

# **CeP nanoparticle-reduced graphene oxide hybrid: an efficient electrocatalyst for NH<sub>3</sub> synthesis under ambient conditions**

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## Experimental section

**Materials:** GO, cerous sulfate ( $\text{CeSO}_4$ ), ammonium chloride ( $\text{NH}_4\text{Cl}$ ), hydrazine hydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ), salicylic acid ( $\text{C}_7\text{H}_6\text{O}_3$ ), sodium citrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ ), sodium hypochlorite ( $\text{NaClO}$ ), sodium hydroxide ( $\text{NaOH}$ ), hydrochloric acid ( $\text{HCl}$ ), ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ), sodium monophosphate ( $\text{NaH}_2\text{PO}_2$ ) and carbon paper (CP) were bought from Beijing Chemical Corporation. Para-(dimethylamino) benzaldehyde ( $\text{C}_9\text{H}_{11}\text{NO}$ ), sodium nitroferricyanide (III) dihydrate ( $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$ ), and Nafion were purchased from Aladdin Ltd. (Shanghai, China). The water used throughout all experiments was purified through a Millipore system. The water used throughout all experiments was purified through a Millipore system. All chemicals were used as received without further purification.

**Preparation of CeP-rGO:** Aqueous solution of  $\text{CeSO}_4$  (50 mL, 0.02 M) and  $\text{NaOH}$  (60 mL, 0.5 M) was dissolved in homogeneous GO aqueous dispersion (1 mg/mL) under stirring for 2 h. After that, the product was separated by centrifuging, and further washing was done with Millipore water. Finally, the nanocomposite sample was freeze-dried for 24 h. The product and  $\text{NaH}_2\text{PO}_2$  (mass ratio 1: 6) were put into two boats separately and then annealed at 200 °C for 2 h under argon flow with a ramping rate of 2 °C  $\text{min}^{-1}$ . In addition, CeP was also prepared according to the same method only without adding GO. In addition, Cu-rGO was also prepared through annealing product at 300 °C for 2 h under  $\text{Ar}/\text{H}_2$  atmosphere (volume ratio = 9:1) atmosphere without adding  $\text{NaH}_2\text{PO}_2$ .

**Preparation of CeP-rGO/CP electrode:** 10 mg CeP-rGO powders and 40  $\mu\text{L}$  of Nafion solution (5 wt%) were dispersed in 960  $\mu\text{L}$  mixed solution containing 720  $\mu\text{L}$  ethanol and 240  $\mu\text{L}$   $\text{H}_2\text{O}$  by 2 h sonication to form a homogeneous ink. Then, 10  $\mu\text{L}$  CeP-rGO was loaded on a CP with area of 1 x 1  $\text{cm}^2$  and dried under ambient condition.

**Characterizations:** XRD patterns were obtained from a Shimadzu XRD-6100 diffractometer with  $\text{Cu K}\alpha$  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.

**Electrochemical measurements:** Before NRR measures, the Nafion proton exchange film was pretreated by heating in 3% H<sub>2</sub>O<sub>2</sub> solution, 0.5 M H<sub>2</sub>SO<sub>4</sub> 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 Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>/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<sub>2</sub> reduction reaction experiments, the HCl electrolyte (0.1 M) was bubbled with high-purity N<sub>2</sub> (99.999%) for 30 min before measurement. All potentials reported in this work were calibrated to RHE, using the following equation:

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

**Determination of NH<sub>3</sub>:** NH<sub>3</sub> concentration was determined by the indophenol blue method.<sup>1</sup> 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 spectrum was measured at a wavelength of 655 nm. The concentration-absorbance curves were calibrated using standard NH<sub>4</sub>Cl solution (0.1 HCl solution as mother solution) with a series of concentrations. The fitting curve ( $y = 0.475x + 0.066$ ,  $R^2 = 0.999$ ) shows good linear relation of absorbance value with NH<sub>3</sub> concentration by three times independent calibrations.

