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A nanoporous CeO₂ nanowire array by acid etching preparation: an efficient electrocatalyst for ambient N₂ reduction†

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It is highly attractive but still remains a key challenge to develop earth-abundant electrocatalysts for efficient NH₃ electrosynthesis via the N₂ reduction reaction (NRR). In this work, a nanoporous CeO₂ nanowire array on a Ti mesh (np-CeO₂/TM) was derived from MnO₂-CeO₂/TM by acid etching of MnO₂ that acts as a pore-forming agent. In 0.1 M HCl, this catalyst achieves a high faradaic efficiency of 4.7% with a NH₃ yield of 38.6 μg h⁻¹ mg⁻¹_{cat.} at -0.3 V vs. reversible hydrogen electrode, outperforming most reported Ce-based NRR electrocatalysts under ambient conditions. It also demonstrates high electrochemical stability and excellent selectivity for NH₃ generation. The acid preparation strategy is highly valuable for future design of active NRR catalysts with desired compositions in various electrocatalysis fields.

As an important industrial chemical, NH₃ has attracted much attention as a potential energy carrier and a fertilizer precursor.^{1,2} With the increase of the population and the decrease of fossil fuels, the large demand for NH₃ has become an urgent social problem, which promotes the in-depth study of artificial NH₃ production technology. Due to the need for hydrogen input and energy consumption from fossil fuels, the traditional industry for producing ammonia (350–550 °C and 150–350 atm) is an energy intensive procedure: the Haber–Bosch process results in a great deal of carbon dioxide.³ Therefore, there is a tough impotunity for the development of facile and sustainable alternative strategies for NH₃ production.

As a kind of nitrogen reduction reaction (NRR) that can synthesize NH₃ at room temperature via using only a high efficiency electrocatalyst,^{4,5} the electrocatalytic NRR plays a significant role in attracting the attention of researchers.^{6–9} Recently, considerable attention has been focused on exploring non-noble-free NRR electrocatalysts.^{10–23} Porous noble metals are displayed to be effectual electrocatalysts for electrochemical storage and energy conversion,^{24–26} which need to be investigated

for the NRR. Instead of homogeneous metal surface, the coordinatively unsaturated active sites on phosphide surface might be beneficial for the bonding of nitrogen-related intermediates, is worth discussing in the NRR. Cerium(IV) oxide (CeO₂) has benefits of desirable electronic/ionic conductivity, and the cerium ion group plays a role as an intermediate in catalytic reaction and adsorption of gas, and is exposed.²⁷ Both element doping²⁸ and interface engineering²⁹ are verified productively to improve the NRR ability of catalysts. Porous nanostructures have the apparent advantage of high surface-area,³⁰ providing good benefit to improve the electrocatalytic NRR catalysis. It is thus trusted that constructing porous Ce-based catalysts is a good strategy to enhance the NRR activity of transition metal catalysts.

Herein, we report our finding that CeO₂ nanowires are a splendid catalyst for NH₃ synthesis under ambient conditions. The key idea is to selectively generate NP-CeO₂ nanowires with different corrosion stability, using oxalic acid on MnO₂ and CeO₂. CeO₂ achieves a high FE (4.7%) and NH₃ yield (38.6 μg h⁻¹ mg⁻¹_{cat.}) at -0.3 V vs. reversible hydrogen electrode (RHE), which are notably higher than those for the MnO₂-CeO₂ precursor (NH₃ yield: 14.3 μg h⁻¹ mg⁻¹_{cat.}, and FE: 1.6%) and most reported Ce-based NRR electrocatalysts under the conditions of 0.1 M HCl.

