

## Supporting Information for

### Direct Electrochemical N<sub>2</sub> Oxidation to Nitrate on Supportive Pt/CeO<sub>2</sub>

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## Experimental

### Catalyst preparation

*Materials.* Cerium nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 99.95 wt%) and platinum tetrachloride ( $\text{PtCl}_4$ , 99.9 wt%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Sodium hydroxide ( $\text{NaOH}$ , 99.5 wt%), Potassium hydroxide ( $\text{KOH}$ , 85 wt%), potassium nitrate ( $\text{KNO}_3$ , 99.0 wt%) and sulfamic acid ( $\text{NH}_2\text{SO}_3\text{H}$ , 99.5 wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ , 99.5 wt%) was purchased from Shanghai Hongguang Chemical Factory. Ethanol was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Carbon black (BP2000) was purchased from Nanjing Xianfeng Nanomaterial Technology Co., Ltd. Nafion was purchased from Kelude Co., Ltd. (5 wt%, DuPont). Carbon paper (HCP030P) was purchased from Guangdong Canrd New Energy Technology Co., Ltd. All chemicals were used as received without further purification.

*Preparation of highly dispersed Pt on  $\text{CeO}_2$  nanocubes.* Typically[1], 0.88 g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was added to 20.0 mL deionized water, stirred until dissolved, and then 15.0 mL of 6.0 mol  $\text{L}^{-1}$  of  $\text{NaOH}$  solution was dropped in, and stirred at room temperature for 30 minutes. The solution was then transferred to a 30 mL PTFE-lined autoclave and reacted at 180°C for 24 h. After washing three times with ethanol and deionized water, and drying at 80°C overnight,  $\text{CeO}_2$  nanocubes (NCs) were obtained. 0.20 g  $\text{CeO}_2$  NCs and 0.25 g  $\text{Na}_2\text{CO}_3$  were weighed into 10.0 mL and 5.0 mL of deionized water, respectively, stirred and sonicated for 2 h until a homogeneous suspension was formed. Different amounts of  $\text{PtCl}_4$  were weighed and added in the above  $\text{CeO}_2$  suspension for reaching different Pt loading on  $\text{CeO}_2$  NCs (0.20, 0.40, or 0.6 wt%), stirred for 10 min, and then added with  $\text{Na}_2\text{CO}_3$  aqueous solution. After stirring for 2 hours, the resulting suspension was filtered and washed with deionized water. The purified samples were transferred to an oven at 80°C for drying, and finally the as-obtained Pt/ $\text{CeO}_2$  was calcined in air at a heating rate of 5°C  $\text{min}^{-1}$  for 3

hours to obtain the final products of  $\text{Pt}_x\text{CeO}_2$ ,  $x=0.20, 0.40, \text{ or } 0.6$ , depending on the amount of  $\text{PtCl}_4$  added for material synthesis. The final  $x$  was precisely measured using inductively coupled plasma optical emission spectrometry (ICP-OES), the  $x$  values in  $\text{Pt}_x\text{CeO}_2$  after justification using ICP-OES are 0.21, 0.44, or 0.58, therefore the prepared samples are named as  $\text{Pt}_{0.21}\text{CeO}_2$ ,  $\text{Pt}_{0.44}\text{CeO}_2$ , or  $\text{Pt}_{0.58}\text{CeO}_2$ , respectively.

