Supporting Information

N, P-codoped Carbon Shells Grafted on Nickel Nanoparticles as Efficient Catalyst for Hydrogen Generation

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S1 Experimental sections

S1.1 Materials and Methods

Nickel (II) acetylacetonate (99.0% purity, Sigma-Aldrich), melamine (97.5% purity), and H_3PO_4 were utilized as starting materials for the preparation of the Ni/NCP sample.

S1.2 Synthesis procedure

In a beaker containing 30 mL of 0.1 M H_3PO_4 aqueous solution, 100 mg of melamine and 150 mg of Nickel (II) acetylacetonate were dispersed. The whole solution was stirred for 30 minutes for homogeneous mixing of reactants. The solution was oven-dried at 60 °C overnight. The obtained solid was placed at one end of a quartz tube, with the opposite end sealed using a nitrogen-filled rubber bladder. This setup was introduced to the tube furnace and heated to 700 °C with a heating rate of 3 °C/min for 30 minutes. Furthermore, the resulting product was collected and washed several times alternately with ethanol and water, then dried again in a hot air oven overnight at 60 °C. Finally, the sample was labeled as Ni/NCP and was prepared for subsequent characterization and electrochemical evaluation.

S1.3 Structural characterization

Several techniques were utilized for the characterization of materials. X-ray diffraction (XRD) was carried out on a PANalytical Xpert Pro system using Cu Kα radiation (λ = 1.541 Å) to confirm the phase purity. The morphology was analyzed using a Zeiss Ultra-55 field-emission scanning electron microscope (FE-SEM) and an FEI Tecnai T20 Super Twin transmission electron microscope (TEM). Raman spectroscopy was carried out using a LabRam HR system with a 532 nm laser to evaluate the defect structure of the samples. X-ray photoelectron spectroscopy (XPS) was executed for compositional analysis using a monochromatic Al Kα X-ray source operated at 15 kV and 6 mA. The elemental composition of the sample was calculated using equation (S1).

$$\text{At. \%} = \frac{\dfrac{A_i}{SF_i}}{\displaystyle\sum_i \dfrac{A_i}{SF_i}} \times 100 \qquad\qquad (S1)$$

where, i = metal/C/N; A_i: area under the curves, $SF_C = 0.25$, $SF_N = 0.42$, $SF_{Ni} = 4.5$, and $SF_P = 0.39$.

S1.4 Electrochemical characterization

Electrochemical experiments were conducted in N_2-saturated aq. 1 M KOH using a three-electrode setup, where a Hg/HgO electrode served as the reference, a graphite rod as the counter, and carbon Toray paper as the working electrode. The catalyst ink was prepared by dispersing 4 mg of the Ni/NCP sample in 1 mL of ethanol, followed by 30 minutes of sonication, together with 10 µL of Nafion solution (5 wt.% in a mixture of lower aliphatic alcohols and 15-20% water). The working electrode was fabricated by drop-casting the catalyst ink onto carbon Toray paper with an active area of approximately 0.04 cm^2, followed by drying at 60 °C for 1 hour. Subsequently, the electrochemical measurements were carried out in an N_2-saturated alkaline electrolyte. The potential was converted to the reversible hydrogen electrode (RHE) scale using equation S2:

$$E_{RHE} = E_{Hg/HgO} + 0.978 \tag{S2}$$

The reference electrode was calibrated to convert its potential to the RHE, as shown in Figure S1(a). The linear sweep voltammetry (LSV) curves were recorded with a scan speed of 10 mV/s. Electrochemical impedance spectra were collected over a frequency range of 100 mHz to 1 MHz at various applied potentials relevant to HER.
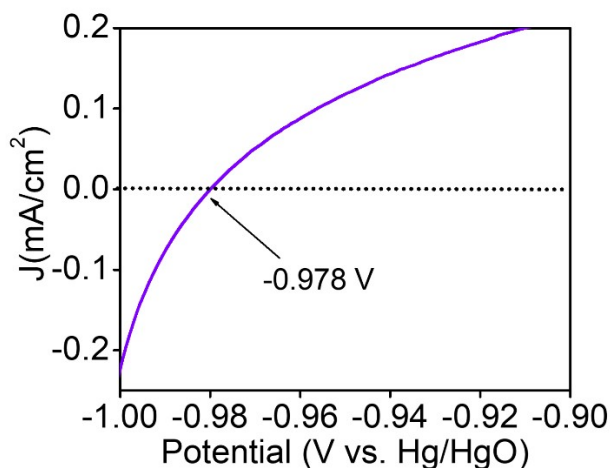

Figure S1 Calibration of the Hg/HgO electrode versus the reversible hydrogen electrode (RHE) in 1 M aqueous KOH solution.

