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Modulating oxygen vacancies of CeO_2 nanospheres by Zn-doping: an efficient electrocatalyst for N_2 reduction under ambient conditions

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Content:

Experimental section

Materials: Cerous(III) nitrate hexahydrate, cerium oxide, and cobalt (II) nitrate hexahydrate were purchased from Beijing Chemical Corporation. Nickel (II) nitrate hexahydrate, copper (II) nitrate trihydrate zinc nitrate hexahydrate, and sodium hydroxide pellets were procured from Beijing Chemical Corporation. Absolute ethanol was procured from Changshu Hongsheng Fine Chemical Co. Ltd. China. Distilled water was produced in our laboratory through a distillation unit.

Preparation of Zn-CeO_2: The preparation process of the Zn-CeO_2 composite is as follows: 2 mmol $Ce(NO_3)_3 \cdot 6H_2O$ and 0.2 mmol metal precursor Zn were dissolved in 5 mL of distilled H_2O in a 50 mL Teflon-lined stainless-steel autoclave. Then, 9 g of NaOH was dissolved in 30 mL of distilled H_2O and added dropwise to the above solution under constant stirring and continued agitation for 20 min. Then, Teflon lined stainless-steel high-pressure reactor was fully tightened and kept at 95 °C for 24 h in an oven (for the synthesis of cube morphology, the autoclave was kept at 180 °C for 24 h). The reactor was allowed to cool to room temperature and the catalyst was washed numerous times with H_2O and then ethanol until the pH reached 7. The resulting catalyst was dried at 80 °C for 10 h and then calcined at 600 °C @ 5 °C min^{-1} for 5 h under static air. Pure CeO_2 and ZnO catalysts were prepared by a similar procedure.

Preparation of Zn-CeO_2 electrode: 10 mg Zn-CeO_2 powders and 40 μL of Nafion solution (5 wt%) were dispersed in 960 μL mixed solution containing 720 μL ethanol and 240 μL H_2O by 2 h sonication to form a homogeneous ink. Then, 10 μL Zn-CeO_2 was loaded on a CP with area of 1 x 1 cm^2 and dried under ambient condition.

Characterizations: XRD patterns were obtained from a Shimazu XRD-6100 diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (Japan). SEM images were collected from the tungsten lamp-equipped SU3500 scanning electron microscope at an accelerating voltage of 20 kV (HITACHI, Japan). TEM images were obtained from a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The UV-Vis absorbance spectra were measured on a SHIMADZU UV-1800 UV-Vis spectrophotometer. energy dispersive X-ray analysis (EDX), and the Brunner−Emmet−Teller method (BET, ASAP 2020, Micromeritics).

Electrochemical measurements: Before NRR measures, the Nafion proton exchange film was pretreated by heating in 3% H_2O_2 solution, 0.5 M H_2SO_4 and ultrapure water at 80 °C for 1.5 h, respectively. Electrochemical measurements were carried out on a CHI 660E electrochemical analyzer (CHI Instruments, Inc., Shanghai) in a three-electrode system using Zn-CeO_2/CP or CP as working electrode, Ag/AgCl as reference electrode, and graphite rod as counter electrode. All experiments were performed at ambient conditions. For N_2 reduction reaction experiments, the HCl electrolyte (0.1 M) was bubbled with high-purity N_2 (99.999%) for 30 min before measurement. All potentials reported in this work were calibrated to RHE, using the following equation:

$$E\ (RHE) = E\ (Ag/AgCl) + (0.197 + 0.059\ pH)\ V$$

Determination of NH_3: NH_3 concentration was determined by the indophenol blue method.[1] The method contains the following details: 2 mL HCl post-NRR electrolyte was collected from the cathodic chamber. Then, 2 mL of 1 M NaOH solution containing 5% salicylic acid and 5% sodium citrate was added into this solution. After mixing and standing at room temperature for 2 h, the UV-Vis absorption absorption spectrum was measured at a wavelength of 655 nm. The concentration-absorbance curves were calibrated using standard NH_4Cl solution (0.1 HCl solution as mother solution) with a serious of concentrations. The fitting curve ($y = 0.475x + 0.066$, $R^2 = 0.999$) shows good linear relation of absorbance value with NH_3 concentration by three times independent calibrations.

