Supporting Information

Atomically Dispersed Janus Nickel Sites on Red Phosphorus for Photocatalytic Overall Water Splitting

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Experimental Section

Hydrothermal treatment of bulk RP: 1 g of commercial bulk red phosphorus (RP) was added to 30 mL of deionized water and then put into a 50-mL Teflon-lined stainless hydrothermal reactor. The reactor was heated to 200 °C and kept there for 12 h to remove the surface oxidation layer of RP. After washing with deionized water 3 times, the obtained powder was vacuum dried at 70 °C and ground into powder for further use. The obtained powder was named HRP.

Synthesis of Ni-HRP photocatalyst: Typically, 60 mg of NiCl₂·6H₂O was dissolved in 80 mL of aqueous methanol solution (CH₃OH, 10 vol%). The solution was stirred for 10 min, then 200 mg of HRP powder was added. After continuous stirring and ultrasonic treatment for another 10 min, the solution was bubbled with Ar flow for 15 min to remove the oxygen in the reactor. The solution was irradiated under full arc irradiation with a 300 W Xe lamp to conduct the photodeposition process. The temperature of the solution was maintained at 30 °C by a circulating water system during the reaction. After washing 4 times with deionized water and centrifuging, the obtained powder was collected and vacuum dried at 70 °C.

Synthesis of Ni-RP control photocatalyst: Ni-RP was prepared similarly to Ni-HRP, except that HRP was replaced with RP during the deposition process.

Photocatalytic reaction for H₂ evolution from pure water: Photocatalytic tests from pure water were measured in a Pyrex glass bottle (110 mL). Typically, 40 mg of the prepared photocatalyst was dispersed into 80 mL of deionized water. After ultrasonically dispersing for 30 s, the solution was bubbled with Ar for 20 min to remove any air in the reaction cell. A 300 W Xe lamp with different cutting-off filters (λ > 430, 530, 620, 800 nm, and full arc irradiation without filters) was used as the light source. The temperature of the system was controlled from 30 to 70 °C with a circulating water bath. The generated gas was tested by gas chromatography using a thermal conductivity detector (TCD).

Electrochemical and photoelectrochemical measurements: 1 mg of the prepared catalyst was ultrasonically dispersed in a mixture of 250 µL of ethanol and 250 µL of deionized water for 30 min. Then 10 µL of Nafion solution (Dupont D1020, 10 wt%) was added to the suspension, followed by
further ultrasonic dispersion for another 30 min. 3.5 µL of the above suspension was then dropped onto the glassy carbon rotating disk electrode (RDE, 3 mm of diameter, CHI 104). The electrode was dried at room temperature overnight for further use as the working electrode. Ag/AgCl (in saturated KCl solution) and Pt plate were used as the reference electrode and the counter electrode, respectively. N2-saturated 0.5 M Na2SO4 solution served as the electrolyte. Mott-Schottky (MS), electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV), and transient photocurrent results were acquired on a CHI 760E electrochemical workstation (Chenhua Instruments Co., Shanghai) in a standard three-electrode configuration. A 300 W Xe lamp coupled with an AM 1.5 filter was used as the light source.

Characterization

Scanning electron microscopy (SEM) was carried out on a JEOL JSM-7800F microscope. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) images were obtained with an FEI Tecnai G2 F30 S-Twin microscope equipped with an OXFORD MAX-80 energy dispersive X-ray (EDX) detector. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image was measured on an ARM200F spherical aberration-corrected electron microscope. X-ray powder diffraction (XRD) was measured with a PANalytical X'pert MPD Pro X-ray diffractometer. Ultraviolet-visible-near infrared (UV-vis-NIR) diffuse reflectance spectra were obtained through a HITACHI U4100 spectrophotometer. The pore size structure and specific surface area were determined by the Brunauer-Emmett-Teller (BET) method through the N2 adsorption-desorption measurement (Micromeritics ASAP-2020). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Fisher ESCALAB X-ray spectrometer. Photoluminescence (PL) spectra were obtained on a PTI QM-4 fluorescence spectrophotometer at room temperature. Fourier transform infrared (FTIR) spectra were acquired on a Bruker Vertex 70 spectrophotometer. X-ray fluorescence (XRF) analysis was carried out on a Bruker S4 PIONEER X-ray fluorescence spectrometer using a Ru target and 4 kW maximum power. Solid-state nuclear magnetic resonance (NMR) was carried out on a Bruker AVWBIII 600 system at a spin rate of 14k Hz with NaH2PO4 as the reference sample. The synchrotron X-ray spectroscopic (XAS) measurements were performed at BL20A, at National Synchrotron Radiation Research Center, Taiwan.
Calculation of apparent quantum efficiency (AQE)

The apparent quantum efficiency of Ni-HRP was measured at 420 nm. The reaction solution was irradiated by a 300 W Xe lamp applying a 420 nm band-pass filter for 2 hours. The AQE was calculated using the following equation (1):

\[
AQE = \left( \frac{AR}{I} \right) \times 100\% \tag{1}
\]

Where \(A\) represents a coefficient (2 for H\(_2\) evolution), \(R\) represents the amount of H\(_2\) molecules generated per hour, \(I\) represents the number of incident photons per hour.

