Nickel antimony oxide (NiSb$_2$O$_6$) nanofibers: amorphization and electrocatalytic nitrogen fixation under ambient conditions

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Abstract. Electrocatalytic Nitrogen Reduction (NRR) under ambient conditions is a potential alternative artificial nitrogen fixation approach to the costly and unsustainable Haber-Bosch process. To realize the practical applications of NRR, it is necessary to develop cost-effective, high-activity electrocatalysts. In this paper, we report amorphous CeO$_2$ doped NiSb$_2$O$_6$ nanofibers as cathode for electrocatalytic NRR. The CeO$_2$ doping exhibits a remarkable synergistic superiority with appropriate annealing temperature, inducing the transforming of NiSb$_2$O$_6$ into amorphous. Amorphous CeO$_2$ doped NiSb$_2$O$_6$ nanofibers benefit from the intrinsic defects of amorphization, showing outstanding electrocatalytic NRR performance with high average yield (NH$_3$: $1.44 \times 10^{-11}$mol s$^{-1}$ cm$^{-2}$, Faradaic efficiency: 12.47%). This work offers a novel approach to optimize the NH$_3$ yields and Faradaic efficiencies by tuning the crystallinity of NRR electrocatalyst.

1. Introduction
One of the greatest inventions of the 20th century is ammonia synthesis from molecular dinitrogen (N$_2$) and hydrogen (H$_2$) by Haber-Bosch process. The century-old route uses Fe-based catalysts under high-temperature (400–600 °C) and high-pressure (150–300 atm) conditions, consuming lots of energy and producing large amounts of greenhouse gases.[1] Hence, as a clean and sustainable alternative approach, the electrochemical reduction of N$_2$ to NH$_3$ under ambient temperature and atmospheric pressure has attracted extensive attention in recent years. To improve NH$_3$ yields and Faradaic efficiencies of nitrogen reduction reaction, screening effective and economical electrocatalysts is of primary importance.

The d orbitals of transition-metals (TMs) are incompletely filled with electrons, which enable TMs to donate or accept electrons from other species easily.[2] It has been reported that applying nickel as a cathode material for NH$_3$ electro-synthesis indicates that Ni-Based catalysts are promising electrocatalysts for the NRR.[3] Ni-Based catalysts can adsorb N; meanwhile, their active sites are also available for H adsorption. To hinder hydrogen evolution reaction (HER) and improve Faradaic efficiencies, we design nickel antimony oxide (NiSb$_2$O$_6$) nanofibers and modulate the crystallinity by calcination temperature control and CeO$_2$ doping, inducing amorphization of NiSb$_2$O$_6$ nanofibers.
2. Experiment

2.1. Materials Synthesis
The CeO$_2$-doping NiSb$_2$O$_6$ nanofibers were prepared by electrospinning and annealing procedures. First of all, 1.825 g Ni(CH$_3$COOH)$_2$·4H$_2$O, 0.996 g SbCl$_3$ and 2 g citric acid were dissolved in 20 mL of N, N-dimethylformamide (DMF) and 15 mL absolute ethanol with magnetic stirring for 4 h. After the above chemicals were fully dissolved, 0.868 g Ce(NO$_3$)$_3$·6H$_2$O was then added into the mixed solution. Afterwards, 10 wt% PVP ($M_w = 1300000$) was added slowly into the above mixture. The clarifying precursor solution were eventually obtained after continuous stirring for 12 h. Pure NiSb$_2$O$_6$ precursor solution were obtained without Ce(NO$_3$)$_3$·6H$_2$O.

All the precursor solution were spun via DXES-4 electrospinning device, at a spinning voltage of 20 kV, a perfusion rate of 1.2 mL h$^{-1}$ and a receive distance of 15 cm. The humidity level was maintained at around 40% RH at room temperature. The as-spun nanofibers were calcinated at a heating rate of 2 °C min$^{-1}$ from 600 °C to 900 °C in the air for 1 h to remove the organic component.

