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High-efficiency electro-synthesis of ammonia with selective reduction of nitrite over an Ag nanoparticle-decorated TiO₂ nanoribbon array†

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Electrochemical nitrite (NO₂⁻) reduction can yield value-added ammonia (NH₃) while removing NO₂⁻ as an environmental pollutant in wastewater; however, it involves a six-electron transfer process and requires highly efficient and selective electrocatalysts. In this study, we report high-efficiency electro-synthesis of NH₃ via NO₂⁻ reduction enabled by an Ag nanoparticle-decorated TiO₂ nanoribbon array on a titanium plate (Ag@TiO₂/TP). When tested in 0.1 M NaOH containing 0.1 M NO₂⁻, such Ag@TiO₂/TP shows a large NH₃ yield of 514.3 μmol h⁻¹ cm⁻² and a high faradaic efficiency of 96.4% at -0.5 V vs. a reversible hydrogen electrode. Significantly, it also demonstrates excellent durability for 12 h electrolysis.

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Ammonia (NH₃) is widely applied to manufacture nitrogen fertilizers, explosives, chemical products, *etc.*, and it is also considered as an attractive hydrogen carrier and zero-carbon fuel.^{1–3} Although the Haber–Bosch method realizes industrial NH₃ synthesis from hydrogen and nitrogen under high temperature and high pressure, this process is highly energy-intensive and emits a mass of greenhouse gases.⁴ Electrochemical nitrogen reduction is thus deemed as a potential alternative to the Haber–Bosch process for ambient NH₃ synthesis, although the competitive hydrogen evolution reaction and unsatisfactory adsorption and cleavage effects of N₂ severely hinder the selectivity and activity of the electrochemical nitrogen reduction reaction.^{5–14}

NH₃ synthesis *via* electrochemical nitrite (NO₂⁻) reduction, in contrast, needs lower energy to cleave the N=O bond with faster reaction kinetics and achieves higher reaction substrate concentrations, leading to a larger NH₃ yield and higher faradaic efficiency (FE).^{1,15,16} In addition, excess NO₂⁻ accumulated in groundwater could destroy the ecological balance and harm human health.¹⁷ Electrochemical conversion of waste NO₂⁻ can produce value-added NH₃ under ambient conditions

and simultaneously remove NO₂⁻, which provides a solution for restoring the imbalance in the global nitrogen cycle. However, the electrochemical NO₂⁻ reduction reaction (NO₂⁻RR) involves a complex six-electron pathway with various possible by-products (N₂H₄, N₂, and H₂), thus requiring highly active catalysts for selective NO₂⁻-to-NH₃ conversion.^{18–27}

Noble metal (Au,²⁸ Pd,^{28,29} Ru,³⁰ Ir,³¹ Pt³²)-based catalysts are active for the NO₂⁻RR, but their scarcity hinders large-scale applications. Compared with the above noble metals, Ag is relatively low in price and high in abundance, and it also performs efficiently in NO₂⁻ reduction electrocatalysis.³³ As an Earth-abundant transition metal oxide with high chemical and structural stability, TiO₂ is widely used as a support to load noble metal nanoparticles for catalysis applications.^{34–39} Our recent studies also suggest that it is active for the NO₂⁻RR and its activity can be enhanced by introducing oxygen vacancies⁴⁰ and P doping.⁴¹ We believe that TiO₂ could be an ideal support for Ag nanoparticles for an enhanced NO₂⁻-to-NH₃ conversion performance with much less usage of noble metals, which, however, has not been reported to date.

In this study, we constructed an Ag nanoparticle-decorated TiO₂ nanoribbon array on a titanium plate (Ag@TiO₂/TP) as a highly selective NO₂⁻RR catalyst for NH₃ synthesis. When tested in NO₂⁻-containing solution, Ag@TiO₂/TP is capable of delivering a large NH₃ yield of 514.3 μmol h⁻¹ cm⁻² with a high FE of 96.4% at -0.5 V vs. a reversible hydrogen electrode (RHE). Furthermore, Ag@TiO₂/TP exhibits robust stability for long-term electrolysis.