Determination of N_2H_4: Concentration of N_2H_4 in the electrolyte was estimated by the method of Watt and Chrisp.[2] Typically, a mixture solution containing p-$C_9H_{11}NO$ (5.99 g), concentrated HCl (30 mL) and ethanol (300 mL) was used as a color reagent. In detail, 2 mL electrolyte removed from the cathodic chamber was added into 2 mL above prepared color reagent. After standing the mixture solution at room temperature for 20 min, UV-Vis absorption spectra were measured at a wavelength of 455 nm. The concentration-absorbance curves were calibrated using standard N_2H_4 solutions with a series of concentrations for three independent calibrations.

Calculations of NH_3 yield and FE: NH_3 yield was calculated using the following equations:

$$R_{NH3}\ (\mu g\ h^{-1}\ mg_{cat.}^{-1}) = (c_{NH3} \times V) / (17 \times t \times m)$$

Where c_{NH3} ($\mu g\ mL^{-1}$) is the measured NH_3 concentration; V (mL) is the volume of electrolyte (in our work 35 mL); t (s or h) is the reaction time; A (cm^2) is the geometric area of the cathode; m (mg) is the mass loading of catalyst on CP.

FE was calculated according to following equation:

$$FE = 3 \times F \times c_{NH3} \times V / (17 \times Q) \times 100\%$$

Where F is Faraday constant (96500 C mol^{-1}); Q (C) is the quantity of applied electricity.

Computational details: The spin polarization DFT is calculated by using photonic crystals. The plane wave based Vienna ab initio simulation software package (VASP) is extended Perdew Burke ernzerhof (PBE) functional gradient approximation method is used to describe the exchange related interactions between electrons.[3] Zn 2p and Ce 3d states are 3.5 eV and 2.0 eV, respectively. Van Der Waals (VDW) correction uses Grime method (DFT-D3) to analyze the interaction molecules/atoms and matrix among single factors.[4] The energy cutoff of the plane wave basis sets the expansion to 500 eV, and the atomic relaxation continues until the energy of the force acting on the atom is less than 0.01 eV Å^{-1}. The surface of CeO_2 (101) was simulated using a 2×2 slab, there are four triple layers (O-Ce-O) on the top, and the triple layers at the bottom are fixed, with a vacuum interval of 15 Å. The Brillouin area has a sampling volume of 3×3×1. The central k-point grid, the width of the coating scheme in the electronic state using the Fermi model is 0.1 eV.

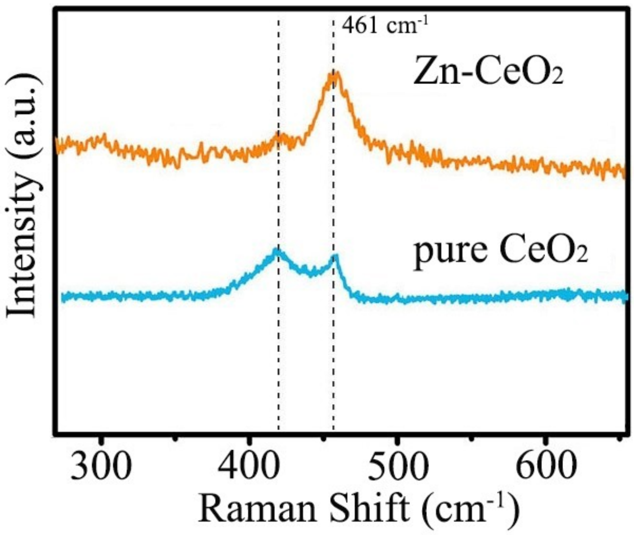

Fig. S1. Raman shift spectra of Zn-CeO_2 and pure CeO_2.