## **Characterizations**

The morphology and microstructures of samples were characterized by transmission electron microscopy (JEM-2100UHR, JEOL). High-resolution transmission electron microscopy (HRTEM, operated at 200 kV) images were recorded using a JEOL 2100 high-resolution transmission electron microscope. Aberration-corrected high-angle annular darkfield scanning transmission electron microscope (HAADF-STEM) images and element mapping images were recorded on a JEOL JEM-ARM200F TEM/STEM with a spherical aberration corrector (operated at 200 kV). The powder XRD patterns of samples were performed on a PANalytical X-ray diffraction meter with  $\text{Cu K}\alpha$  radiation at a scan rate of  $10^\circ \text{ min}^{-1}$  in a  $2\theta$  range from 5 to  $75^\circ$ .  $\text{N}_2$  adsorption-desorption measurements were performed on a Micromeritics Tristar 3020 adsorption analyzer. Specific surface areas were calculated by the Brunauer-Emmert-Teller (BET) method. Pore volumes and sizes were estimated from the pore-size distribution curves from the desorption isotherms using the density functional theory (DFT) calculations. Raman spectra were acquired with a LabRAM Aramis Raman spectrometer (HORIBA Jobin Yvon) with a 532 nm line of Ar laser as the excitation source. Electron paramagnetic resonance (EPR) data were obtained using a Bruker A-300. The temperature-programmed desorption ( $\text{N}_2$ -TPD) spectrum was performed on a Xianquan TP-5080. X-ray photoelectron spectroscopy (XPS) data were obtained using an Escalab 250Xi (X-ray Source: Al). The ultraviolet-visible (UV-vis) spectrum was performed on an Analytikjena SPECORD plus210. Precise elemental analysis of Pt on  $\text{CeO}_2$  NCs was conducted by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 720es).

## Electrochemical measurements

All the electrochemical measurements were carried out on a CHI-760E electrochemical station (Shanghai, Chenghua). A standard three-electrode setup was used with the carbon paper loaded with catalyst as the working electrode, a graphite rod as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. All the voltage were normalized to the standard hydrogen electrode following Equation 1. Before e-NOR tests, the electrolyte (1.0 mol L<sup>-1</sup> KOH) was saturated with N<sub>2</sub> for at least 30 min. The catalyst ink was prepared by ultrasonically blending the mixture of 5.0 mg of catalyst, 500 μL of ethanol, 10 μL of 5.0 wt% Nafion solution and 1.0 mg of carbon black. Then, 15.0 μL of catalyst ink was coated onto the carbon paper and dried at room temperature, resulting in a catalyst loading of 0.15 mg cm<sup>-2</sup>.

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.224 \text{ V} + 0.059 \text{ V} \times \text{pH} \quad (1)$$

*Determination of nitrate hydrate.* Nitrate produced in the electrolyte were firstly measured using UV spectrophotometry[2]. 1.0 mL of electrolyte was taken out of the electrolytic cell and diluted to 5.0 mL with deionized water, and then 0.1 mL of 1.0 M HCl and 0.01 mL of 0.8 wt% sulfamic acid solution were added to the above solution. The absorption spectra were measured using a UV-Vis spectrophotometer and the absorption intensity at 220 nm and 275 nm were recorded. The final absorbance value is calculated by the following Equation 2:

$$A = A_{220 \text{ nm}} - 2A_{275 \text{ nm}} \quad (2)$$

The concentration-absorbance curves were made using a series of potassium nitrate standard solutions, and the potassium nitrate crystals were pre-dried at 105-110°C for 2 hours. The content of the produced nitrate was further determined using an ion chromatography workstation (Daian DX-120) with an anion chromatography column<sup>[13]</sup>. The yield of nitrate is calculated by the following Equation 3:

$$\text{NO}_3^- \text{ yield} = (C \times V) / (t \times \text{area}_{\text{cat.}}) \quad (3)$$

where C is the increased nitrate mass concentration; V is the volume of electrolyte; t is the electrochemical oxidation reaction time; area<sub>cat.</sub> is the geometric area of the

electrocatalyst. The nitrate faradaic efficiency (FE) for nitrate production can be calculated as[3]:

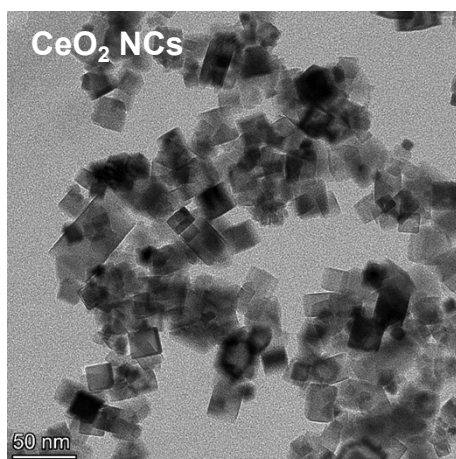
$$FE = (5 \times C \times V \times F) / (M \times Q) \quad (4)$$

where F is the Faraday constant; C is the increased nitrate mass concentration; V is the volume of electrolyte; M is the relative molecular mass of nitrate, and Q is the total charge passing through the electrodes during electrolysis.

