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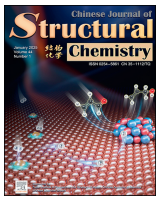

News&Views

Electrosynthesis of hydroxylamine from earth-abundant small molecules

With the rapid evolution of contemporary society, there is an increasing demand for the production of bulk chemicals such as fertilizers, fuels, and pharmaceuticals. However, current synthetic approaches for these bulk chemicals predominantly depend on conventional fossil fuel-based chemical refining processes. This dependence poses a substantial challenge to both environmental sustainability and energy resources [1]. An example of this issue is the synthesis of hydroxylamine (NH_2OH).

As a highly reactive nitrogenous feedstock, NH_2OH has been extensively employed in the synthesis of nitrogen-containing compounds across various fields, including chemical, agrochemical and pharmaceutical industries [2]. The conventional synthesis of NH_2OH typically necessitates the use of highly corrosive and polluting sulfur dioxide as a reducing agent, leading to the generation of a substantial quantity of by-products ($(NH_4)_2SO_4$) [3]. Alternative methods, such as the nitric oxide (NO) and nitric acid (HNO_3) reduction techniques, involve the utilization of precious metals like Pt and Pd as the catalysts [3]. These approaches also entail the use of H_2 as both a reducing agent and hydrogen source. Consequently, not only are these strategies expensive but they also result in significant carbon emissions during production.

In light of these challenges, researchers have explored the direct synthesis of NH_2OH using simpler feedstocks. Among the emerging synthetic pathways, two attractive directions are plasma synthesis and electrochemical synthesis [4]. These methods employ earth-abundant small molecules (e.g., air and H_2O) as feedstocks and harness electricity to drive the reactions, thereby reducing reliance on traditional energy-intensive feedstocks and minimizing the negative impact on the environment. Nevertheless, the practical application of such approaches faces significant hurdles. For instance, the direct synthesis of NH_2OH from N_2 poses challenges due to the low reactivity and high energy consumption required by N_2 [4]. Additionally, the selection of catalysts and the control of reaction conditions during the synthesis need further research and optimization.

Writing in *Nature Sustainability*, Zeng's team has proposed a new model of plasma-electrochemical cascade catalysis for the green and sustainable synthesis of NH_2OH at ambient temperature and pressure, using air and H_2O as the reactants and electrical energy as the driving force [5]. Initially, the plasma nitrogen fixation strategy was employed to produce HNO_3 solution by activating air into nitrogen oxides (NO_x) through high-pressure plasma discharge, with water serving as the NO_x absorber. Subsequently, the HNO_3 solution was subjected to cathodic selective reduction to produce NH_2OH, utilizing a novel bismuth-based catalyst. The reaction process and its advantages are depicted in Fig. 1(a).

The efficient activation and conversion of nitrogen molecules is a prerequisite for the resourceful use of nitrogen species. Inspired by the natural phenomenon of "thunderstorm crop", researchers have developed a plasma-parallel arc discharge device capable of producing HNO_3 solution with a concentration as high as 120.1 mM. Following this, the team employed bismuth nanoparticles loaded on carbon fibre paper (Bi film/CFP, Fig. 1(b)) as the catalyst for electrocatalytic reduction of HNO_3 to NH_2OH. The Bi film/CFP demonstrates a faradaic efficiency (FE) of 81% for NH_2OH, with product selectivity exceeding 96%. At −1.2 V *vs.* RHE, the yield rate for NH_2OH using Bi film/CFP is as high as 713.1 μmol cm^{-2} h^{-1} (Fig. 1(c)). As illustrated in Fig. 1(d), following 12 cycles of stabilisation, the electrolyte was collected, purified, and concentrated for crystallisation, resulting in the production of 1.887 g of high-purity hydroxylamine sulphate ($2NH_2OH{\cdot}H_2SO_4$). The analysis of reaction pathways reveals that the key to NH_2OH preparation lies in the adsorption of $*NH_2OH$ on the catalyst surface. Specifically, when $*NH_2OH$ exhibits weak adsorption on the catalyst surface, it can be desorbed directly to obtain the free state NH_2OH. Conversely, strong adsorption of $*NH_2OH$ on the catalyst will result in further proton-coupled electron transfer, leading to the formation of deep-reduction product NH_3. Density-functional theory (DFT) calculations indicate that an easier desorption accompanied by a more difficult dissociation of $*NH_2OH$ accounts for the selective generation of NH_2OH on the Bi (012) surface relative to other metal surfaces.

It is noteworthy that the work combined plasma discharge with electroreduction processes, resulting in the sustainable synthesis of NH_2OH from ambient air and H_2O. The proposed mechanism not only mitigates the energy consumption problem during NH_2OH electrosynthesis but also reduces the emission of NO_x. Furthermore, it provides an important scientific reference for the renewable electrosynthesis of NH_2OH and other nitrogen-containing compounds. Nevertheless, the large-scale synthesis of HNO_3 plasma continues to present significant challenges, including high energy consumption and low air conversion efficiency. In particular, the key to industrialisation is the further realisation of high-concentration HNO_3, the advancement of scale-up and low-cost preparation of catalytic electrodes, and the rational construction of reactive electrostack.

