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Article

Commercial indium-tin oxide glass: A catalyst electrode for efficient N₂ reduction at ambient conditions

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ABSTRACT

The typical Haber technical process for industrial NH₃ production involves plenty of energy-consumption and large quantities of greenhouse gas emission. In contrast, electrochemical N₂ reduction proffers environment-friendly and energy-efficient avenues to synthesize NH₃ at mild conditions but demands efficient electrocatalysts for the N₂ reduction reaction (NRR). Herein we report for the first time that commercial indium-tin oxide glass (ITO/G) can be used as a catalyst electrode toward artificial N₂ fixation, as it demonstrates excellent selectivity at mild conditions. Such ITO/G delivers excellent NRR performance with a NH₃ yield of 1.06×10^{-10} mol s⁻¹ cm⁻² and a faradaic efficiency of 6.17% at -0.40 V versus the reversible hydrogen electrode (RHE) in 0.5 M LiClO₄. Furthermore, the ITO/G also possesses good electrochemical stability and durability. Finally, the possible reaction mechanism for the NRR on the ITO catalysts was explored using first-principles calculations.

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1. Introduction

NH₃ is considered as an essential activated nitrogen source that facilitates the production of dyes, resins, fertilizers, medicaments, etc, and helps the transportation sector in the form of an attractive carbon-free energy carrier [1,2]. Whereas, the use of famous Haber-Bosch's major bottleneck is energy consumption and carbon emissions [3]. Consequently, devel-

oping an energy-saving and robust NH₃-production technique is crucial to solving this problem.

Electrochemical N₂ reduction has come forth as a replaceable approach for ambient N₂ fixation conversion utilizing water as the hydrogen source and efficient electrocatalysts that can efficiently decrease the large activation barrier of N≡N and promote its dissociation for the N₂ reduction reaction (NRR) [4–6]. Catalysts on the basis of precious metals (Au [7,8], Ag [9],

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Pd [10–12], and Ru [13,14]) are efficient NRR catalysts, but the scarce reserves and high cost of such catalysts impede their practical application. Hence, high-efficiency and cost-effective electrocatalysts have been explored as propitious alternatives [15–40]. Recent work shows that SnO₂ is active for ambient electrocatalytic N₂ reduction [41,42], but its low conductivity limits the NRR performance. This issue has been fixed via fluorine doping [43] and graphene hybridization [44]. Indium-tin oxide (ITO) is widely applied as an electrode for catalyst loading [45–47] due to its high conductivity. Although it may be an efficient electrocatalyst for NRR, it has yet to be explored.

In this report, we describe our latest experimental verification that commercial ITO glass (ITO/G) can be directly utilized as a catalyst electrode for efficient N₂ electrocatalytic reduction to NH₃. The ITO/G exhibits excellent electrocatalytic N₂ reduction performance, which provides a NH₃ yield of 1.06×10^{-10} mol s⁻¹ cm⁻² (6.51 μg h⁻¹ cm⁻²) and a superior faradaic efficiency (FE) of 6.17% at -0.40 V against the reversible hydrogen electrode (RHE) in 0.5 M LiClO₄. Especially, it also exhibits high electrochemical and structural durability. The possible reaction mechanism for NRR on the ITO catalyst was investigated using first-principles calculations on account of the density functional theory (DFT).

2. Experimental

2.1. Materials

Ammonium chloride (NH₄Cl), LiClO₄, hydrazine hydrate (N₂H₄·H₂O), sodium hypochlorite (NaClO), sodium hydroxide (NaOH), sodium salicylate (C₇H₅O₃Na), ethanol (CH₃CH₂OH), and carbon paper were originated from Beijing Chemical Corporation. Para-(dimethylamino) benzaldehyde (C₉H₁₁NO), sodium nitroferricyanide (III) dihydrate (Na₂Fe(CN)₅NO·2H₂O), and Nafion were bought from Aladdin Ltd.. The Indium-tin-oxide glass was acquired from Luoyang Shangzhao Technology Co. Ltd. (Henan, China).

2.2. Characterizations

X-ray diffraction (XRD) patterns were collected on LabX XRD-6100 X-ray diffractometer, using Cu K_α radiation (SHIMADZU, Japan). Scanning electron microscopy (SEM) measurements were taken using an XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. X-ray photoelectron spectroscopy (XPS) data were performed using an ESCALABMK II X-ray photoelectron spectrometer employing Mg as the source. Ultraviolet-Visible (UV-Vis) absorption spectra were measured on a SHIMADZU UV-1800 UV-Vis spectrophotometer.

2.3. Electrochemical measurements

The electrochemical performance measurements were performed in a H-type cell separated with a standard three-electrode system on a CHI 660E electrochemical analyzer. In terms of electrochemical N₂ reduction, electrolyte was

purged with N₂ for half an hour before conducting the chronopotentiometry tests.