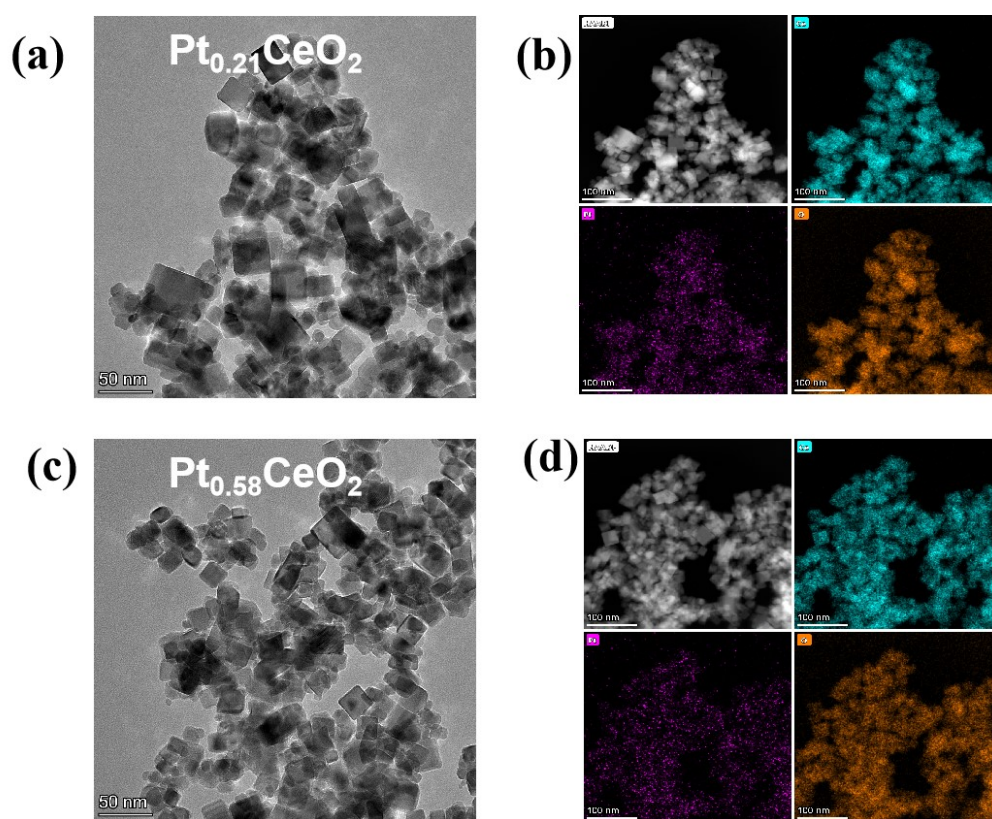
### **The Experiments of the $^{15}\text{N}$ Isotopic**

The  $^{15}\text{N}$  isotopic labeled experiment were performed using the  $^{15}\text{N}_2$  isotope with the  $^{15}\text{N}$  (99.99%) to certify the  $\text{N}_2$  origination of  $\text{NO}_3^-$ . Firstly, the  $^{15}\text{NO}_3^-$  solution (30 ml, 50  $\mu\text{g}/\text{mL}$ -250  $\mu\text{g}/\text{mL}$ ) was concentrated in a decompression distillation plant, and then determined by  $^{15}\text{N}$  nuclear magnetic resonance (NMR, JEOL ECA400).  $\text{D}_2\text{O}$  was used as the solvent, and the reaction time of NMR tests for samples was 11 hours with 11000 scans. Then, a calibration curve of  $^{15}\text{N}$ -NMR spectra was established.