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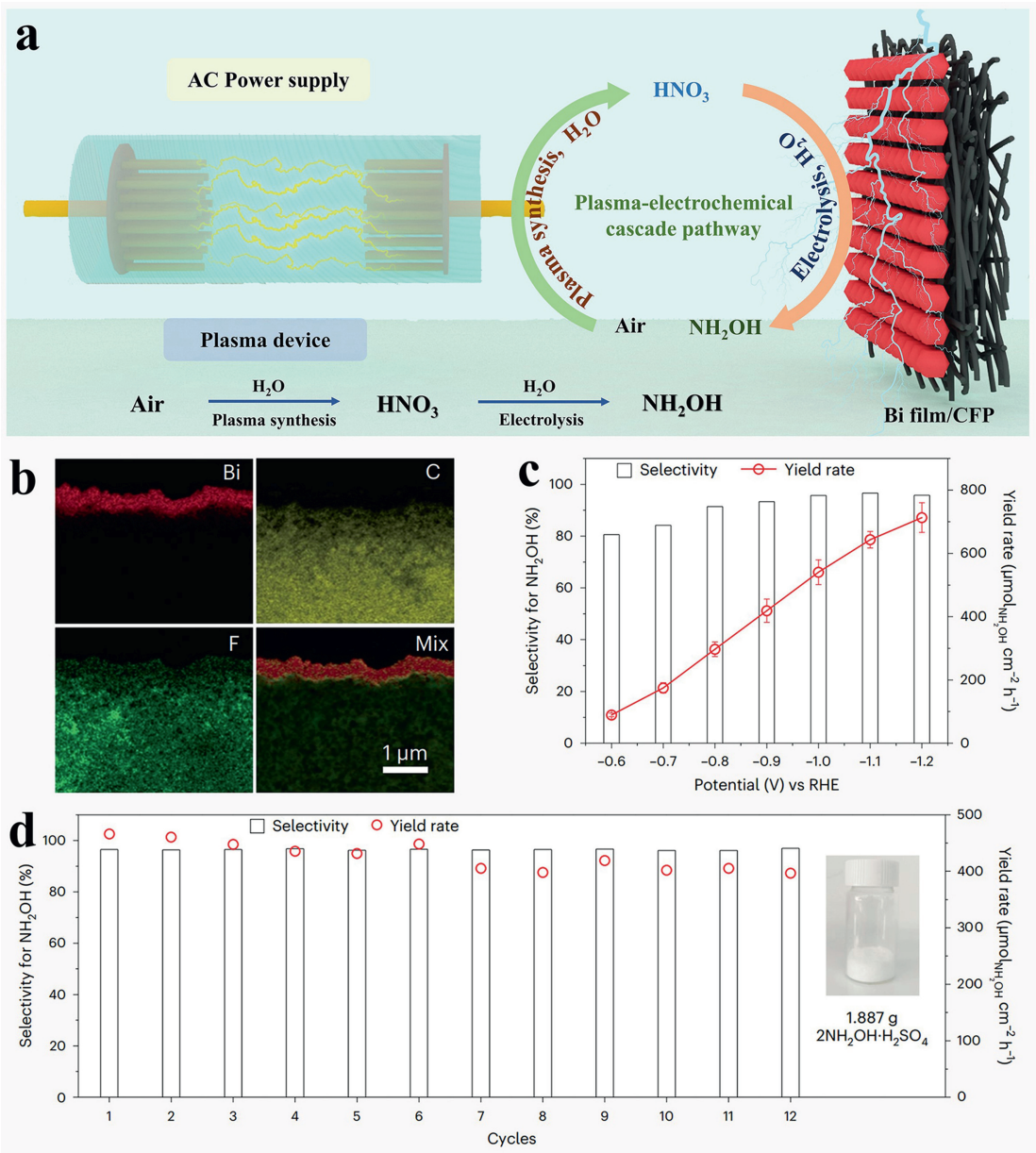

Fig. 1. (a) Schematic illustration of the synthetic pathways for NH_2OH production: the sustainable plasma-electrochemical cascade pathway from ambient air and H_2O. (b) Energy-dispersive X-ray elemental mapping images of the crosssectional Bi film/CFP. (c) The selectivity and yield rate for NH_2OH in NO_3^- electroreduction using Bi film/CFP. Experimental data were acquired via a 1 h chronoamperometry test at various applied potentials in 0.5 M H_2SO_4 and 0.1 M plasma-generated HNO_3. (d) Cyclic stability test in NO_3^- electroreduction using Bi film/CFP for each cycle for a 5 h continuous electrolysis. Inset: solid $2NH_2OH{\cdot}H_2SO_4$ product separated after 12 cyclic tests. Figure (b, c and d) panels reproduced from Ref. [5] with permission. Copyright 2023, Springer Nature.

CRediT authorship contribution statement

Wen-Bo Wei: Writing – original draft, Investigation. **Qi-Long Zhu:** Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors state that there is not any conflict of interests for this paper.

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