Electrodeposition of Pt-Decorated Ni(OH)$_2$/CeO$_2$ Hybrid as Superior Bifunctional Electrocatalyst for Water Splitting

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The facile synthesis of highly active and stable bifunctional electrocatalysts to catalyze water splitting is attractive but challenging. Herein, we report the electrodeposition of Pt-decorated Ni(OH)$_2$/CeO$_2$ (PNC) hybrid as an efficient and robust bifunctional electrocatalyst. The graphite-supported PNC catalyst delivers superior hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) activities over the benchmark Pt/C and RuO$_2$, respectively. For overall water electrolysis, the PNC hybrid only requires a cell voltage of 1.45 V at 10 mA cm$^{-2}$ and sustains over 85 h at 1000 mA cm$^{-2}$. The remarkable HER/OER performances are attributed to the superhydrophilicity and multiple effects of PNC, in which Ni(OH)$_2$ and CeO$_2$ accelerate HER on Pt due to promoted water dissociation and strong electronic interaction, while the electron-pulling Ce cations facilitate the generation of high-valence Ni OER-active species. These results suggest the promising application of PNC for H$_2$ production from water electrolysis.

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1. Introduction

Hydrogen is the ideal alternative of fossil fuels as an important clean energy and industrial material [1, 2]. Water electrolysis using electricity from renewable energy is a facile and attractive technique to produce hydrogen with high purity [3, 4]. Electrocatalysts play the paramount role in overcoming the slow dynamics of both hydrogen and oxygen evolution reactions (HER and OER) [5–7]. While Pt and Ru/Ir-based compounds are highly efficient to catalyze HER and OER, respectively [8, 9], their fancy price, extremely low elemental reserves, and unsatisfactory durability limit large-scale applications [10–12], calling for strategies to improve stability and reduce noble metal loading [13–15].

In alkaline media, although Pt is the benchmarking HER catalyst, its catalytic activity is still restrained by water dissociation due to the lack of oxophilic surfaces to cleave the O–H bond of H$_2$O [16, 17]. The synergistic effect mechanism of Pt and Ni(OH)$_2$ has been indicated in previous studies: Ni(OH)$_2$ promotes the water dissociation and the generation of hydrogen atoms, which are absorbed at Pt sites nearby to recombine into hydrogen molecules [18–24]. In addition, using a bifunctional catalyst could avoid different synthetic processes of electrocatalysts and simplify the water electrolysis device to lower the cost [25]. However, Pt/Ni(OH)$_2$ catalysts do not favor the OER due to sluggish kinetics. The electronic structure of Ni could be modulated through the integration of CeO$_2$ in Ni(OH)$_2$, which could further promote to form γ-NiOOH, making the Ni(OH)$_2$/CeO$_2$ a superb OER catalyst [26, 27]. Meanwhile, Ce can impose large electronic perturbation to Pt nanoparticles, which may enhance the HER ability of the neighboring Pt sites [28]. Therefore, the Pt-Ni(OH)$_2$/CeO$_2$ hybrid has great potential for electrocatalysis of both HER and OER but has not been reported previously. Besides, the Pt-based hybrid catalysts usually suffer from complicated preparation procedures, particle agglomeration, and weak adhesion between catalyst and substrate [29–31].

In this study, we report a facile electrodeposition method to synthesize ultrafine Pt nanoparticles (NPs) decorated...
Ni(OH)$_2$/CeO$_2$ nanosheets (abbreviated as PNC) via anion intercalation and cathodic electrodeposition method. The Pt NPs with an average size of 3.1 nm are homogeneously deposited on the Ni(OH)$_2$/CeO$_2$ (abbreviated as NC) nanosheets, which could increase the exposure area of active sites and improve the utilization of Pt. Additionally, the mosaic-structured NC nanosheets not only effectively catalyze the OER but also enhance the HER activity of Pt due to electronic modulation and promoted dissociation of water. Furthermore, anion intercalation and in situ growth of the hybrid catalyst on graphite construct interfaces with strong adhesion, resulting in efficient electron transportation and enhanced stability. As a result, the prepared PNC electrocatalyst exhibits superior activity and stability to catalyze overall water electrolysis.

