Self-template synthesis of hierarchically structured $\text{Co}_3\text{O}_4@\text{NiO}$ bifunctional electrodes for selective nitrate reduction and tetrahydroisoquinolines semi-dehydrogenation

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ABSTRACT The rational design and synthesis of hierarchically hollow nanostructures with controlled spatial architecture and composition are significant in electrocatalysis owing to their abundant active sites and the expedited electron/mass transfer. Electrocatalytic nitrate reduction to ammonia is of great interest from the points of environmental protection and energy saving. However, the development of this technology is hindered by the lack of efficient nitrate-to-ammonia electrocatalysts and the kinetically sluggish oxygen evolution reaction at the anode. Herein, a novel self-template conversion method was developed for the synthesis of $\text{Co}_3\text{O}_4@\text{NiO}$ hierarchical nanotubes ($\text{Co}_3\text{O}_4@\text{NiO}$ HNTs) with NiO porous nanosheets assembled on Co_3O_4 nanotubes. The as-obtained $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs exhibited an outstanding performance for both the cathodic nitrate electroreduction to ammonia reaction and the anodic tetrahydroisoquinolines (THIQs) semi-dehydrogenation to dihydroisoquinolines (DHIQs). Importantly, a two-electrode system of $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs || $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs was constructed for the simultaneous synthesis of ammonia and DHIQs with high selectivity and robust stability.

Keywords: hierarchically hollow structure, self-template, cation exchange, electrocatalysis, bifunctional electrodes

INTRODUCTION

Construction of hierarchically structured nanomaterials with hollow interior is of great interest in both materials science and energy storage/conversion [1–8]. Specially, the unique features of hierarchically hollow structure bring promising potential in the area of electrocatalysis

owing to their abundant active sites and the expedited electron/mass transfer [9–12]. However, the conventional synthetic methods are usually less efficient in preparing hierarchically hollow structures with well-defined shapes [13]. In the past decades, self-template conversion, which involves various physical/chemical processes to convert precursor templates into target materials, has been proved as an efficient strategy to produce diverse nanostructures because the as-obtained daughter nanomaterials are endowed with the inherited architecture of their parental precursors [14–17]. For instance, Lu *et al.* [18] developed a facile self-template approach to fabricate Ni-doped FeP/C hollow nanorods based on the etching and coordination reaction. He *et al.* [19] reported the transformation of solid palladium nanocrystals to hollow palladium nanocrystals *via* a Kirkendall cavitation process. Although great progress has been made in this area, the synthesis of hierarchically hollow structures with controlled spatial architectures and compositions, as well as the understanding of structure conversion mechanism, is still a big challenge [20].

Excessive nitrate in groundwater can cause serious health problems and need to be removed. Electrocatalytic nitrate reduction to ammonia has been considered as a promising approach [21]. Precious metal-based electrocatalysts show high performance for electrocatalytic nitrate reduction, but the high cost and the scarcity limit their wide application [22]. Thus, searching for advanced materials with low cost and high activity is highly needed. Moreover, the kinetically sluggish oxygen evolution reaction (OER) at the anode seriously hinders the overall

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electrochemical efficiency [23]. Exploring thermodynamically favorable reaction with the production of value-added fine chemicals to replace OER is an efficient strategy [24–26]. Dihydroisoquinolines (DHIQs) play an important role in the pharmaceutical industry and can be produced by the tetrahydroisoquinolines (THIQs) semi-dehydrogenation [27]. Nevertheless, the highly selective preparation of DHIQs is still difficult because of the easy formation of complete dehydrogenation products of isoquinolines (IQs) [28]. Recently, our group reported that Ni_2P could realize the semi-dehydrogenation of THIQs on the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ redox [29]. In this regard, developing a novel strategy to construct hierarchically hollow materials with high performance for integrating THIQs semi-dehydrogenation with nitrate reduction is highly promising.

