

Electronic Supplementary Information for

## **Solar Driven High Efficiency Hydrogen Evolution Catalyzed by Surface Engineered Ultrathin Carbon Nitride**

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**Preparation of Pt/2D-C<sub>3</sub>N<sub>4</sub>:** The Pt cocatalyst was loaded on the surface of 2D-C<sub>3</sub>N<sub>4</sub> by in-situ photo-reduction. 100 mg 2D-C<sub>3</sub>N<sub>4</sub> was dispersed in 50 mL H<sub>2</sub>O, then 2000  $\mu$ L of H<sub>2</sub>PtCl<sub>6</sub> solution (4 mg/mL H<sub>2</sub>PtCl<sub>6</sub> 6H<sub>2</sub>O) was injected into the suspension. The above suspension was irradiated by 300 W Xe lamp for 30 min under constant stirring to obtain Pt/2D-C<sub>3</sub>N<sub>4</sub>.<sup>1</sup>

**Preparation of Au/2D-C<sub>3</sub>N<sub>4</sub>:** 100 mg 2D-C<sub>3</sub>N<sub>4</sub> was dissolved in 10 mL H<sub>2</sub>O under ultrasonic treatment, then 2 mL NH<sub>3</sub> H<sub>2</sub>O, 10 mg Na<sub>2</sub>SO<sub>3</sub> and 10 mL isooctane were added into the above mixed solution respectively. The solution was transferred to an oil bath (95°C) under stirring, and then 2.1 mg of HAuCl<sub>4</sub> 4H<sub>2</sub>O was added into the mixed solution under stirring for 1 h. Afterwards, the sample was collected by centrifugation and washed several times with pure water, and finally freeze-dried.<sup>2</sup>

**Preparation of Ag/2D-C<sub>3</sub>N<sub>4</sub>:** 3.2 mg of AgNO<sub>3</sub> was initially dissolved in 6 mL H<sub>2</sub>O and 10 mL Ethylene glycol (EG). Subsequently, 48.5 mg poly(vinyl pyrrolidone) (PVP, M.W.≈55000) was added under stirring. Then, 100 mg 2D-C<sub>3</sub>N<sub>4</sub> was added into mixed solution under stirring and sonicating. After 30 min stirring and 30 min sonicating, the suspension was added into 25 mL Teflon-lined autoclave and subsequently heated at 150°C for 4 h. The resulting product was separated by centrifuging and washed several times with acetone and ethanol. The resulting samples were finally freeze-dried.<sup>3</sup>

**Preparation of Pd/2D-C<sub>3</sub>N<sub>4</sub>:** The Pd was prepared as follows: 8.0 mL of an aqueous solution containing 105 mg of poly(vinyl pyrrolidone) (PVP, M.W.≈55000), 60 mg of L-ascorbic acid (AA), 5 mg of KBr and 185 mg KCl were placed in a 20 mL vial, and pre-heated in air under stirring at 80°C for 10 min. Then, 3 mL solution containing 57 mg of Na<sub>2</sub>PdCl<sub>4</sub> was added. After the vial had been capped, the reaction was allowed to proceed at 80°C for 3 h. The Pd was finally collected after washing with water for several times. The Pd/2D-C<sub>3</sub>N<sub>4</sub> was obtained as follows: 0.5 mg of Pd with 100 mg of 2D-C<sub>3</sub>N<sub>4</sub> in 25 mL water uniformly, and then the mixed suspension was transferred into a 50 mL Teflon-lined autoclave and heated at 140°C for 4 h. The resulting samples were finally freeze-dried.<sup>4</sup>

**Preparation of Ni/2D-C<sub>3</sub>N<sub>4</sub>:** The Ni cocatalyst was loaded on the surface of 2D-C<sub>3</sub>N<sub>4</sub> by in-situ

photo-reduction. 10 mg 2D-C<sub>3</sub>N<sub>4</sub> and 4.95 mg Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O was dispersed in 100 mL of aqueous solution which contained 10 mL of triethanolamine and 90 mL water. The solution was then irradiated by a 300 W Xenon lamp (PLS-SXE 300C (BF) with an optical filter ( $\lambda > 400$  nm), Perfectlight, Beijing) with continuous stirring for 2 h.