2. Result and Discussion

The PNC catalyst was synthesized through a two-step cathodic electrodeposition process as illustrated schematically in Figure 1(a). Graphite substrate was pretreated by applying a positive potential to allow nitrate ions inserting into graphite layers to enhance the interface of catalyst and graphite. The potential was reversed to realize the cathodic coelectrodeposition of cerium dioxide and nickel hydroxide on graphite. Subsequently, Pt NPs were deposited on the NC nanosheets to obtain the PNC hybrid electrode. In this two-step deposition process, the Pt loading can be reduced and the exposure of Pt is increased to enhance the utilization of Pt, outperforming the reverse sequence when Pt is deposited prior to transition metal hydroxide. The involved reactions in the preparation of PNC are described by equations (1)–(4). For comparison, Pt/G and Pt-Ni(OH)$_2$ (abbreviated as PN) electrodes were obtained through a similar process.

\[
\begin{align*}
\text{NO}_3^- + H_2O + 2e^- & \rightarrow 2OH^- + NO_2^- \\
\text{Ni}^{2+} + 2OH^- & \rightarrow \text{Ni(OH)}_2 \\
4\text{Ce}^{3+} + 12OH^- + O_2 & \rightarrow 4\text{CeO}_2 + 6H_2O \\
\text{PtCl}_6^{2-} + 2H_2O & \rightarrow \text{Pt}^4 + 4H^+ + 6Cl^- + O_2 \\
\end{align*}
\]

Figure 1(b) shows the X-ray diffraction (XRD) patterns of the prepared Pt, PN, and PNC. In addition to the reflections of graphite substrate, the diffraction peaks centered at 2\(\theta\) of 40.0 and 46.5\(\degree\) correspond to the (111) and (200) planes of the face-centered cubic (fcc) Pt (space group of Fm-3m), respectively. The Ni(OH)$_2$ and CeO$_2$ signals are not observed in XRD because of weak crystalline state of Ni(OH)$_2$ and low content of CeO$_2$ (supplementary Figure S1). The morphology and microstructure were investigated by a scanning electron microscope (SEM) and transmission electron microscope (TEM). The prepared PN and PNC are composed of aggregated nanoparticles with interparticle pores and flat nanosheets with a thickness of 5–10 nm.
while the control Pt/G is granular (Figure 1(c) inset and supplementary Figure S2). This rimos texture and interlinked lamellar morphology would facilitate the penetration of electrolyte inside the electrode and increase the active site exposure area. Contact angle tests indicate superhydrophilic property of PNC (supplementary Figure S3), which can be attributed to the rimos texture and the presence of O−H bond in hydroxide nanosheets. TEM images (Figure 1(c) and supplementary Figure S4) show uniform dispersion of Pt NPs on the hydroxide support. The average size of Pt NPs is 3.1 nm in PNC, smaller than PN (3.4 nm) and Pt/G (13.2 nm). The superhydrophilic surfaces of NC favor the nucleation and growth of Pt, leading to smaller NPs and uniform distribution [32, 33]. The high dispersion of Pt NPs on the mosaic structure of CeO2 and the weak crystallinity of Ni(OH)2 would enrich the interface between metal and oxide/hydroxide. High-resolution TEM (HRTEM) reveals lattice spacings of 0.314 and 0.227 nm (Figure 1(d)), which are separately assigned to the (111) planes of fcc CeO2 and fcc Pt. Energy dispersive spectroscopy (EDS) mapping further confirms the homogenous distribution of Pt, Ni, Ce, and O in PNC (supplementary Figure S5). As detected by EDS and inductively coupled plasma atomic emission spectroscopy (ICP-AES) (supplementary Figure S6), the Pt loadings are 8.8 and 8.2 wt.% in PN and PNC, respectively. The Pt content could be tuned by adjusting the electrodeposition time in H2PtCl6 solution (supplementary Table S1).