Herein, we developed a novel two-step self-template conversion method to prepare $\text{Co}_3\text{O}_4@\text{NiO}$ hierarchical nanotubes, denoted as $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs, by adopting Co-aspartic acid nanowires (Co-Asp NWs) as precursors. Co-Asp NWs firstly underwent the cation-exchange reaction with Ni^{2+} to produce Co-Asp@Ni-Asp hierarchical nanowires (Co-Asp@Ni-Asp HNWs), which were further converted into $\text{Co}_3\text{O}_4@\text{NiO}$ hierarchical nanotubes ($\text{Co}_3\text{O}_4@\text{NiO}$ HNTs) *via* a Kirkendall cavitation process. The conversion mechanism was well revealed by characterizing the intermediates. The as-prepared $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs exhibited superior performance in both selective nitrate reduction to ammonia and THIQs semi-dehydrogenation to DHIQs. Online differential electrochemical mass spectrometry (DEMS) and *in situ* Raman spectra were carried out to identify the reaction intermediates during nitrate reduction and reactive species for semi-dehydrogenation over $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs electrodes. Importantly, a two-electrode system of $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs || $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs was constructed for the simultaneous preparation of ammonia and DHIQs with high selectivity and robust stability.

EXPERIMENTAL SECTION

Synthesis of Co-Asp NWs

In a typical procedure, 3 mmol of cobalt (II) nitrate hexahydrate, 3 mmol of *L*-aspartic acid, and 3 mL of NaOH (2 mol L^{-1}) aqueous solution were added to a mixture solution of 15 mL of deionized water and 18 mL of glycol. After vigorous stirring for 1 h, the solution was transferred to a 50-mL Teflon-lined autoclave and maintained at 180°C for 5 h. After cooling down to room temperature naturally, the pink precipitates of Co-Asp NWs were obtained by centrifugation and dried at 40°C

for 12 h.

Synthesis of Co-Asp@Ni-Asp HNWs

The as-prepared 0.075 g of Co-Asp NWs were dispersed in 20 mL of ethanol. Then, 10 mL of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ethanol solution (0.1 mol L^{-1}) was injected into the above-mentioned Co-Asp NWs ethanol solution with constant stirring. The mixed solution was transferred to a 50-mL Teflon-lined stainless-steel autoclave and maintained at 180°C for 6 h. The Co-Asp@Ni-Asp HNWs were collected by centrifugation and dried at 40°C for 12 h.

Synthesis of $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs

The $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs were prepared by annealing Co-Asp@Ni-Asp HNWs in air at 300°C for 4 h.

Electrochemical measurements

Preparation of the working electrode

First, carbon paper ($3 \text{ cm} \times 1 \text{ cm} \times 0.1 \text{ cm}$) was ultrasonicated with anhydrous alcohol for 5 min. After being rinsed with ultrapure water, carbon paper was cooked at 60°C for 24 h in a mixture of water, concentrated nitric acid and concentrated sulfuric acid with a volume ratio of 1:1:1. Then, carbon paper was washed with ultrapure water and dried at ambient conditions for further use. Two milligram of $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs was mixed with 0.75 mL of deionized water, 0.25 mL of isopropanol and 15 μL of 5% Nafion solution followed by 30 min sonication to form a homogeneous ink. Finally, the ink was loaded onto carbon paper to obtain the working electrode of $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs.

Electrochemical measurement of selective nitrate reduction

Electrochemical nitrate reduction reaction was carried out in a three-electrode system consisting of a working electrode of $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs, a platinum plate counter electrode (CE), and a saturated calomel electrode (SCE) reference electrode with a CHI 650E electrochemical analyzer (CH Instruments, Inc., Shanghai). Na_2SO_4 solution (70 mL , 0.5 mol L^{-1}) was used as an electrolyte and evenly distributed to the cathode and anode compartment separated by a membrane. NaNO_3 (200 ppm NO_3^- -N) was added into the cathode compartment as the reactant. The polarization curve for nitrate reduction was carried out at a scan rate of 10 mV s^{-1} . Then, the chronoamperometry test was carried out at different potentials for 3 h under stirring. All the measured potentials were referred to reversible hydrogen electrode (RHE) based on

Equation (1):

$$E(\text{RHE}) = E(\text{SCE}) + 0.2415 \text{ V} + 0.059 \times \text{pH}. \quad (1)$$

