

Pt Nanoparticles Dispersed Ni(OH)₂ nanosheets via Pulsed Laser Deposition Method to Efficiently Enhance Hydrogen Evolution Reaction Performance at Alkaline Conditions

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Experimental Section

Reagents and Materials

85% Potassium hydroxide (KOH) was purchased from Shanghai Titan Scientific Co., Ltd. Urea ($\text{CO}(\text{NH}_2)_2$) and Ammonium fluoride (NH_4F) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Nickel nitrate hexahydrate was ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) purchased from Sinopharm Chemical Reagent Co., Ltd. deionized water. Ni foam was purchased from Suzhou Keshenghe Metallic Products Co., Ltd. All the reagents and solvents were commercially obtained and used without further purification.

Synthesis of $\text{Ni}(\text{OH})_2$

Self-supporting layered nickel hydroxide salts were prepared by the vapor-phase hydrothermal (VPH) method. In detail, nickel foam ($3 \times 3.5 \text{ cm}^2$) was put into the hydrochloride, ultrapure water, ethanol and acetone in ultrasonic processing respectively for 10 minutes, to remove nickel foam (NF) surface oxide layer and organic impurities. Then 4mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2mmol NH_4F , and 5mmol $\text{CO}(\text{NH}_2)_2$ was added into the 50 mL deionized water. After magnetic stirring after 20 minutes, the mixture was placed on a Teflon holder. The VPH reaction was operated at 120°C for 12 hours.

Synthesis of $\text{Pt-Ni}(\text{OH})_2$ -X, X=deposition time

The $\text{Pt-Ni}(\text{OH})_2$ -X sample was synthesized by the pulsed laser deposition method. In detail, the above as-prepared $\text{Ni}(\text{OH})_2$ was $3 \times 3.5 \text{ cm}^2$ firstly. Then laser irradiation of Pt target formed the plasma plume. After that, the plasma plume was further deposited on the surface of $\text{Ni}(\text{OH})_2$ to form the $\text{Pt-Ni}(\text{OH})_2$ -X. X represents the beginning of laser irradiation to the end of deposition. The laser emission voltage is 25 KV. The distance between platinum target and $\text{Ni}(\text{OH})_2$ @NF was 6 cm. The laser emission energy is 300 mj. The fabrication process of $\text{Pt-Ni}(\text{OH})_2$ -5, $\text{Pt-Ni}(\text{OH})_2$ -7.5, $\text{Pt-Ni}(\text{OH})_2$ -10 was similar to that of $\text{Pt-Ni}(\text{OH})_2$ -2.5, only the deposition time was different.

Characterization

X-ray diffraction analysis (XRD, Philips X'pert PRO) equipped with Nifiltered monochromatic $\text{CuK}\alpha$ radiation ($\lambda\text{K}\alpha 1 = 1.5418 \text{ \AA}$) at 40 kV and 40 mA was used for the crystalline structures of electrodes. The field emission scanning electron microscopy (FESEM, Quanta 200FEG) and transmission electron microscopy (TEM, JEOL 2010) with an energy dispersive X-ray spectrometer (EDS Oxford, Link ISIS) were used for characterizing the electrode morphology and microstructure. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, America) equipped with Al $\text{K}\alpha_{1,2}$ monochromatized radiation at 1486.6 eV X-ray source.

Electrochemical Measurements.

The electrocatalytic performance of all the electrodes were conducted on the CHI 660E electrochemical workstation (CH Instruments, Inc.). The as-prepared $\text{Pt-Ni}(\text{OH})_2$ -X was directly cut into the working electrode was $1.0 \times 1.5 \text{ cm}^2$ and the electrode area used in our work was $1.0 \times 1.0 \text{ cm}^2$. The $\text{Pt-Ni}(\text{OH})_2$ -X, Hg/HgO electrode and Pt mesh were used for working electrode, reference electrode and the counter electrode, respectively. All the electrochemical performances were carried out in 1 M KOH (pH=14) solution. And the potential was reflected, relative to reversible hydrogen electrode (RHE) was according to the Equation (1).

$$E(\text{RHE}) = 0.059 \cdot \text{pH} + 0.098 + E(\text{Hg}/\text{HgO}) \quad (1)$$

where RHE is reversible hydrogen electrode, Hg/HgO is reference electrode.