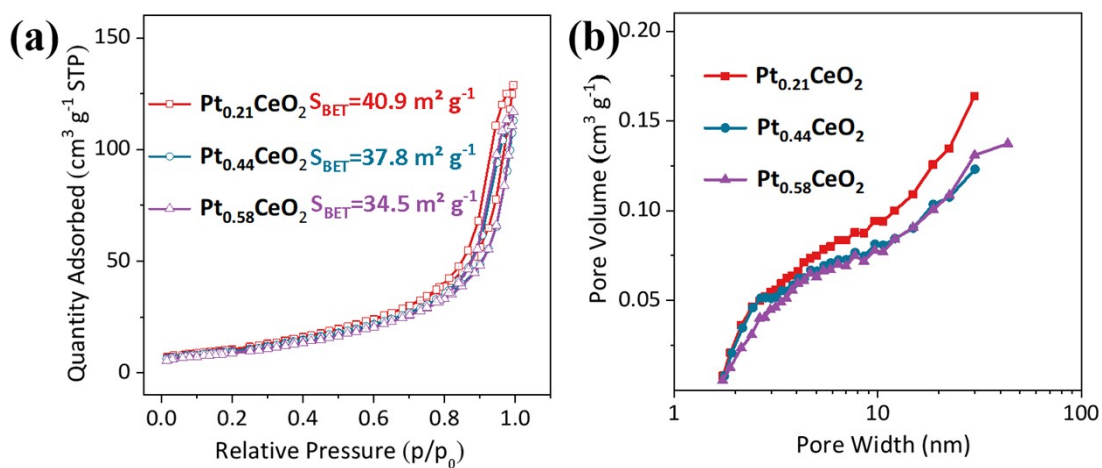
After 2 h of NOR with  $^{15}\text{N}_2$  feeding gas, the obtained  $^{15}\text{NO}_3^-$  containing electrolyte concentrated via distilling was analyzed by  $^{15}\text{N}$  nuclear magnetic resonance.  $\text{D}_2\text{O}$  was applied as the solvent and the reaction time of each NMR test was 11 hours with 11000 scans.



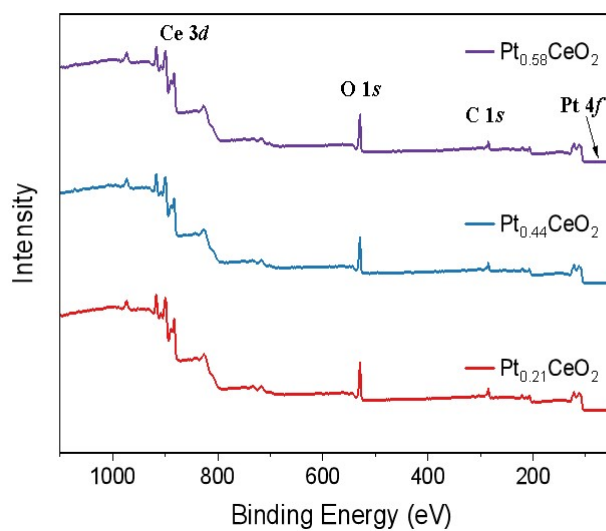
**Fig. S1.** HRTEM images of CeO<sub>2</sub> nanocubes