X-ray diffraction (XRD) results for CeO₂ (scratched down from TM) are shown in Fig. 1a. CeO₂ shows six peaks at 28.5°, 33.9°, 47.8°, 56.2°, 58.5°, and 69.1° indexed to the (111), (200), (220), (311), (222), and (400) facets of CeO₂ (JCPDS No. 43-1002), proposing the effective etching of MnO₂. As it is shown in the SEM image, MnO₂-CeO₂ nanowire arrays are anchored on TM (Fig. S1, ESI†), indicating that the construction of np-CeO₂/TM maintains the nanowire array feature (Fig. 1b). The transmission electron microscopy (TEM) image of etched np-CeO₂ is shown in Fig. 1e, which expresses a truth that the high-resolution TEM (HRTEM) supports interplanar distance of 0.313 nm corresponding to the (111) plane of CeO₂ (Fig. 1c).

The Brunauer–Emmett–Teller (BET) pore-size distribution curves of np-CeO₂ (Fig. 1e) exhibit an extensive peak centering at 8.6 nm, associated excellently with the TEM data. Meanwhile, the energy-dispersive X-ray (EDX) elemental mapping images of

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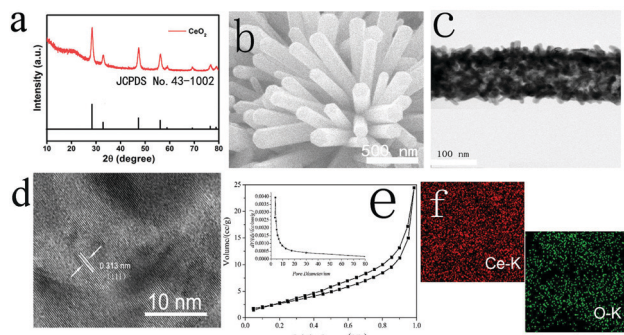


Fig. 1 (a) XRD patterns for np-CeO₂. SEM image of (b) np-CeO₂. TEM image of one single nanowire of (c) np-CeO₂. (d) HRTEM image of np-CeO₂. (e) Nitrogen adsorption/desorption isotherm plots and pore diameter of np-CeO₂. (f) EDX mapping images of CeO₂.

CeO₂ clearly show that Ce and O elements are evenly distributed on the surface. All these measurements absolutely prove the convincing formation of MnO₂-CeO₂ resulting in high surface area nanoporous CeO₂ nanowires under the condition of etching *via* acid.

X-ray photoelectron spectroscopy (XPS) was used to investigate the elemental composition and chemical valence states of porous CeO₂. As shown in Fig. 2b, high-resolution Ce 1s spectra (Fig. 2a) display binding energies of about 882.6 and 901.2 eV matching to Ce 3d_{5/2} and Ce 3d_{3/2}, accordingly.³¹ For O 1s, we can attribute it to three characteristic peaks. The two peaks at 530.1 and 531.7 eV correspond well to the ordered lattice oxygen ions of CeO₂, and the oxygen vacancy. For the peak at 533.3 eV, it can be defined to the absorbed hydroxyl on the surfaces of the CeO₂ from water molecules.^{32,33} The difference of peak area at 531.2 eV indicated that the oxygen vacancy of CeO₂ increased significantly during hydrogen reduction after acid treatment.^{34,35}

Conventional NRR is a conventional hydrogenation reduction after N₂ bubbling at the cathode surface, where H⁺ could convert the electrolyte to product NH₃ by reacting with CeO₂/N₂. For our experiment, the NRR tests were conducted in a two-chamber cell separately at ambient conditions, which is partitioned by a Nafion membrane (115). For our research, the NH₃ obtained at the cathode is formed by the interaction of N₂ and H⁺ by avoiding oxidation of the produced NH₃ at the anode, by avoiding passing through the spaced cell. At a moderate temperature and atmospheric pressure, the voltage was corrected by means of a reversible hydrogen electrode (RHE). The NH₃ and N₂H₄ produced by electrocatalytic reaction were determined *via* the indophenol blue

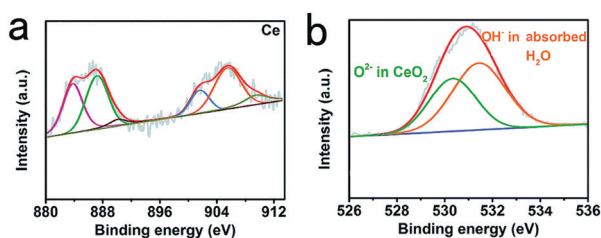


Fig. 2 XPS spectra of np-CeO₂ in the (a) Ce 3d and (b) O 1s regions.