**Determination of N<sub>2</sub>H<sub>4</sub>:** Concentration of N<sub>2</sub>H<sub>4</sub> in the electrolyte was estimated by the method of Watt and Chrisp.<sup>2</sup> Typically, a mixture solution containing p-C<sub>9</sub>H<sub>11</sub>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<sub>2</sub>H<sub>4</sub> solutions with a series of concentrations for three

independent calibrations.

**Calculations of NH<sub>3</sub> yield and FE:** NH<sub>3</sub> yield was calculated using the following equations:

$$R_{\text{NH}_3} (\mu\text{g h}^{-1} \text{ mg}_{\text{cat.}}^{-1}) = (c_{\text{NH}_3} \times V) / (17 \times t \times m)$$

Where  $c_{\text{NH}_3}$  ( $\mu\text{g mL}^{-1}$ ) is the measured NH<sub>3</sub> concentration;  $V$  (mL) is the volume of electrolyte (in our work 35 mL);  $t$  (s or h) is the reaction time;  $A$  ( $\text{cm}^2$ ) is the geometric area of the cathode;  $m$  (mg) is the mass loading of catalyst on CP.

FE was calculated according to following equation:

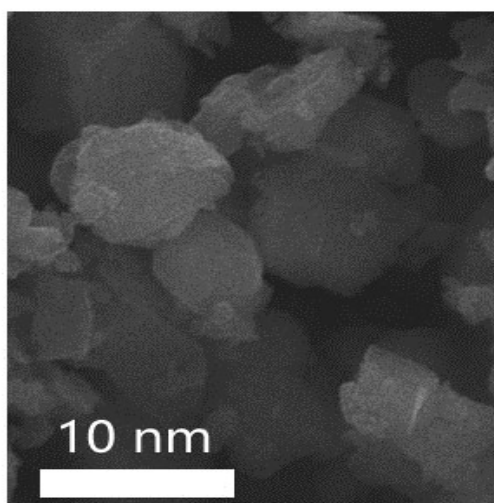
$$\text{FE} = 3 \times F \times c_{\text{NH}_3} \times V / (17 \times Q) \times 100\%$$

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

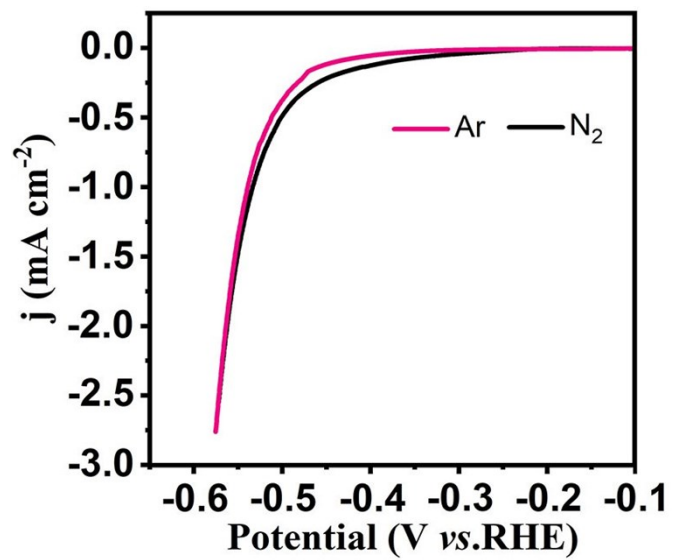
**Computational details:** To gain more in-depth insights into the mechanism for nitrogen reduction reaction (NRR) on  $\text{Ti}_3\text{C}_2\text{T}_x$  ( $X = \text{F}, \text{OH}$ ) nanosheet, density functional theory (DFT) calculations are carried out using the Vienna ab initio simulation package (VASP). Exchange-correlation energy is described by Perdue-Burke-Ernzerhof (PBE) version of the generalized gradient approximation (GGA). The projector-augmented wave (PAW) method is used to represent the core-valence electron interaction. The calculations also adopt long-range dispersion interactions (DFT-D3 (BJ)) A Hubbard  $U$  term is introduced to the PBE functional, with  $U_{\text{eff}} = 4.2 \text{ eV}$  for Ti on its d orbital. An energy cutoff of 480 eV for basis-set expansion is used. A  $2 \times 2$  supercell and the corresponding  $5 \times 5 \times 1$  k-point mesh are modeled in the calculations. A vacuum region of about 20 Å is set to decouple the periodic replicas. Two F and OH groups attached to the hollow sites between the three neighboring carbon atoms are added on each side of  $\text{Ti}_3\text{C}_2\text{T}_x$  monolayer according to previous literatures. A OH group is removed to expose active sites for N<sub>2</sub> adsorption. The force tolerance and total energy for the relaxations are converged to 0.02 eV Å<sup>-1</sup> and 10<sup>-5</sup> eV, respectively. The Gibbs free energy is calculated via the computational hydrogen electrode model proposed by Nørskov et al.<sup>3</sup>