The oxidation states of Pt, Ni(OH)2, and CeO2 were detected by X-ray photoelectron spectroscopy (XPS) spectra (Figure 2). The survey spectra confirm the presence of Pt, Ni, and O in PN and additional Ce in PNC (Figure 2(a)). As shown in Figure 2(b), Pt 4f spectra display two pairs of peaks (4f7/2 and 4f5/2), corresponding to dominant Pt(0) (75.9%) and surface Pt(II) (24.1%) in PNC. For PN, the atomic ratio of Pt(0) and Pt(II) is 90.7% and 9.3%, respectively. The higher Pt(II) content and 0.3 eV positive shift of Pt(0) peaks in PNC compared to PN suggest partial oxidation of Pt and electronic interaction between Pt and NC [28, 34, 35]. The peak shift also indicates a downshift of the d-band center of Pt in PNC, which could favor hydrogen adsorption on Pt and accelerate the recombination of H2 to form H2 [36–38].

As discerned by Ni 2p XPS spectra (Figure 2(c)), both Ni (II) (855.6 eV) and Ni (III) (857.1 and 856.8 eV) exist in PN and PNC. There is a 0.3 eV positive shift of Ni(III) in PNC compared to PN suggest partial oxidation of Pt and electronic interaction between Pt and NC [28, 34, 35]. The peak shift also indicates a downshift of the d-band center of Pt in PNC, which could favor hydrogen adsorption on Pt and accelerate the recombination of H2 to form H2 [36–38].
shows deconvoluted peaks at 528.6, 530.5, 531.6, and 532.6 eV assigned to CeO$_2$, Ni(OH)$_2$, NiOOH, and H$_2$O, respectively [26, 40]. Collecting XPS results suggest strong electron interaction and synergy effect between Pt and Ce-Ni oxide/hydroxide in PNC, which would favor the formation of more electrocatalytically active species [26, 41].

The electrocatalytic HER performances were investigated by linear sweep voltammetry (LSV). As shown in Figure 3(a),

**Figure 3: HER performance.** (a) HER LSV curves and (b) Tafel plots of Pt/C, Pt/G, PN, and PNC in 1.0 M KOH. (c) EIS Nyquist plots. (d) Pt mass activities at the overpotential of 150 mV. (e) Turnover frequency (TOF) deduced from the LSV curves at overpotential of 150 mV. (f) LSV curves of PNC before and after 1000 cycles. The inset shows the chronopotentiometry (E-t) curves of PNC and Pt/C at 1000 mA cm$^{-2}$. 

Potentials (V vs. RHE): 

-0.20 –0.15 –0.10 –0.05 0.00

Current density (mA cm$^{-2}$)

0 50 100 150

At 150 mV

0.316 0.145 2.011 3.144

At 150 mV

0.455 0.254 2.127 3.488

At 150 mV

0 0.5 1.0 1.5 2.0 2.5

Potential (V vs. RHE)

0.0 0.05 0.1 0.15 0.2

Initial PNC

After 1000 CV cycles
the onset potential of PNC is near 0 mV and it needs only 76 mV overpotential at 100 mA cm$^{-2}$, significantly outperforming PN (105 mV), Pt/G (124 mV), and 20 wt.% Pt/C (153 mV). At a high applied current density, rapid generation and release of bubbles occur while no catalyst desquamating from the electrode surface is observed for PNC (supplementary Movie S1). The results indicate superior mechanical stability of the electrodeposited hybrid material, which is favorable for industrial application operating under large current density.