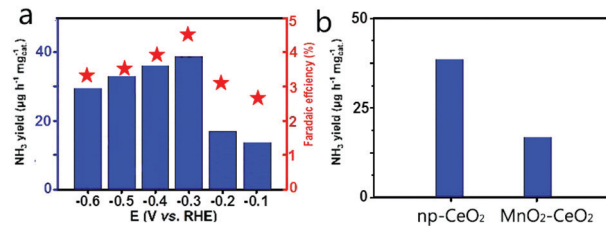


Fig. 3 (a) NH₃ yields and FEs at each given potential. (b) NH₃ yields with different catalysts at -0.3 V vs. RHE under ambient conditions.

method,³⁶ as well as by the Watt and Chrisp method.³⁷ The electrolyte was colored with indophenol indicator after 2 h electrocatalytic NRR reaction at constant potentials for collecting UV-Vis absorption spectra (Fig. S2 and S3, ESI†).

Np-CeO₂/GCE (0.3 mg cm⁻²) demonstrates exceptional selectivity without N₂H₄-production (Fig. S4, ESI†). Fig. 3b exhibits average NH₃ yields, and FEs at different potentials. In the study of the effect of load on catalytic activity, it was found that when the load was 0.3 mg, the best NRR activity was shown (Fig. S5, ESI†). The optimum NRR rate is fixed at -0.3 V vs. RHE, causing an average yield of 38.6 μg h⁻¹ mg⁻¹_{cat} NH₃, and 4.7% FE. As a catalyst with good performance, it has a great advantage over most reported NRR catalysts, including Au nanorods (6.042 μg h⁻¹ mg⁻¹_{cat}, 4%),³⁸ Cu₃P-rGO (26.38 μg h⁻¹ mg⁻¹_{cat}, 1.9%),³⁹ γ-Fe₂O₃ (0.212 μg h⁻¹ mg⁻¹_{cat}, 1.9%),⁴⁰ and N-doped nanocarbon (27.2 μg L⁻¹ h⁻¹, 1.42%).⁴¹ Detailed comparison is presented in Table S1 (ESI†). Fig. 3a displays that the yield increases with the increase of potential. In view of the surface competitive adsorption between N₂ and H, the catalyst performance is significantly reduced when the voltage transcends -0.3 V. For comparison, we provide hydrogen yield rates for hydrogen evolution reactions (Fig. S5, ESI†). By comparing the pH test paper of the electrolyte solution before and after electrolysis (Fig. S6, ESI†), it can be concluded that the pH hardly changed in the experiment, which shows that the whole system has not transformed through the reaction. In Fig. 3b, np-CeO₂/GCE exerts a speedier NRR rate than MnO₂-CeO₂/GCE (14.3 μg h⁻¹ mg⁻¹_{cat}), demonstrating that the element N plays an important role in NRR. Meanwhile, in the whole process, the weak signal value expressed by the blank GCE is completely offset. To confirm that the sensed NH₃ is produced through NRR of np-CeO₂/GCE, a series of control experiments is conducted (experimental conditions: Ar for carrier gas, -0.3 V vs. RHE for open-circuit potential and 20 h for electrochemical reaction). Moreover, in 0.1 M HCl, we tested the NRR performance of the nanoporous CeO₂ nanowires deposited on carbon paper, and it also shows the greatest NH₃ yield of 34.6 μg h⁻¹ mg⁻¹_{cat} and a high FE of 4.6% (Fig. S7, ESI†). For comparison purposes, the NH₃ yield and FE of the MnO₂-CeO₂ are shown in Fig. S8 (ESI†), and this result also demonstrates that np-CeO₂ has better NRR performance. Meanwhile, in 0.1 M H₂SO₄, our catalyst achieves a high FE of 4.61% along with a NH₃ yield of 36.9 μg h⁻¹ mg⁻¹_{cat} at -0.3 V vs. RHE, and it shows almost no changes when measured in 0.1 M HCl and in 0.1 M H₂SO₄ (Fig. S9, ESI†).