To convert the measured potential to the RHE scale, the following procedure was used. A Hg/HgO electrode served as the reference, while Pt wire/mesh acted as both the working and counter electrodes. Current density was recorded as a function of applied potential in H_2-

saturated 1 M KOH at a scan rate of 10 mV/s, as shown in Figure S1. From the plot, the current density reaches zero at -0.978 V, indicating that all Hg/HgO potentials in our measurements were converted to RHE by adding 0.978 V.
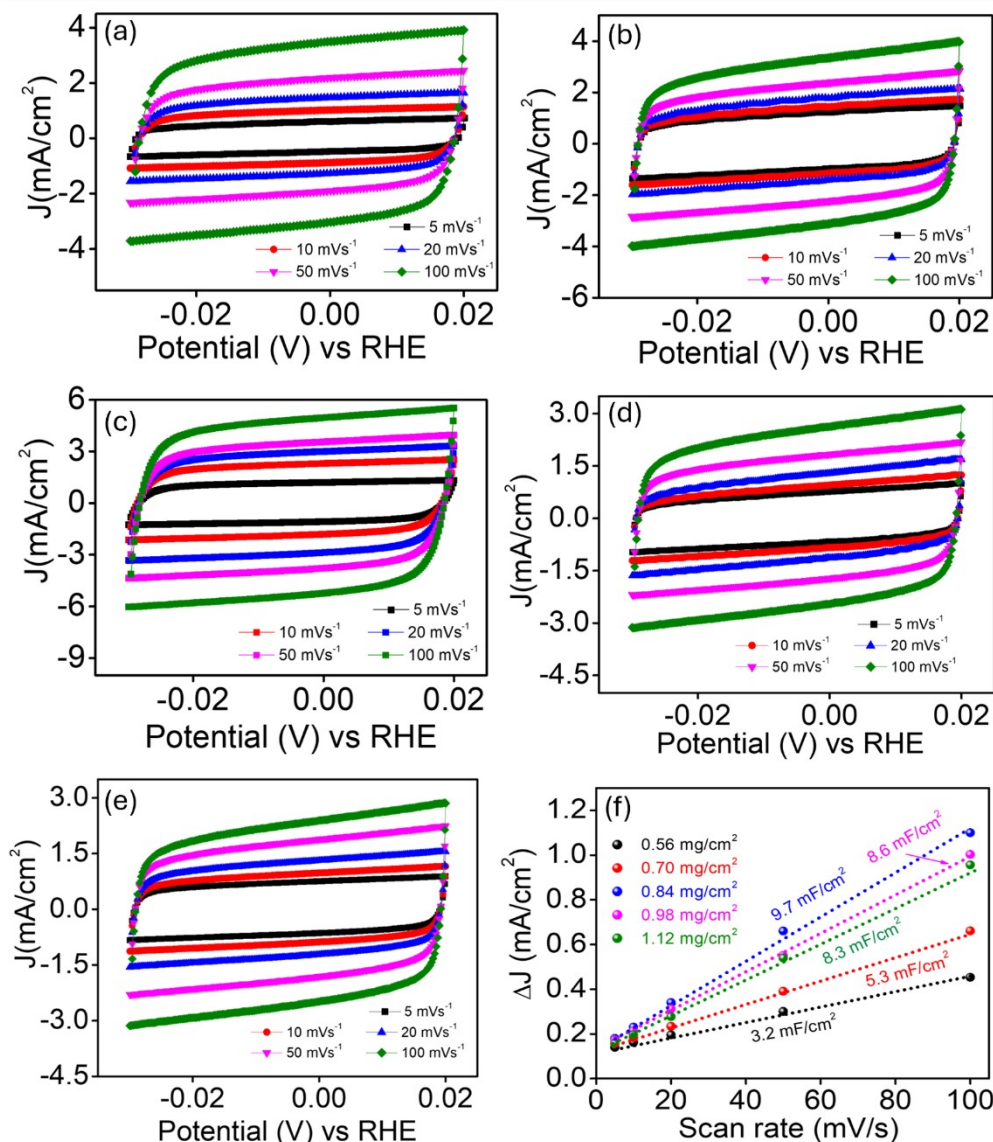

Figure S2 Cyclic voltametry (CV) curves at scan speed of 5, 10, 20, 50, and 100 mV/s for mass loadings of (a) 0.56 mg/cm^2, (b) 0.70 mg/cm^2, (c) 0.84 mg/cm^2, (d) 0.98 mg/cm^2, and (e) 1.12 mg/cm^2, and corresponding to the (f) double layer capacitance (C$_{dl}$) estimation for Ni/NCP sample.

