity of the electrolyte (0.01 cm <sup>2</sup> S<sup>-1</sup>),  ${}^D O_2$  is diffusion coefficient of O<sub>2</sub> (1.8 × 10 <sup>-5</sup> cm <sup>2</sup> S <sup>-1</sup>), and 0.2 is a constant used as rotation speed quoted in rpm. The K-L plot is the  $J^{-1}$  versus  $\omega^{-0.5}$  graph with an intercept and slope of  $J_k^{-1}$  and B<sup>-1</sup>, respectively.

#### 1.4 Electrochemical production analysis of H<sub>2</sub>O<sub>2</sub>

Electrochemical  $H_2O_2$  production was tested in a custom-made two-compartment H-type cell separated by a Nafion 117 membrane. The Nafion membrane was pretreated with 10% (v/v)  $H_2SO_4$  for 1 h. Both the cathode and anode compartments were filled with 40 mL of 1.0 M KOH electrolyte. The loading amount of catalyst on the working electrode was fixed at 0.4 mg/cm<sup>2</sup>, by dropping 160 µL of the catalyst ink (5 mg mL<sup>-1</sup>) onto the surface of carbon paper (CP) within the area of 20 × 20 mm for each side. While dropping, the heating plate was heated up to dry the electrode. Each electrode was weighed before and after drop-casting to quantify the catalyst loading.

The time-dependent concentration of  $H_2O_2$  generated through bulk ORR electrolysis was determined using the cerium sulfate (Ce(SO<sub>4</sub>)<sub>2</sub>) titration method. The titration was conducted by adding of the electrolyte into a Ce(SO<sub>4</sub>)<sub>2</sub> solution containing 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 mM Ce(SO<sub>4</sub>)<sub>2</sub>. The H<sub>2</sub>O<sub>2</sub> concentration was determined by measuring the decrease in the concentration of Ce<sup>4+</sup> in the solution, which reacted according to the Eq. S6

$$2Ce^{4+} + H_2O_2 \rightarrow 2Ce^{3+} + 2H^+ + O_2 \tag{6}$$

The  $H_2O_2$  concentration accumulated in the H-cell was utilized to evaluate the bulk electrolysis of the catalyst. The catalytic performance was evaluated through the Faraday efficiency (FE) which is calculated by the Eq. S7 for the catalyst for  $H_2O_2$ .

$$FE(\%) = \frac{2 \times Total \ amount \ of \ generated \ H_2O_2 \times Faraday \ constant}{Total \ amount \ of \ change} \left(\int_{0}^{t} Idt\right)$$

(7)

At near-zero overpotential, the kinetic current density  $(j_K)$  can be determined using the Eq. S4 and Eq. S5.

The kinetic current equation normalized by the BET surface area and expressed in terms of the KL value (at near-zero overpotential) can be expressed as follows Eq. S8:

$$j_{k}^{norm} = \frac{J_{k}}{S_{BET}}$$
(8)

#### **1.5 Theoretical calculation**

Density functional theory (DFT) based first-principles calculations are performed

using the projected augmented wave (PAW) method implemented in the Vienna ab initio simulation package (VASP). The generalized gradient approximation (GGA) with Perdew Burke-Ernzerhof (PBE) functional and the projector augmented wave (PAW) potential were employed. The kinetic energy cut-off was set to 450 eV. The Brillouin-zone (BZ) integration is carried out using the Monkhorst-Pack sampling method with a density of  $3 \times 3 \times 1$  for simulations. A sufficiently large vacuum region of 15 Å was used for all the systems to ensure the periodic images were well separated. The convergence criterion of force and energy were set to 0.02 eV Å<sup>-1</sup> and 10<sup>-5</sup> eV, respectively. The ORR pathways on the considered models were calculated in detail according to the electrochemical framework developed by Norskov et al. The catalytic activity of these catalysts was evaluated by calculating the change of Gibbs free energy ( $\Delta G$ ) of each elementary step in the ORR reaction, based on the computational hydrogen electrode model proposed by Nørskov, <sup>2</sup> which is expressed by the Eq. S9:

$$\Delta G = \Delta E_{ads} + \Delta ZPE - T\Delta S - eU - kBT \ln(10) \times pH$$
(9)

where  $\Delta E_{ads}$ ,  $\Delta ZPE$ , T,  $\Delta S$ , eU, kBTln(10)×pH are adsorption energy, zero-point energy, temperature, entropy change, change of free energy due to applied potential on electrode, the correction of the H<sup>+</sup> free energy resulted from the acidity and alkalinity of the solution.