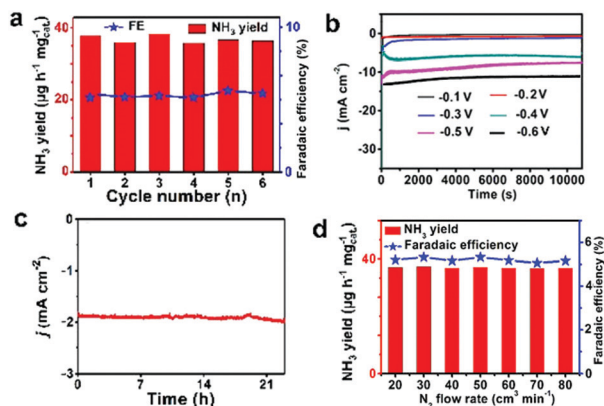


Fig. 4 (a) NH₃ yields and FEs at a potential of -0.3 V vs. RHE during recycling tests for 6 times. (b) Time-dependent current density curves for np-CeO₂ at different potentials. (c) Time-dependent current density curve for np-CeO₂ at -0.3 V vs. RHE. (d) NH₃ yields and FEs of the catalyst with different N₂ flow rates.

Stability is an additional significant parameter to estimate the catalyst behavior. np-CeO₂/TM has insignificant changes in NH₃ yield and FE through recycling experiments for 6 times (Fig. 4a). Fig. 4b displays the long-term electrolysis at a set of potentials, which indicates good stability of np-CeO₂/TM. Moreover, a slight change occurred after the NRR reaction at -0.3 V for 24 h (Fig. 4c). The XRD (Fig. S10, ESI[†]) and XPS (Fig. S11, ESI[†]) show almost no changes before and after the long test, and they also demonstrate high electrochemical stability. The FE for np-CeO₂ demonstrates slight loss compared to the initial one after long-term testing. Based on the experimental data, it can be concluded that np-CeO₂ is exceptionally stable and durable for the NRR under ambient reaction conditions. The influence of N₂ flow rate on electrocatalytic N₂ reduction was examined concurrently. What is shown in Fig. 4d is that there is inapparent fluctuation in FEs and NH₃ yields following a series of N₂ flow-rates, suggesting that the rate of reduction is impartial to the gas–solid interface. What is more, N₂ is transported toward the cathodic catalyst surface within the N₂ of the electrolyte. In addition, since the speed of electrocatalytic reaction is independent of N₂ concentration, it can be concluded that the diffusion of N₂ is not the decisive step of the reaction.

In summary, np-CeO₂ nanowire is proven as an efficient and selective electrocatalyst for NH₃ electrocatalysis from N₂ and water in acidic media. The np-CeO₂ nanowires attain a NH₃ yield of $38.6 \mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat}}$ and an FE of 4.7% at a potential of -0.3 V. Besides, what is surprising is that np-CeO₂ possesses appealing selectivity and long-term stability for electro-hydrogenation under ambient conditions. This investigation is not only the first demonstration of applying np-CeO₂ for efficient and stable NRR electrocatalysis, but would expose a stimulating new path to the advancement of transition metal nitrides as attractive low-cost NRR catalyst materials for implementations.

Conflicts of interest

There are no conflicts to declare.

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