2.2. Material Characterization
Hitachi SU 5000 field emission scanning electron microscope (FE-SEM) operated at a voltage of 20 kV was used to observe the morphology of the samples. X-ray diffraction (XRD) was performed by a Bruker D8 Advance X-ray diffractometer, and the diffraction patterns were collected from 20 ° to 90 °. Thermogravimetric analysis (TGA) was performed by a TA-SDT Q600 analyzer. Raman spectra were collected on the LabRAM HR Evolution Raman microscopes. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were carried out on a Talos F200S microscope operated at an accelerating voltage of 120 kV. UV-vis diffuse reflectance spectra were acquired by a Persee TU-1810 spectrometer. The chronoamperometry curves were recorded by a Bio-Logic VSP electrochemical workstation.

2.3. Electrocatalytic NRR tests
The NRR experiments were carried out in a two-compartment electrocatalysis tank filled with 50 mL 0.1 M Na$_2$SO$_4$ under ambient conditions, and the two chambers were separated with Nafion 211 membrane. 1 × 1 cm$^2$ of NiSb$_2$O$_6$ nanofibrous membrane was tested as the cathode, a platinum mesh as the anode, and a saturated calomel electrode as the reference electrode. Bubbles of nitrogen or argon of high purity (99.999%) were pumped into the electrolytic cell for at least 30 minutes to remove the air before electrolysis. The electron potentials were converted to the reversible hydrogen electrode (RHE) according to the following equation:

$$E_{\text{vs. RHE}} = E_{\text{vs. Hg/HgO}} + 0.059 \times \text{pH} + 0.245 \text{ V}$$

3. Result and discussion
Initially, SEM data were used to examine the microstructural evolution of the nanofibers as a function of annealing temperature. SEM images show that the surface of the nanofibers becomes rough from smooth by degrees with the increase of temperature, on account of nucleation of NiSb$_2$O$_6$ and growth of the grain size. At the same temperature, the doped NiSb$_2$O$_6$ nanofibers are coarser and smoother than the undoped nanofibers on average.
Figure 1. (a) images of NiSb$_2$O$_6$ nanofibers calcined at various temperatures from 600 °C to 900 °C, (b) images of CeO$_2$ doped NiSb$_2$O$_6$ nanofibers.

Figure 1a shows a TGA curve of as-spun CeO$_2$ doped NiSb$_2$O$_6$ nanofibers. First of all, residual DMF, ethanol and water in the as-spun nanofibers were slowly vaporized below decomposition temperature (300 °C). When 300 °C was first reached, pyrrolidone groups in PVP and the organic group of citric acid coordination began to degrade. The weight loss below 500 °C was attributed to the decomposition of the unsaturated carbon backbone and remnants of the organic composites. As the temperature rose, the weight loss was little. After heat treatment at 600 °C, the weight remained constant, indicating the completion of the thermal decomposition.

In order to identify the crystalline phase of the doped and undoped NiSb$_2$O$_6$ nanofibers, we carried out XRD analyses on the nanofibers calcined at different heat treatment temperatures. The XRD spectra show that while the after doping NiSb$_2$O$_6$ nanofibers calcined at 700 °C maintain amorphous nature with only broad halo (as shown in Figure 2c), there are obvious crystalline peaks (as shown in Figure 2b) reflecting the pure nanofibers begin to crystallize at 600 °C. Up until to 900 °C calcination, the diffraction peaks of CeO$_2$ doped NiSb$_2$O$_6$ nanofibers are well-matched with the characteristic peaks of CeO$_2$ and NiSb$_2$O$_6$, whereas no peak is assignable to CeO$_2$ phase of pure NiSb$_2$O$_6$ nanofibers determines the successful inclusion of the CeO$_2$ in NiSb$_2$O$_6$ nanofibers and the construction of amorphous NiSb$_2$O$_6$ nanofibers induced by CeO$_2$. This result is further verified by the Raman spectroscopy.