$$\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S$$

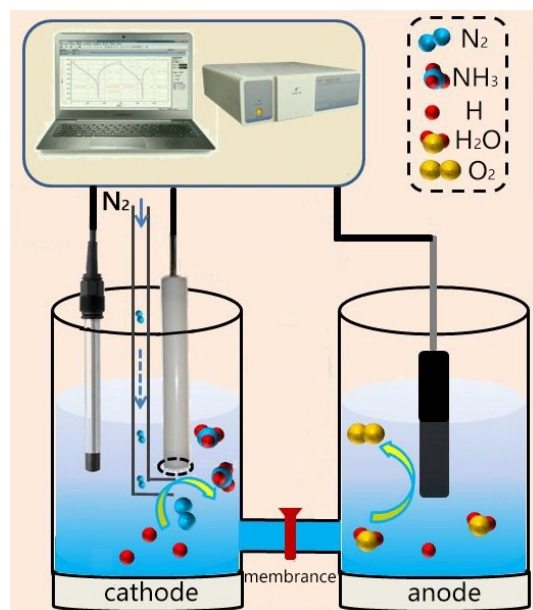
$T$  and  $\text{pH}$  value are set to be 298.15K and 0 in this work, respectively. For adsorbates, ZPE and  $S$  are determined by vibrational frequencies calculations. For molecules, those are taken from the NIST database.



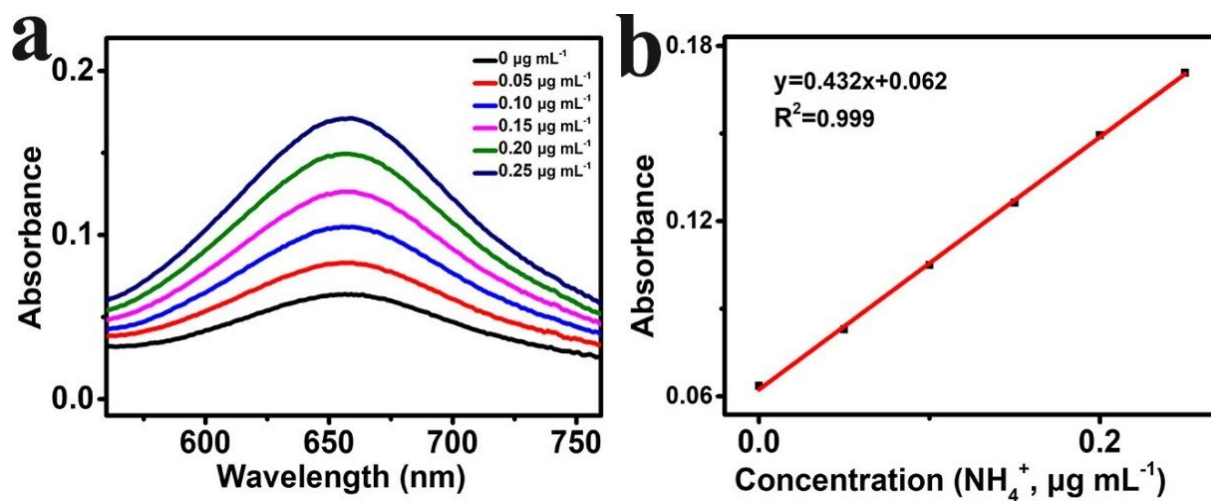
**Fig. S1.** SEM image of CeP-rGO.