Electrochemical measurement for the semi-dehydrogenation of THIQs

The electrochemical semi-dehydrogenation of THIQs was carried out in a three-electrode system consisting of a working electrode of $\text{Co}_3\text{O}_4/\text{NiO}$ HNTs, a platinum plate CE, and a Ag/AgCl reference electrode with a CHI 650E electrochemical analyzer (CH Instruments, Inc., Shanghai). The solution of 1.0 mol L^{-1} KOH with or without 0.5 mmol THIQs was employed as electrolytes. The polarization curves for the semi-dehydrogenation of THIQs were carried out at a scan rate of 10 mV s^{-1} . Then, the chronoamperometry test was carried out at 1.55 V vs. RHE , and the time of chronoamperometry tests was set according to the passing charge of $\sim 100 \text{ C}$. All the measured potentials were referred to RHE based on Equation (2):

$$E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + 0.197 \text{ V} + 0.059 \times \text{pH}. \quad (2)$$

Electrochemical measurements for THIQs semi-dehydrogenation coupled with nitrate electroreduction over bifunctional electrodes of $\text{Co}_3\text{O}_4/\text{NiO}$ HNTs || $\text{Co}_3\text{O}_4/\text{NiO}$ HNTs

For two-electrode electrolysis, $\text{Co}_3\text{O}_4/\text{NiO}$ HNTs electrodes were employed as both anode and cathode. The

scan rate of linear sweep voltammetry (LSV) curves was 10 mV s^{-1} . The electrolytes in cathode and anode chamber were 0.5 mol L^{-1} Na_2SO_4 with 200 ppm NO_3^- -N and 1.0 mol L^{-1} KOH with 0.5 mmol of THIQs, respectively, and were separated by a membrane. All experiments were carried out at room temperature. The chronoamperometry test was carried out at 2.0 V vs. CE with $\sim 100 \text{ C}$ of total passing charge.

RESULTS AND DISCUSSION

The first-step conversion from Co-Asp NWs to Co-Asp@Ni-Asp HNWs is illustrated in Fig. 1a. First, one-dimensional (1D) Co-Asp NWs were fabricated based on our previous report [30]. The scanning electron microscopy (SEM) image (Fig. 1b) and transmission electron microscopy (TEM) image (inset in Fig. 1b) show their smooth surface. X-ray diffraction (XRD) pattern and Fourier transform infrared spectroscopy (FTIR) (Fig. S1 in the Supplementary information) confirm the Co-Asp NWs as inorganic-organic hybrid materials [31,32]. After mixing the Co-Asp NWs and Ni^{2+} ions in pure ethanol, the cation-exchange reaction proceeded at 180°C . The surface of Co-Asp NWs was consumed to produce Ni-Asp 2D nanosheets (Ni-Asp NSs). When a thick layer of Ni-Asp NSs formed on the surface to hinder the further exchange of interior Co-Asp, the core@shell structured Co-Asp@Ni-Asp HNWs with Co-Asp NWs core and Ni-

Figure 1 (a) Schematic illustration for the conversion from Co-Asp NWs to Co-Asp@Ni-Asp HNWs. SEM images of (b) Co-Asp NWs and (c) Co-Asp@Ni-Asp HNWs. The insets are the corresponding TEM images. (d) STEM-EDS elemental mapping images of the Co-Asp@Ni-Asp HNWs.

Asp NSs shell were produced. SEM image (Fig. 1c) and TEM image (inset in Fig. 1c) clearly show the 1D NWs@2D NSs structure in the cation-exchange product. The scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) elemental mapping images (Fig. 1d) reveal the elemental distribution. Cobalt and nickel distribute in core and shell, respectively, while oxygen exists in both core and shell. XRD pattern

(Fig. S2) confirms the cation-exchange products as inorganic-organic hybrid materials. The aforementioned results demonstrate the successful preparation of Co-Asp@Ni-Asp HNWs through the cation-exchange reaction between Co-Asp NWs and Ni^{2+} .