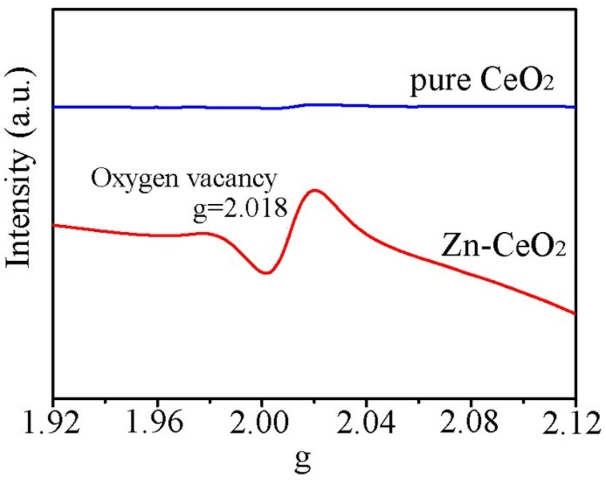

Fig. S2. Room-temperature ESR spectra of Zn-CeO_2 and pure CeO_2.

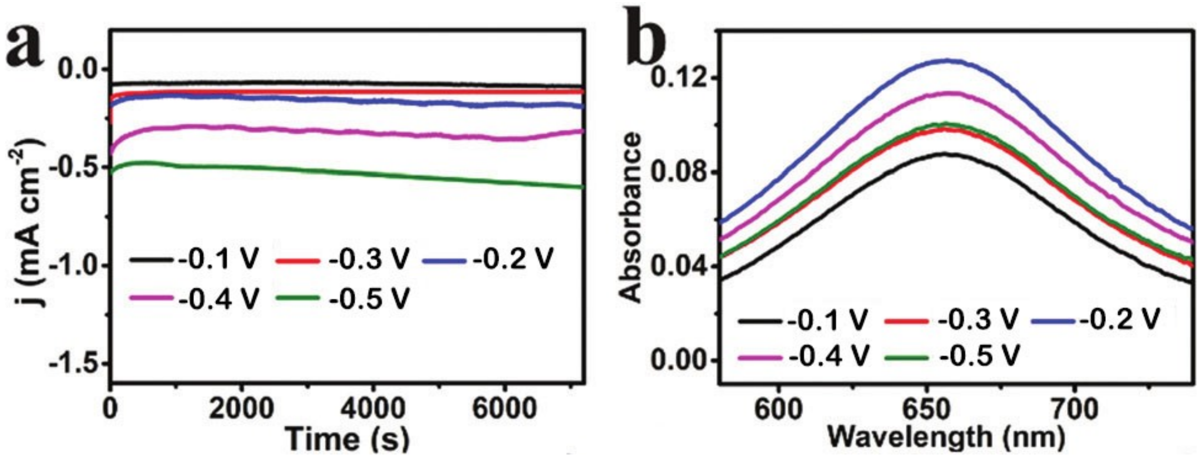

Fig. S3. (a) Chronoamperometry curves of Zn-CeO_2 in a 0.1 M Na_2SO_4 solution at different potentials. (b) UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after NRR electrolysis at different potentials for 2 h.

