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Nanoporous CeO\textsubscript{2} nanowire array by acid etching preparation: An efficient electrocatalyst for ambient N\textsubscript{2} reduction

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It is highly attractive but still remain a key challenge to develop earth-abundant electrocatalysts for efficient NH\textsubscript{3} electrolysens via N\textsubscript{2} reduction reaction (NRR). In this work, nanoporous CeO\textsubscript{2} nanowire array on Ti mesh (np-CeO\textsubscript{2}/TM) was derived from MnO\textsubscript{2}·CeO\textsubscript{2}/TM by acid etching of MnO\textsubscript{2} that acts as a pore-forming agent. In 0.1 M HCl, this catalyst achieves a high Faradaic efficiency of 4.7% with a NH\textsubscript{3} yield of 38.6 µg h\textsuperscript{-1} mg\textsuperscript{-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 NH\textsubscript{3} generation. The acid preparation strategy is highly valuable for future design of active NRR catalysts with desired compositions toward various electrocatalysis fields.

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

As a kind of nitrogen reduction reaction (NRR) which can synthesize NH\textsubscript{3} at room temperature only via using high efficiency electrolystalyst,\textsuperscript{4,5} the electrocatalytic NRR plays a significant role in attracting the attention of researchers.\textsuperscript{6-8} the electrocatalytic NRR plays a significant role in attracting the attention of researchers. Recently, considerable attention has focused on exploring non-noble-free NRR electrocatalysts.\textsuperscript{10-23} Porous noble metals are displayed to be effectual electrocatalysts for electrochemical storages and energy conversions,\textsuperscript{24-26} which are assuring to be investigated for NRR. Over the homogeneous metal surface, the application prospect of forming unsaturated active sites on the surface of phosphide which is beneficial to the bonding of nitrogen-related intermediates is worth discussing in NRR. Cerium(IV) oxide (CeO\textsubscript{2}) benefits desire electronic/iono conductivity, cerium ion group plays a role as intermediate in catalytic reaction and adsorbed gas , as well as they are exposed.\textsuperscript{27} Both element doping\textsuperscript{28} and interface energinerring\textsuperscript{29} are verified productively to improve the NRR ability of catalysts. Porous nanostructures are of apparent advantages of high surface-area,\textsuperscript{30} providing good benefit to improve the electrocatalytic NRR catalysis. It is thus expected that constructing of porous Ce-based catalysts is a good strategy to enhance the NRR activity of transition metal catalysts.

Herein, we report our finding that CeO\textsubscript{2} nanowire is splendid catalyst for N\textsubscript{2} synthesis at ambient conditions. The key idea is to selectively generate NP-CeO\textsubscript{2} nanowires with different corrosion stability of oxalic acid on MnO\textsubscript{2} and CeO\textsubscript{2}. CeO\textsubscript{2} achieves a high FE (4.7 %) and NH\textsubscript{3} yield (38.6 µg h\textsuperscript{-1} mg\textsuperscript{-1}cat.) at −0.3 V vs. reversible hydrogen electrode (RHE), which are notably higher than that for MnO\textsubscript{2}-CeO\textsubscript{2} precursor (NH\textsubscript{3} yield: 14.3 µg h\textsuperscript{-1} mg\textsuperscript{-1}cat., FE: 1.6%) and most reported Ce-based NRR electrocatalysts at the condition of 0.1 M HCl.

X-ray diffraction (XRD) results for CeO\textsubscript{2} are shown in Fig. 1a (scratched down from TM). CeO\textsubscript{2} submits 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 CeO\textsubscript{2} (JCPDS No.43-1002), proposing the effective etching of MnO\textsubscript{2}. As it shown in SEM image, MnO\textsubscript{2}-CeO\textsubscript{2} nanowire arrays are anchored on TM (Fig. S1). Indicating that the constructing np-CeO\textsubscript{2}/TM maintains nanowire array feature (Fig. 1b). The transmission electron microscopy (TEM) image of etching np-CeO\textsubscript{2} is shown in Figure 1e, which expresses a truth that the High-resolution TEM (HRTEM) supports interplanar distance of 0.313 nm corresponding to (111) plane of CeO\textsubscript{2} (Fig. 1c).
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The Brunauer-Emmett-Teller (BET) pore-size distribution curves of np-CeO$_2$ (Fig. 1e) exhibits a extensive peak centering at 8.6 nm, associating excellent with TEM data. Meanwhile, the energy-dispersive X-ray (EDX) elemental mapping images of CeO$_2$ clearly show that Ce and O elements evenly distribute on the surface. All these measurements absolutely approve the convincing formation of MnO$_2$-CeO$_2$ resulted high surface area nanoporous CeO$_2$ nanowires under the condition of etching via acid.

Fig. 1. (a) XRD patterns for np-CeO$_2$. SEM image of (b) np-CeO$_2$. TEM image taken from one single nanowire of (c) np-CeO$_2$. (d) HRTEM image taken from np-CeO$_2$. (e) Nitrogen adsorption/desorption isotherm plots of np-CeO$_2$. (f) EDX mapping images of CeO$_2$.

Fig. 2. XPS spectra for np-CeO$_2$ in the (a) Ce 3d and (b) O 1s regions.

