

Supporting Information

Multifunctional sandwich structure with plentiful active sites to achieve electronic transferring modulation and its application in energy storage and conversion

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1. Experimental

1.1. Synthesis of SiO₂/N-carbon spheres

SiO₂/N-carbon spheres were synthesized by a one-step method involving the formation of spherical SiO₂ cores and the coating of polydopamine. Briefly, a mixture containing 25 mL of anhydrous ethanol, 5 mL of ammonia (25%) and 40 mL of deionized water was stirred for 30 mins. Tetraethoxysilane (TEOS) was poured into the mixture. Subsequently, dopamine hydrochloride (0.04 g) was added into the above solution and kept stirring for 36 h. After centrifugation and washed with purified water three times. SiO₂/N-carbon spheres were obtained after calcination at 900 °C for 1 h under nitrogen (N₂) atmosphere.

1.2. Synthesis of NHC@Ni₃S₂ composite

0.1 g SiO₂@N-carbon spheres was added in 40 mL of water by sonication for 1 h, the addition of Na₂S (0.4 mmol), NiCl₂ (0.5 mmol), NH₄Cl (5 mmol), NH₃·H₂O (0.5

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mL) and $\text{CO}(\text{NH}_2)_2$ under stirring for 1 h. The mixture solution was transferred into a Teflon-lined autoclave and maintained at 160 °C and reaction for 12 h. NHC/ Ni_3S_2 composites were obtained by washing and drying.

1.3. Synthesis of NHC/ Ni_3S_2 /RGO composite

The graphene oxide nanosheets (GO) were synthesized by a modified Hummers procedure. To prepare NHC/ Ni_3S_2 /RGO hybrids, 250 mg GO (100620, from Nanjing XFNANO) was dispersed in deionized water (40 mL) and stirred vigorously, and then the mixed solution was treated with ultrasound for 30 mins to form a homogeneous solution. Later, NHC/ Ni_3S_2 (1 g) was added to the homogeneous solution under intense magnetic stirring for 60 mins. The mixed solution was transferred into Teflon-lined stainless-steel autoclaves with a capacity of 100 mL. Subsequently, the sample was heated at 160 °C for 10 h to form a graphene-based 3D hydrogel. After cooling to room temperature, the composites were obtained by washing with ethanol and deionized water for four times. Finally, the products were processed with freeze drying a night to maintain the 3D frame structure, and NHC/ Ni_3S_2 /RGO hybrids were thus obtained.

1.4. Preparation of electrode

1.4.1 Prepare the counter electrodes of DSSCs

The CEs were made by respectively mixing 0.06 g NHC/ Ni_3S_2 /RGO with 0.02 g polyethylene glycol powder and disperse into 2 mL absolute ethyl alcohol and following grinded with an agate mortar to form a colloid. The colloid was coated on FTO glass by using a doctor-blading method to form an exposed surface of 0.5×0.5 cm², which can be assisted by a 3 M Scotch tape. Followed by drying naturally and then the CEs were obtained after annealing at 400 °C for 60 min under the protection of argon.

1.4.2 Prepare the working electrodes of supercapacitors

The nickel foam was cut into a rectangle (2×1 cm²) and treated with alcohol

ultrasound for 5 times, each time for 3 minutes, and vacuum dried for 2 hours. The rectangle was bent along the middle into an L shape. Then, a blend solution with PTFT: carbon black: material = 1:1:8, was prepared, wherein, the ratio of PTFT to alcohol solution was $1\text{mg}\cdot\text{mL}^{-1}$. After the sample solution was prepared, it was ground evenly, and then was evenly applied to the 90 degree surface of L shaped nickel foam with a clean small brush, and vacuum dried for another 12 h. After that, it was folded into a $1\times 1\text{ cm}^2$ double-layer nickel foam and pressed into thin sheets at a pressure of 20 MP.

1.4.3 Prepare the working electrodes of HER

The catalyst material of 5 mg was evenly dispersed in a mixture of 300 UL isopropanol, 700 UL deionized water and 50 UL Nafion solution. The catalyst solution of $5\text{ mg}\cdot\text{mL}^{-1}$ was prepared by ultrasonic treatment until the solution was uniform and wall-hanging phenomenon appeared. The temperature during ultrasonic treatment should not exceed $25\text{ }^\circ\text{C}$. Finally, the prepared catalyst solution was absorbed by a 10 UL pipette gun and evenly modified on a 25 mm diameter glassy carbon electrode, then dried naturally.