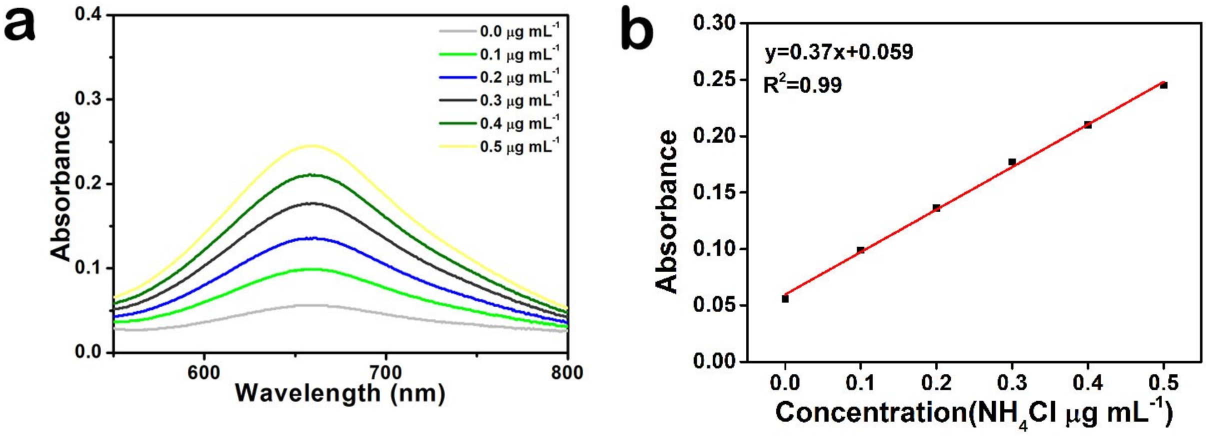

Fig. S4. (a) UV-Vis absorption spectra of indophenol assays with NH^{4+} concentrations after incubated for 2 h at room temperature. (b) Calibration curve used for calculation of NH^{4+} concentrations.

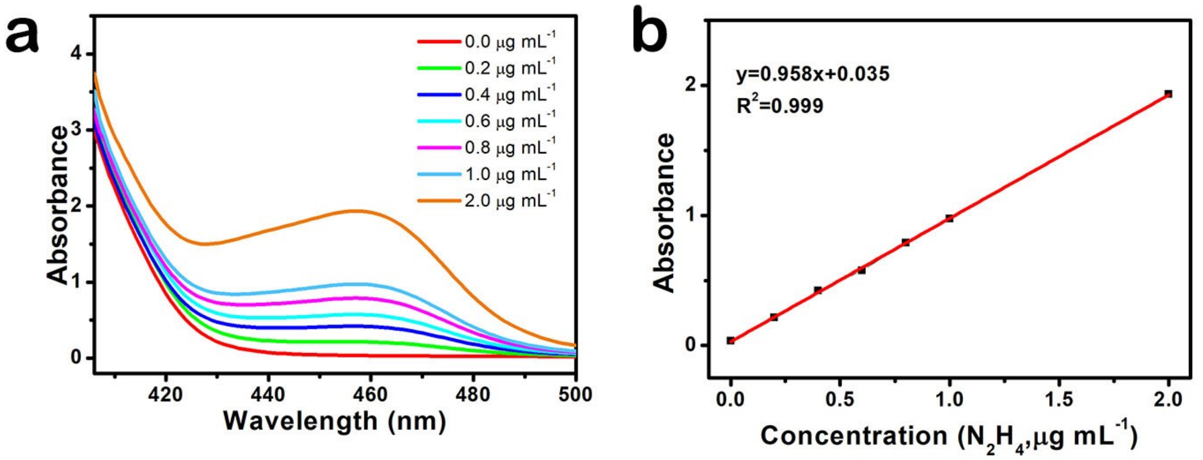

Fig. S5. (a) UV-Vis absorption spectra of various N_2H_4 concentrations after incubated for 15 min at room temperature. (b) Calibration curve used for calculation of N_2H_4 concentrations.