As shown in Fig. 1a, Ag@TiO₂/TP was synthesized through a hydrothermal method in an alkaline solution, Ag⁺ exchange,

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Fig. 1 (a) Schematic illustration of the fabrication process of Ag@TiO₂/TP. (b) XRD pattern and (c) and (d) SEM images of Ag@TiO₂/TP. (e) SEM and corresponding elemental mapping images of Ag@TiO₂/TP. (f) TEM and (g) HRTEM images of Ag@TiO₂.

and an annealing process under an Ar/H₂ atmosphere (see the ESI† for details). Fig. 1b depicts the X-ray diffraction (XRD) pattern of Ag@TiO₂/TP. The diffraction peaks at 38.15°, 44.30°, 64.43°, and 77.50° correspond to the (111), (200), (220), and (311) lattice planes of Ag, respectively (JCPDS No. 04-0783),³³ while the other diffraction peaks can be assigned to metallic Ti (JCPDS No. 44-1294) and TiO₂ (JCPDS No. 21-1272), and these are in accordance with those for TiO₂/TP (Fig. S1†). As depicted in Fig. S2 and S3,† the scanning electron microscopy (SEM) images show that the TiO₂ nanoribbon array was grown on TP. With regard to Ag@TiO₂/TP, plenty of nanoparticles are decorated on the surface of the TiO₂ nanoribbon (Fig. 1c and d). Additionally, the SEM image and corresponding energy-dispersive X-ray (EDX) elemental mapping images of Ag@TiO₂/TP confirm the existence of Ag, Ti, and O elements with a homogeneous distribution (Fig. 1e). Furthermore, the result of the EDX spectrum confirms that the Ag content in Ag@TiO₂/TP is approximately 13.63% (Fig. S4†). The transmission electron microscopy (TEM) image also provides evidence of the formation of a large number of nanoparticles without agglomeration on the nanoribbon, as shown in Fig. 1f. A high-resolution TEM (HRTEM) image taken from one such nanoparticle displays a lattice spacing of 0.236 nm indexed to the (111) plane of Ag (Fig. 1g). All these observations confirm the successful fabrication of an Ag nanoparticle-decorated TiO₂ nanoribbon array.

The X-ray photoelectron spectroscopy (XPS) survey spectrum (Fig. 2a) also shows the presence of Ag, O, and Ti elements. The Ag 3d region spectrum (Fig. 2b) is divided into two peaks at 368.28 and 374.28 eV, which are ascribed to Ag 3d_{5/2} and Ag 3d_{3/2}, respectively.^{42,43} In the Ti 2p spectrum, two fitting peaks at 459.38 and 465.08 eV are assigned to Ti 2p_{3/2} and Ti 2p_{1/2}, respectively (Fig. 2c).^{44,45} In addition, two fitting peaks in the O 1s spectrum are attributed to metal–oxygen bonds (M–O,

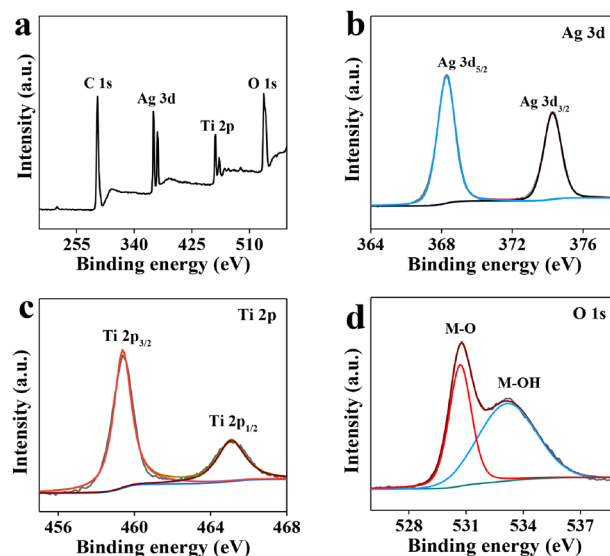


Fig. 2 (a) XPS survey spectrum, and high resolution XPS spectra in the (b) Ag 3d, (c) Ti 2p, and (d) O 1s regions of Ag@TiO₂.