Tafel slope is a figure-of-merit to assess HER kinetics of electrocatalysts. In Figure 3(b), the PNC represents a Tafel slope of 38 mV dec$^{-1}$, which is much smaller than PN, Pt/C, and Pt/G (45, 56, and 58 mV dec$^{-1}$) and indicates rapid HER kinetics in PNC (Tafel-Volmer mechanism). The HER process in alkaline condition includes the Volmer adsorption step ($\text{H}_2\text{O} + e^- \rightarrow \text{H}_\text{ad} + \text{OH}^-$) combined with the Heyrovsky desorption step ($\text{H}_\text{ad} + \text{H}_2\text{O} + e^- \rightarrow \text{H}_2 + \text{OH}^-$) or the Tafel recombination step ($\text{H}_\text{ad} + \text{H}_\text{ad} \rightarrow \text{H}_2$) [42, 43]. In alkaline media, the Volmer step is suggested to determine the HER rate of Pt, due to the sluggish dissociation of water [44, 45]. For the PNC hybrid, the metal (hydro)oxides are efficient to split O–H bond and accelerate the Volmer step, leading to an improvement in HER kinetics. The electrode kinetics of the HER process is further investigated by conducting the EIS experiments, where the equivalent circuit was composed of an electrolyte resistance ($R_\ell$) in series with a parallel connection of a constant phase element (CPE) and a charge-transfer resistance ($R_\text{ct}$) [46]. From the Nyquist plots (Figure 3(c)) recorded at the potential of −0.026 V vs. RHE, PNC has a smaller $R_\text{ct}$ compared to Pt/C, Pt/G, and PN. The enhanced charge transfer is attributed to the interfacial electron interaction, plate-like nanostructure with shorter diffusion pathway, and rioso texture that allows facile electrolyte access.

The mass activities were calculated to evaluate the utilization ratio of Pt in the catalysts (Figure 3(d)). At the overpotential of 150 mV, the PNC electrode achieves a remarkable current density of 3.144 A mg$^{-1}$ Pt, which is almost 10 and 1.6 times those of the counterpart 20 wt.% Pt/C and PN (0.316 and 2.011 A mg$^{-1}$ Pt). The improvement of the mass activity of Pt could be ascribed to the high dispersion and enhanced charge transfer is attributed to the interfacial electron interaction, plate-like nanostructure with shorter diffusion pathway, and rioso texture that allows facile electrolyte access.

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constructed using PNC as a bifunctional electrode for water electrolysis. As shown in Figure 5(a), the cell delivers a current density of 10 mA cm$^{-2}$ at an applied voltage of 1.5 V, 100 mV lower than that of the benchmark Pt/C $|$ RuO$_2$ couple (1.55 V). The PNC hybrid competes favorably with most electrocatalysts reported previously for overall water splitting (supplementary Table S4). Remarkably, in the extended stability test at a large current density of 1000 mA cm$^{-2}$, a constant potential of 2.06 V can be well maintained for 85 h with the faintest degradation (Figure 5(b)). A large amount of bubbles release uniformly from the electrode surfaces without any shedding (supplementary Movie S3). Moreover, the volumes of collected H$_2$ and O$_2$ match well with the theoretical values as a function of time during electrolysis at 1000 mA cm$^{-2}$ (supplementary Figure S16), indicating nearly 100% faradaic efficiency of PNC $|$ PNC electrolyzer. Excitingly, the PNC-based device can be actuated by a 1.5 V battery for vigorous, stable generation, and release of gas (supplementary Figure S17 and Movie S3), again confirming the high efficiency of PNC to electrolyze water.

Figure 5(c) schematically shows the reaction mechanism of the electrolyzer. We propose that metal hydroxide in PNC promotes the rupture of O−H in water and the generation of adsorbed H atoms (H$_{ads}$), which adsorb on the Pt surface to recombine into hydrogen molecule. Meanwhile, the OH$^-$ ions are transformed into O$_2$ on the anode with different metal centers [22, 26, 49]. To gain further insight into the water dissociation process, we performed preliminary DFT calculations on the configuration and evolution of PNC hybrid and dissociation energy of H$_2$O on the interface (Figure 5(d) and supplementary Movie S4). The water is adsorbed at the interface of Ni(OH)$_2$ and CeO$_2$, where O is connected with the Ni atom in Ni(OH)$_2$ and H forms a weak hydrogen bond interaction with O in CeO$_2$. These interactions jointly promote the activation of water, resulting in the fracture of O−H bond in water and the formation of the final structure in Figure 5(d). The
process is exothermic (about $-2.74 \text{ eV}$), indicating that water dissociation can proceed spontaneously at this interface. Accordingly, the superior performance of PNC can be attributed to the synergistic effect among Pt, Ni(OH)$_2$, and CeO$_2$ in the hybrid, together with the beneficial texture, microstructure, and wettability.

