Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information

Photoinduced decoration of NiO nanosheets/Ni foam with Pd Nanoparticles towards carbon-free and self-standing cathode for lithium-oxygen battery with low overpotential and long cycle life

Methods

Chemicals and materials:

$Ni(NO_3)_2•6H_2O$, Na_2PdCl_4, TEGDME and $LiCF_3SO_3$ were purchased from Aladdin Reagent.

Pd/NiO nanosheets @Ni foam cathode preparation. The synthesis procedure for the Pd/NiO@Ni foam cathode was described by Vijay et al with a slight modification. In a typical process, 50 ml of an aqueous 0.15 M $Ni(NO_3)_2$ $6H_2O$ solution was obtained by dissolving an appropriate amount of $Ni(NO_3)_2$ $6H_2O$ into 50 ml of DI water and stirring it for 30 min. The three-electrode system consisting of NF as the working electrode, platinum foil as the counter electrode, and silver/silver chloride (Ag/AgCl) as the reference electrode was used to deposit the $Ni(OH)_2$ nanostructure on NF. Potentiodynamic electrodeposition mode was employed within the potential window of 0 to 1.1 V (vs. Ag/AgCl) at a 20 mV s^{-1} scan rate for 30 cycles.

After deposition, the $Ni(OH)_2$ electrodes were washed several times with DI water and dried at room temperature. Furthermore, $Ni(OH)_2$ electrodes were calcined at 473 K for 2 h to obtain NiO. Next, the obtained NiO@Ni foam cathode was directly immersed into Na_2PdCl_4 aqueous solution (5 mM) and exposed to light for 30 min. The cathode was finally rinsed with deionized water several times and dried in an air oven at 60℃. The active mass of each electrodeposited NiO electrode was estimated by calculating the weight difference beteen the pristine Ni foam and NiO@Ni foam cathode.

NiO nanosheet@Ni foam cathode preparation. The NiO@Ni foam cathode was fabriacated with the same procedure as Pd/NiO@Ni foam cathode without the step of further photoreduction.

Pd/NiO film@Ni foam cathode preparation. The Pd/NiO film @Ni foam cathode was prepared with the following steps. First, the Ni foam was annealed in air at 350℃ for 2h to

obtain NiO film covering on the surface of Ni foam. Then, the obtained NiO film @Ni foam cathode was directly immersed into Na_2PdCl_4 aqueous solution (5 mM) and exposed to light for 30 min.

Characterization. The morphologies and structures of materials were analysed with various physiochemical techniques, including PXRD, field emission scanning electron microscopy (SEM), TEM, nitrogen adsorption/desorption isotherms. The reaction products were characterized with SEM.

Li-O_2 cell preparation and electrochemical measurements. The electrochemical performance of the Li-O_2 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 $LiCF_3SO_3$ in TEGDME. The Pd/NiOnanosheet@Ni foam cathode, were used directly without any ploymer binder. The electrochemical performances of the Pd/NiO @Ni foam 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. LSV with a scan rate of 0.02 mV s^{-1} was also performed in the range of 2.0–3.0 V.

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. TEM was performed using an FEI Tecnai G2 S-Twin transmission electron microscope with a field emission gun operating at 200 kV. Nitrogen adsorption measurements were performed on a Micromeritics ASAP 2020 adsorption analyser. Specific surface areas were calculated by the Brunaure–Emmert–Teller method. Pore volumes and sizes were estimated from the pore-size distribution curves from the adsorption isotherms using the Barrett–Joyner–Halenda method. Li-O_2 cell were

tested on a LAND CT2001A multi-channel battery testing system. Electrochemical impedance spectroscopy and LSV were performed on a BioLogic VMP3 electrochemical workstation. A xenon light source (PLS-SXE300C) was employed for the photochemical deposition of Pd nanoparticles.

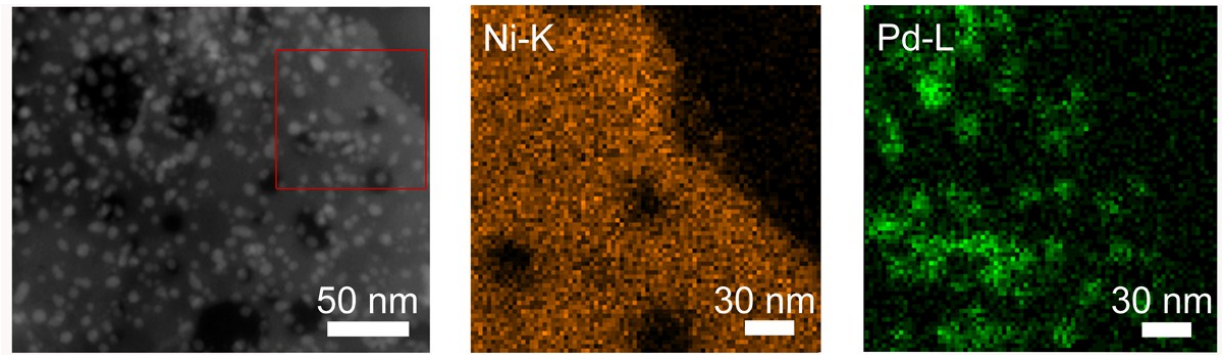

Figure S1. TEM mapping images. TEM image of PNS cathode and the corresponding elemental mapping images of Ni and Pd.