The second-step conversion from Co-Asp@Ni-Asp HNWs to Co_3O_4 @NiO HNTs is illustrated in Fig. 2a. The conversion intermediates were obtained by aborting an-

Figure 2 (a) Schematic illustration for the conversion from Co-Asp@Ni-Asp HNWs to Co_3O_4 @NiO HNTs with the intermediates of Co-Asp@ Co_3O_4 @NiO HNSs. (b) SEM image, (c) TEM image and (d) STEM-EDS elemental mapping images of Co-Asp@ Co_3O_4 @NiO HNSs intermediates. (e) SEM image, (f, g) TEM images, (h) STEM-EDS elemental line scanning image, (i) nitrogen adsorption/desorption isotherms (inset: pore size distribution) and (j) XRD pattern of the Co_3O_4 @NiO HNTs.

nealing at 1 h. SEM image (Fig. 2b) and TEM image (Fig. 2c) clearly show the yolk@core@shell hierarchical nanostructures (HNSs) of the intermediates with 1D NWs yolk, 1D NTs core and 2D NSs shell. As displayed in the STEM-EDS elemental mapping images (Fig. 2d), nickel exists in 2D NSs shell, while oxygen distributes in the overall materials. Notably, cobalt could be found in both 1D NWs yolk and 1D NTs core. A possible mechanism involving the Kirkendall effect was proposed for the formation of the intermediates. Upon annealing Co-Asp@Ni-Asp HNWs, Ni-Asp NSs shell decomposed to produce NiO NSs shell. Owing to the big size of Co-Asp NWs, the surface of Co-Asp NWs first decomposed to Co_3O_4 . The concentration gradient would drive the outward diffusion of Co^{2+} and the inward diffusion of oxygen. The difference of the diffusion rates between Co^{2+} and oxygen (i.e. Kirkendall effect) [33–35] led to the formation of a unique structure with interior Co-Asp NWs and external Co_3O_4 NTs. Combining with NiO NSs shell, the Co-Asp@ Co_3O_4 @NiO HNSs intermediates were obtained. Further prolonging the reaction time to 4 h, a typical core@shell structured 1D NTs@2D NSs were obtained as displayed in SEM and TEM images (Fig. 2e and f) when the interior Co-Asp NWs were completely consumed. TEM image reveals that pores appear in the 2D NSs shell after annealing treatment owing to the thermal

decomposition of aspartic acid (Fig. 2g). STEM-EDS elemental line scanning images (Fig. 2h) show that cobalt and nickel distribute in 1D NTs core and 2D NSs shell, respectively, while oxygen exists in both core and shell. The pores with size centered at ~ 6.5 nm provide a specific surface area as high as $184.2 \text{ m}^2 \text{ g}^{-1}$ (Fig. 2i and its inset). XRD pattern (Fig. 2j) and X-ray photoelectron spectroscopy (XPS) spectra (Fig. S3) identify the final decomposition products as a mixture of Co_3O_4 (JCPDS No. 43-1003) and NiO (JCPDS No. 44-1159). Thus, the final conversion products are Co_3O_4 @NiO HNTs with Co_3O_4 NTs core and NiO NSs shell.

The selective electroreduction of nitrate to ammonia was tested in an H-type electrolytic cell (Fig. 3a). The electrolyte in the cathode chamber is $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution with 200 ppm NO_3^- -N. Before nitrate electroreduction, LSV curves were swept until a steady state. As shown in Fig. 3b, the current density exhibits obvious promotion with nitrate, indicating the reduction of nitrate [36]. The concentrations of reactants and products were determined by a UV-Vis spectrophotometer (Fig. S4) [37]. From -0.65 to -0.80 V in Fig. 3c, there is almost no obvious difference in selectivity of ammonia, and the yield rate of ammonia keeps increasing (Fig. S5), but the Faradaic efficiency of ammonia displays a volcanic shape curve with a maximum value at -0.70 V. Thus,

Figure 3 (a) Schematic illustration for selective nitrate reduction to ammonia. (b) LSV curves of Co_3O_4 @NiO HNTs in electrolyte with and without nitrate. (c) Potential-dependent Faradaic efficiency and selectivity of ammonia over Co_3O_4 @NiO HNTs. (d) The ammonia yield rate of consecutive recycling test at -0.70 V over Co_3O_4 @NiO HNTs. (e) The ammonia yield rate over Co_3O_4 @NiO HNTs in $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ electrolyte with and without NO_3^- . (f) DEMS measurements of Co_3O_4 @NiO HNTs for nitrate electroreduction.