3. Conclusion

In summary, we report the electrodeposition of Pt-Ni(OH)$_2$-CeO$_2$ hybrid on graphite and its application for efficient electrocatalysis of water splitting. In 1.0 M KOH, the PNC electrode needs only overpotentials of 76 and 186 mV to afford 100 mA cm$^{-2}$ current density for HER and OER, respectively. The turnover frequency and Pt-based mass activity towards HER are significantly improved on PNC than the benchmark Pt/C. Remarkably, when PNC electrode is directly utilized as the anode and cathode, the assembled symmetric water electrolyzer well works at a low applied cell voltage of 1.45 V. Additionally, respectable stability of PNC is attained at 1000 mA cm$^{-2}$. The superior activity is due to high dispersion of Pt NPs and electronic interaction among Pt, Ni(OH)$_2$, and CeO$_2$ while the durability is ascribed to strong deposit/graphite adherence, electrode hydrophilicity, and facilitated release of gas bubbles. The results indicate that Pt-decorated hydroxide/oxide electrodeposited on graphite is a promising electrocatalyst for overall water electrolysis.

4. Materials and Methods

4.1. Material Synthesis. To prepare the PNC hybrid, cathodic galvanostatic electrodeposition was applied and performed using a two-electrode system in a 50 ml electrolytic bath at 25°C. The working and counter electrode are two graphite
plates (1 × 2 cm) [26]. The graphite plate was first preprocessed by applying an anodic current of 20 mA cm⁻² for 300 s to realize NO₃⁻ intercalation in the interlamination. Then, a cathodic current of −20 mA cm⁻² was applied for 300 s in a nitrate solution containing 0.09 M Ni(NO₃)₂ and 0.01 M Ce(NO₃)₃. After that, cathodic depositions at −20 mA cm⁻² were performed for different time (50, 100, 150, and 200 s) in 0.02 M H₂PtCl₆ solution. For comparison, PN was obtained from electrodeposition in 0.1 M Ni(NO₃)₂ and 0.02 M H₂PtCl₆ using a similar process, while Pt/G was prepared in 0.02 M H₂PtCl₆ at 20 mA cm⁻² for 300 s.

4.2. Material Characterizations. A JEOL JSM-7500F microscope was used to obtain SEM images. TEM and HRTEM were carried out on a FEI Talos F200X G2 system equipped with EDS. A Rigaku MiniFlex 600 diffractometer was used to measure the XRD patterns. XPS data were collected with a Kratos Axis Ultra DLD spectrometer. Elemental analysis was obtained on ICP-AES (PerkinElmer Optima 83000).

4.3. Electrochemical Measurements. All electrochemical tests were performed by a three-electrode system on AMETEK Parstat 4000 electrochemical workstation in 1.0 M KOH. The electrodeposited electrodes, Hg/HgO, and graphite rod were employed as the working, reference, and counter electrode, respectively. To study the HER performance, LSV curves were recorded at different scan rates. The ECSA of the prepared catalysts was calculated according to

\[ ECSA = \frac{C_{dl}}{C_s}, \]

where \( C_{dl} \) is the double-layer capacitance and \( C_s \) is the specific capacitance (0.040 mF cm⁻²) [50].

The TOF was determined by the following equation [51, 52]:

\[ TOF = \frac{J \times A}{2 \times F \times m}, \]

where \( J \) is the current density at a given overpotential (150 mV), \( F \) is the Faraday constant (96,485 C mol⁻¹), \( A \) is the electrode surface area (1 cm²), and \( m \) is the number of moles of active species on the electrode. The Pt content in PN and PNC was quantified by ICP-AES. In TOF calculation, Pt atoms are counted as the active sites in PN and PNC.

