**Supplementary Information for**

**Nanoengineered ultralight and robust all-metal cathode for high-capacity, stable lithium–oxygen batteries**

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This PDF file includes: Methods, Supplementary Figures 1 to 16, and Table 1.

**Table of Contents**

Methods and Materials S2-S5

Supporting Figures and Details S6-S21

Supporting Table S22

References S23
Supporting Information: Methods and Materials

1. Chemicals and materials

Lithium Carbonate (Li_2CO_3), Lithium acetate (CH_3CO_2Li), and Lithium formate (HCO_2Li) were purchased from Sigma–Aldrich; Lithium peroxide (Li_2O_2) was purchased from Acros; Lithiated Nafion was purchased from DuPont Company; Nickel nitrate hexahydrate (Ni_2NiO_3·6H_2O), Nickel(II) acetate tetrahydrate (Ni(CH_3COO)_2·4H_2O), Glycine (C_2H_5NO_2), Nickel chloride hexahydrate (NiCl·6H_2O), Chloroauric Acid (HAuCl_4·3H_2O), N-methyl-2-pyrrolidinone (NMP), Tretraethylene glycol dimethyl ether (TEGDME), Lithium triflate (LiCF_3SO_3), Brij30, n-octane, Nickel chloride hexahydrate (NiCl·6H_2O), Sodium borohydride (NaBH_4) and Deuterium oxide (D_2O) were purchased from Aladdin Reagent; Nickel foam (Ni) was purchased from Changde Liyuan Co., Ltd; Hydrazine hydrate (N_2H_4·H_2O, 85 wt%) and Ethanol (EtOH) were purchased from Sinopharm Chemical Reagent Co. Ltd.

2. AuNi/NPNi/FNi cathode preparation

All reagents were of analytical grade and used as received without further purifications. Deionized water was used throughout the experiments. A typical synthetic process to fabricate the AuNi/NPNi/FNi cathode is as follows. Ni_2NiO_3·6H_2O (1.85 g), Ni(CH_3COO)_2·4H_2O (1.85 g), N_2H_4·H_2O (0.95 g) and C_2H_5NO_2 (0.09 g) were dissolved in deionized water (25 mL) and the resulting solution was stirred vigorously for 5h to form a turbid precursor of the metal complex. Then, the nickel foam was soaked in obtained precursor of the metal complex for 10 min, and the excess solution was removed. The samples were dried at 70 °C for 3 h under vacuum and heated at 300 °C for 5 min under a air atmosphere to produce and then calcined at 500 °C for 5 h under an argon–hydrogen atmosphere to tips-riveting NPNi onto the framework of FNi and forming NPNi/FNi. Then, an adequate amount of Au is in situ-deposited uniformly onto the surface of the
NPNi/FNi by redox replacement. Au deposition was performed by dipping the NPNi/FNi into 1 mM HAuCl₄ solution for Ni replacement. The morphology and amount of deposited Au could be effectively controlled by holding at a temperature, concentration, and/or time of replacement-reaction. Finally, the AuNi alloy was also formed by rapid atoms interdiffusion between Au overlayer and NPNi/FNi surface at elevated temperatures (300-500 °C).

3. Au/NPNi/FNi cathode preparation

The Au/NPNi/FNi cathode was prepared by a similar process to the AuNi/NPNi/FNi cathode, except for the absence of alloying process. Loading density is 20 ± 0.1 mg_{Au/NPNi} cm⁻² or 0.09 mg_{Au} cm⁻².

4. AuNi/NPNi preparation

The Au/NPNi/FNi cathode was prepared by a similar process to the AuNi/NPNi/FNi cathode, except for the absence of nickel foam.

5. AuNi/NPNi@FNi cathode preparation

The oxygen cathodes were prepared by coating homogenous ink composed of the mixture of 80 wt% AuNi/NPNi and 20 wt% lithiated Nafion onto the a nickel foam with a loading density of 20 ± 0.1 mg_{AuNi/NPNi} cm⁻² or 0.106 mg_{AuNi} cm⁻².

6. Standard Auₓ₁₋ₓNiₓ (x = 0, 0.10, 0.15, 0.20, 0.30) alloy preparation

The pure Ni and Au nanoparticles were chemically prepared through a redox-transmetalation method in reverse microemulsion. The reaction was carried out under argon protection at room temperature and stirred at a given speed. Brij30 and n-octane were used as the surfactant and the oil phase, respectively. The pure Ni and Au nanoparticles were prepared by the reduction of Ni²⁺
and HAuCl₄ with NaBH₄, and the ω value (molar ratio of water to surfactant) of 7 was selected. The product was washed several times with ethanol. Ni and Au nanoparticles with atom ratio of 10:90, 15:85, 20:80, 30:70, were thoroughly mixed and heated at 500 °C for 5 h under an argon–hydrogen atmosphere.

7. Characterization

The morphologies and structures of materials were analyzed with various physiochemical techniques, including PXRD, field emission scanning electron microscopy (SEM), TEM, nitrogen adsorption/desorption isotherms, inductively coupled plasma optical emission spectrometry (ICP-OES). The reaction products were characterized with PXRD, FTIR spectroscopy and SEM. The electrolyte stability was decided by ¹H NMR.