530.78 eV) and adsorbed surface hydroxyl groups (M–OH, 533.18 eV) (Fig. 2d).^{42,45}

The electrochemical experiments of Ag@TiO₂/TP, Ag/TP, and TiO₂/TP toward the NO₂[−]RR were implemented in Ar-saturated NO₂[−]-free and NO₂[−]-containing 0.1 M NaOH electrolytes. UV-vis spectra and related calibration curves are depicted in Fig. S5 and S6.† Linear scanning voltammetry (LSV) of Ag@TiO₂/TP was firstly conducted. Obviously, a markedly enhanced current density (*j*) emerges upon the addition of NO₂[−] (Fig. 3a), verifying that Ag@TiO₂/TP enables efficient NO₂[−] reduction. In comparison, Ag/TP and TiO₂/TP display lower *j* with NO₂[−]-containing electrolytes (Fig. S7†), confirming that the electrocatalytic NO₂[−]RR activity of Ag@TiO₂/TP is superior to those of Ag/TP

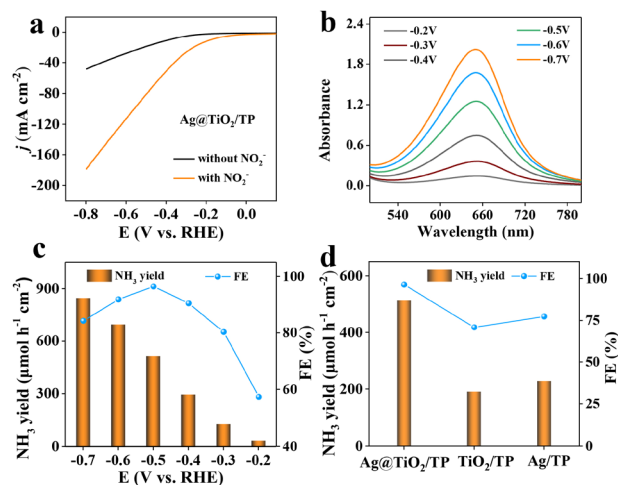


Fig. 3 (a) LSV curves of Ag@TiO₂/TP in 0.1 M NaOH with/without 0.1 M NO₂[−]. (b) UV-vis spectra of Ag@TiO₂/TP at various potentials. (c) NH₃ yields and FEs of Ag@TiO₂/TP at various potentials. (d) Comparison of NH₃ yields and FEs of Ag@TiO₂/TP, TiO₂/TP, and Ag/TP at −0.5 V.

and TiO₂/TP. Chronoamperometry (CA) measurements at given potentials (from -0.2 V to -0.7 V) were then executed to study the NH₃-generation ability of Ag@TiO₂/TP (Fig. S8†), where the peak intensity of the relevant UV-vis spectra strengthens with an increase in the given potential (Fig. 3b), manifesting that a more negative potential results in more NH₃. Furthermore, we evaluated NH₃ FEs and yields of Ag@TiO₂/TP in test windows (Fig. 3c). Noticeably, as the cathode potential negatively shifts, the NH₃ yields of Ag@TiO₂/TP progressively increase, and eventually the largest value of 846.3 μmol h⁻¹ cm⁻² (14 387.1 μg h⁻¹ cm⁻²) at -0.7 V is obtained. Furthermore, the maximum FE of NH₃ production is 96.4% at -0.5 V with an NH₃ yield of 514.3 μmol h⁻¹ cm⁻² (8743.1 μg h⁻¹ cm⁻²), confirming an excellent NO₂⁻RR electrocatalyst. The NH₃ yields and FEs of Ag@TiO₂/TP exceed those of most reported NO₂⁻RR electrocatalysts (Table S1†). As shown in Fig. 3d, Ag@TiO₂/TP exhibits a much better performance than Ag/TP (77.38%, 228.5 μmol h⁻¹ cm⁻²) and TiO₂/TP (70.8%, 190.9 μmol h⁻¹ cm⁻²).

The NO₂⁻ reduction process of Ag@TiO₂/TP was further assessed by quantifying various by-products (N₂H₄, H₂, and N₂). As exhibited in Fig. S9,† no N₂H₄ signals were monitored as was proved by identical UV-vis absorption spectral peaks at different potentials. Meanwhile, traces of H₂ and N₂ were detected (Fig. 4a) with the maximal H₂ and N₂ yields being 2.82 μmol h⁻¹ cm⁻² and 1.85 μmol h⁻¹ cm⁻², with FEs of 4.9% and 1.42%, respectively, much lower than that of NH₃ at every

potential, verifying the superb selectivity of such Ag@TiO₂/TP electrocatalysts for NH₃ synthesis. Furthermore, the partial current densities (j_{partial}) of Ag@TiO₂/TP for NH₃ reach -122.1 mA cm⁻² at -0.7 V, clearly higher than that of H₂ (-4.1 mA cm⁻²) and N₂ (-1.04 mA cm⁻²) (Fig. 4b), again proving great NO₂⁻RR selectivity towards NH₃ electrosynthesis. Control experiments were then performed to determine whether the synthesized NH₃ just comes from the NO₂⁻RR on Ag@TiO₂/TP. It is clearly seen that the amounts of NH₃ generated after 1 h of electrolysis in a blank solution (0.29 μg) and open circuit potential (OCP, 0.66 μg) are extremely small (Fig. S10†), which excludes possible interference factors from the electrolytic solution and device.