2.4. NH₃ determination

The content of generated product was spectrophotometrically evaluated using the previously reported indophenol blue method [48]. The A solution was composed of NaClO (pCl = 4–4.9) and NaOH (0.75 M). And B solution was prepared including of 320 mM NaOH and 400 mM C₇H₅O₃Na. The C solution was 1 wt% Na₂[Fe(CN)₅NO]. Generally, 4 mL cathodic electrolyte after reaction was added with A solution (50 μL), B solution (500 μL), and C solution (50 μL) in turn and keep it for one hour. Absorbance measuring values were exhibited at λ = 650 nm. A series of standard NH₄⁺ solution with various concentrations were utilized to calibrate the concentration-absorbance curve.

2.5. N₂H₄ measurement

N₂H₄ was reckoned by the method of the reported literature [49]. In detail, we prepared a series of N₂H₄ solutions of generally known concentrations as standards. Secondly, we added 5 mL of the color reagent to above N₂H₄ solution, separately, and allowed it to stand for 20 min at ambient environment. Finally, the absorbance of the electrolyte was revealed at 460 nm. As a result, the obtained fitting regression equation presents a good linear relation ($y = 0.197x + 0.054$, $R^2 = 0.999$) through conducting the independent experiment in triplicate.

3. Results and discussion

Fig. 1(a) shows the XRD pattern for the ITO/G, the diffraction peaks at 21.5°, 30.2°, 35.0°, 37.7°, 50.4°, and 60.0° are indexed to the (211), (222), (400), (411), (440), and (622) planes for the In₂O₃ (JCPDS No. 04-0416). Notably, no pattern is ascribed to SnO₂, which is in accordance with a previous study [50]. The SEM images show a well-defined nanofilm morphology (Fig. 1(b) and Fig. 1(c)). The energy-dispersive X-ray (EDX)

Fig. 1. (a) XRD pattern of ITO/G; (b,c) SEM images of ITO/G; (d) SEM and corresponding EDX elemental mapping images of In, Sn, and O elements for ITO/G.

spectrum of the ITO/G (Fig. S1) reveals the existence of In, Sn, and O elements with the atomic ratios of 32.11:3.16:64.74. SEM and corresponding EDX elemental mapping spectra (Fig. 1(d)) further indicate the uniformly dispersion of In, Sn, and O elements on the thin film. The side-view SEM image (Fig. S2) shows that the thickness of the ITO layer is about 267 nm.

Fig. 2(a) shows the XPS analysis of ITO/G, identifying the presence of In, Sn, and O elements. XPS spectrum for In 3d illustrated in Fig. 2(b) presents two major peaks centered at binding energies (BEs) of 444.3 and 451.8 eV, assignable to In 3d_{5/2} and In 3d_{3/2}, respectively, which is feature of In³⁺ in the In₂O₃ phases [51]. Additionally, there are two satellites peaks at 445.3 and 452.9 eV. In the Sn 3d region (Fig. 2(c)), the peaks at BEs of 486.3 and 494.8 eV which match Sn 3d_{5/2} and Sn 3d_{3/2}, respectively, show the Sn⁴⁺ in the SnO₂ phases [52]. For the O 1s region (Fig. 2(d)), the peaks at 529.9 and 531 eV are ascribed to In-O and Sn-O, respectively [52]. The higher binding energy at 532.1 eV is associated with the oxygen of the free hydroxyl group, which is perchance attributable to the water molecules absorbed on the surface.

All electrochemical measurements of ITO/G were tested in a LiClO₄ electrolyte (0.5 M) utilizing a two-compartment cell. The desired product of ammonia was spectrophotometrically assessed [48] and the existence of possible by-products (N₂H₄) was ensured [49]. Fig. S3 and Fig. S4 provide corresponding calibration curves. Fig. 3(a) displays the linear sweep voltammetry (LSV) curves of ITO/G. An evident augmentation in current density can be monitored in the N₂-saturated solution, evidencing effective N₂ electroreduction. The chronoamperometry curves display a stable current density for 2 h in a range of potentials from −0.30 to −0.50 V (Fig. 3(b)). After 2 h electrolysis, these electrolytes, which were stained with an indophenol indicator, were measured (Fig. 3(c)), connoting the NRR process can carry. Fig. 3(d) displays the NH₃ yields and FEs of the ITO/G. As observed, the ITO/G offered a large NH₃ yield of 1.06 × 10^{−10} mol s^{−1} cm^{−2} (6.51 μg h^{−1} cm^{−2}) as well as an attractive FE of 6.17% at −0.40 V, defeating the great mass of NRR catalysts in