The solvation effect was not considered in determining the value of  $\Delta G_{OOH^*}$ , as previous works, which governs a reasonable comparison. The surface Pourbaix diagrams were constructed following the procedure proposed in the works by Siahrostami et al. for 2e-ORR.<sup>3</sup>

#### 1.6 Degradation analysis of RhB

RhB degradation measurements were conducted in a single-chamber device, where Pt plate ( $20 \times 20$  mm in area) and catalyst loaded on the CP were used as the counter electrode and the working electrode, respectively. The concentration of RhB was controlled to be 5 ppm. For a dual-cathode system, another cathode was stainless steel mesh (20 ×20 mm in area), which was used to further decompose the *in-situ* generated  $H_2O_2$  to form hydroxyl radicals. During the degradation of RhB, the sample was taken at 5-minute intervals to measure the organic concentration with UV-Visible spectrophotometer (UV-2600). The specific standard curves for RhB degradation were obtained as follows: A 5 mg L<sup>-1</sup> RhB solution was diluted fivefold with 1 M KOH, and UV tests were subsequently performed to generate the concentration versus UV absorbance curve, as depicted in Fig. S18.



Fig. S1 XPS survey spectrum of x%-Bi-CeO<sub>2</sub> (x=0, 0.5, 1, 2, 5).



**Fig. S2** (a-e) SEM images, (f-g) TEM images and (h) average particle size distribution of the CeO<sub>2</sub>.



Fig. S3 (a-e) SEM images and (f) average particle size distribution of the 0.5%-Bi-CeO<sub>2</sub>.



Fig. S4 (a-c) TEM images, (d) HRTEM image, (e) SAED image, (f) STEM image and (g-i) Mapping images of the 0.5%-Bi-CeO<sub>2</sub>.



Fig. S5 (a-e) SEM images and (f) average particle size distribution of the 1%-Bi-CeO<sub>2</sub>.



Fig. S6 (a-e) SEM images and (f) average particle size distribution of the 2%-Bi-CeO<sub>2</sub>.



Fig. S7 (a-e) SEM images and (f) average particle size distribution of the 5%-Bi-CeO<sub>2</sub>.



Fig. S8 (a-b) TEM images, (c) HRTEM image, (d-e) SAED image, (f) STEM image and (g-i) Mapping images of the 5%-Bi-CeO<sub>2</sub>.



Fig. S9 Nitrogen adsorption-desorption tests of (a) 1%-Bi-CeO<sub>2</sub> and (b) CeO<sub>2</sub>.



Fig. S10 CV curves of 1%-Bi-CeO<sub>2</sub> in O<sub>2</sub>- and N<sub>2</sub>- saturated 1 M KOH solution.



Fig. S11 (a) RRDE polarization curves of  $CeO_2$  and x%-Bi-CeO<sub>2</sub> in 0.1 M KOH solution; (b) Corresponding Faraday efficiency (%) and  $H_2O_2$  selectivity (%) of  $CeO_2$  and x%-Bi-CeO<sub>2</sub> in 1 M KOH solution



Fig. S12 Electron-transfer number of  $CeO_2$  and x%-Bi-CeO<sub>2</sub> at various potentials in 1 M KOH (a) and 0.1 M KOH solution (b).



Fig. S13 (a) Polarization curves of 1%-Bi-CeO<sub>2</sub> at different rotational speeds in 1 M

KOH solution, and (b) corresponding K-L plots.



**Fig. S14** (a) Polarization curves of 1%-Bi-CeO<sub>2</sub> at different rotational speeds in 0.1 M KOH solution, and (b) corresponding K-L plots.