Cyclic voltammetry curves recorded in the non-Faradaic region at different scan rates for various mass loadings of Ni/NCP catalyst. The double-layer capacitance (C$_{dl}$) was determined from the slope of the linear fit obtained by plotting current density versus scan rate at -0.01 V

vs. RHE, as illustrated in Figure S2(f). The C_{dl} value is estimated using the following equation. The relationship is expressed as-

$$j = \upsilon \times C_{dl} \tag{S3}$$

where j represents the change in current density and υ denotes the scan rate. The electrochemically active surface area (ECSA) is then determined using ECSA = C_{dl} / C_S, with C_S being the specific capacitance. For a flat, smooth surface, C_S is typically taken as 0.040 mF cm^{-2}.
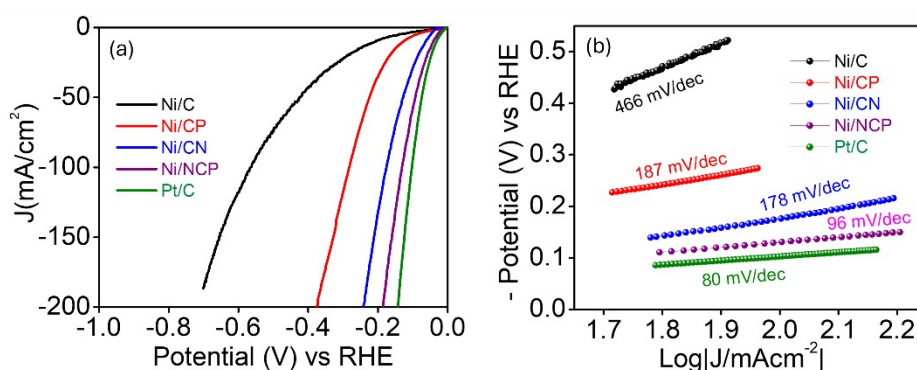

Figure S3 (a) LSV curves for Ni/C (without doped), Ni/CP (P-doped), Ni/CN (N-doped), Ni/NCP, and Pt/C samples, and (b) Tafel plot for all samples.
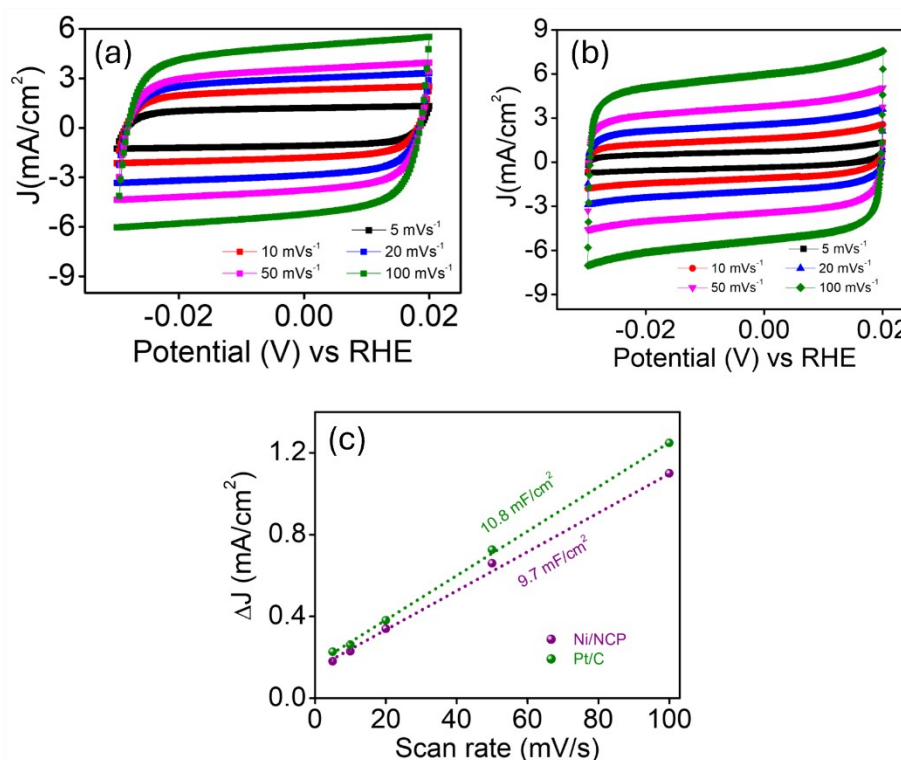
Figure S4 CV curves at different scan speeds for (a) Ni/NCP and (b) Pt/C samples, and corresponding C_{dl} estimation for Ni/NCP and Pt/C samples.

Table S1 The R_{ct} comparison at various applied potentials for the Ni/NCP sample.

-Potential (mV)	R_{ct} (Ohm)
50	2.66
100	2.39
150	2.23
200	2.06

Gas collection setup: In this arrangement, a constant voltage is applied to create hydrogen gas by an electrochemical reaction. The electrode and electrolyte are contained in the reaction flask. An inverted measuring cylinder filled with water is immersed in a water trough and connected to a flask via a delivery tube. To stop gas leaks, the delivery tube is positioned with its tip submerged in the water inside the inverted cylinder, and all connections are sealed tightly. Hydrogen gas is generated during the experiment and passes down the delivery tube into the inverted cylinder submerged in water. A comparable volume of water is displaced downward into the trough as the hydrogen gas builds up. As more gas is gathered, the water level in the cylinder progressively drops.