we chose -0.70 V as the operation potential to further investigate the activity of $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs. The ammonia yield rate exhibited no evident decrease after six cycling tests (yield rate: $6.93 \text{ mmol h}^{-1} \text{ g}^{-1}$), implying the excellent stability of $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs (Fig. 3d). Moreover, the blank control experiment was performed in order to exclude the pollution of nitrogen-containing species from the external environment and/or catalyst. The ignorable ammonia was detected without the addition of nitrate in the electrolyte and the difference of ammonia yield rate with and without nitrate was very huge (Fig. 3e), confirming that the produced ammonia originated from nitrate electroreduction and external environment and/or catalyst exhibited no effect on ammonia quantification. Notably, the Faradaic efficiency and yield rate of ammonia were much higher than all the reported values of nitrogen electroreduction and among the best for the electroreduction of nitrate into ammonia (Table S1). In addition, online DEMS was employed for *in situ* detection of the molecular intermediate and product (Fig. 3f). The m/z signals of 30 and 17 corresponding to NO and NH_3 were detected upon the continuous cyclic test. This result proves NO as one of the intermediates during the nitrate electroreduction procedure, which is consistent with the previous report [38].

The electrocatalytic THIQs semi-dehydrogenation over the $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs anode was studied in a typical H-type electrolytic cell by adopting 1.0 mol L^{-1} KOH aqueous solution as the electrolyte (Fig. 4a). The 1,2,3,4-tetrahydroisoquinoline (**1a**) was selected as a model substrate. The current density dramatically increased with the presence of **1a**, indicating the more thermodynamically favorable **1a** semi-dehydrogenation compared with OER (Fig. 4b). To get insight into the reactive species for electrocatalytic semi-dehydrogenation of THIQs, *in situ* Raman spectroscopy was investigated. When the electrolyte was pure KOH solution, the potential-dependent *in situ* Raman spectra started to show two peaks of NiOOH centered at 472 and 553 cm^{-1} from 1.45 V [39] and their intensity increased gradually with the increase of the applied potentials (Fig. 4c). Meanwhile, the Raman peak of NiO (732 cm^{-1}) started to disappear from 1.45 V [40]. Note that the peaks of Co_3O_4 (482 , 521 and 691 cm^{-1}) maintained with the increase of the applied voltage [41]. Thus, time-dependent Raman spectra were tested at 1.45 V (Fig. 4d). The NiOOH peaks weakened gradually after adding **1a** and disappeared in about 10 s , and NiO appeared at the same time. The $\text{Ni}^{\text{III}}\text{-OOH}$ species on the surface of $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs could quickly capture the electrons from **1a** to form Ni^{II} , which

led to the disappearance of $\text{Ni}^{\text{III}}\text{-OOH}$. Thus, the formation of $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ redox served as the active species for THIQs semi-dehydrogenation [29,42,43]. $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs could drive a semi-dehydrogenation of **1a** with 98.0% selectivity. 6-methoxy-1,2,3,4-tetrahydroisoquinoline (**1b**) and 6-chloro-1,2,3,4-tetrahydroisoquinoline (**1c**) were converted to the corresponding DHIQs (**2b** and **2c**) with 95% and 98% selectivity, respectively, suggesting the good group tolerance of the semi-dehydrogenation of THIQs over $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs anode (Fig. 4e and Fig. S6).

A $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs || $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs two-electrode electrolyzer was constructed to simultaneously produce ammonia at the cathode and DHIQs at the anode (Fig. 5a). The current density in cathode and anode both increased in the two-electrode electrolyzer after the addition of **1a** (Fig. S7), indicating that the cell potential of the two-electrode system could be decreased after coupling the THIQs semi-dehydrogenation with nitrate reduction. As shown in Fig. 5b, the selectivity of ammonia and **2a** over the $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs || $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs two-electrode electrolyzer shows no apparent decline after three cycles (Ammonia: 53.0%, **2a**: 98.0%). Moreover, the morphology and crystalline structure of $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs after both cathode and anode tests remained well (Fig. S8). These results demonstrate the high activity and durability of the bifunctional $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs in the two-electrode electrolyzer.