Six alternative-cycle measurements were then carried out in NO₂⁻-free/NO₂⁻-containing electrolytes at -0.5 V, and NH₃ only is generated in NO₂⁻-containing electrolytes (Fig. 4c), demonstrating that NH₃ just originates from NO₂⁻ via the NO₂⁻RR on Ag@TiO₂/TP. Additionally, stability is an extremely important parameter of the NO₂⁻RR process for NH₃ synthesis. We thus implemented a 12 h electrolysis test, as displayed in Fig. 4d, and the Ag@TiO₂/TP electrode maintained an initial j of nearly 100% with almost no fluctuation, confirming the excellent tolerance of our catalyst. Furthermore, we carried out 8 consecutive measurements on Ag@TiO₂/TP at -0.5 V, and the volatility of NH₃ yields and FEs was negligible, again proving the durability of Ag@TiO₂/TP (Fig. 4e and S11†), which is also in good accordance with the LSV curve (Fig. S12†), XRD pattern (Fig. S13†), and SEM images (Fig. S14†) of Ag@TiO₂/TP after long-term electrolysis. These results suggest that Ag@TiO₂/TP has excellent stability for the electrocatalytic reduction of NO₂⁻ to NH₃.

In summary, a Ag nanoparticle-decorated TiO₂ nanoribbon array is proved to be an efficient and stable NO₂⁻RR catalyst for NO₂⁻-to-NH₃ conversion in an alkaline electrolyte, producing a remarkable NH₃ yield of 8743.1 μg h⁻¹ cm⁻² with a large FE of 96.4%. This study not only offers a highly selective electrocatalyst for ambient NH₃ synthesis via NO₂⁻ reduction, but also opens up a new avenue to construct a nanostructured Ag/TiO₂ hybrid array for applications.

Conflicts of interest

There are no conflicts to declare.

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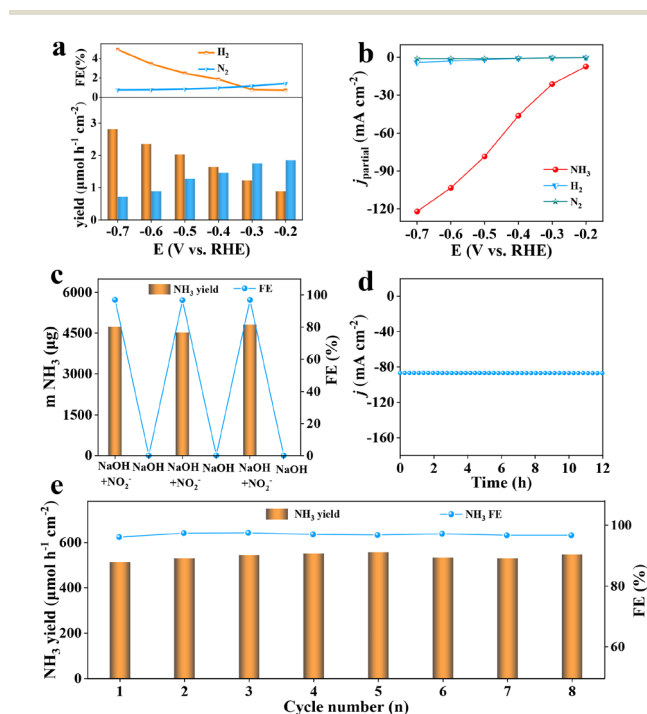


Fig. 4 (a) Yields and FEs of N₂ and H₂ of Ag@TiO₂/TP at different potentials. (b) j_{partial} of NH₃, N₂, and H₂ of Ag@TiO₂/TP at different potentials. (c) NH₃ yields and FEs of Ag@TiO₂/TP during the alternating cycling tests. (d) Time-dependent current density curve during 12 h electrolysis of Ag@TiO₂/TP at -0.5 V. (e) Recycling tests of Ag@TiO₂/TP at -0.5 V.

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