8. Electrolytes

Lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) was the preferred lithium salt for all the experiments reported in this manuscript. 1 M LiTFSI in tetraethylene glycol dimethylether (TEGDME) was prepared. The water content in TEGDME electrolyte, measured by KarlFischer titration, is < 40 ppm.

9. Li–O₂ cell preparation and electrochemical measurements

The electrochemical performance of the Li–O₂ cell was tested in a 2025-type coin cell. All of the cells were assembled in a glove box under an Ar atmosphere with a lithium metal foil anode, a glass fiber separator, an oxygen cathode and an electrolyte containing 1 M LiCF₃SO₃ in TEGDME. The AuNi/NPNi@FNi cathode was prepared by coating homogenous ink composed of a mixture of 80 wt% AuNi/NPNi powder and 20 wt% lithiated Nafion onto the FNi current collector. And the conventional SP carbon cathode was prepared in the same manner. Assuming
complete oxidation, the artificially Li$_2$O$_2$-loaded electrode has a calculated capacity of 1000 mA h g$^{-1}$. The electrochemical performances of the cathodes were tested in a specific capacity-controlled mode under various current densities. The electrochemical impedance spectroscopy of the cell was evaluated using a BioLogic VMP3 electrochemical workstation within a frequency range of $10^6$ to $10^2$ Hz. CV with a scan rate of 0.05 mV s$^{-1}$ was performed in the range of 2.0–4.5 V.

10. Instrumentation

PXRD measurements were performed on a Rigaku-MiniFlex600 power X-ray diffractometer with Cu Ka radiation. SEM was performed on a field emission Hitachi S-4800 instrument operating at an accelerating voltage of 10 kV. Samples for SEM were prepared by dispersing the as-prepared product in ethanol by sonicating for around 4 min and then depositing onto an indium tin oxide glass attached to an SEM brass stub. TEM was performed using an FEI Tecnai G2 S-Twin transmission electron microscope with a field emission gun operating at 200 kV. FTIR analysis was carried out on a Nicolet 6700 spectrometer. Nitrogen adsorption measurements were performed on a Micromeritics ASAP 2020 adsorption analyzer. Specific surface areas were calculated by the Brunauer–Emmett–Teller method. Pore volumes and sizes were estimated from the pore-size distribution curves from the adsorption isotherms using the Barrett–Joyner–Halenda method. $^1$H NMR spectra were examined on a Bruker Avance II 400 spectrometer. Li–O$_2$ cell were tested on a LAND CT2001A multi-channel battery testing system. Electrochemical impedance spectroscopy and CV were performed on a BioLogic VMP3 electrochemical workstation.
Supporting Figures and Details