Fig. 3. (a) LSV curves of ITO/G in Ar- and N₂-saturated 0.5 M LiClO₄ with a scan rate of 2 mV s^{−1}; (b) Chronoamperometry curves of ITO/G at various potentials for 2 h; (c) UV-Vis absorption spectra of the electrolytes colored with indophenol indicator; (d) Corresponding NH₃ yields and FEs for ITO/G at all potentials.

a neutral electrolyte (Table S1). Due to the hydrogen evolution reaction, both NH₃ yield and FE decrease with the continuous increase of the negative potential [53,54]. In addition, N₂H₄ was not discovered in the electrolytes after an electrocatalytic reaction at −0.40 V (Fig. S5), implying that the ITO/G has outstanding selectivity for NH₃ accumulation. The NRR performance of the ITO/G treated with HCl and Zn powder, suggesting it still shows good NRR performance (Fig. S6). The NRR performance of the ITO/G sourced from another company was also studied under the same ambient conditions. As shown in Fig. S7, this ITO/G is also capable of effectively catalyzing the NRR. Notably, the In-to-Sn ratio, although not controlled in the commercial ITO glass, may affect the catalytic performances, which is an interesting topic for future work.

For verifying that the source of NH₃ derives from the N₂ electroreduction of the ITO/G, two comparative trials were carried. The result indicates no NH₃ formation in either case (Fig. 4(a)). As observed in Fig. 4(b), NH₃ is solely resultant in the N₂-saturated solution. Additionally, ¹⁵N isotopic labeling experiment was conducted. Fig. S8 indicate that the got NH₃ was formed through N₂ electrocatalysis by the ITO/G.

Invariability is another critical criterion for valuating the performance of electrocatalysts. As such, the duration of continuous six cycling tests were operated in the N₂-saturated electrolyte. As observed in Fig. S9 and Fig. 4(c), both the NH₃ yields and FEs were well retained. The chronoamperometry curve of ITO/G at −0.40 V for 24 h reveals a trifling decline in current density (Fig. S10). The NRR performance of post-NRR ITO/G was tested. As shown in Fig. 4(d) and Fig. S11, apparent decline in NH₃ yield and corresponding FE did not emerge, further indicating that the ITO/G still sustains excellent stability after long-term electrolysis. Almost no ammonia was detected in the anodic solutions stained with the indophenol indicator (Fig. S12). Moreover, the pH value of the LiClO₄ aqueous solution before and after electrocatalytic NRR hardly changed significantly as shown in Fig. S13. In addition, XRD (Fig. 5(a)),

Fig. 2. (a) XPS survey spectrum for ITO/G; XPS spectra of ITO/G in the In 3d (b), Sn 3d (c), and O 1s (d) regions.

Fig. 4. (a) UV-Vis absorption spectra of the electrolytes stained with indophenol indicator at -0.40 V under different electrochemical conditions using ITO/G; (b) NH_3 yields and FEs of ITO/G at -0.40 V with alternating at the interval of 2 h cycles between Ar-saturated and N_2 -saturated electrolytes; (c) Cycling stability over ITO/G at -0.40 V; (d) NH_3 yields and FEs at -0.40 V for 2 h over initial ITO/G and ITO/G subjected to 24 h operation.

SEM (Fig. 5(b)) and EDX (Fig. S14) data of post-NRR ITO/G show that the ITO/G has high structural stability. Electrochemical impedance spectroscopy analysis (Fig. S15) shows that ITO/G has good electrical conductivity.

First-principles calculations at the DFT level were performed. The computational details for such are presented in Supporting Information. The ITO (400) surfaces were investigated, which are the most abundant according to the XRD pattern in Fig. 1(a). The atomic models of the ITO (400) surface are presented in Fig. S16, built according to Ref. [55]. Our calculation results indicate that the NRR active site on the ITO (400) surface is the In atom neighboring the doped Sn atom, and in certain reaction steps the Sn atom also participates in the intermediate binding. NRR has several pathways based on the specific adsorption modes of nitrogen molecules [56,57]. As for the end-on adsorption of N_2 herein, NRR may occur following the alternating or distal mechanism. In the case of alternating pathway, the two N atoms are alternately reduced to produce NH_3 by the electron-proton pair, while the electron-proton pair attack the distal N atom to produce the first NH_3 , followed by the reduction of the second N atom in the detail pathway. The free energy profiles of the reaction intermediates via alternating and distal mechanisms and corresponding adsorption sites on ITO(400) surfaces are given in Fig. 6 and Fig. S17. The initial N_2 adsorption requires a free energy input only of 0.39 eV, suggesting the favorable N_2 capture. In the following hydrogenation process, only the steps of $\text{*N-N} \rightarrow \text{*N-NH}$ and $\text{*N-NH} \rightarrow \text{*NH-NH}$ show free energy uphill by 1.18 and 0.1 eV, respectively. Though the second NH_3 desorption needs 0.4 eV free energy, the adsorption site should be renewed energetically because the released free energy in previous reaction processes (1.12 eV) can sufficiently compensate the needed free energy input. Thus, the potential-determining step is determined as the first hydrogenation step with a 1.18 eV free energy uphill in both pathway. In the second hydrogenation step, the free en-

Fig. 5. (a) XRD pattern and (b) SEM images of ITO/G after stability test.