1.5. Characterization and measurements

Photocurrent density-voltage (J-V) curves of photovoltaic effect were measured by a solar light simulator under an illumination of $100\text{ mW}\cdot\text{cm}^{-2}$, AM 1.5 and using a digital source meter (Keithley 2410). Cyclic voltammetry (CV) curves were recorded in the range from -0.4 to 1.1 V at a scan rate of $25\text{ mV}\cdot\text{s}^{-1}$ in a supporting electrolyte consisting of 10 mM LiI , 1 mM I_2 , and 100 mM LiClO_4 in acetonitrile and carried out in a three-electrode system. Pt thin film was used as the CE and Ag/AgCl as reference electrode. In DSSCs, a symmetrical cell is widely used in EIS and Tafel polarization measurements. Electrochemical impedance spectroscopy (EIS) of symmetrical cells was recorded in a frequency range of $0.1 \sim 10^6\text{ Hz}$ and at alternating current voltage amplitude of 10 mV . Tafel polarization measurements were also performed in a symmetrical cell and kept quasi stationary conditions with the voltage range -1 to 1 V at a scan rate of $50\text{ mV}\cdot\text{s}^{-1}$. EIS and Tafel measurements were carried out in dark

environment.

Cyclic voltammetry (CV) curves, galvanostatic charge-discharge (GCD) curves and electrochemical impedance spectroscopy (EIS) of supercapacitor were in a supporting electrolyte consisting of 6 M KOH solution, carried out in a three-electrode system. Pt thin film was used as the CE and Ag/AgCl as reference electrode. CV curves were recorded in the range from -0.6 to 0 V at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$. GCD curve were recorded in the range from $0 \sim 0.6$ V at a current density of $1 \text{ A}\cdot\text{g}^{-1}$. EIS was recorded in a frequency range of $0.01 \sim 10^5$ Hz and at alternating current voltage amplitude of 10 mV .

The linear scanning voltammetry (LSV) curves of HER were in a supporting electrolyte consisting of $0.5 \text{ M H}_2\text{SO}_4$, carried out in a three-electrode system (Wave Vortex 10 Rotator, Model number: AF01WV10, Pine Research Instrumentation). The graphite electrode was used as the counter electrode and Ag/AgCl as reference electrode, catalyst-loaded glass carbon electrode (GCE, 25 mm in diameter) as working electrode. All potentials were referenced to the reversible hydrogen electrode (RHE) according to the conversion of $E (\text{vs. RHE}) = E (\text{vs. Ag/AgCl}) + 0.059 \text{ pH} + 0.197$.

The surface morphologies of CEs were observed via a field-emission scanning electron microscope (SEM, JSM-6701F, JEOL accelerating voltage of 5 kV), transmission electron microscopy (TEM, JEOL-2010, operating voltage of 200 kV), and high-resolution TEM (HRTEM, JEOL-2010). All samples were prepared by depositing a drop of diluted suspensions in ethanol on a carbon-film-coated copper grid. The crystalline structures of NHC/Ni₃S₂ and NHC/Ni₃S₂/S-RGO powders were recorded via Raman spectroscopy and a Rigaku/Max-3A X-ray diffractometer with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). X-ray photoelectron spectroscopy was conducted using a Smart Lab 9 KW to study the chemical states.