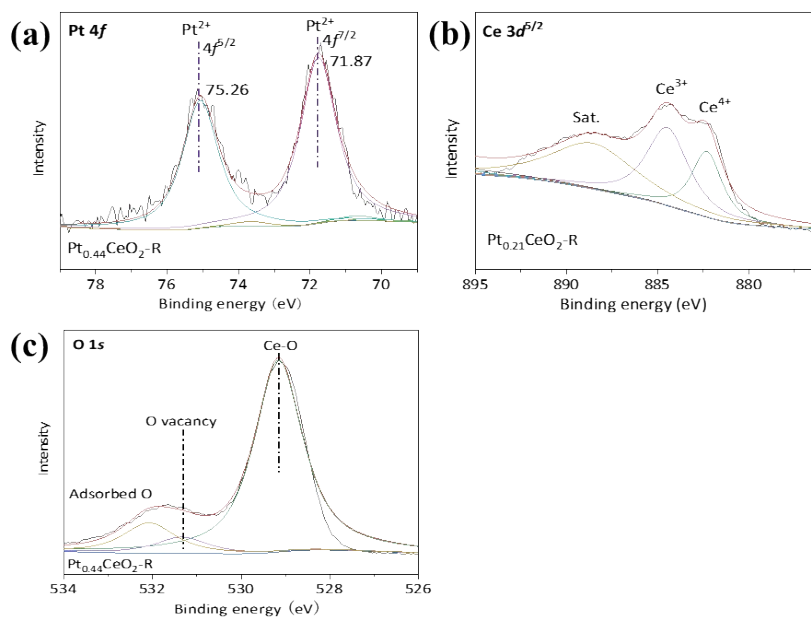
**Fig. S2.** (a) HRTEM and (b) HAADF-STEM and element mapping images of Pt<sub>0.21</sub>CeO<sub>2</sub>. (c) HRTEM and (d) HAADF-STEM and element mapping images of Pt<sub>0.58</sub>CeO<sub>2</sub>.



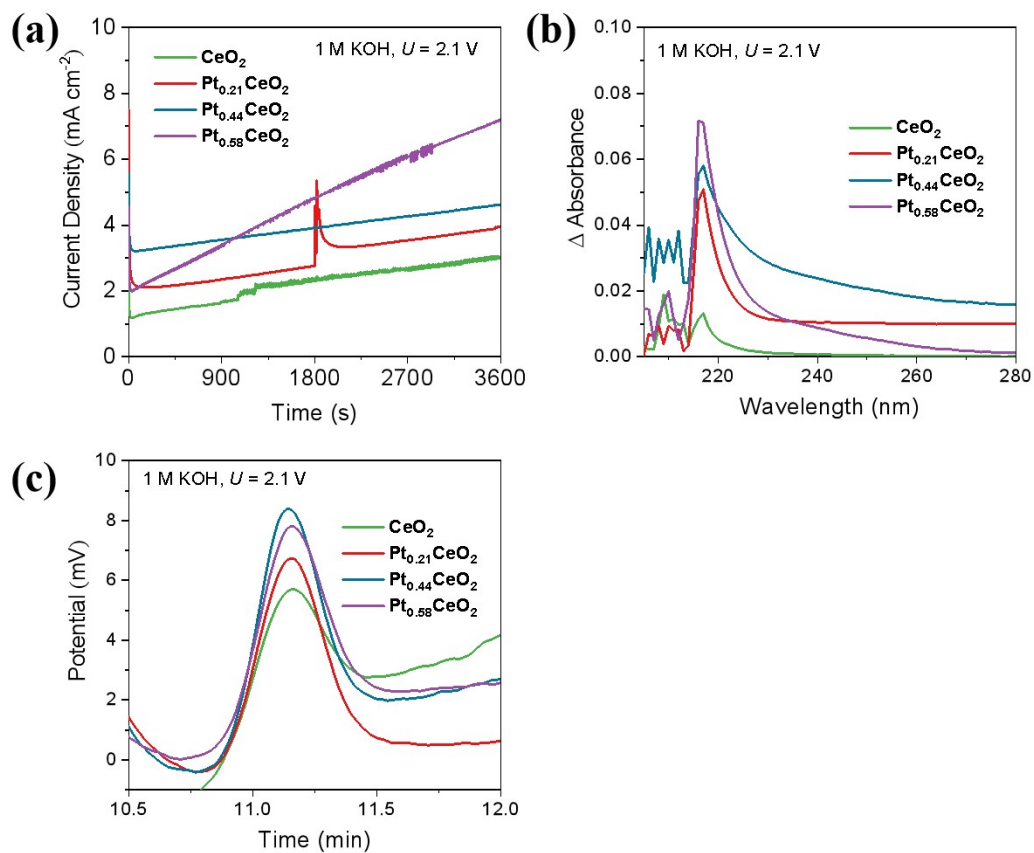
**Fig. S3.** (a) N<sub>2</sub> adsorption/desorption isotherms and (b) Pore size distribution curves of Pt<sub>x</sub>CeO<sub>2</sub>, x=0.21, 0.44, or 0.58