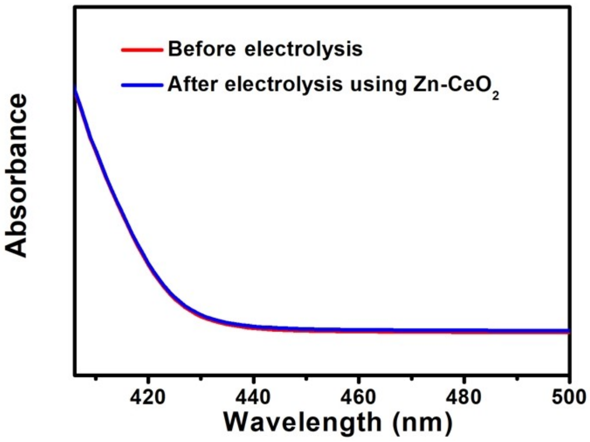

Fig. S6. UV-Vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp before and after 2 h electrolysis in N_2 atmosphere at –0.2 V.

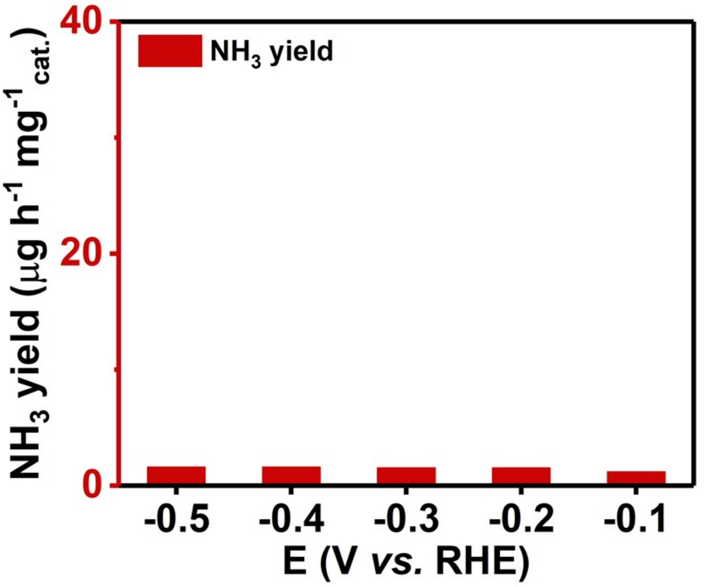

Fig. S7. The amount of NH_3 detected in the Ar-saturated electrolyte at each potential.

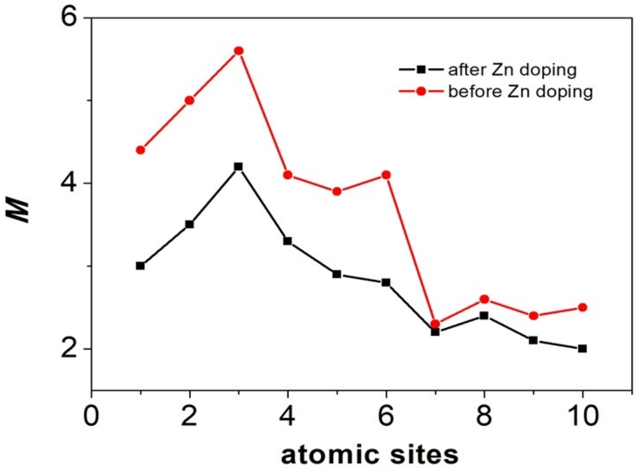

Fig. S8. Spin magnetic moment (M in μ B) of atomic sites before and after Zn doping.

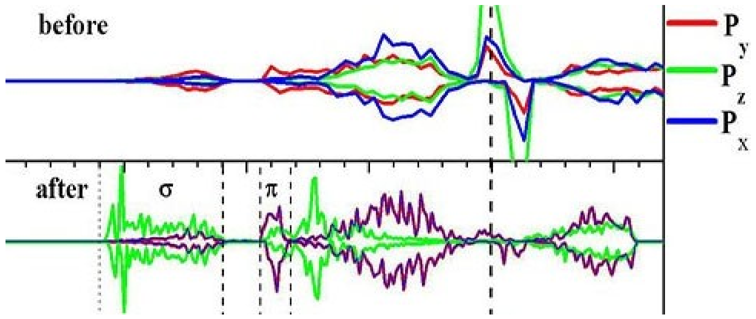

Fig. S9. DOS of Zn active site before and after N_2 adsorption in CeO_2 (111) surface.