**Preparation of Ni(OH)<sub>2</sub>/2D-C<sub>3</sub>N<sub>4</sub>:** 50 mg of 2D-C<sub>3</sub>N<sub>4</sub> was firstly dispersed in 12 mL water in a 25 mL Teflon-lined autoclave with continuous stirring, then 22.8 mg Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O and 22.0 mg HMT were added in and kept stirring, after about half an hour, the autoclave was putted in an oven and heated to 120 °C, kept for 12 h, then cooled down to room temperature. The product was collected and washed using ethanol and distilled water for several times, then freeze-dried for over one day. The obtained sample was denoted as 10% Ni(OH)<sub>2</sub>/2D-C<sub>3</sub>N<sub>4</sub>. The ratio of Ni(OH)<sub>2</sub> to 2D-C<sub>3</sub>N<sub>4</sub> differed as the amount of Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O and HMT, and the molar ratio of [HMT]/[Ni<sup>2+</sup>] was a fix value of 2.

**Preparation of NiO/2D-C<sub>3</sub>N<sub>4</sub>:** The obtained Ni(OH)<sub>2</sub>/2D-C<sub>3</sub>N<sub>4</sub> power was putted into a combustion boat and heated at 380 °C in air for 2 h with a heating rate of 5 °C/min.

**Preparation of Ni<sub>3</sub>N/2D-C<sub>3</sub>N<sub>4</sub>:** Ni(OH)<sub>2</sub>/2D-C<sub>3</sub>N<sub>4</sub> power was putted into a combustion boat and heated at 380 °C in NH<sub>3</sub> atmosphere for 3 h with a heating rate of 5 °C/min.<sup>5</sup>

**Preparation of MoS<sub>2</sub>/2D-C<sub>3</sub>N<sub>4</sub>:** 2D-C<sub>3</sub>N<sub>4</sub> (100 mg) and MoCl<sub>5</sub> (0.35 mg) were dispersed in dimethylformamide (DMF). Then, 0.0450 g Thioacetamide (TAA) was added into the solution. After sonicating it for 30 min, the suspension was transferred to a Teflon-lined stainless steel autoclave (50 mL capacity), and then heated at 200 °C for 24 h. When the autoclave cooled down to room temperature, the obtained samples were separated by centrifugation and washed with water and ethanol. Finally, they were freeze-dried for 24 h.<sup>6</sup>

**Preparation of WS<sub>2</sub>/2D-C<sub>3</sub>N<sub>4</sub>:** The 1T-WS<sub>2</sub> was synthesized through a solvothermal process. Typically, 1 mmol of WCl<sub>6</sub> and 10 mmol TAA were dissolved in 30 mL of DMF and then stirred for 1 h and sonicated for another 1h. Subsequently, the solution was transferred to a 40 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 24 h. Afterwards, the black product was washed

using ethanol for several times, and dried in vacuum oven at 50 °C for 12 h. The obtained 1T-WS<sub>2</sub> was dispersed in hexane (1.3 mg mL<sup>-1</sup>). 30 mg of 2D-C<sub>3</sub>N<sub>4</sub> and 1T-WS<sub>2</sub> suspension (4.5 mg 1T-WS<sub>2</sub>) were added in an agate mortar and ground efficiently to dryness. Then another 3 mL of ethanol was added and ground again. The solution containing the composites was washed by ethanol for several times, and then the final sample was freeze-dried.<sup>7</sup>