**Fig. S4.** XPS survey of Pt<sub>x</sub>CeO<sub>2</sub>, x=0.21, 0.44, or 0.58

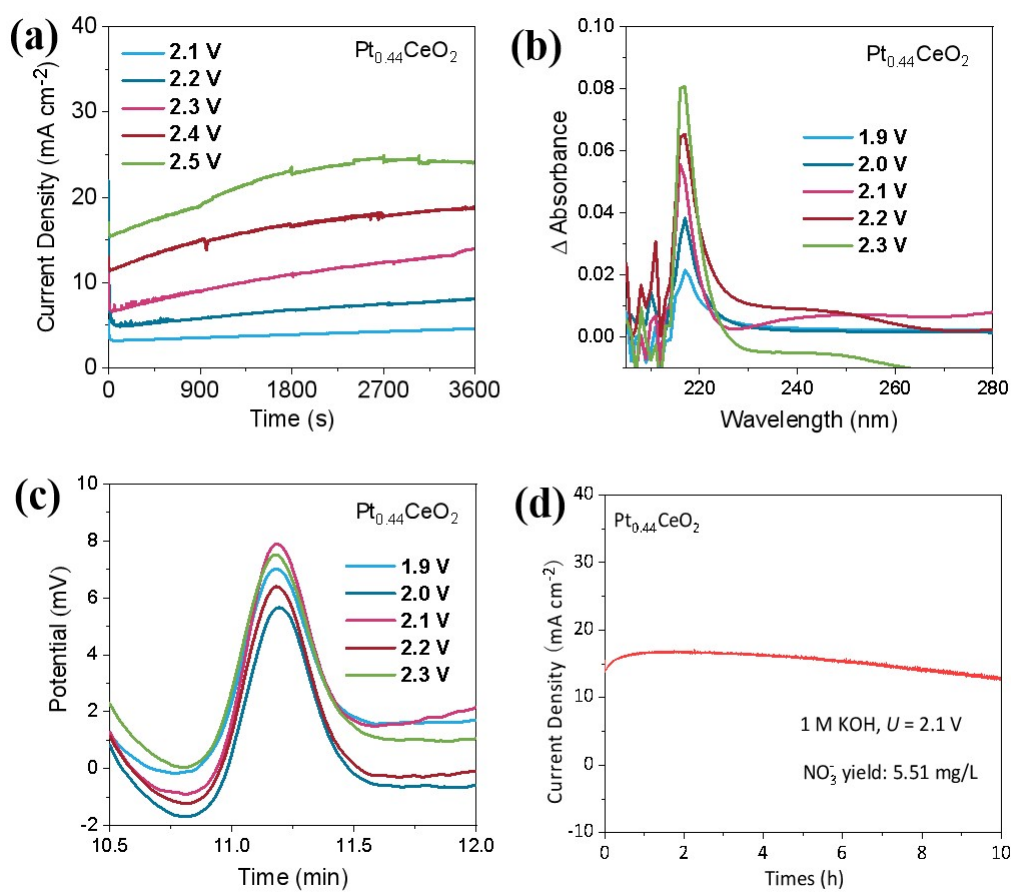


**Fig. S5.** (a) XPS Pt 4f spectra, (b) XPS Ce 3d spectra, and (c) XPS O 1s spectra of Pt<sub>0.44</sub>CeO<sub>2</sub>-R.