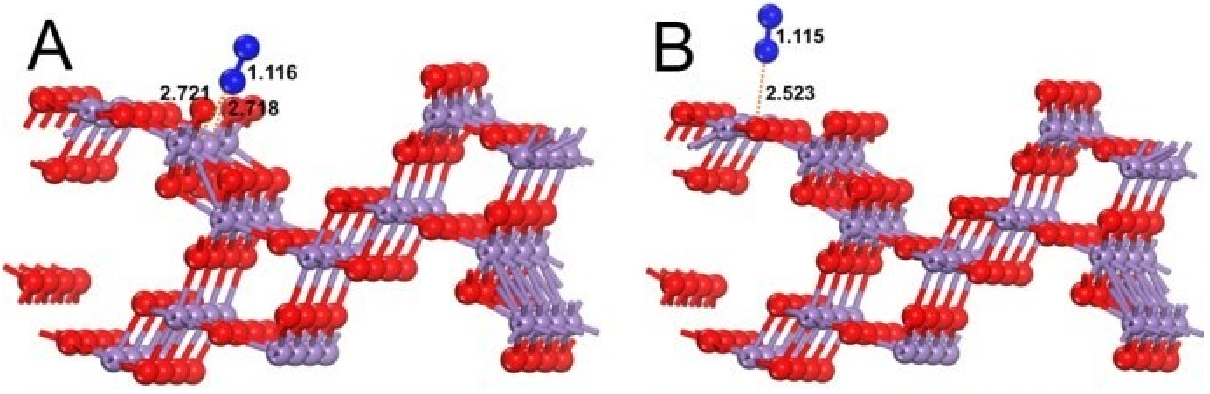

Fig. S10. Selected bond lengths (Å) are given. Red and blue isosurfaces (0.001 a.u.) represent charge accumulation and depletion, respectively.

Table S1. Comparison of electrocatalytic N_2 reduction performance for Zn-CeO_2 with other aqueous-based electrocatalysts under ambient conditions.

Catalyst	**Electrolyte**	**NH_3 yield rate ($\mu g\ h^{-1}\ mg_{cat.}^{-1}$)**	**FE (%)**	**Ref.**
Zn-CeO_2	**0.1 M Na_2SO_4**	**29.01**	**10.3**	**This work**
α-Au/CeO_x -RGO	-	8.3	10.1	5
TA-reduced Au/TiO_2	-	21.4	8.11	6
MoN NA/CC	-	18.42	1.15	7
MoO_3	-	29.43	1.9	8
VN/TM	-	5.14	2.25	9
$Bi_4V_2O_{11}/CeO_2$	-	23.21	1.16	10
Mo_2N	-	78.4	4.5	11
NPC	0.05 M H_2SO_4	23.8	1.42	12
CuO/RGO	0.1 M Na_2SO_4	11.02	3.9	13
TiO_2-rGO	0.1 M Na_2SO_4	15.13	3.3	14
γ-Fe_2O_3	0.1 M KOH	0.212	1.9	15
Fe_2O_3 nanorods	0.1 M Na_2SO_4	15.9	0.94	16
Co-PCN	0.1 M Na_2SO_4	49.69	32.2	17
Ce-Bi_2WO_6	0.1 M HCI	22.5	15.9	18
Mo-$W_{18}O_{49}$	0.1 M Na_2SO_4	5.3	12.1	19
FeSC	0.1 M KOH	8.8±1.3	6.1± 0.9	20
h-BNNS	0.1 M HCI	22.4	4.7	21
Au NPs/CoOx	0.05 M H_2SO_4	15	19	22
Fe-MoS_2	0.05 M K_2SO_4	8.63	18.5	23

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