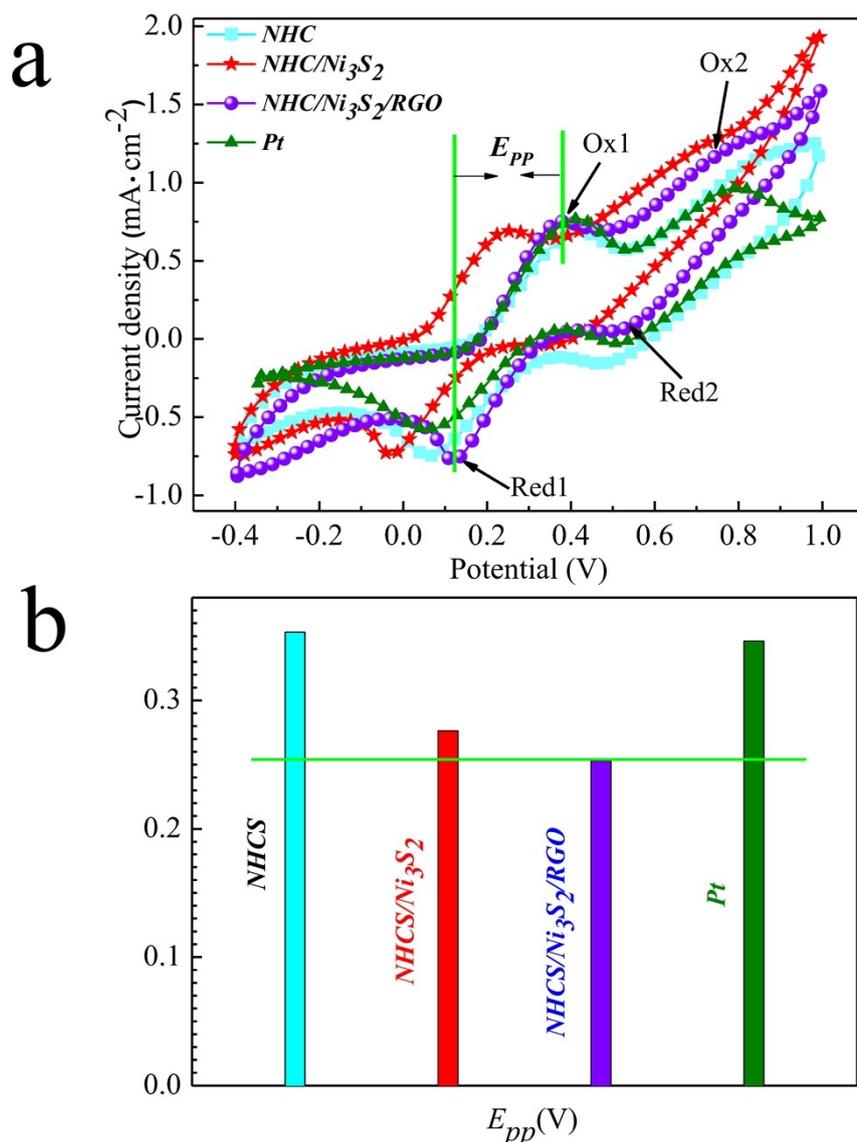


Fig. S1 (a) the CV curves of prepared materials (NHC, NHC/Ni₃S₂, and NHC/Ni₃S₂/RGO). (b) The E_{pp} value of prepared materials (NHC, NHC/Ni₃S₂, and NHC/Ni₃S₂/RGO).