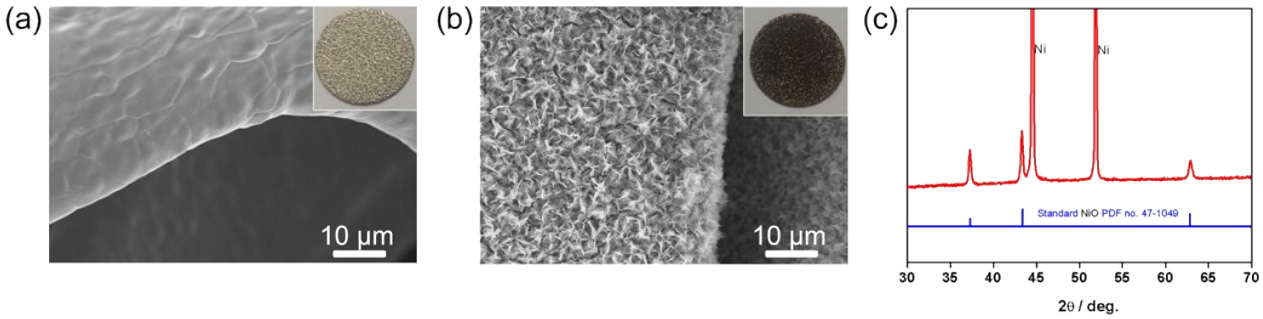

Figure S2. (a) SEM image and photograph (inset) of pristine Ni foam. (b) SEM image and photograph (inset) of NiO nanosheets grwon on the Ni foam. (c) X-ray diffraction patterns of the NiO nanosheets grown on the Ni foam cathode. The patterns for standard NiO are also shown for reference.

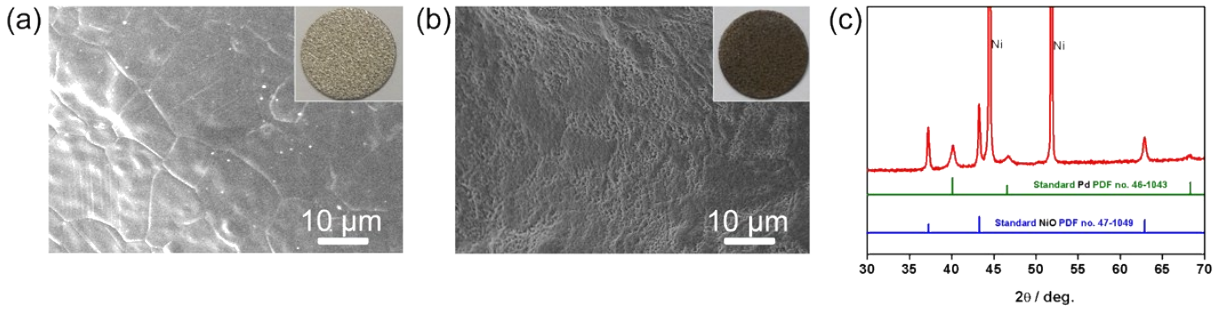

Figure S3. (a) SEM image and photograph (inset) of pristine Ni foam. (b) SEM image and photograph (inset) of Pd nanoparticles modified NiO film grwon on the Ni foam. (c) X-ray diffraction patterns of Pd nanoparticles modified NiO film grwon on the Ni foam cathode. The patterns for standard NiO and Pd are also shown for reference.