The argon (Ar) feeding gas with a flow rate of 10 mL min^{-1} was successively purged to drive

dissolved oxygen, carbon dioxide, and other gases from the solution. The cyclic voltammetry (CV) was measured 0.174-0.274 v (vs. RHE) on both sides of open circuit voltage. The number of scanning segment is 2 turns. Sensitivity is 0.1 A V⁻¹. Scanning rate is 30, 60, 90, 120, 150 mV s⁻¹. The LSV curves were corrected with 95% IR-correction. Then, the LSV experiments were carried out at the potential range of 0.424 V - -0.975 V vs. RHE. The scanning rate was 5 mV s⁻¹. The sample interval was 0.001 V, and the sensitivity was 0.1 A V⁻¹. The electrochemically active surface area was calculated using the following equation (2)

$$ECSA=C_{dl}/C_s$$

where ECSA is electrochemically active area, C_{dl} is electric double layer capacitor, C_s is specific capacitance.



Scheme S1. The HER pathway in alkaline electrolyte follows the Volmer–Heyrovsky or Volmer–Tafel mechanisms shown in Equations (1) and (2).¹

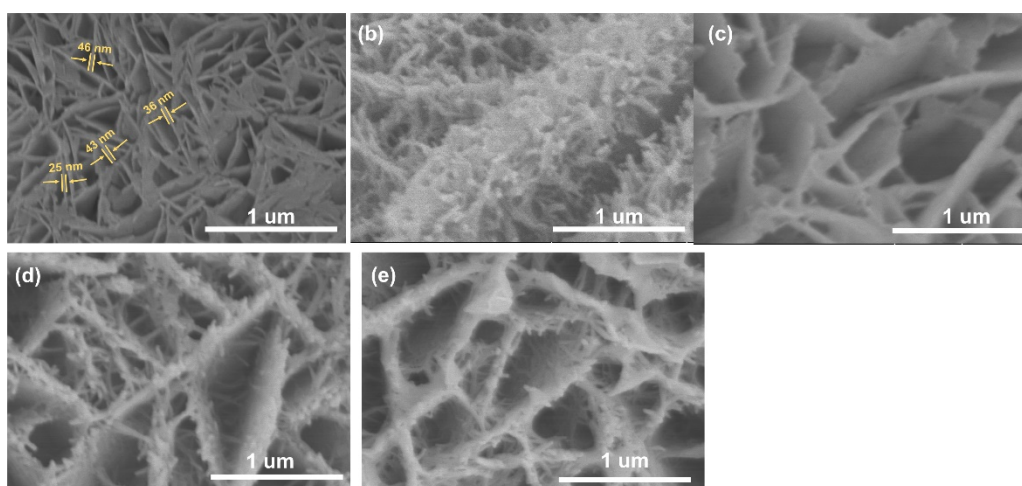


Figure S1. SEM images of the different deposition thickness Pt nanoparticles dispersed Ni(OH)₂ nanosheets. (a) Ni(OH)₂, (b) Pt-Ni(OH)₂-2.5, (c) Pt-Ni(OH)₂-5, (d) Pt-Ni(OH)₂-7.5, (e) Pt-Ni(OH)₂-10.