N$_2$ and H$^+$ by avoiding the oxidation of produced NH$_3$ through spaced cell can at anode. At moderate temperature and atmospheric pressure, the voltage was corrected by means of a reversible hydrogen electrode (RHE). The NH$_3$ and H$_2$ production by electrocatalytic reaction were determined via the indophenol blue method, as well as the Watt and Chrisp method. 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).

Fig. 3. (a) NH$_3$ yields and FEs at each given potential. (b) NH$_3$ yields with different catalysts at –0.3 V vs. RHE under ambient conditions.

Np-CeO$_2$/GCE (0.3 mg/cm$^2$) demonstrates exceptional selectivity without N$_2$H$_4$-production (Fig. S4). Fig. 3b exhibits average NH$_3$ yields, as well as 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). The optimum NRR rate fixes at –0.3 V vs. RHE, causing an average yield of 38.6 μg h$^{-1}$ mg$^{-1}$cat NH$_3$ and 4.7 % FE. Over most reported NRR catalysts, as a catalyst with good performance, it has a great advantage, including Au nanorod (6.042 μg h$^{-1}$ mg$^{-1}$cat NH$_3$, 4%), Cu$_3$P-rGO (26.38 μg h$^{-1}$ mg$^{-1}$cat, 1.9%), γ-Fe$_2$O$_3$ (0.212 μg h$^{-1}$ mg$^{-1}$cat, 1.9%), and N-doped nanocarbon (27.2 μg L$^{-1}$ h$^{-1}$, 1.42%). Detailed comparison is presented in Table S1. Fig. 3a displays that the yield increases with the increase of potential. In view of the surface competitive adsorption between N$_2$ and H, the catalyst performance is significantly reduced when the voltage transcents –0.3 V. For comparison, we provide hydrogen yield rates for hydrogen evolution reactions (Fig. S5). By comparing the pH test paper of electrolyte solution before and after electrolysis (Fig. S6), 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-CeO$_2$/GCE exposit spreed NRR rate than MnO$_2$-CeO$_2$/GCE (14.3 μg h$^{-1}$ mg$^{-1}$cat), demonstrating the N element 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 the sensed NH$_3$ is produced through NRR of np-CeO$_2$/GCE, a series of controlled experiments are conducted (experiments’ 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 performances of the nanoporous CeO$_2$ nanowires deposited on carbon paper, it also acquires the greatest NH$_3$ yield of 34.6 μg h$^{-1}$ mg$^{-1}$cat, as well as a high FE of 4.6 % (Fig. S7). For comparison purpose, NH$_3$ yield and FE of MnO$_2$-CeO$_2$ were shown in Fig. S8, the result also demonstrates np-CeO$_2$ has
better NRR performance. Meanwhile, in 0.1 M \( \text{H}_2\text{SO}_4 \) our catalyst achieves high FE of 4.61% in the company of a \( \text{NH}_3 \) yield of 36.9 µg h\(^{-1}\) mg\(^{-1}\) cat. at \(-0.3\) V vs. RHE, it shows almost no changes when measuring in 0.1 M HCl and \( \text{H}_2\text{SO}_4 \) (Fig. S9).

Stability is an additional significant parameter to estimate catalyst behavior. np-CeO\(_2\)/TM has insignificant changes in \( \text{NH}_3 \) yield and FE through recycling experiments for 6 times (Fig. 4a). The Fig. 4b displays the long-term electrolysis at a set of potentials, which indicate good stability of np-CeO\(_2\)/TM. Moreover, a slight change occurred after the NRR reaction at \(-0.3\) V for 24 h (Fig. 4c). The XRD (Fig. S10) and XPS (Fig. S11) show almost no changes before and after the long test, they also demonstrate high electrochemical stability. The FEs for np-CeO\(_2\) demonstrate slight loss came up to the initial one after long-term testing. Based on the experimental data, it can be concluded that np-CeO\(_2\) is exceptionally stable and durable for the NRR through ambient reaction conditions. The influence of \( \text{N}_2 \) flow rate on electrocatalytic \( \text{N}_2 \) reduction was examined concurrently. What is shown in Fig. 4d is that there is inapparent fluctuation in FEs and \( \text{NH}_3 \) yields following a series of \( \text{N}_2 \) flow-rates, suggesting that the rate of reduction is impartial of the gas-solid interface. What’s more, \( \text{N}_2 \) is transported toward the cathodic catalyst’s surface within the \( \text{N}_2 \) the electrolyte. In addition, Since the speed of electrocatalytic reaction is independent of \( \text{N}_2 \) concentration, it can be concluded that the diffusion of \( \text{N}_2 \) is not the decisive step of the reaction.

In summary, np-CeO\(_2\) nanowire is confirmed as a high-efficiency and selective electrocatalyst for qualify leading \( \text{NH}_3 \) synthesis of \( \text{N}_2 \) to \( \text{NH}_3 \) in acidic media. The np-CeO\(_2\) nanowire attains a \( \text{NH}_3 \) yield of 38.6 µg h\(^{-1}\) mg\(^{-1}\) cat. as well as a FE of 4.7% at potential of \(-0.3\) V. Besides, what’s surprising is that np-CeO\(_2\) possesses appealing selectivity and long-term stability for electro-hydrogenation under ambient conditions. This investigation is not only the first demonstration of applying np-CeO\(_2\) 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.
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