Fig. S15(a) CV curves of CeO<sub>2</sub> at different scan rates. (b) CV current density versus

scan rate (the liner slope is equivalent to the double-layer capacitance  $(C_{dl})$ ) of CeO<sub>2</sub>, (c) CV curves of 1%-Bi-CeO<sub>2</sub> at different scan rates. (d) CV current density versus scan rate (the liner slope is equivalent to the double-layer capacitance  $(C_{dl})$ ) of 1%-Bi-CeO<sub>2</sub>



Fig. S16  $j_{K}^{norm}$  versus potential derived from the polarization curves of Fig. 4a and BET surface area of Fig. S9.



**Fig. S17** (a) Faraday efficiency (%) in hydrogen peroxide production at different potentials and (b) different cycle number (oxygen saturation).



**Fig. S18** (a) UV absorbance spectra of standard RhB solution in 1 M KOH solution, (b) Corresponding linear relationship between the concentration of RhB and the absorbance.

Table S1 Ce , O and Bi species content of x%-Bi-CeO $_2$  calculated from the fitted high-

Sample	Ce Species		O Species				<b>Bi Species</b>	
	Ce <sup>3+</sup>	Ce <sup>4+</sup>	H <sub>2</sub> O	OH-/O <sub>2</sub>	O <sub>2</sub> <sup>2-</sup> /O	- O <sup>2-</sup>	Bi	Bi <sup>3+</sup>
CeO <sub>2</sub>	15.3	84.7	6.3	21.2	37.9	34.6	/	/
0.5%-Bi-CeO <sub>2</sub>	16.6	83.4	5.0	29.2	16.3	49.5	6.2	93.8
1%-Bi-CeO <sub>2</sub>	12.8	87.2	4.4	22.0	31.4	35.2	7.4	92.6
2%-Bi-CeO <sub>2</sub>	15.7	84.3	1.5	18.7	26.7	53.1	6.0	94.0
5%-Bi-CeO <sub>2</sub>	17.6	82.4	5.3	14.4	35.3	45.0	1.7	98.3

resolution XPS spectra.

Catalysts	Experimental conditions	FE in bulk electrolysis	Optimized productivity in bulk electrolysis	Refs
α-Fe <sub>2</sub> O <sub>3</sub>	0.1 M KOH	NM	454 mmol $g_{cat}^{-1} h^{-1}$	4
R-GO	0.1 M KOH	43.6%	224.8 mmol $g_{cat}^{-1}$ h <sup>-1</sup>	5
Exfoliated GR	0.1 M KOH	NM	12.68 mmol $g_{cat}^{-1}$ h <sup>-1</sup>	6
NiNb <sub>2</sub> O <sub>6</sub>	0.1 M KOH	NM	996 mmol $g_{cat}^{-1} h^{-1}$	7
Py-TD-COF	0.1 M KOH	~70%	218 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	8
OCNS900	0.1 M KOH	~80%	$0.77 \text{ mol } g_{\text{cat}}^{-1} \text{ h}^{-1}$	9
Co <sub>1</sub> @GO	0.1 M KOH	60%-70%	1.0 mg cm <sup>-2</sup> h <sup>-1</sup>	10
Co <sub>1</sub> @NG(O)	0.1 M KOH	60%-65%	$0.42 \text{ mol } g_{cat}^{-1} h^{-1}$	11
NCMK3IL50_800T	0.1 M KOH	>70%	$0.56 \text{ mol } g_{cat}^{-1} h^{-1}$	12
N-doped porous carbon	0.1 M KClO <sub>4</sub>	NM	121.5mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	13
Oxidized carbon	1M KOH	NM	$116 \text{ mmol } g_{cat}^{-1} \text{ h}^{-11}$	14
NiFe-LDH	1M KOH	NM	47.62 mmol $g_{cat}^{-1}$ h <sup>-1</sup>	15
1%-Bi-CeO <sub>2</sub>	1М КОН	56%	$1.16 \text{ mol } g_{cat}^{-1} h^{-1}$	This work

Table S2 Comparison of the  $H_2O_2$  production rate of 1%-Bi-CeO<sub>2</sub> with the state-of-art

catalysts from previous literature.

Note: FE means faradaic efficiency, R-GO means reduced graphene oxide, GR means graphene, NM: not measurable.

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