Electronic Supplementary Information

Thiocarboxylate Ligand Modified Ni(OH)$_2$ Nanosheets for High Performance Alkaline Battery

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Experimental Section:

1. Preparation of Ni(OH)$_2$ ultrathin nanosheets

The preparation of Ni(OH)$_2$ ultrathin nanosheets was followed a previous method [1]. In a typical procedure, Ni(NO$_3$)$_2$·6H$_2$O (1.45 g, 5 mmol) and hexamethylenetetramine (HMT) (1.40 g, 10 mmol) were dissolved in 35 mL H$_2$O under the aid of sonication to form a clear solution. Nickel foam (about 5 cm x 1.5 cm x 0.1 cm) was firstly cleaned with mixed solution of *i*-propanol, acetone, and H$_2$O with ratio of 1:1:1 under sonication for 15 mins to remove the possible oil layer. Afterwards, the nickel foam was immersed in concentrated HCl solution in an ultrasound bath for 5 min to remove the oxidized nickel compounds. Then the nickel foam was cleaned by deionized water and absolute ethanol in sequence. *We suggest that it is better not to dry the nickel foam at this stage in ambient environment with electric oven above 60ºC for long time. Otherwise the newly formed nickel surface would be seriously oxidized to yellow-colored nickel oxide again. We recommend to used low-temperature gas flow (air or N$_2$) to quickly remove the liquid remain on the foam to avoid the oxidation.* After weighing, the dried nickel foam and aqueous Ni(NO$_3$)$_2$/HMT solution were transferred to a 40 mL Teflon-lined stainless-steel autoclave was sealed and heated at 100 °C for 10 h in an electric oven. Then the autoclave was allowed to cool to room temperature. The nickel foam was taken out from the solution, washed with ethanol/water mixture in a beaker with slight sonication to remove the excess Ni(OH)$_2$. The residual solution was centrifuged to obtain the powdered Ni(OH)$_2$ nanoflowers. The Ni(OH)$_2$ grown on nickel foam was dried at 60ºC and the Ni(OH)$_2$ powder was freeze-dried.

2. Preparation of thiocarboxylate acid sodium salt

The detailed preparation and characterization of thiocarboxylate acid sodium salts was described in our previous publication [2].
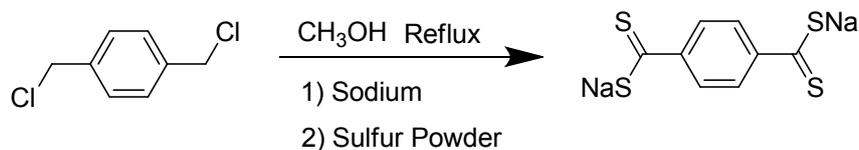
Sodium (0.92 g, 0.04 mol) and sulfur powder (1.28 g, 0.04 mol) was dissolved in dry methanol (100 mL). This mixture was heated to reflux for 4 h under argon in a two-necked flask equipped with a reflux condenser. Then, p-xylylene dichloride (1.75 g, 0.01 mol) was added to the reaction mixture in small portions over a period of 1 h. The reaction was allowed to reflux for additional 15 h, generating a red solution with some solids suspended. After the solution was cooled at room temperature, methanol was removed under reduced pressure. The dark red solid was re-dissolved in THF (50 mL), and then the solution was filtered. Hexane (20 mL) was added to the filtrate, and cooled to -15°C. The precipitation was collected by filtration to yield compound **c** as dark red solid. Yield: 1.64 g (60%).

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3. Preparation of NiTHC ultrathin nanosheets

The thiocarboxylate acid sodium salt was dissolved in 15 mL DMF with concentration of 10 mmol L^{-1}. A piece of $Ni(OH)_2$/nickel foam with diameter of 1.2 cm (or 50 mg of powered $Ni(OH)_2$) was then immersed in this solution. The mixture was then transferred to a 20 mL Teflon-lined stainless-steel autoclave and heated at $80^{\circ}C$ for 5h. After cooling down to room temperature, the nickel foam was then taken out from the solution. For powder NiTHC sample, the reaction mixture was centrifuged and washed with H_2O and ethanol in sequence. The light-green $Ni(OH)_2$ turned to dark blue after sulfurization, indicating the surface of $Ni(OH)_2$ was modified with sulfur-containing molecules. The nickel foam/NiTHC was dried at $60^{\circ}C$ and the powder NiTHC was freeze-dried.