CONCLUSIONS

In summary, a two-step self-template conversion method was developed for the synthesis of $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs with controlled spatial architecture and composition. In the first step, Co-Asp NWs were converted into Co-Asp@Ni-Asp HNWs via the cation-exchange reaction. Next, the Kirkendall effect induced the conversion from Co-Asp@Ni-Asp HNWs to $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs. The conversion mechanism was proved by characterizations on the intermediates. The as-obtained $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs exhibited high activity and stability toward both cathode nitrate electroreduction to ammonia (selectivity: 62.29%; Faradaic efficiency: 54.97%; yield rate: $6.93 \text{ mmol h}^{-1} \text{ g}^{-1}$) and anodic THIQs semi-dehydrogenation to DHIQs (selectivity: 98.0%). The combined results of online DEMS measurement and *in situ* Raman spectroscopy revealed the key intermediate for nitrate reduction and the active species for THIQs semi-dehydrogenation. Importantly, a $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs || $\text{Co}_3\text{O}_4@\text{NiO}$ HNTs two-electrode electrolyzer was constructed and simultaneously exhibited high selectivity and stability for both

Figure 4 (a) Schematic illustration for the electrocatalytic THIQs semi-dehydrogenation. (b) LSV curves of $\text{Co}_3\text{O}_4/\text{NiO}$ HNTs in 1.0 mol L^{-1} KOH solution with and without 0.5 mmol **1a**. (c) Potential-dependent *in situ* Raman spectra of $\text{Co}_3\text{O}_4/\text{NiO}$ HNTs. (d) *In situ* Raman spectra collected under chronoamperometry test in 0.1 mol L^{-1} KOH solution without **1a** (initial) and after the addition of **1a**. (e) Substrate scope of selective THIQs semi-dehydrogenation over $\text{Co}_3\text{O}_4/\text{NiO}$ HNTs.

Figure 5 (a) Schematic illustration for coupling **1a** semi-dehydrogenation with nitrate reduction in a $\text{Co}_3\text{O}_4/\text{NiO}$ HNTs || $\text{Co}_3\text{O}_4/\text{NiO}$ HNTs two-electrode cell. (b) Cycle-dependent selectivity of ammonia and **2a** in a $\text{Co}_3\text{O}_4/\text{NiO}$ HNTs || $\text{Co}_3\text{O}_4/\text{NiO}$ HNTs two-electrode cell at 2.0 V vs. CE.

electroreduction and electrooxidation reaction. This work offers a facile strategy to construct hierarchically structured electrocatalysts for integrating nitrate-to-ammonia reduction with the oxidative synthesis of value-added fine chemicals.

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Author contributions Yu Y and Liu C conceived and directed the project. Wang Y carried out the experiments and wrote the paper. Zhang B revised the paper. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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自模板法合成等级结构Co₃O₄@NiO双功能电极用于选择性硝酸根还原和四氢异喹啉类半脱氢

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摘要 等级中空结构的纳米材料具有丰富的活性位点和畅通的电子/物质传递通道, 因此在电催化领域具有广阔的应用前景. 从环保和节能的角度考虑, 电催化硝酸根还原合成铵具有重要意义. 高效电催化剂短缺, 以及动力学缓慢的阳极析氧反应, 严重限制了该技术的发展. 本论文发展了一种新颖的自模板转化法, 将无机有机杂化的钴基纳米棒成功转化为Co₃O₄纳米管@NiO多孔纳米片等级材料. 该材料在阴极硝酸根电还原为铵和阳极四氢异喹啉类半脱氢为二氢异喹啉类物质的反应中均表现出了优异的性能. 更重要的是, 合成的Co₃O₄@NiO等级纳米管还可作为双功能电极, 同时合成铵和二氢异喹啉化合物, 并具有良好的选择性和稳定性.