**Fig. S2.** LSV curves of CeP-rGO/CP electrolytes in N<sub>2</sub>- and Ar-saturated 0.1 M HCl electrolytes with a scan rate of 5 mV s<sup>-1</sup>.

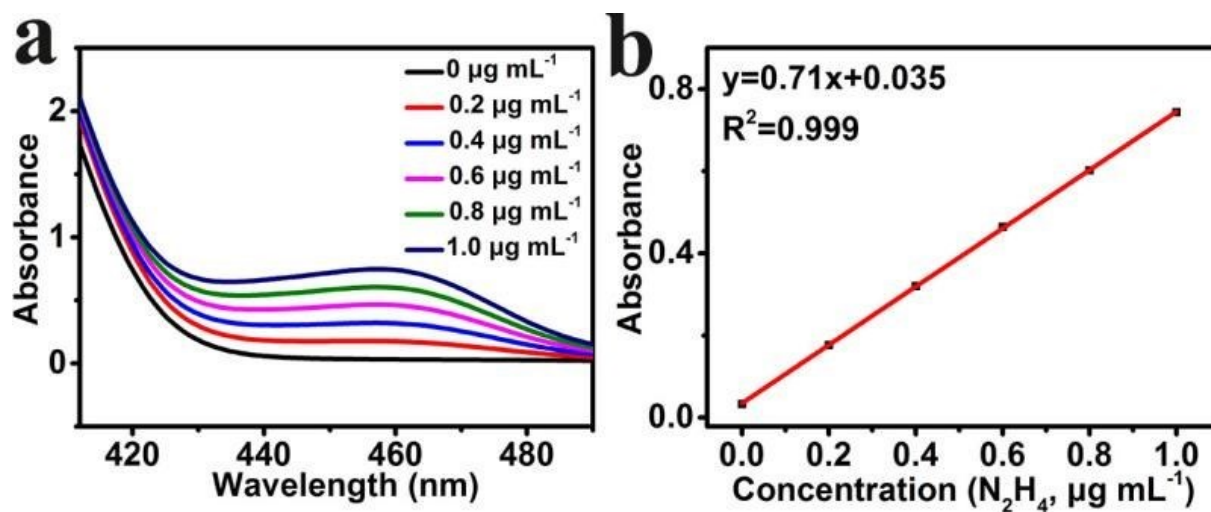


**Fig. S3.** Schematic graph to illustrate the electrocatalytic setup for the NRR test.

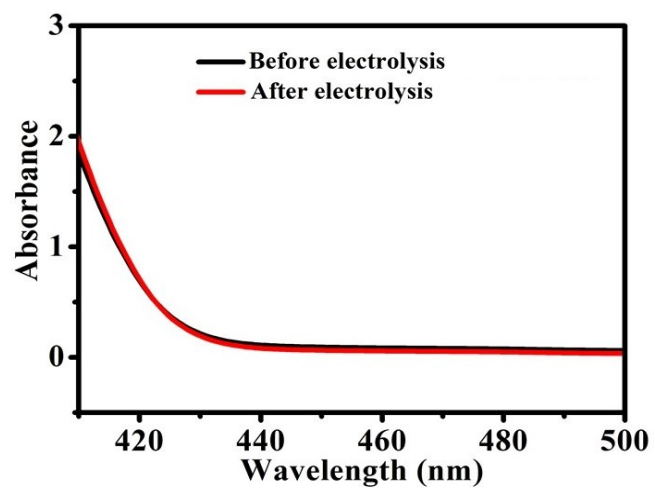


**Fig. S4.** (a) UV-Vis absorption spectra of indophenol assays with  $\text{NH}_4^+$  concentrations after incubated for 2 h at room temperature. (b) Calibration curve used for calculation of  $\text{NH}_4^+$  concentrations.