**Preparation of MoSe<sub>2</sub>/2D-C<sub>3</sub>N<sub>4</sub>:** 8.0 mg of MoCl<sub>5</sub> and 6.5 mg of SeO<sub>2</sub> were dissolved or dispersed in 5 mL octylamine respectively. 30 mg of 2D-C<sub>3</sub>N<sub>4</sub> were dispersed in 10 mL octylamine in a 25 mL Teflon-lined autoclave and kept stirring. Afterwards, 400 μL of MoCl<sub>5</sub> solution and SeO<sub>2</sub> dispersion were injected into the autoclave. After stirring for several minutes, the autoclave was kept in an oven at 180 °C for 12 h, then cooled down to room temperature. The product was collected and washed using absolute ethanol and distilled water several times, and freeze-dried.<sup>8</sup>

**Preparation of MoN/2D-C<sub>3</sub>N<sub>4</sub>:** To prepare the MoO<sub>3</sub> nanowires, 15 mL of H<sub>2</sub>O<sub>2</sub> (30%) was stirred rapidly, and 1 g of molybdenum powder was added slowly under ice-cooling until the clear orange sol was obtained, it is the H<sub>2</sub>MoO<sub>4</sub>. Then, the sol was transferred into a Teflon-lined autoclave and kept at 180 °C for 48 h. The autoclave was cool to room temperature, and the precipitate was collected by centrifuge and washed with deionized water three times. Finally, the sample was freeze-dried, the obtained product was MoO<sub>3</sub> nanowires. Then, 500 mg MoO<sub>3</sub> sample was calcined in tube furnace at 750°C for 6 h with a heating rate at 10°C /min in NH<sub>3</sub> atmosphere. A certain time of pretreatment to remove air before heating is very important. Finally, the obtained black sample is MoN. Finally, 10 mg MoN was dissolved in 10 mL hexane followed with a 30 min ultrasonic treatment. Then, 50 mg 2D-C<sub>3</sub>N<sub>4</sub> and 5 mL MoN solution were put into a beaker containing 10 mL of hexane under stirring until a dried sample formed. The dried gray sample was washed by ethanol and deionized water, and followed freeze-drying for 24 h. Finally, the sample was annealed at 400 °C in NH<sub>3</sub> atmosphere for 1 h at a heating rate of 10 °C min<sup>-1</sup>.<sup>9</sup>

**Preparation of Mo<sub>2</sub>C/2D-C<sub>3</sub>N<sub>4</sub>:** To obtain Mo<sub>2</sub>C nanoparticles, glucose (0.25 g) and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>•4H<sub>2</sub>O (1 g) were dissolved in 25 ml DI water. The mixture was sonicated for approximately 20 min and magnetic stirring 30 min at room temperature until a homogeneous solution was achieved. Then, the solution was transferred to a 50 mL Teflon-lined stainless steel

autoclave and heated in an oven at 200 °C for 12 h with no intentional control of ramping or cooling rate. The black product was collected by centrifugation at 10000 rpm for 3 min and washed with DI water and ethanol for at least 3 times followed by freeze-drying. The dried sample was calcined in tube furnace at 750 °C for 5 h with 3 °C/min heating rate at 5% H<sub>2</sub>/Ar mixture gas atmosphere. The resulting powder is Mo<sub>2</sub>C and can be collected after the tube furnace cooling down to room temperature. Then, 5 mg of Mo<sub>2</sub>C was dispersed in 10 mL hexane and after 30 min ultrasonic treatment, a homogeneous solution was formed. Then, 30 mg of 2D-C<sub>3</sub>N<sub>4</sub> and a certain amount of Mo<sub>2</sub>C solution were dosed into a beaker containing 10 mL of hexane. Under stirring for another 20 min, a dried sample formed. After the reaction was completed, the obtained grey product was washed with DI water and ethanol. The product then underwent freeze-drying process.<sup>10</sup>