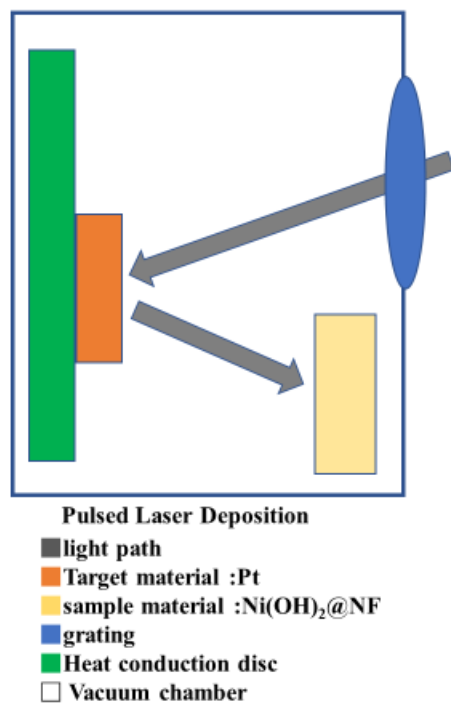


Figure S2. Scheme of the pulsed laser deposition for the fabrication of Pt-Ni(OH)_{2-x}.

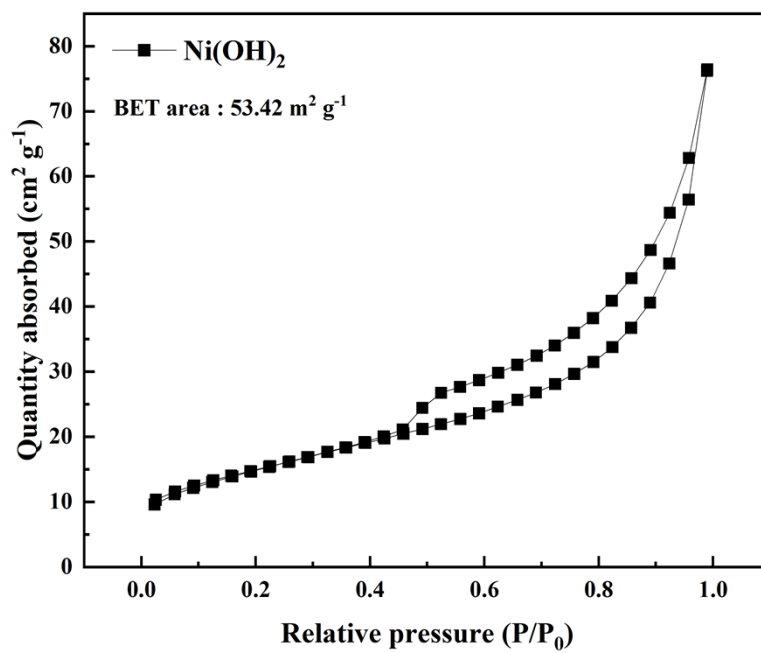


Figure S3. The BET surface areas and particle diameters of Ni(OH)₂ electrocatalyst.

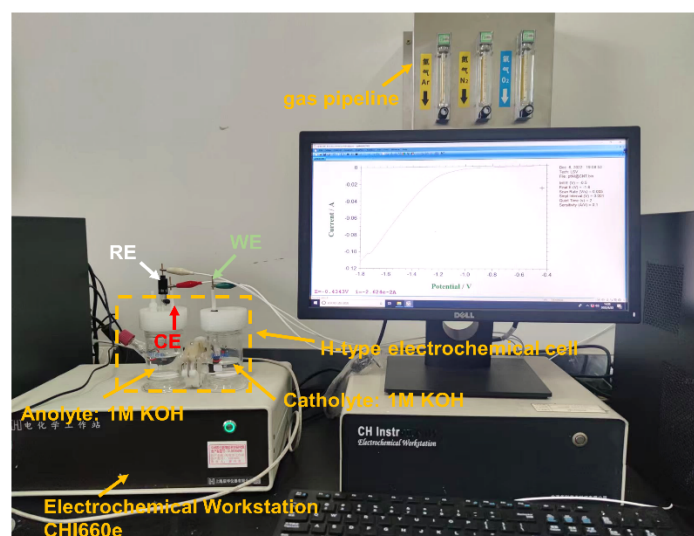


Figure S4. Photograph of electrochemical experimental setup.