Figure S1. Scheme for the fabrication and structure of the AuNi/NPNi/FNi cathode.
**Figure S2. TEM mapping images.** TEM image of AuNi/NPNi and the corresponding elemental mapping images of Au and Ni. The complete overlap between Au and Ni elements has effectively evidenced the existence of AuNi overlayer.
Figure S3. Structure of standard Au$_{1-x}$Ni$_x$ alloy. PXRD patterns of the as-prepared indicated Au$_{1-x}$Ni$_x$ alloy (x = 0, 0.10, 0.15, 0.20, 0.30).
Figure S4. Influence of alloying degree on discharge/charge voltage of Li–O$_2$ cells. (a) PXRD patterns of the Au$_{1-x}$Ni$_x$/NPNi/FNi (x = 0, 0.10, 0.15, 0.20, 0.30) cathodes. (b) First charge–discharge voltage platforms of the Au$_{1-x}$Ni$_x$/NPNi/FNi cathodes. It was noted that the diffraction angles of Au$_{1-x}$Ni$_x$/NPNi/FNi increased with increasing Ni content. These changes may be caused by the crystal lattice compression due to the substitution of partial Au atom by Ni atom. Especially, compared with the Au/NPNi/FNi cathodes, Au$_{1-x}$Ni$_x$/NPNi/FNi significantly suppresses the ORR and especially OER overpotentials and thus improves the round-trip efficiency. This may be explained by the increased d bond hole and the atom rearrangement on the Au surface due to the incorporation of Ni$^{1-3}$. The Au$_{85}$Ni$_{15}$ has a higher catalytic activity than other alloy.
Figure S5. Influence of AuNi alloy overlayer thickness on discharge/charge voltage of Li−O\textsubscript{2} cells. (a) TEM image of the AuNi/NPNi with different overlayer thickness. (b) PXRD patterns of the AuNi/NPNi with different overlayer thickness. (c) First charge–discharge voltage platforms of the AuNi/NPNi with different AuNi alloy overlayer thickness. When the overlayer thickness is < 2 nm, the ORR and OER overpotentials of Li−O\textsubscript{2} cells are suppressed significantly with the increase of the overlayer thickness. When the thickness is > 2 nm, the overpotentials is almost unchanged, which is maintained between 0.68−0.73 V.
Figure S6. Cathode morphology. (a) FESEM image of the pristine FNi cathode. (b) FESEM image of the AuNi/FNi cathode. (c) FESEM image of the AuNi/NPNi@FNi cathode. (d) FESEM image of the Au/NPNi/FNi cathode.
Figure S7. Structure of the cathode. PXRD patterns of the pristine FNi, AuNi/FNi, AuNi/NPNi@FNi, and Au/NPNi/FNi cathodes.
Figure S8. Electrochemical performance of artificially Li_2O_2-loaded cathodes. Voltage profile on charge for Li−O_2 cells with Li_2O_2-loaded FNi, NPNi/FNi, Au/NPNi/FNi, and AuNi/NPNi/FNi cathodes at a current density of 1.0 A g$^{-1}$. In order to avoid complications from possible electrolyte decomposition during a prolonged discharge reaction, the four artificially Li_2O_2-loaded cathodes are also subjected to electrochemical oxidation in Li−O_2 cells. It can be seen that a similar reduction in the charge voltage is obtained for the oxidation of the Li_2O_2 on AuNi/NPNi/FNi versus other cathodes, as observed in the charge profile shown in Figure 2a.
Figure S9. Scheme for structure and discharge/charge mechanism of the AuNi/NPNi/FNi cathode.
**Figure S10.** The PXRD patterns of the discharged cathodes. The PXRD peaks can be assigned to \( \text{Li}_2\text{O}_2 \), although the morphology of the discharge product is different.
Figure S11. Impedance spectra. The equivalent-circuit parameters were obtained by curve fitting using the Zview software with the equivalent circuit shown in the inset. Data points are the measured values and the solid line is the calculated impedance curve using the equivalent circuit. $R_{\text{ohm}}$ is Ohmic resistance of the Li–O$_2$ cell. $R_{\text{int}}$ is interfacial resistance between the Li anode and the electrolyte. $R_{\text{int}2}$ is interfacial resistance between the cathode and the electrolyte. $W_l$ is Warburg impedance arising from the Li$^+$ concentration gradients. According to the equivalent circuit, the resistance components were analyzed by the nonlinear least squares fit program. The fitting values of $R_{\text{int}2}$ are 113.8 and 48.28 $\Omega$ cm$^{-2}$ for AuNi/NPNi@FNi and AuNi/NPNi/FNi cathodes, respectively.
Figure S12. Electrochemical performance of Ar-filled cells. The discharge curves of the Ar-filled cells with FNi, NPNi/FNi, Au/NPNi/FNi, and AuNi/NPNi/FNi cathodes at a current density of 1.0 A g\(^{-1}\). To exclude possible electrochemical contributions from lithium ions (Li\(^+\)) intercalation into cathode materials, the initial discharge curves of Li–O\(_2\) cells in Ar atmosphere are also tested for comparison. The background discharge capacity is negligible within the voltage range, which suggests that the high discharge capacities of the Li–O\(_2\) cells are derived from the oxygen reduction.
Figure S13. FTIR spectra of the pristine and recharged Au/NPNi/FNi, AuNi/NPNi@FNi, and AuNi/NPNi/FNi cathodes after the 1st and 50th cycle. The spectra for Li$_2$CO$_3$, HCO$_2$Li and CH$_3$CO$_2$Li are also shown for reference.
Figure S14. Electrochemical stability of electrolyte and cathode. (a) Voltage profile on charge for undischarged Li–O₂ cells with FNi, NPNi/FNi, Au/NPNi/FNi, and AuNi/NPNi/FNi cathodes at a current density of 1.0 A g⁻¹. PXRD patterns of undischarged (b) FNi, (c) NPNi/FNi, (d) Au/NPNi/FNi, and (e) AuNi/NPNi/FNi cathodes after the charge at a current density of 1.0 A g⁻¹.
Figure S15. PXRD patterns of the pristine and recharged Au/NPNi/FNi, AuNi/NPNi@FNi, and AuNi/NPNi/FNi cathodes after the 1st and 50th cycle. The patterns of the as-prepared Au$_{85}$Ni$_{15}$ alloy, standard Au and Ni are also shown for reference.
Figure S16. FESEM image of the conventional SP carbon cathode.
Supporting Table

Table S1. Constituent of AuNi/NPNi. The AuNi content of AuNi/NPNi with ~ 2.13 nm overlayer in thickness was verified to be 0.53 at.% by inductively coupled plasma optical emission spectrometry (ICP-OES).

| No. | Thickness / nm | Ni / ppm  | Au / ppm | Ni+Au / ppm | Au/Ni+Au | AuNi/Ni+Au |
|-----|---------------|-----------|----------|-------------|----------|------------|
| 1#  | 1.52          | 984400    | 2166     | 896566      | 0.0024   | 0.0028     |
| 2#  | 2.13          | 956800    | 4349     | 961149      | 0.0045   | 0.0053     |
| 3#  | 3.02          | 941800    | 5276     | 947076      | 0.0056   | 0.0066     |
| 4#  | 5.23          | 874200    | 7271     | 881471      | 0.0082   | 0.0096     |
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