Raman spectral analysis is shown in Figure 2b. A strong Raman band at around 450 cm$^{-1}$ exactly corresponds to the reported value of Ce=O band. Besides, the Raman band of CeO$_2$ doped NiSb$_2$O$_6$ nanofibers locates at nearly the same position when taking pure crystalline NiSb$_2$O$_6$ nanofibers as a reference, confirming the construction of amorphous NiSb$_2$O$_6$ nanofibers rather than the composite of NiO and Sb$_2$O$_5$. The band shifts and smaller force constants can be due to the lattice distortion and disordered in amorphous CeO$_2$ doped NiSb$_2$O$_6$ nanofibers.
Figure 2. (a) TGA curve of As-spun CeO₂ doped NiSb₂O₆ nanofibers, (b) Raman spectra of pure crystalline NiSb₂O₆ nanofibers and CeO₂ doped NiSb₂O₆ nanofibers calcined at 600 °C, (c) XRD of CeO₂ doped NiSb₂O₆ nanofibers at different temperature treatment, (d) XRD of pure NiSb₂O₆ nanofibers.

Figure 3. (a) HRTEM image and SAED pattern, (b) TEM image and the corresponding EDS mapping of amorphous CeO₂ doped NiSb₂O₆ nanofiber.

Blurry halo and fuzzy lattice fringes can be seen in Figure 3a, respectively. Thus, in good agreement with the previous analyses, the amorphous feature of CeO₂ doped NiSb₂O₆ nanofibers is
conclusively confirmed.[7] The energy-dispersive X-ray (EDX) elemental mapping analysis in Figure 3b reveals the homogeneous distribution of Ce, Sb, Ni and O.

Figure 4. (a) Chronoamperometry curves, (b) UV-vis absorption spectra, (c) ammonia yields and Faradaic efficiencies at different potentials, (d) amorphous CeO$_2$ doped NiSb$_2$O$_6$ nanofibers in N$_2$ or Ar electrolyte at −0.65 V vs. RHE.

Figure 4a shows the chronoamperometry curve at each potential. The NiSb$_2$O$_6$ nanofibrous membrane was directly used as a cathode. The electrolysis was conducted from −0.45 to −0.75 V vs. RHE for 2 h. The electrolytes were collected and tested by UV-vis spectroscopy based on the indophenol blue method to obtain the ammonia concentration (Figure 4b).[8] According to the standard ammonia curve equation: $y = 0.3097x + 0.0381$, the ammonia yields and Faradaic efficiencies can be calculated (Figure 4c). It can be seen that the highest average yield and corresponding Faradaic efficiency occur at −0.65 V vs. RHE, being approximately $1.44 \times 10^{-11}$ mol s$^{-1}$ cm$^{-2}$ and 12.47%, respectively. To clarify the origin of the produced ammonia, a control experiment was conducted in which the electrolysis took place in argon-saturated Na$_2$SO$_4$ at −0.65 V vs. RHE. The result verifies that the detected ammonia indeed originated from nitrogen by electrocatalysis rather than from contamination, illustrating the superiority of amorphous CeO$_2$ doped NiSb$_2$O$_6$ nanofibers as the NRR catalyst.

4. Conclusion
In conclusion, the CeO$_2$-doping NiSb$_2$O$_6$ nanofibers were prepared by simple electrospinning and subsequent calcination. The CeO$_2$ doping exhibits a remarkable synergistic superiority with the appropriate annealing temperature, inducing the transforming of NiSb$_2$O$_6$ into amorphous. Thus, as-fabricated CeO$_2$-doping NiSb$_2$O$_6$ electrocatalyst delivers the highest ammonia yield and Faradaic efficiency of $1.44 \times 10^{-11}$ mol s$^{-1}$ cm$^{-2}$ and 12.47% in a neutral electrolyte of 0.1 M Na$_2$SO$_4$, which
represents a successful attempt at N\textsubscript{2} fixation under ambient conditions.

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