**Preparation of CoSe<sub>2</sub>/2D-C<sub>3</sub>N<sub>4</sub>:** 50 mg 2D-C<sub>3</sub>N<sub>4</sub> was dispersed in a 25 mL Teflon-lined autoclave containing 12 mL DI and kept stirring. Afterwards, 6.6866 mg Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 6.4568 mg Hexamethylenetetramine (HMT) with mole ratio of 1:2 were added into the suspension forming pink solution. Then, the autoclave was heated in an oven at 120°C for 12 h. After the autoclave cooled down, the synthesized product was separated, washed and freeze-dried to obtain the Co(OH)<sub>2</sub>/2D-C<sub>3</sub>N<sub>4</sub>. The obtained Co(OH)<sub>2</sub>/2D-C<sub>3</sub>N<sub>4</sub> was then dispersed in a 25 mL Teflon-lined autoclave containing 12 mL N,N-Dimethylformamide (DMF) solution. Afterwards, 120 mg of Se powder was added into the suspension and kept stirring for 15 mins to disperse uniformly. The autoclave was then put into an oven and heated at 200°C for 24 h. The product was washed, freeze-dried to obtain o-CoSe<sub>2</sub>/2D-C<sub>3</sub>N<sub>4</sub>. Finally, the o-CoSe<sub>2</sub>/2D-C<sub>3</sub>N<sub>4</sub> was placed in a tube furnace and annealed at 350°C in Ar atmosphere for 2 h to remove the excess amount of Se powder.<sup>11</sup>

### **Characterizations**

The powder X-ray diffraction (XRD) patterns of the samples were recorded on Bruker D8 Advance diffractometer with monochromatized Cu K $\alpha$  radiation. The surface electron microscopy (SEM) observations were performed on JEOL-JSM-7800F and elemental mappings were collected by EDAX. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were performed on JEOL-JEM-2100 with an acceleration voltage of 200 kV. The photoluminescence (PL) spectra and fluorescence decay curves (FL) were recorded on

QuantaMaster & TimeMaster Spectrofluorometer. Ultraviolet-visible diffused reflectance spectra (UV-vis) were obtained by Thermo Fisher UV-3600 plus spectrophotometer with BaSO<sub>4</sub> as the reflectance standard. Raman spectra were recorded at room temperature excited with 532 nm laser by Thermo Scientific DXR Raman Microscope. The Fourier transform infrared spectra (FT-IR) of the materials were analyzed using Nicolet Nexus 470 spectrometer. X-ray photoelectron spectroscopy (XPS) was tested on ESCALab MKII X-ray photoelectron spectrometer using Mg K $\alpha$  radiation.

### *Theoretical calculations*

Density functional theory (DFT) calculations were performed in the Vienna ab initio simulation package (VASP). A spin-polarized GGA PBE functional, all-electron plane-wave basis sets with an energy cutoff of 520 eV, and a projector augmented wave (PAW) method were adopted. Ni<sub>3</sub>N is simulated using a surface model of p (2  $\times$  2) unit cell periodicity. A (3  $\times$  3  $\times$  1) Monkhorst-Pack mesh was used for the Brillouin-zone integrations to be sampled. The conjugate gradient algorithm was used in the optimization. The convergence threshold was set  $1 \times 10^{-4}$  eV in total energy and 0.05 eV/Å in force on each atom.

The Gibbs free-energy ( $\Delta G_{H^*}$ ) is expressed as:  $\Delta G_{H^*} = \Delta E_{H^*} + \Delta E_{ZPE} - T\Delta S$ . Where  $\Delta E_{H^*}$ ,  $\Delta E_{ZPE}$  and  $\Delta S$  are the adsorption energy of atomic hydrogen on the given surface, zero point energy correction and entropy change of H\* adsorption, respectively. The zero point energy correction can be estimated by the equation  $\Delta E_{ZPE} = E_{ZPE}(H^*) - 1/2 E_{ZPE}(H_2)$ .  $\Delta S$  can be calculated by the equation  $\Delta S = S(H^*) - 1/2 S(H_2) \approx -1/2 S(H_2)$ , due to the negligible of the entropy of hydrogen in adsorbed state.  $\Delta E_{H^*}$  is calculated as  $\Delta E_{H^*} = E_{tot} - E_{sub} - 1/2 E_{H_2}$ , where  $E_{tot}$  and  $E_{sub}$  are energies of H adsorbed system and the clean given surface, and  $E_{H_2}$  is the energy of H<sub>2</sub> molecular in gas phase.