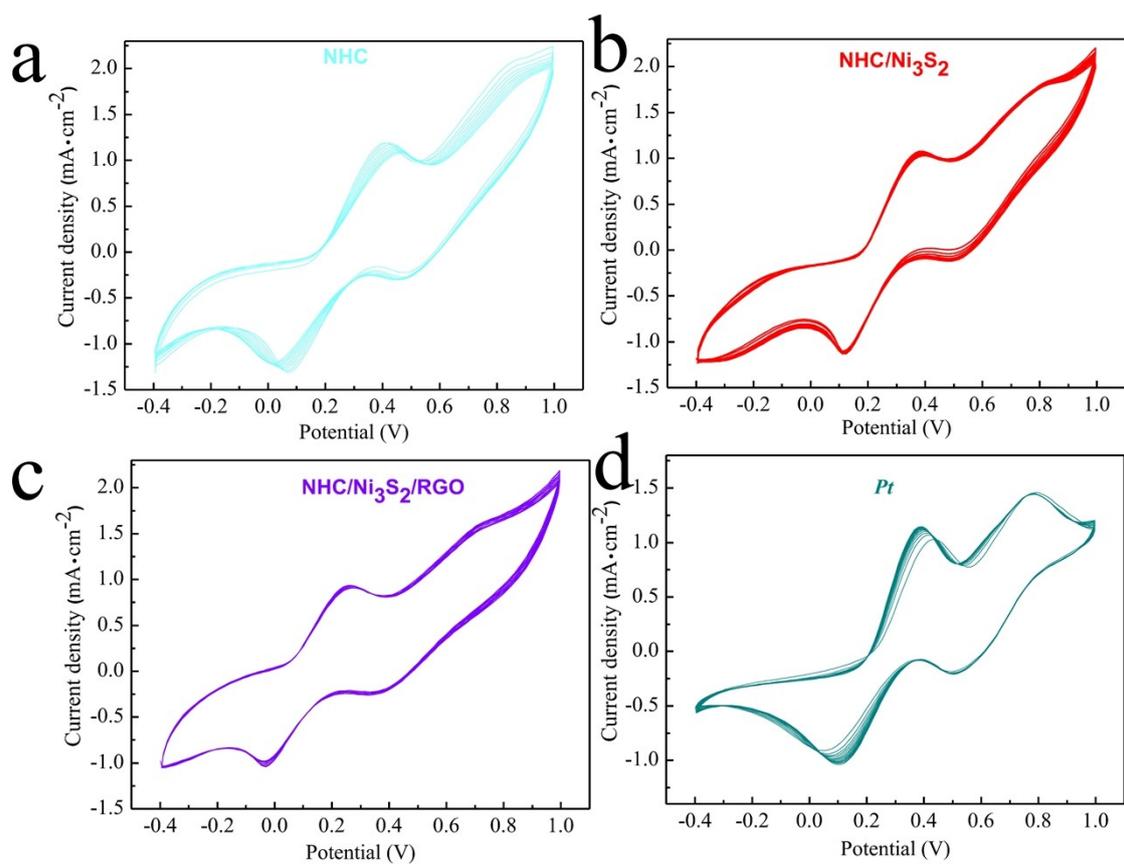


Fig. S2 the CV curves of prepared materials after 30 cycles (NHC, NHC/Ni₃S₂, and NHC/Ni₃S₂/RGO).

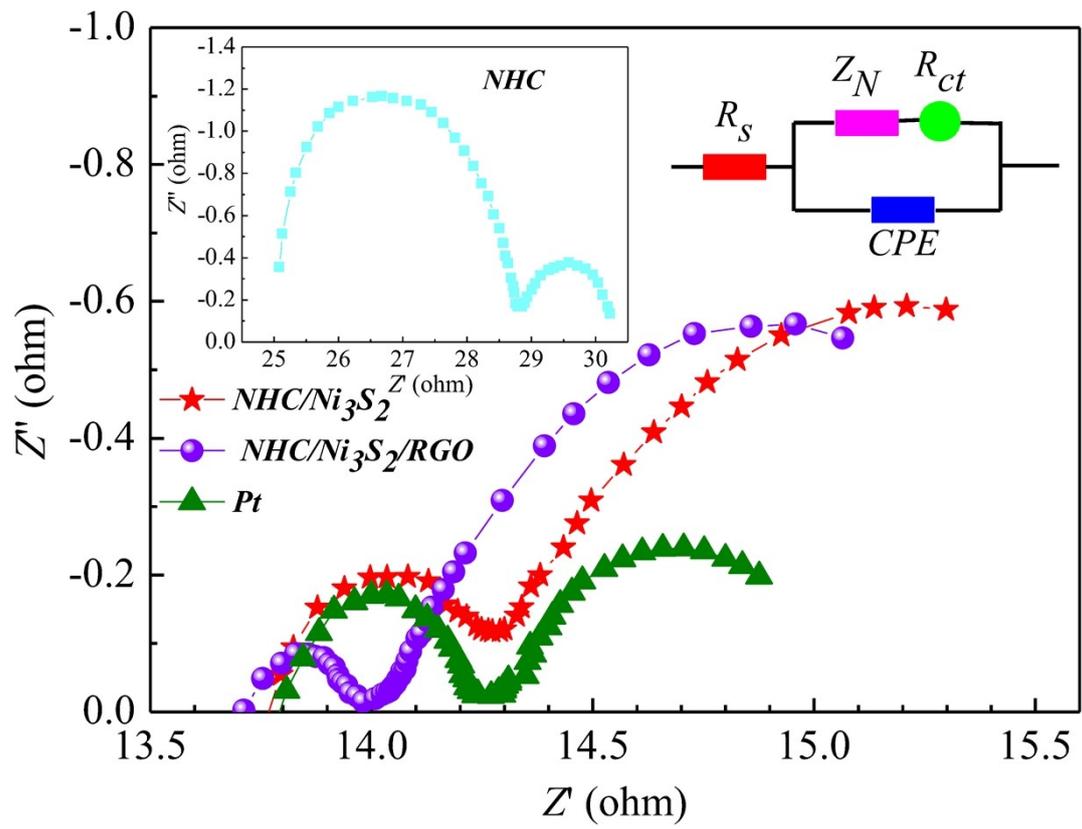


Fig. S3 EIS of prepared materials (NHC, NHC/Ni₃S₂, and NHC/Ni₃S₂/RGO).