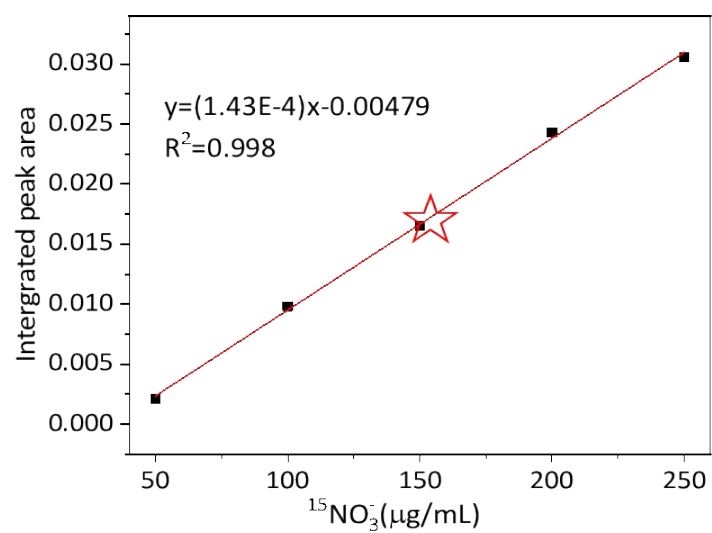


**Fig. S6.** (a) Chronoamperometric response curves of Pt<sub>x</sub>CeO<sub>2</sub> under a potential of 2.1 V (vs. RHE), x=0.21, 0.44, or 0.58. (b) UV absorption spectra and (c) ion chromatography spectra of electrolyte after one-hour e-NOR working on Pt<sub>x</sub>CeO<sub>2</sub>





**Fig. S7.** (a) Chronoamperometric response curves of Pt<sub>0.44</sub>CeO<sub>2</sub> under different potentials (vs. RHE). (b) UV absorption spectra and (c) ion chromatography spectra of electrolyte after one-hour e-NOR promoted by Pt<sub>0.44</sub>CeO<sub>2</sub> at different potentials. (d) Long-term durability test of Pt<sub>0.44</sub>CeO<sub>2</sub> at 2.1 V (vs. RHE)



**Fig. S8.**  $^{15}\text{N}$ -NMR calibration for standard  $^{15}\text{NO}_3^-$ . Our work data comes from isotope NOR test by  $\text{Pt}_{0.44}\text{CeO}_2$  for 2 h at 2.1 V vs RHE.

**Table S1.** XPS element contents of Pt<sub>x</sub>CeO<sub>2</sub>, x=0.21, 0.44, or 0.58

| Sample                              | C (at%) | Ce (at%) | O (at%) | Pt (at%) |
|-------------------------------------|---------|----------|---------|----------|
| Pt <sub>0.21</sub> CeO <sub>2</sub> | 32.96   | 15.91    | 50.97   | 0.16%    |
| Pt <sub>0.44</sub> CeO <sub>2</sub> | 30.06   | 15.65    | 54.10   | 0.19%    |
| Pt <sub>0.58</sub> CeO <sub>2</sub> | 30.67   | 15.36    | 53.73   | 0.24%    |

**Table. S2.** XPS analysis of Pt<sub>x</sub>CeO<sub>2</sub> and Pt<sub>0.44</sub>CeO<sub>2</sub>-R

| Sample  | Pt <sub>0.21</sub> CeO <sub>2</sub> | Pt <sub>0.44</sub> CeO <sub>2</sub> | Pt <sub>0.58</sub> CeO <sub>2</sub> | Pt <sub>0.44</sub> CeO <sub>2</sub> -R |
|---|-------------------------------------|-------------------------------------|-------------------------------------|--|
| Ce <sup>3+</sup> /Ce <sup>4+</sup>                | 1.323                               | 1.412                               | 1.401                               | 1.409                                  |
| O <sub>V</sub> /(O <sub>V</sub> +O <sub>L</sub> ) | 0.147                               | 0.176                               | 0.165                               | 0.172                                  |