4. Synthesis of PAQS

PAQS was synthesized by a reported method[3]: 1,5-dichloroanthraquinone (2 mmol) and anhydrous Na_2S (2 mmol) were dissolved in 5 mL N-methyl pyrrolidone (NMP). The mixture was refluxed under N_2 for 24 h. The product was washed repeatedly by acetone/hot water for several times and finally dried in vacuum.

5. Structural Characterization

The morphologies of the samples were examined by scanning electron microscope (Quanta FEI 250) and transmission electron microscope (Hitachi HT-7700). HRTEM and EDS images were obtained on a high-resolution transmission electron microscope (JEM-2100). XPS (PHI Quantera SXM instrument equipped with an Al X-ray excitation source (1486.6 eV)) was conducted to analyze of the composition of the sample surface. XRD patterns were obtained by Rigaku SmartLab, using Cu Kα radiation (40 kV, 30 mA). Raman spectra were conducted using a LabRAM HR Evolution laser Raman spectrometer with green laser (532 nm) for excitation.

6. Electric Conductivity Measurement.

The powder samples were pressed into pellets with diameter of 4 mm and a thickness of about 0.1 mm (Ultrathin nanosheet is ductile that enables the fabrication of thin pellet, or the pellet will be extremely fragile with such small thickness). Electric conductivity of samples was measured in a two-point measurement with a picoameter (Keithley 6485) and a source meter (Keithley 2400). Two copper strips were used as the conducting wire, and conductive silver paste was used to stick the copper foil and the samples. Current-voltage (I-V) curves were scanned at various voltage ranges according to the resistance of the samples and the sensitivity of the instrument. The conductivity was calculated by the plots of current density versus electric field strength (J-E curves) based on Ohm's law:

$$\sigma = J/E,$$
$$J = I/S,$$
$$E = V/L$$

where σ is the conductivity, J is the current density, E is the electric field strength, I is the current, V is the voltage, S is the cross-sectional area of the sample, and L is the thickness of the sample

7. Electrochemical Measurement

Electrode preparation:

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For kinetics study, we adopted glassy carbon electrode with diameter of 5 mm. 4 mg of the powder samples and 1 mg single-wall carbon nanotubes (SWNTs) were dispersed in 2 mL ethanol/water (1:1) mixed solution with 100 μL Nafion (5%) solution. The mixture was then sonicated for 30 min until a homogeneous suspension was obtained. 20 μL of the suspension was transferred on the glassy carbon electrode. The glassy carbon electrode was then dried under ambient temperature. The active material mass loading on the glassy carbon electrode was about 0.2 mg/cm^{-2}. It should be noted that the use of SWNTs instead of commonly used carbon black would generate a much smoother electrode surface with strong binding. Therefore, the active material can be anchored firmly on the electrode even when small amount of bubbles was generated.

For the test of Galvanostatic charge/discharge and full cell test, active material grown on nickel foams were directly used as electrode with high mass loading of ~5 mg cm^{-2}.

The PAQS anode was prepared by a traditional slurry-coating method. 10 mg PAQS, 2 mg Ketjen black, and 2 mg PTFE (40 μL 5% in H_2O) were well mixed with the aid of small amount of ethanol. The paste-like slurry was then pressed into a piece of nickel foam. After the nickel foam was dried at 60°C, the electrode was sandwiched into two piece of nickel foam and hydraulic pressed at 5 MPa.

Measurement equipment and cell configuration:

Electrochemical experiments were performed with Autolab PGSTAT302N Electrochemical Workstation. The cycle stability test was performed on LANHE battery test system. For three-electrode measurement, the electrochemical cell was equipped with the working electrode, a platinum foil (4 cm^2) as the counter electrode and a standard Ag/AgCl reference electrode. The reference electrodes were calibrated once a week. 1 M KOH was used as the electrolyte. Cyclic voltammetry (CV) measurements were tested at scanning rate varied from 0.2 to 50 mV/s with a voltage window of 0-0.5 V. Galvanostatic charge–discharge test was carried in the cut-off potential range from 0 V to 0.5 V with current density range from 1 to 10 A g^{-1}. The Tafel slope was derived from LSV curves at the scan rate of 10 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) was carried out with the frequency ranged from 0.01-10^{-5} Hz with the open-circuit potential *vs.* Ag/AgCl.