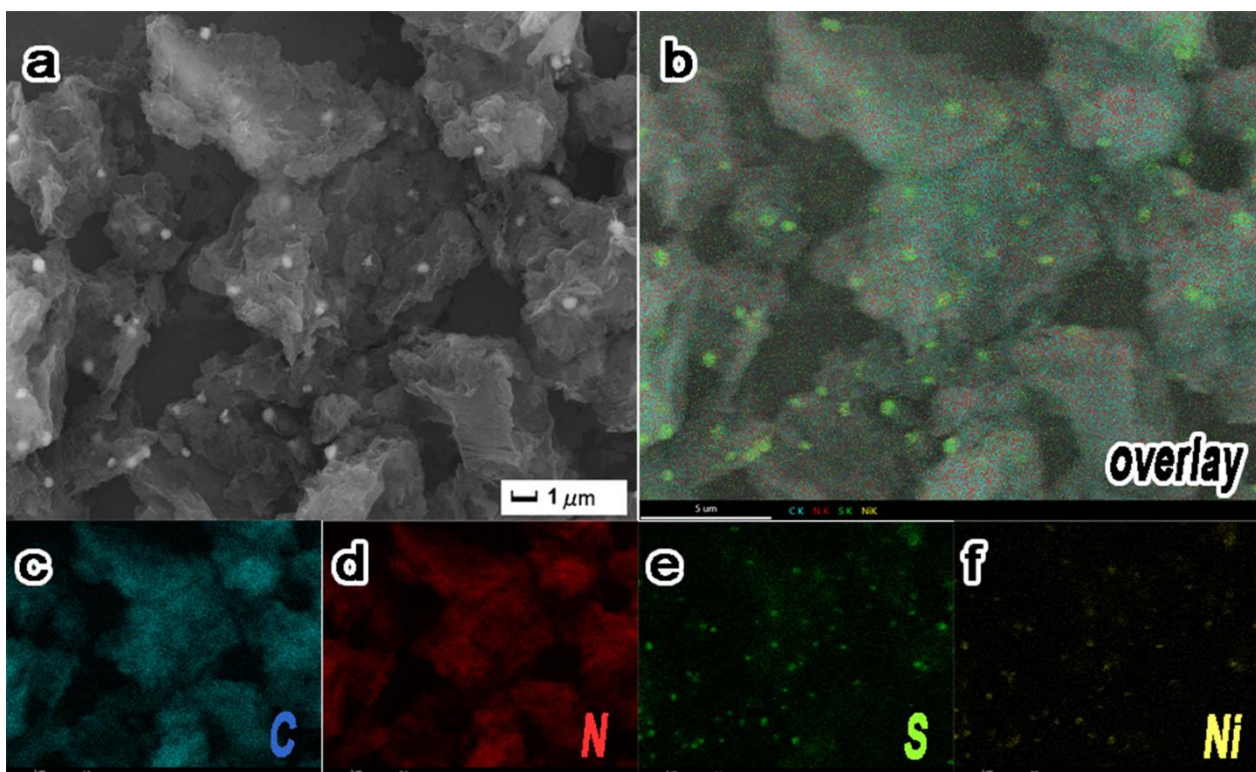


Figure S1. SEM images of NSCN and corresponding elemental mapping.