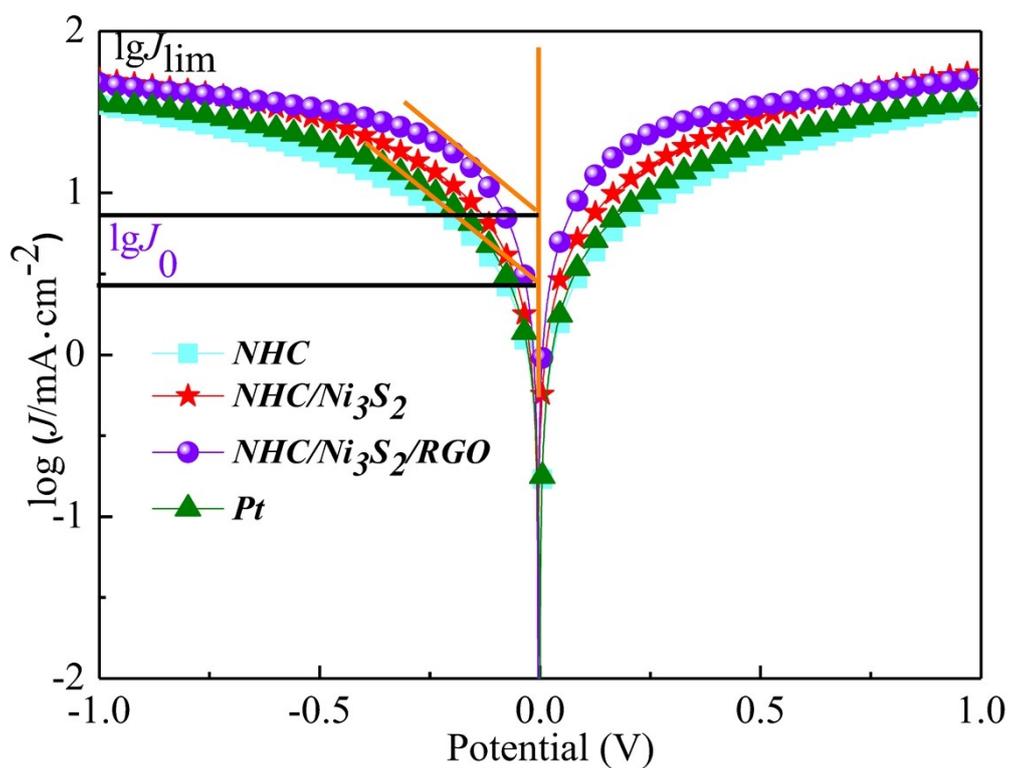


Fig. S4 the Tafel curves of all prepared materials (NHC, NHC/Ni₃S₂, and NHC/Ni₃S₂/RGO).

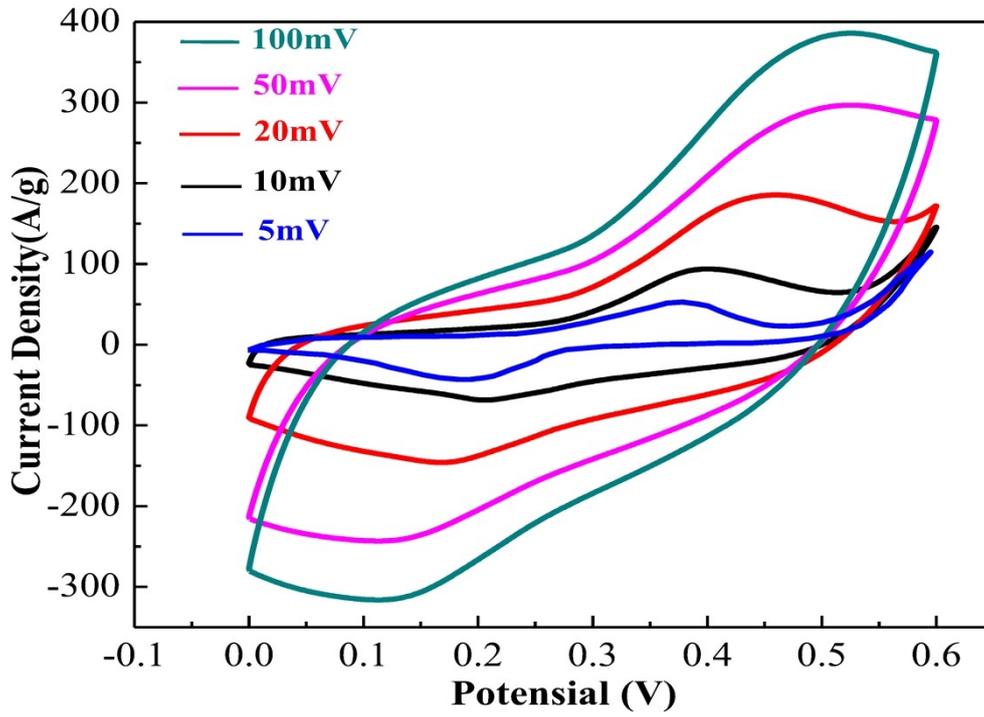


Fig. S5 CV curves of all prepared materials (NHC, NHC/Ni₃S₂, and NHC/Ni₃S₂/RGO) under different scan rate (5 mV·s⁻¹ to 100 mV·s⁻¹).