For two-electrode configuration testing the full-cell performance, Electrochemical properties were test with stainless-steel CR2032 coin cells. It should be noted that due to the full-cell in this work is with relative low cell voltage of 1.17 V, stainless-steel cells are fully capable. For alkaline battery with relative high voltage, nickel layer and tin layer should be plated on cathode and anode cap reepectively in order to avoid the gas evolution [4]. The batteries were assembled with the as-prepared Ni(OH)$_2$ or NiTHC cathodes, separator (glass fiber mat) and PAQS anodes. The electrolyte was composed of 1 M of KOH aqueous solution. Galvanostatic charge–discharge test was carried in the cut-off potential range from 0.5 V to 1.3 V on LAND cell test system. Cyclic voltammetry (CV) measurements were test on a Autolab PGSTAT302N electrochemical workstation at scanning rate varied from 2 to 100 mV/s with a voltage window of 0.5-1.3 V.
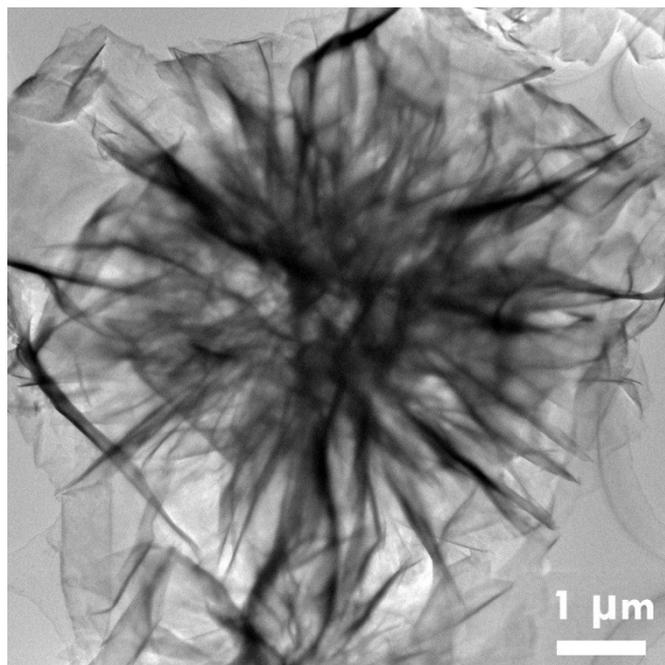
Figure S1. TEM image of NiTHC ultrathin nanosheet.
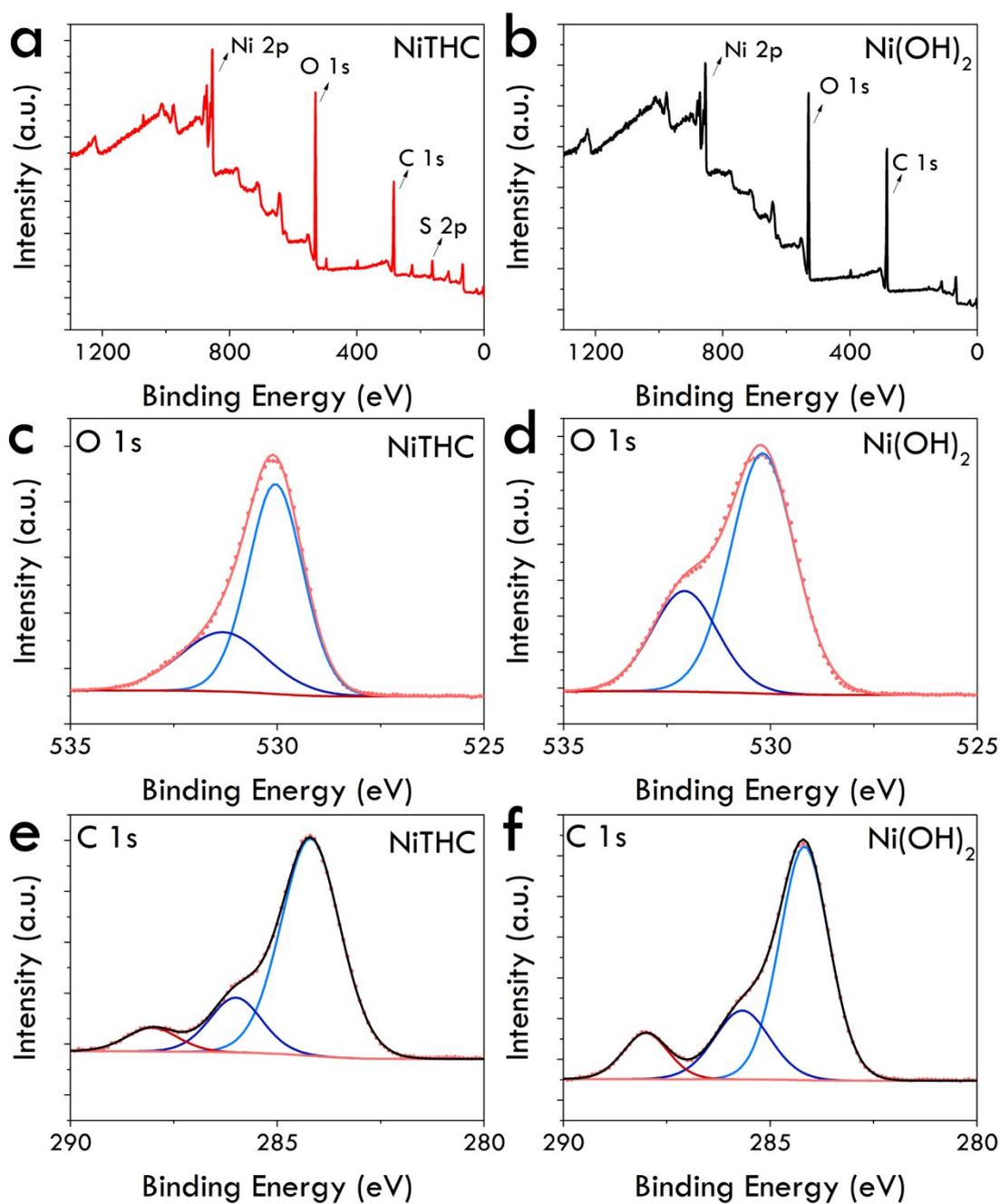
Figure S2. XPS measurement of NiTHC and Ni(OH)$_2$ nanosheets. (a) and (b): XPS survey of two samples. (c) and (d): O 1s signal. (e) and (f): C 1s signal.