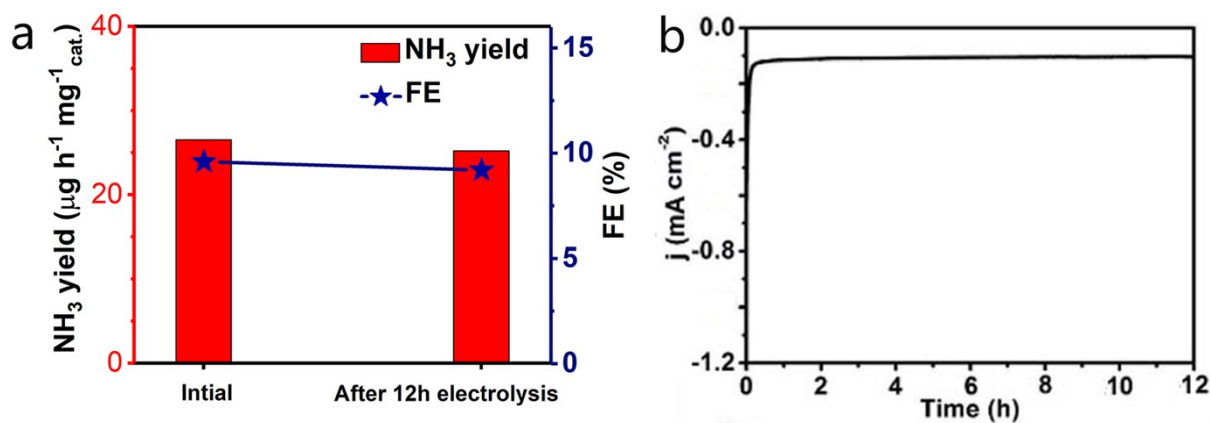




**Fig. S5.** (a) UV-Vis absorption spectra of various  $\text{N}_2\text{H}_4$  concentrations after incubated for 10 min at room temperature. (b) Calibration curve used for calculation of  $\text{N}_2\text{H}_4$  concentrations.



**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<sub>2</sub> atmosphere at -0.40 V.



**Fig. S7.** (a) NH<sub>3</sub> yields and FEs at -0.4 V with the initial CeP-rGO/CP and the CeP-rGO/CP after 12 h electrolysis. (b) Time-dependent current density curve of CeP-rGO/CP at -0.40 V.

**Table S1.** Comparison of electrocatalytic N<sub>2</sub> reduction performance for CeP-rGO with other aqueous-based electrocatalysts under ambient conditions.

Catalyst	Electrolyte	NH <sub>3</sub> yield rate ( $\mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$ )	FE (%)	Ref.
<b>CeP-rGO</b>	<b>0.1 M HCl</b>	<b>28.69</b>	<b>9.6</b>	<b>This work</b>
$\alpha$ -Au/CeO <sub>x</sub> -RGO	-	8.3	10.1	4
TA-reduced Au/TiO <sub>2</sub>	-	21.4	8.11	5
MoN NA/CC	-	18.42	1.15	6
MoO <sub>3</sub>	-	29.43	1.9	7
VN/TM	-	5.14	2.25	8
Bi <sub>4</sub> V <sub>2</sub> O <sub>11</sub> /CeO <sub>2</sub>	-	23.21	1.16	9
Mo <sub>2</sub> N	-	78.4	4.5	10
NPC	0.05 M H <sub>2</sub> SO <sub>4</sub>	23.8	1.42	11
CuO/RGO	0.1 M Na <sub>2</sub> SO <sub>4</sub>	11.02	3.9	12
TiO <sub>2</sub> -rGO	0.1 M Na <sub>2</sub> SO <sub>4</sub>	15.13	3.3	13

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