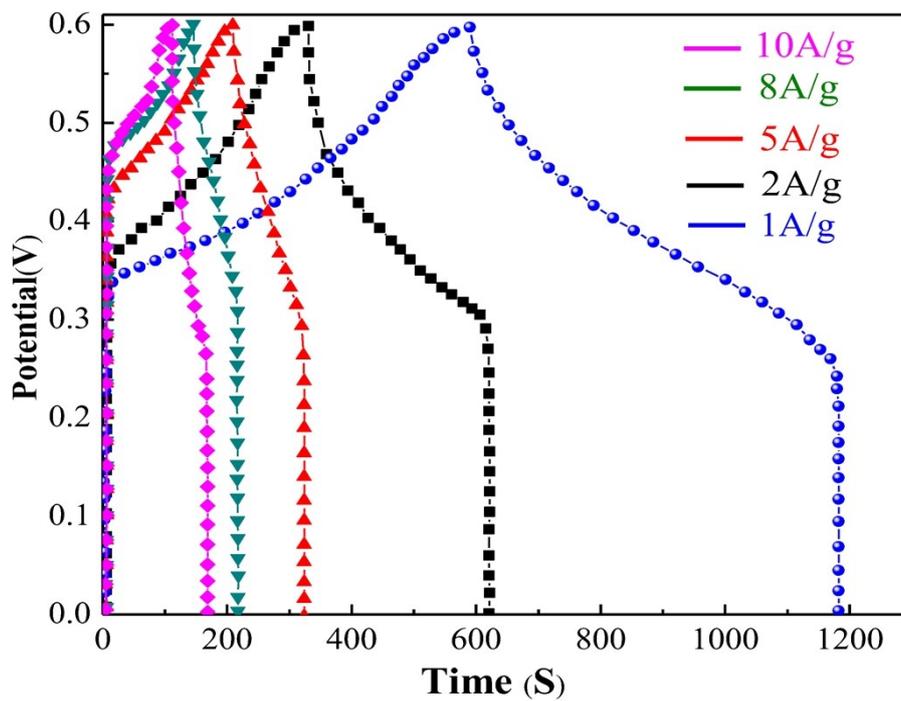


Fig. S6 GCD curves of all prepared materials (NHC, NHC/Ni₃S₂, and NHC/Ni₃S₂/RGO) under different current density (1 A·g⁻¹ to 10 A·g⁻¹).