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Table S1. XPS signal comparison of C 1s and O 1s of NiTHC and Ni(OH)$_2$ samples

Signal	Peak Binding Energy (eV)	Atomic %
C 1s	**NiTHC**	
	284.19	46.59
	286	10.38
	288.02	4.41
O 1s	530.04	26.7
	531.31	11.91
C 1s	**Ni(OH)$_2$**	
	284.17	44.11
	285.67	14.55
	288	7.85
O 1s	530.19	23.4
	532.07	10.1
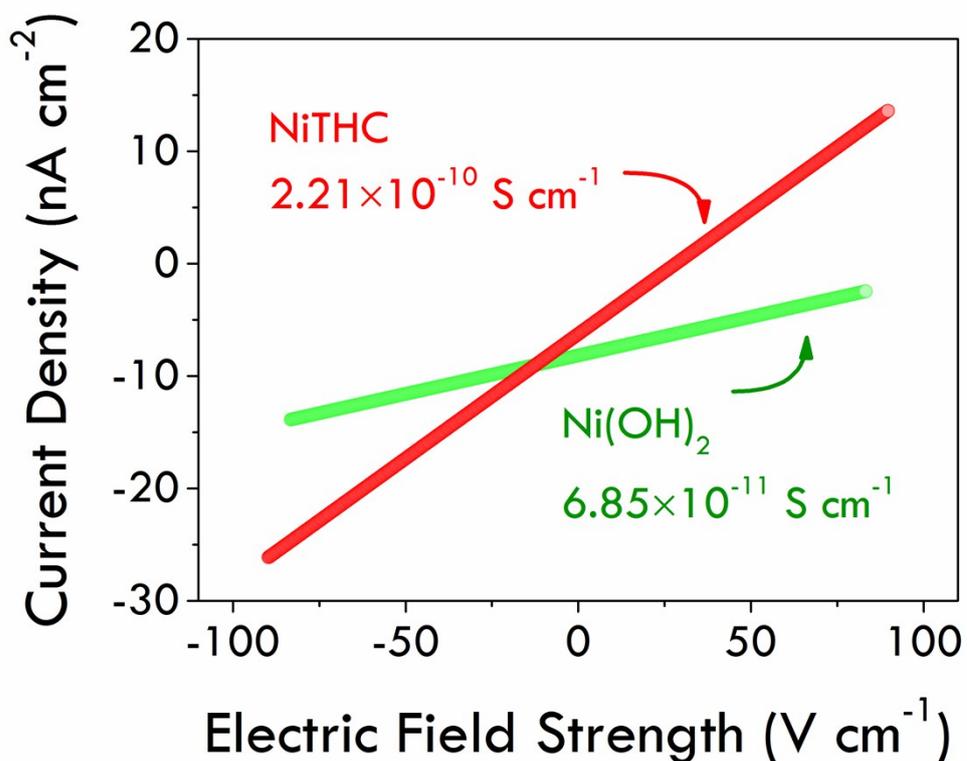
Figure S3. Electric conductivity measured by I-V curves of NiTHC and Ni(OH)$_2$ nanosheets.
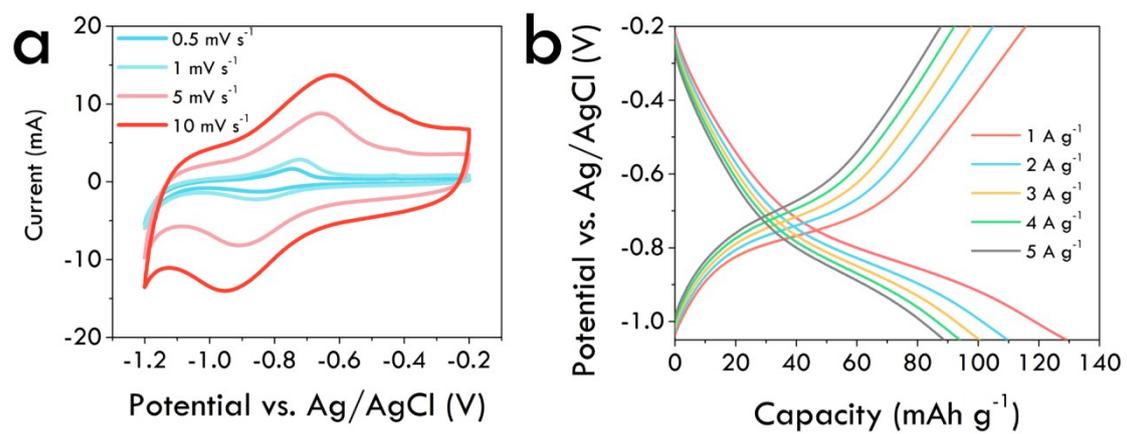
Figure S4. Electrochemical performance of PAQS anode with three-electrode measurement configuration.
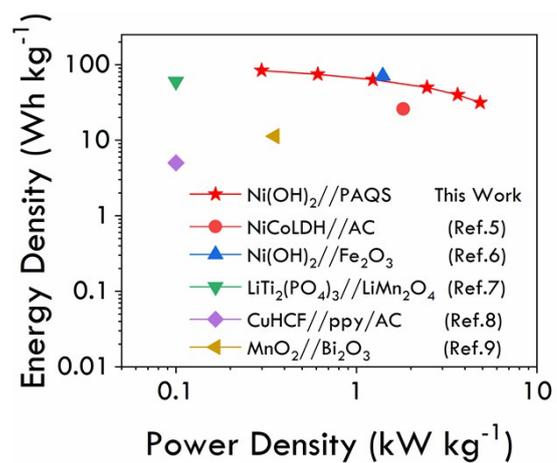
Figure S5. Ragone plot of NiTHC//PAQS full cell with comparison of typical aqueous batteries.

Table S2. Energy density and power density of NiTHC//PAQS full cell

Power Density (kW kg^{-1})	0.29	0.61	1.23	2.46	3.63	4.84
Energy Density (Wh kg^{-1})	83.60	74.54	63.30	50.00	40.00	31.50

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