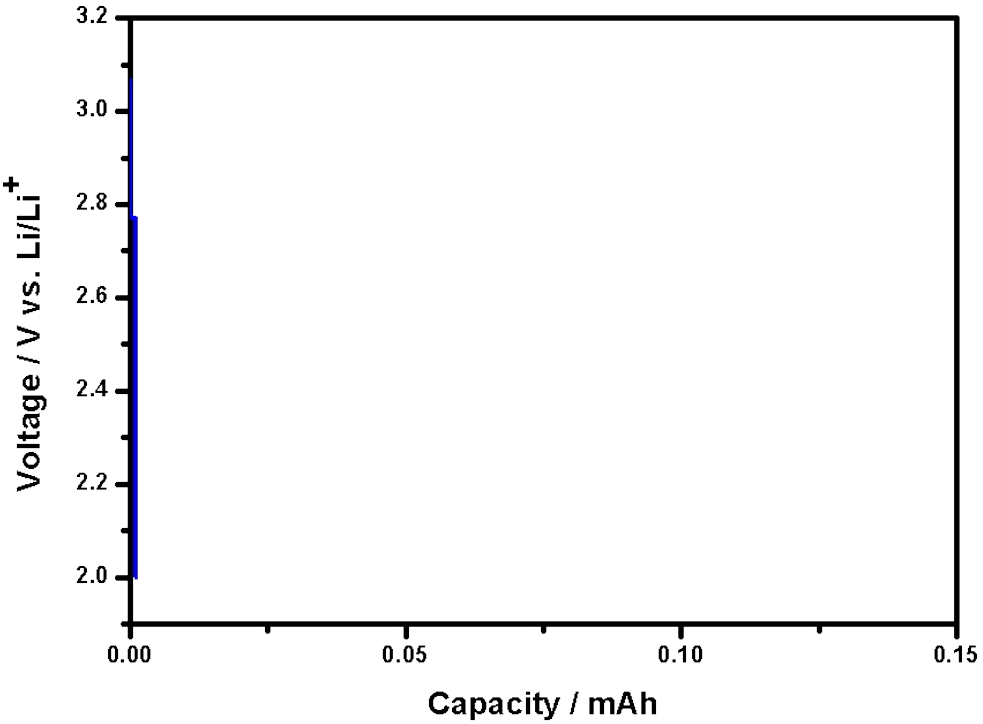

Figure S4. The discharge performance of lithium-oxygen (Li-O_2) cell with PNS cathode in Ar.

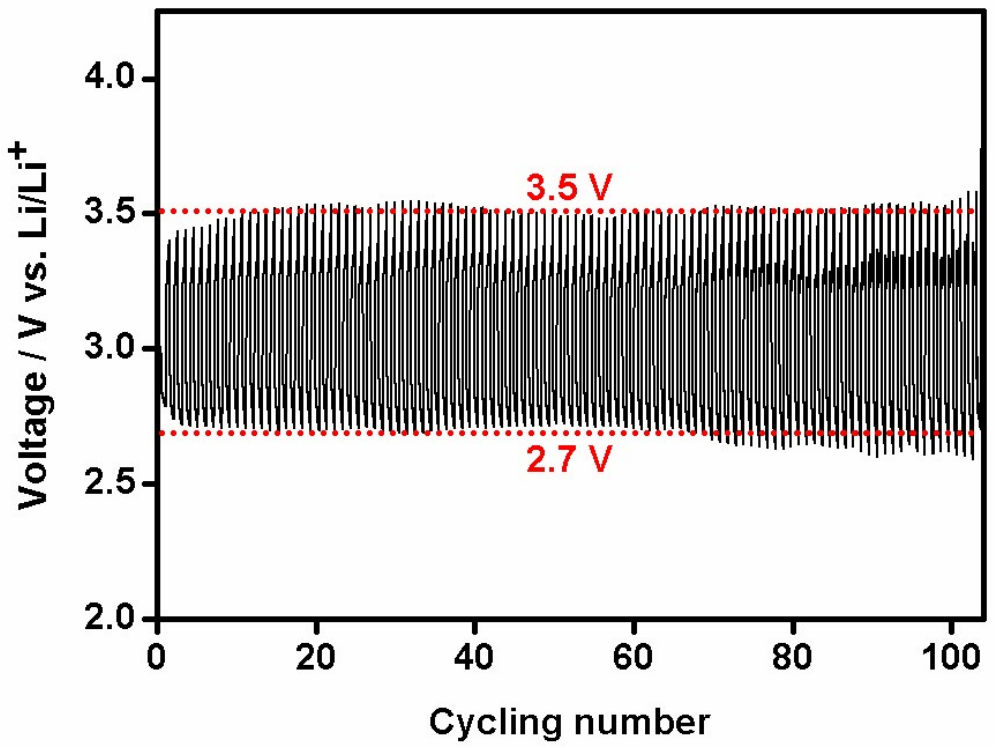

Figure S5. Discharge-charge profiles of the PNS cathode with a fixed capacity of 1000 mAh g_{Pd}^{-1} at 200 mA g_{Pd}^{-1}.

Table S1. Composition of Pd/NiO. The Pd content of Pd/NiO was verified to be 1.55 at.% by inductively coupled plasma optical emission spectrometry (ICP-OES).

No.	Ni/ppm	Pd/ppm	Ni+Pd/ppm	Pd/Ni+Pd
1#	465400	7312	472712	0.0155