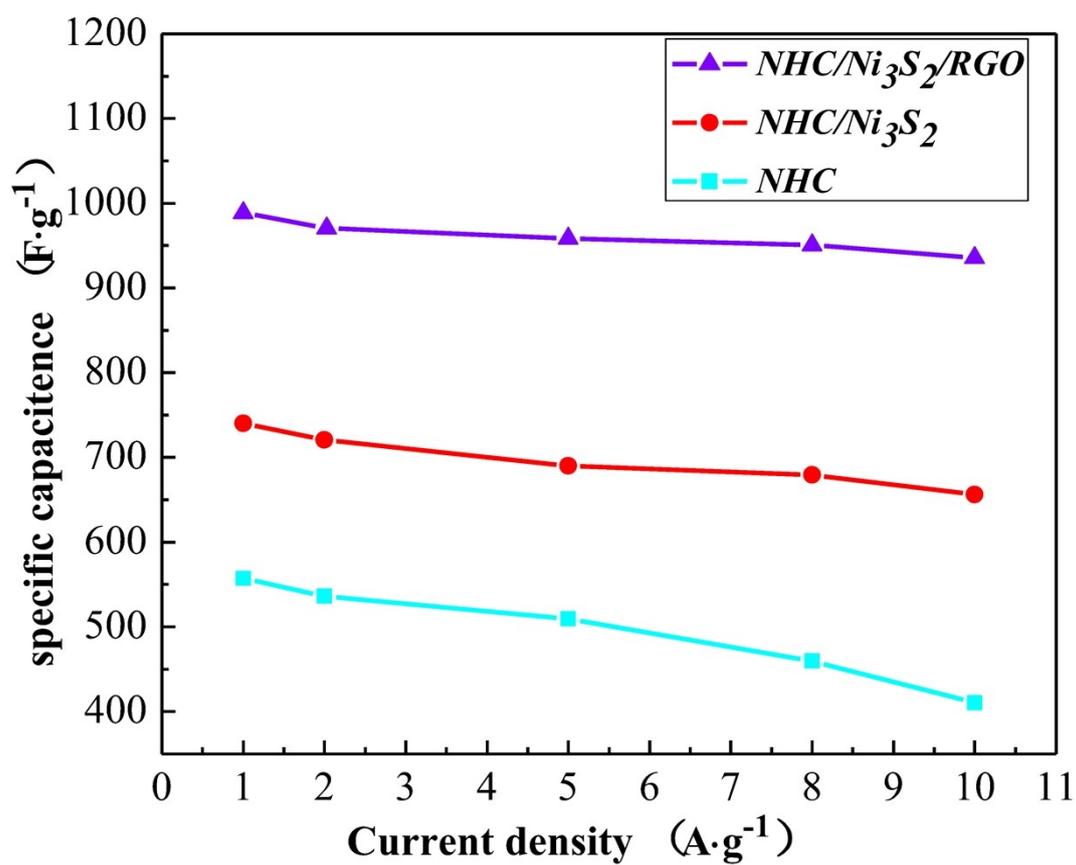


Fig. S7 The specific capacity of all prepared materials (NHC, NHC/Ni₃S₂, and NHC/Ni₃S₂/RGO) under different current density (1A·g⁻¹ to 10A·g⁻¹).

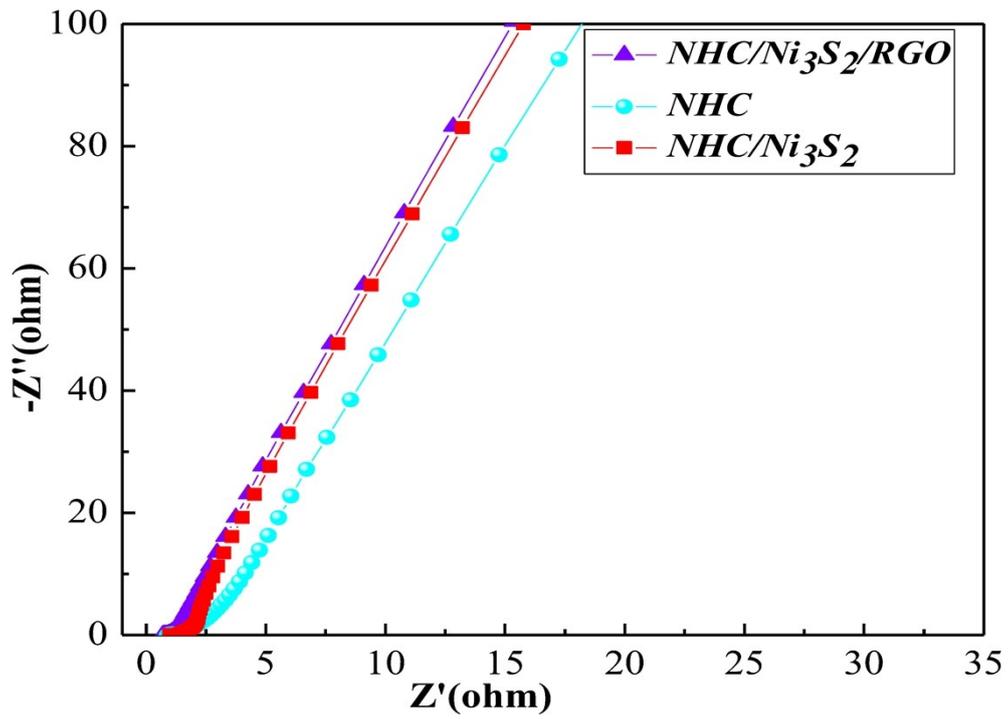


Fig. S8 The EIS of all prepared materials (NHC, NHC/Ni₃S₂, and NHC/Ni₃S₂/RGO).