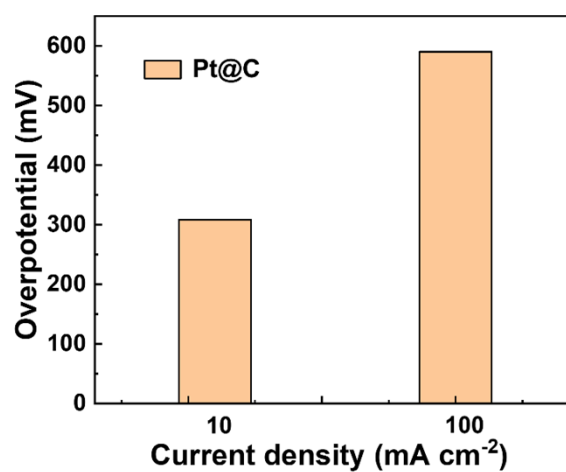


Figure S5. The overpotential of commercial Pt/C (60 wt%).

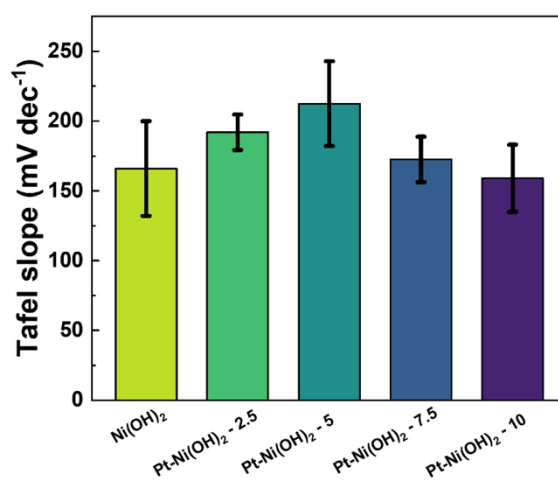


Figure S6. The corresponding Tafel plots of Ni(OH)₂, Pt-Ni(OH)₂-2.5, Pt-Ni(OH)₂-5, Pt-Ni(OH)₂-7.5, Pt-Ni(OH)₂-10.

