Supplementary Information (SI) for RSC Advances.

# Electronic Supporting Information

# Synergistic Enhancement of Hydrogen Evolution Reaction via N and Ni Co-doping in $TiO_2$-Modified Pt/C Catalysts

**Xufeng Lin[1,2,*], Huijie Wei[1], Yixuan Zhang[1], Hua Chi[1], Xiaofan Liu[1], Yanyan Xi[3,*]**

[1]College of Chemistry and Chemical Engineering, China University of Petroleum (East China), Qingdao, P. R. China, 266580

[2]State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Qingdao, P. R. China, 266580

[3]Advanced Chemical Engineering and Energy Materials Research Center, China University of Petroleum (East China), Qingdao, P. R. China, 266580

## Catalyst characterization

The crystallinity and phase composition of the catalysts were analyzed using an X-ray diffractometer (X'Pert Pro MPD) with a scanning range of 3-80° and a scanning rate of 4°/min. Low-temperature $N_2$ adsorption-desorption isotherms were measured using an ASAP 2020 analyzer (Micromeritics, USA). Prior to analysis, samples were degassed under vacuum at 200 °C for 6 h. Transmission electron microscopy (TEM) images were obtained using a JEM-2100EX microscope (JEOL, Japan) operated at 200 kV. Raman spectra were collected on a Renishaw Micro-Raman system 2000 using a 532 nm laser source, with a spectral range of 100-2000 cm$^{-1}$. The elemental composition and chemical states of the catalysts were analyzed using X-ray photoelectron spectroscopy (XPS) on an Escalab 250 Xi instrument (Thermo Fisher Scientific, USA). Although ICP-OES could precisely quantify Ni and N, it was unavailable during this study due to instrument downtime and limited sample amounts. Instead, controlled synthesis using precisely weighed precursors ensures nominal Ni loadings of 1 wt% and 3 wt% are reliably achieved. XPS confirms Ni and N are present in expected chemical states, and systematic trends—increasing BET surface area and optimal HER performance at 1% Ni—correlate with Ni content. These consistent property–activity relationships, together with spectroscopic validation and synthesis control, confirm successful and controlled incorporation of Ni and N.

# Performance evaluation of catalytic hydrogen evolution reaction

Electrochemical measurements were conducted using a standard three-electrode system in a $N_2$-saturated 1.0 M KOH solution. A graphite sheet and a Hg/HgO electrode were used as the counter and reference electrodes, respectively. The working electrode was prepared by depositing catalyst ink on a glassy carbon electrode. A schematic diagram of the three-electrode system and its connection with the electrochemical workstation is shown in Figure S1.

The potential measured against the Hg/HgO electrode was converted to the reversible hydrogen electrode (RHE) scale using the following equation:

$$E(\text{RHE}) = E(\text{Hg/HgO}) + 0.059 \times \text{pH} + 0.098 \qquad (1\text{-}1)$$

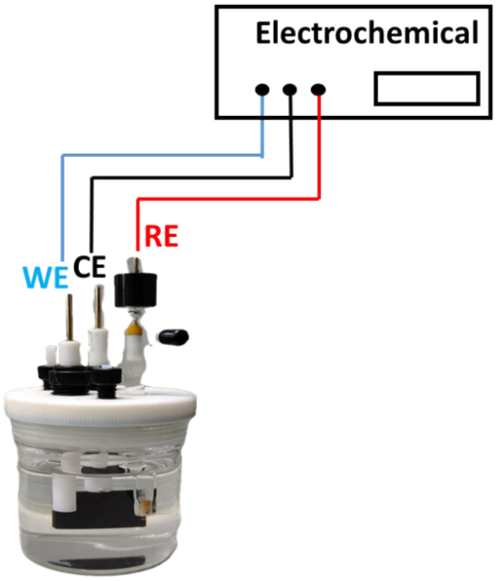

**Figure S1 Schematic diagram of the three-electrode system and its connection with the electrochemical workstation**

Tests of the three-electrode system were conducted in a nitrogen-saturated 1.0 M KOH solution. Cyclic voltammetry (CV) activation was performed in the potential range of 0.3 to -0.9 V (vs. Hg/HgO). Linear sweep voltammetry (LSV) was conducted from -0.9 to -1.7 V (vs. Hg/HgO) at a scan rate of 5 mV/s. Electrochemical impedance spectroscopy (EIS) measurements were carried out over a frequency range of $10^5$ to 0.01 Hz. Catalyst stability was evaluated using chronoamperometry (i-t) at a fixed potential by monitoring the current decay over time.

It should be noted that while direct quantification of hydrogen evolution rate (e.g., in $\mathrm{mmol \cdot h^{-1} \cdot g^{-1}}$) would provide additional validation of catalytic performance, such measurements require specialized gas collection and analysis setups that are currently unavailable in our laboratory. Nevertheless, the combination of overpotential, Tafel slope, and charge transfer resistance—all standard and widely accepted metrics in the electrocatalysis community—provides a comprehensive and reliable assessment of HER activity. These three complementary measurements collectively support the relative performance trends and mechanistic conclusions presented in this work.