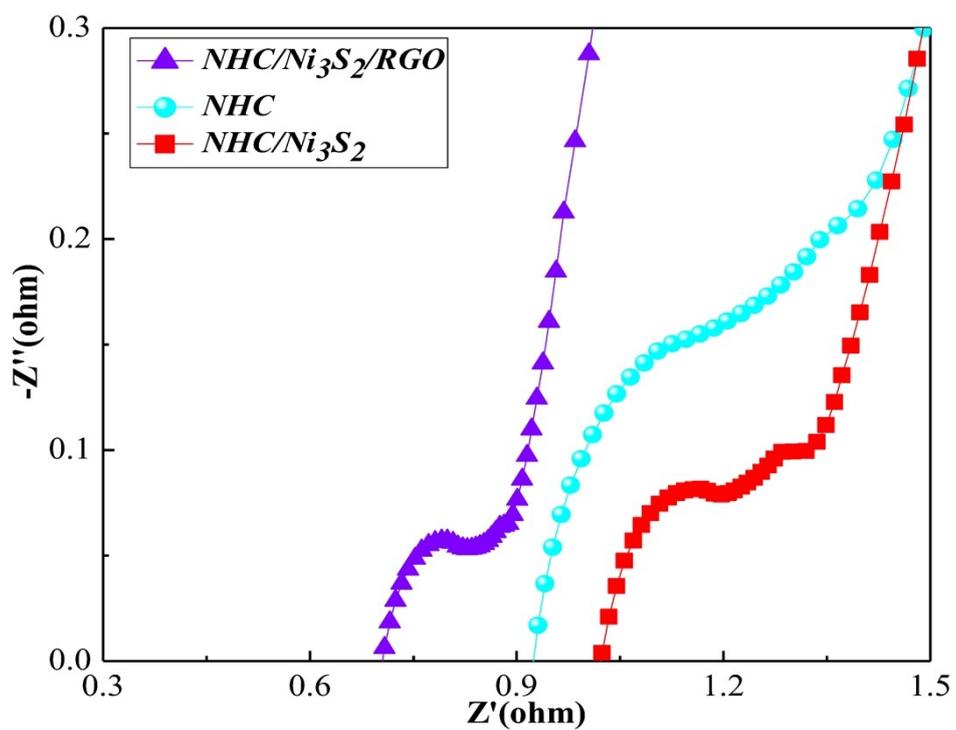


Fig. S9 The EIS high frequency region of all prepared materials (NHC, NHC/Ni₃S₂, and NHC/Ni₃S₂/RGO).

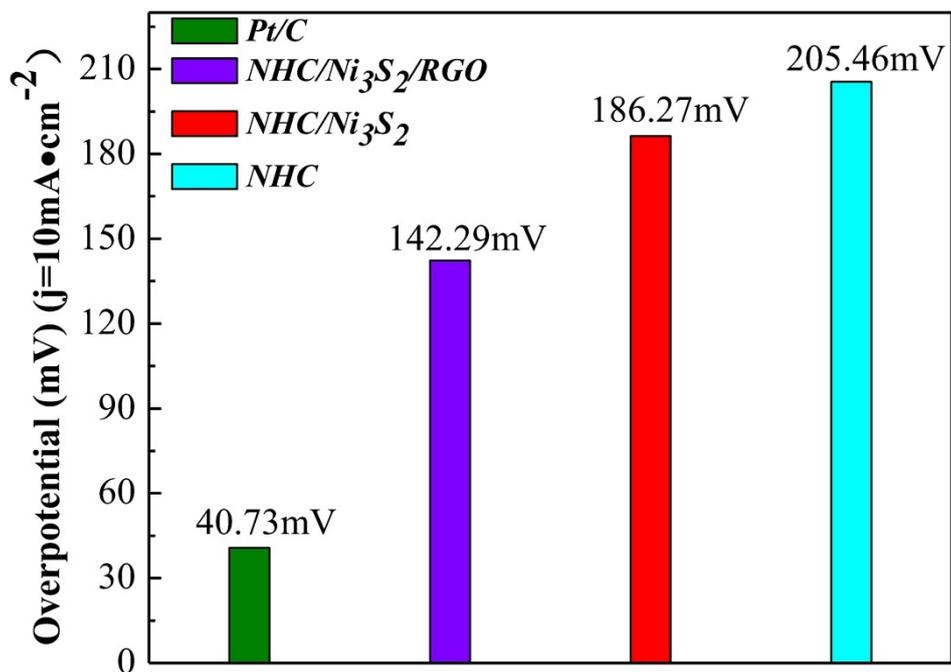


Fig. S10 The value of overpotential for different catalysts at the the current density of 10 A·cm⁻².