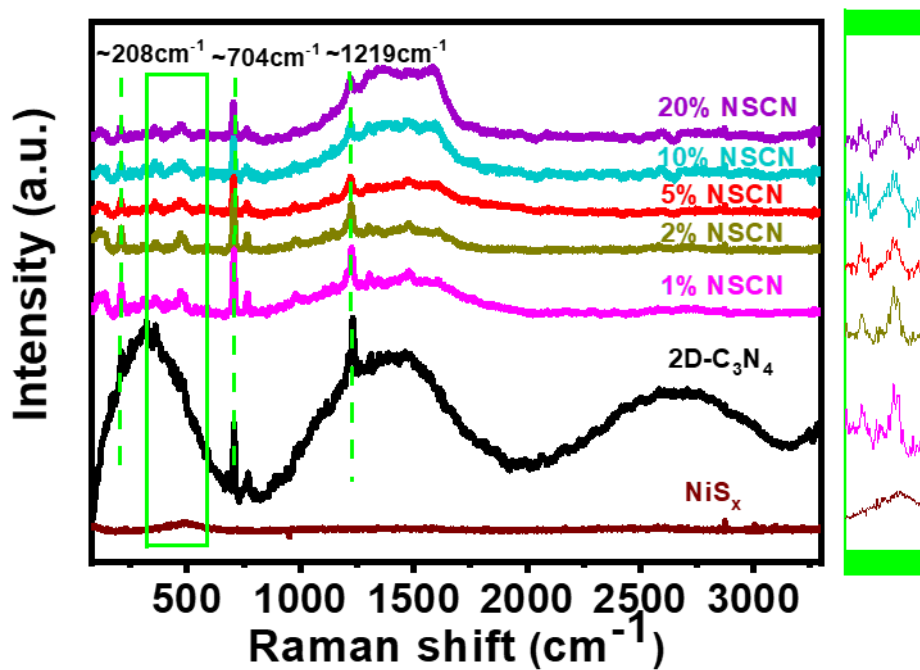


Figure S2. Raman spectra of the synthesized catalysts.

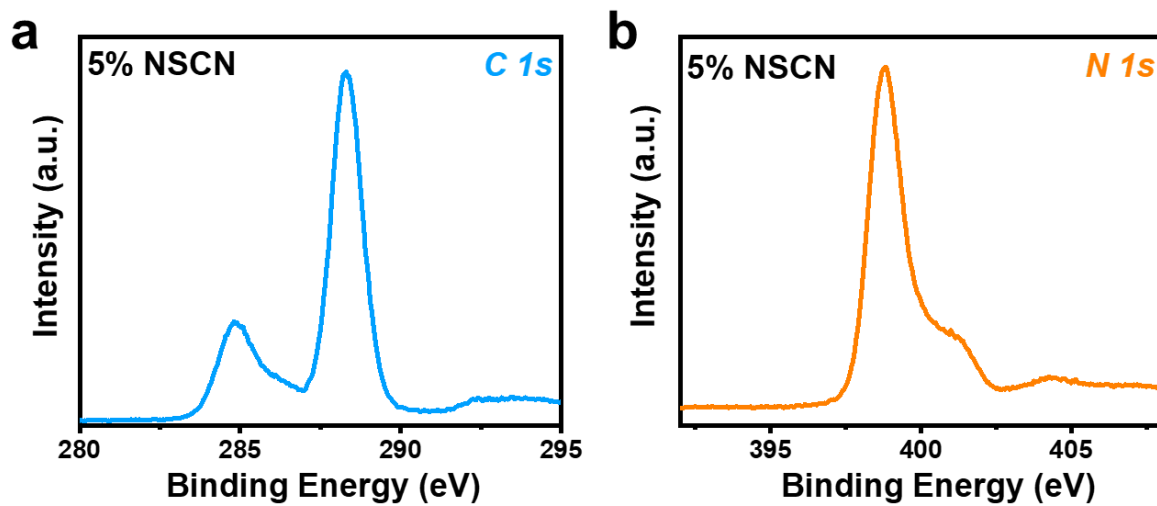


Figure S3. High-resolution XPS spectra of C 1s and N 1s for 5% NSCN.