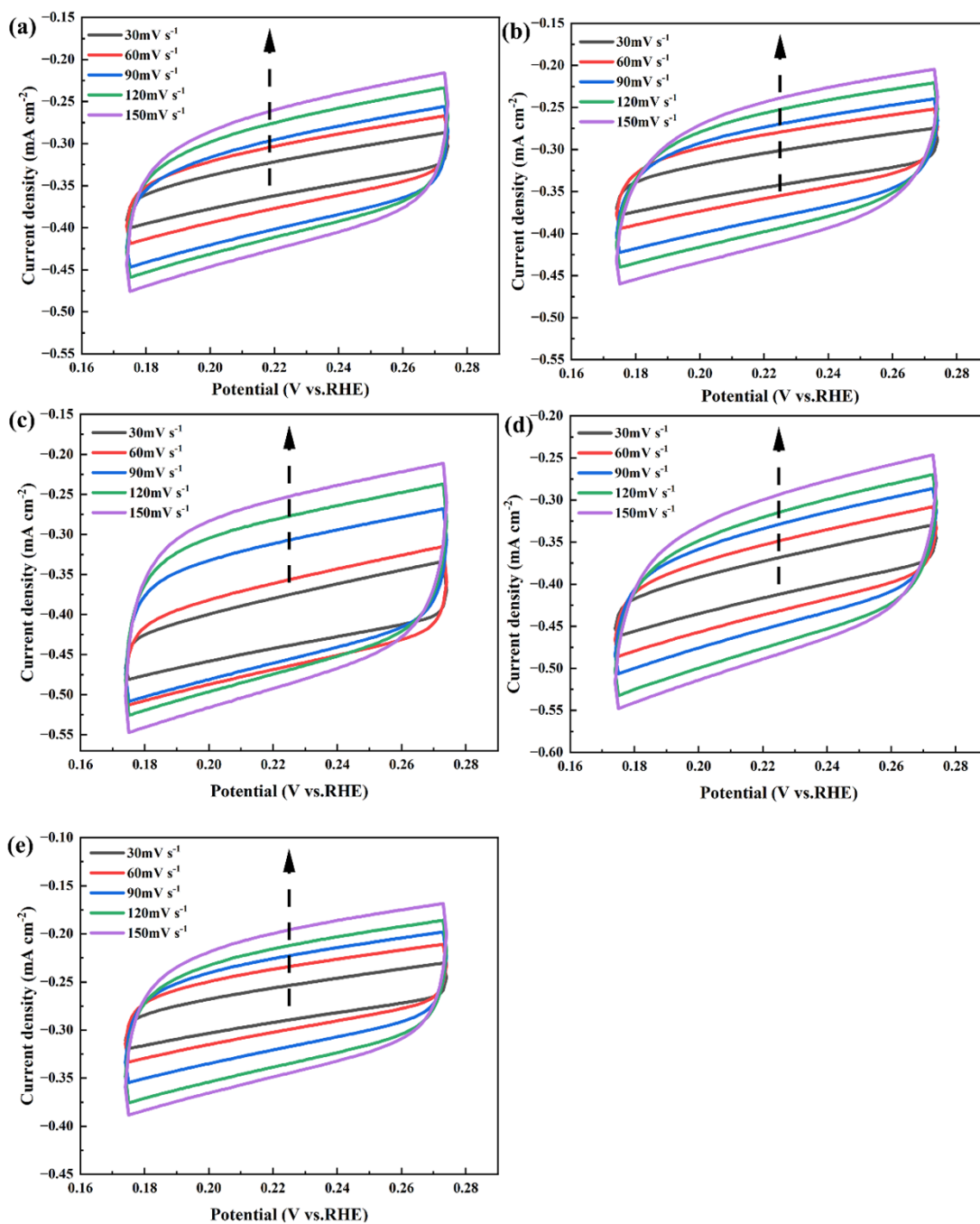


Figure S7. CV curves at different scan rates between 0.174 and 0.274 V vs. RHE for (a) Ni(OH)₂, (b) Pt-Ni(OH)₂-2.5, (c) Pt-Ni(OH)₂-5, (d) Pt-Ni(OH)₂-7.5, (e) Pt-Ni(OH)₂-10.

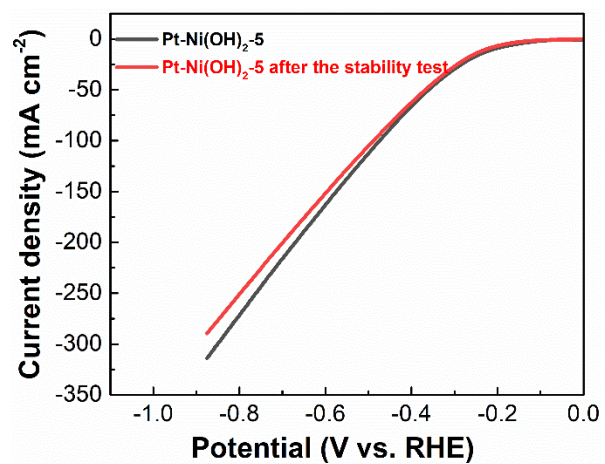


Figure S8. The stability test of Pt- Ni(OH)₂-5 for 10 hours.

Reference

- 1 H. Li, P. Wen, Q. Li, C. Dun, J. Xing, C. Lu, S. Adhikari, L. Jiang, D. L. Carroll and S. M. Geyer, Earth-Abundant Iron Diboride (FeB₂) Nanoparticles as Highly Active Bifunctional Electrocatalysts for Overall Water Splitting, *Adv. Energy Mater.*, 2017, **7**, 1700513.