**Table S3.** The peak area of ion chromatography curves and the calculated concentration increments of nitrate in electrolyte after e-NOR on Pt<sub>x</sub>CeO<sub>2</sub>

| Sample                              | Peak area | Concentration increment<br>(mg L <sup>-1</sup> h <sup>-1</sup> ) |
|-------------------------------------|-----------|--|
| Initial                             | 74178.89  | —  |
| CeO <sub>2</sub>                    | 116015.40 | 0.39   |
| Pt <sub>0.21</sub> CeO <sub>2</sub> | 125709.50 | 0.48   |
| Pt <sub>0.44</sub> CeO <sub>2</sub> | 132970.94 | 0.55   |
| Pt <sub>0.58</sub> CeO <sub>2</sub> | 129404.39 | 0.51   |

**Table S4.** Comparison of e-NOR performance of Pt<sub>0.44</sub>CeO<sub>2</sub> with previously reported electrocatalysts

| Catalyst                                | Electrolyte                           | Substrate           | FE (%)     | Production rate ( $\mu\text{g mg}^{-1} \text{h}^{-1}$ ) | Stability (h) | Ref              |
|---|---------------------------------------|---------------------|------------|---|---------------|------------------|
| Pd-s PNSs                               | 0.1 M KOH                             | Ti plate            | 2.5        | 18.56   | 72            | 4                |
| ZnFeCoO <sub>4</sub>                    | 1.0 M KOH                             | graphite paper      | 10.1       | 9.96  | 24            | 5                |
| Ru/TiO <sub>2</sub>                     | 0.1 M Na <sub>2</sub> SO <sub>4</sub> | carbon paper        | 26.1       | 9.92  | 10            | 6                |
| Pd <sub>0.9</sub> Ru <sub>0.1</sub>     | 0.1 M KOH                             | Ti plate            | 0.61       | 4.83  | 5             | 7                |
| Fe-SnO <sub>2</sub>                     | 0.05 M H <sub>2</sub> SO <sub>4</sub> | carbon paper        | 0.84       | 42.80   | 10            | 8                |
| Ru-Mn <sub>3</sub> O <sub>4</sub>       | 0.1 M Na <sub>2</sub> SO <sub>4</sub> | carbon paper        | 28.9       | 35.30   | 50            | 9                |
| MnPc                                    | 0.05 N H <sub>2</sub> SO <sub>4</sub> | Ti - foam           | 33.9       | 32.33   | 10            | 10               |
| <b>Pt<sub>0.44</sub>CeO<sub>2</sub></b> | <b>1.0 M KOH</b>                      | <b>carbon paper</b> | <b>8.8</b> | <b>76.72</b>  | <b>10</b>     | <b>this work</b> |

**Table S5.** The peak area of ion chromatography curves and the calculated concentration increments of nitrate in electrolyte after e-NOR on Pt<sub>0.44</sub>CeO<sub>2</sub>

| Potential (V vs. RHE) | Peak area | Concentration increment ( $\text{mg L}^{-1} \text{h}^{-1}$ ) |
|-----------------------|-----------|--|
| Initial               | 74178.89  | —  |
| 1.9                   | 118578.20 | 0.41   |
| 2.0                   | 128739.50 | 0.51   |
| 2.1                   | 132970.94 | 0.55   |
| 2.2                   | 136623.60 | 0.58   |
| 2.3                   | 138423.10 | 0.60   |

**Table S6.** The peak area of ion chromatography curves and the calculated concentration increments of nitrate in electrolyte after e-NOR on Pt<sub>0.44</sub>CeO<sub>2</sub>

| Ambience       | Peak area | Concentration increment<br>(mg L <sup>-1</sup> h <sup>-1</sup> ) |
|----------------|-----------|--|
| Initial        | 117526.70 | —  |
| N <sub>2</sub> | 138510.50 | 0.51   |
| Ar             | 110568.51 | close to 0   |

**Table S7.** The peak area of ion chromatography curves and the calculated concentration increments of nitrate in electrolyte after e-NOR on Pt<sub>0.44</sub>CeO<sub>2</sub> for 10 hours

| Operational time | Peak area  | Concentration increment<br>(mg L <sup>-1</sup> h <sup>-1</sup> ) |
|------------------|------------|--|
| 0 h              | 188450.609 | —  |
| 5 h              | 463735.537 | 5.51   |

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