4.4. DFT Calculation. Density function theory calculation was performed by using the CP2K package [53]. PBE functional [54] with Grimme D3 correction [55] was used to describe the system. Unrestricted Kohn-Sham DFT has been used as the electronic structure method in the framework of the Gaussian and plane wave method [56, 57]. The Goedecker-Teter-Hutter (GTH) pseudopotentials [58, 59] and DZPMOLOPT-GTH basis sets [56] were utilized to describe the molecules. A plane-wave energy cut-off of 500 Ry has been employed.

Conflicts of Interest

The authors declare no conflict of interest.

Authors’ Contributions

F. Y. Cheng and Z. H. Yan supervised the research. H. H. Liu carried out the experiments, measured and analyzed the data, and drafted the manuscript. X. Chen, J. H. Li, and L. Zhang participated in electrochemical measurements. J. H. Li, F. M. Liu, and G. L. Fan assisted material characterization and DFT calculation. All the authors participated in the discussion of results and manuscript.

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Supplementary Materials

Figure S1: powder XRD patterns of Ni(OH)₂ and NC scratched down from the Ti mesh. Figure S2: SEM images of Pt/G (a, b), PN (c, d), and PNC (e, f) at low (a, c, e) and high (b, d, f) magnification. Figure S3: contact angles measured on graphite substrate (a) before and (b–d) after the electrodeposition of Pt (b), PN (c), and PNC (d). Figure S4: (a, b) TEM images and particle size distribution of Pt/G. Figure S5: elemental mapping images of PNC. Figure S6: EDS spectra of (a) Pt, (b) PN, and (c) PNC. Figure S7: HER polarization curves of (a) PN and (b) PNC hybrid with different Pt loadings. Figure S8: CV curves of (a) Pt/C, (b) electrodeposited Pt, (c) PN, and (d) PNC. (e) The corresponding linear fitting of the current density versus scan rates. (f) Comparison of ECSA. Figure S9: (a) Specific and mass activities derived from the HER polarization curves at 150 mV. Figure S10: polarization curves of 20 wt.% Pt/C before and after 1000 HER cycles. Figure S11: (a) SEM, (b) TEM, (c) HRTEM, and (d) elemental mapping images of PNC after 70 h of HER stability test at 1000 mA cm⁻². Insets (a) and (b) show high-magnification SEM image and size distribution of Pt nanoparticles, respectively. Figure S12: (a) XRD pattern of PNC after HER stability test for 70 h at 1000 mA cm⁻². High-resolution XPS spectra of (b) Pt 4f, (c) Ni 2p3/2, and (d) O 1s of PNC after stability test.
S13: polarization curves of RuO2 before and after 1000 OER cycles. Figure S14: (a) SEM, (b) TEM, (c) HRTEM, and (d) elemental mapping images of PNC after 70 h of OER stability test at 1000 mA cm\(^{-2}\). Insets (a) and (b) show high-magnification SEM image and size distribution of Pt nanoparticles, respectively. Figure S15: (a) XRD patterns of PNC after OER stability test. High-resolution XPS spectra of (b) Pt 4f, (c) Ni 2p3/2, and (d) O 1s regions of PNC after stability test. Figure S16: generated and theoretical volumes of H\(_2\) and O\(_2\) over time at a constant current density of 1000 mA cm\(^{-2}\) in PNC || PNC electrolyzer. Figure S17: digital photographs of the PNC || PNC electrolyzer powered by a 1.5 V battery. Table S1: Pt contents in PN and PNC with different electrodeposition time in the H\(_2\)PtCl\(_6\) precursor solutions. Table S2: the comparison of HER performances of PNC with other electrocatalysts. Table S3: the comparison of OER performances of PNC with other electrocatalysts. Table S4: comparison of water splitting performance of PNC electrocatalyst with other bifunctional electrocatalysts reported before. Movie S1: the formation and release of bubbles on the PNC electrode surface for HER at different current densities. Movie S2: the formation and release of bubbles on the PNC electrode surface for OER at different current densities. Movie S3: the process of water splitting at different densities and the gas generation and release on electrode surface when the PNC || PNC electrolyzer is powered by a 1.5 V battery. Movie S4: the movie of DFT calculated the water dissociation process on the PNC interface. (Supplementary Materials)

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