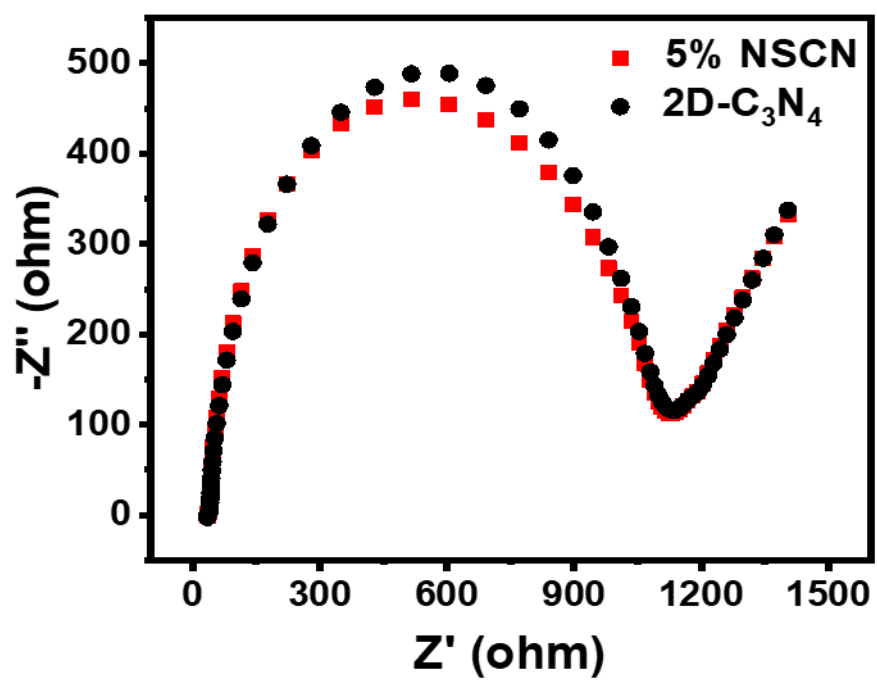
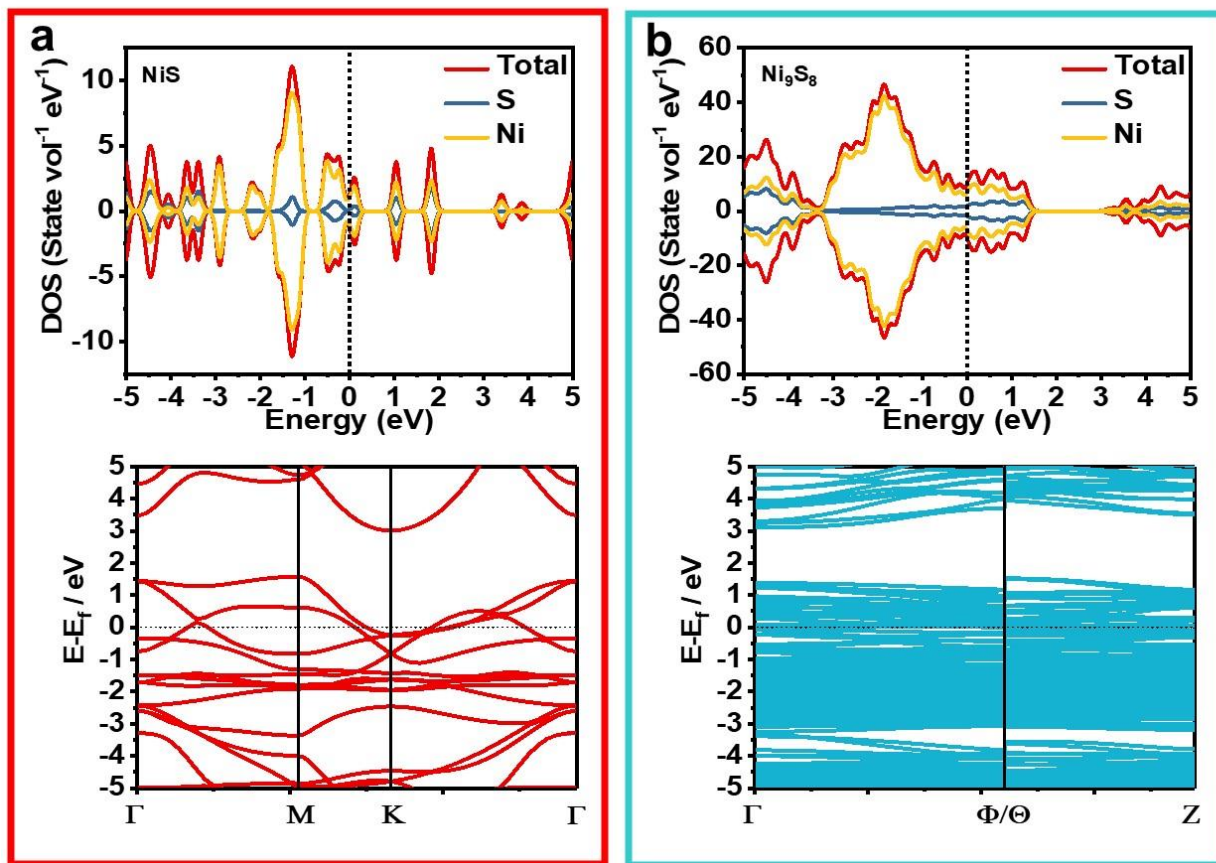
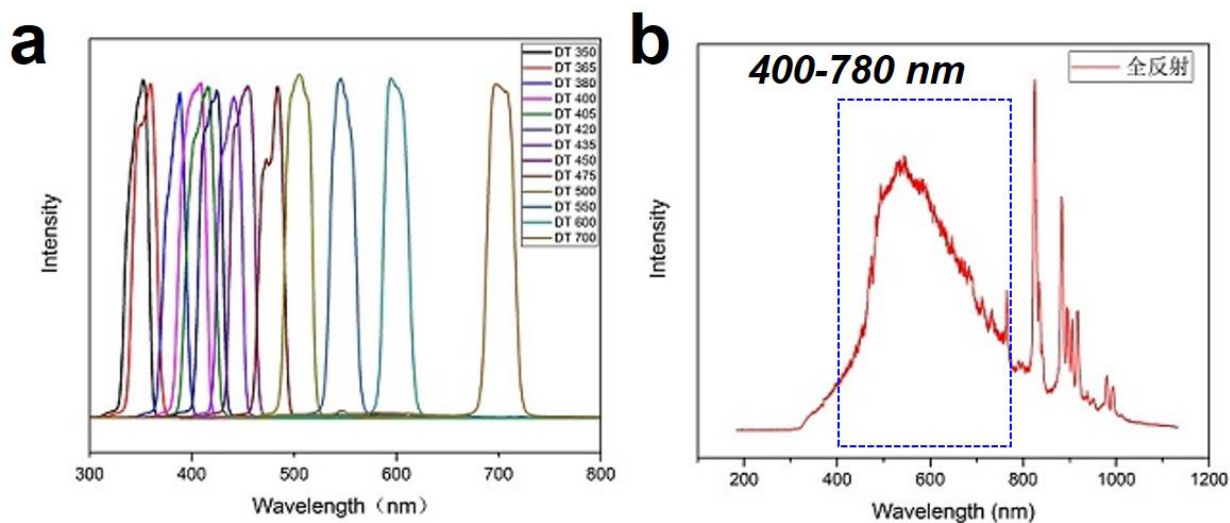


Figure S4. EIS Nyquist plots of prepared catalysts.





**Figure S5.** The calculated band structure and total density of states for a)  $\text{NiS}_x$  and b)  $\text{Ni}_9\text{S}_8$ .



**Figure S6.** The power spectra of the monochromatic light (a) and visible light (b) used in the study.

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