Fig. 6. Free energy (in eV) diagrams and the local atomic structures of the reaction intermediates for the NRR on the ITO (400) surface through the alternating pathway. The blue, green, pink, red, and grey spheres represent the N, H, In, O, and Sn atoms, respectively.

ergy uphill of the distal pathway (0.26 eV) (Fig. S17) is much higher than that of the alternating pathway (0.1 eV). Therefore, it is proposed that the alternating pathway rather than the distal pathway is preferred for NRR on the ITO (400) surface.

4. Conclusion

In summary, commercial ITO glass has been proposed as an effective catalyst electrode to convert N_2 into NH_3 under ambient environments. In 0.5 M LiClO_4 , the FE and NH_3 yield rate can reach 6.17% and 1.06×10^{-10} mol s⁻¹ cm⁻² ($6.51 \mu\text{g h}^{-1}$ cm⁻²) at -0.40 V, respectively. Notably, the ITO film preserves high electrochemical stability after NRR electrolysis. The result described here not only supplies us an effective earth-abundant electrocatalyst for ambient NRR but also identifies an exhilarating new means in the development of ITO-based nanostructures for artificial N_2 -fixing applications.

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Graphical Abstract

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Commercial indium-tin oxide glass: A catalyst electrode for efficient N₂ reduction at ambient conditions

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Commercial indium-tin oxide glass acts as an efficient electrocatalyst for the conversion of N₂ to NH₃ in 0.5 M LiClO₄, achieving a large NH₃ yield of 1.06×10^{-10} mol s⁻¹ cm⁻² and a high FE of 6.17%.

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商用氧化铟锡玻璃：室温高效还原氮气的催化剂电极

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摘要: NH₃作为一种必需的活化氮源,在化肥、染料、爆炸物和药物等的制造中起到了关键作用;同时,它也是一种在交通运输领域具有吸引力的无碳能源载体.工业上生产氨气使用典型的哈伯-博世工艺,但是此工艺涉及大量的能源消耗和碳排放,给环境带来巨大的压力.电化学氮还原反应(NRR)能够在温和环境下实现环境友好、节能的氨合成,但此过程需要高效的电催化剂.高效的NRR催化剂(Au、Ag、Pd和Ru)储量少、成本高,阻碍了它的实际应用.因此,设计和开发由地球上丰富的元素制成的具有成本效益的催化剂来代替NRR催化剂意义重大.本课题组最近的研究(*Chem. Commun.*, **2018**, 54, 12966–12969)表明,SnO₂在环境条件下具有电催化氧化活性,但其低电导率限制了其性能,可通过氟掺杂或石墨烯杂化予以解决.氧化铟锡(ITO)作为一种含SnO₂的材料,导电性好,可望用于NRR的高效电催化剂中.因此,本文采用商用氧化铟锡玻璃(ITO/G)作为催化剂电极,在温和环境条件下进行N₂-NH₃的电化学转化,并呈现出对生成氨气有较高的选择性.XRD和XPS结果表明,商用ITO/G中存在In、Sn和O元素;SEM显示ITO/G具有清晰的纳米薄膜结构和267 nm的截面厚度;相应的EDX谱图显示In、Sn和O元素分布均匀,且原子比为32.11:3.16:64.74.采用紫外-可见光谱及线性扫描伏安和恒电位极化等电化学测试研究了商用ITO/G的NRR活性.在0.5 M LiClO₄电解液中测试时,于−0.40 V vs. RHE条件下,ITO/G的NH₃产率为1.06 × 10^{−10} mol s^{−1} cm^{−2},其法拉第效率为6.17%.¹⁵N同位素标记实验证实了所测到的NH₃是由ITO/G催化的N₂电还原反应生成的.利用第一性原理计算探讨了在ITO催化剂上可能的NRR反应机理,确定了ITO催化剂的NRR活性位点、N₂化学吸附活性位点以及NRR的反应途径.此外,24 h恒电位(−0.40 V vs. RHE)极化测试和2 h恒电位极化(−0.40 V vs. RHE)测试后的XRD和SEM结果表明,该催化剂具有较高的电化学稳定性.综上所述,商用ITO/G用作在环境条件下将N₂转化为NH₃的有效催化剂电极,将为开发人工固定氮气的ITO基纳米结构提供一种研究途径.

关键词: N₂还原反应; NH₃; 铟-锡氧化物; 电催化剂; 环境条件; 密度泛函理论

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