The amount of generated H\(_2\) per hour was measured to be 24.8 \(\mu\)mol. The number of incident photons per hour was measured to be \(3.36 \times 10^{20}\). Thus, the AQE of 420 nm was calculated to be:

\[
AQE = \left( 2 \times 6.02 \times 10^{23} \times 24.8 \times 10^{-6} \right) / \left( 3.36 \times 10^{20} \right) \times 100\% = 8.9\%
\]

Test of electron transfer number

The electron transfer number (\(n\)) was measured in a rotating ring-disk electrode (RRDE) testing system with a rotating speed of 1600 rpm. N\(_2\)-saturated deionized water was used in the experiment. Typically, the disk potential was set at open circuit potential to avoid water oxidation from the electrochemical catalytic procedure. The ring potential was set at 0.9 V vs. RHE to ensure that H\(_2\)O\(_2\) could decompose into O\(_2\). The experiments were carried out on a CHI 600E electrochemical workstation (Chenhua Instruments Co., Shanghai). The electron transfer number (\(n\)) can be calculated according to the following equation (2):

\[
n = \frac{4I_d}{I_d + I_r / N} \tag{2}
\]

where \(I_d\) and \(I_r\) represent the disk current and ring current, respectively. \(N\) is the H\(_2\)O\(_2\) collection fraction from the disk electrode, which is tested to be 0.4745.\[^{[S1]}\]

In this work,

\[
I_r = (0.5648-0.4917) \mu A = 0.0731 \mu A
\]
\[
I_d = (0.3453-0.1786) \mu A = 0.1667 \mu A
\]

\[
n = 4 \times 0.1667 / (0.1667 + 0.0731 / 0.4745) = 2.08
\]

H\(_2\)O\(_2\) detection by electrochemical method

H\(_2\)O\(_2\) was also detected in a three-electrode system by an electrochemical method. A platinum disk, an
Ag/AgCl electrode, and a platinum plate worked as the working electrode, reference electrode, and counter electrode, respectively. The solution after the photocatalytic reaction was used as the electrolyte. The current-time (I-t) curves were measured to confirm the existence of H$_2$O$_2$ in the solution.\cite{S1}

**H$_2$O$_2$ detection by titration method**

The actual amount of H$_2$O$_2$ after the photocatalytic reaction was detected through the titration method. Typically, the reaction solution (after photocatalytic reaction for 5 h at 30 °C and 70 °C) was centrifuged to remove the residual photocatalyst. The concentrated sulfuric acid was diluted by additional deionized water. 10 mL of the centrifuged reaction solution was mixed with 10 mL of diluted H$_2$SO$_4$. Then the mixed solution was transferred into a 100 mL beaker and placed on a magnetic stirring plate. 2 mM of KMnO$_4$ solution was used as the titrant and added dropwise into the mixed solution using a buret until the solution changed to a pinkish color. The reaction can be illustrated by the following equation (3):

\[
2\text{KMnO}_4 + 5\text{H}_2\text{O}_2 + 3\text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2
\]  

(3)

The H$_2$O$_2$ concentration (C) could be determined by the following equation (4):

\[
C = \frac{(5/2) \times V_{EP} \times C_{KMnO_4}}{V_{Al}}
\]  

(4)

where $V_{EP}$ is the volume of titrant added into the solution in milliliters, $C_{KMnO_4}$ is the standardized concentration of 2 mM, $V_{Al}$ is the volume of reaction aliquot (10 mL).\cite{S2}

For the reaction solution at 30 °C, $V_{EP}$ was 0.4 mL. Here $C_{30^\circ\text{C}}$ was calculated to be:

$C_{30^\circ\text{C}} = (5/2 \times 0.4 \text{ mL} \times 2 \text{ mmol/L})/10 \text{ mL} = 0.2 \text{ mmol/L}$

The volume of the reaction solution was 80 mL, so the actual H$_2$O$_2$ at 30 °C was

0.2 mmol/L $\times$ 0.08 L = 0.016 mmol = 16 μmol

Where the amount of H$_2$ at 30 °C was determined to be 17.45 μmol by the gas chromatography, corresponding to a theoretical H$_2$O$_2$ amount of 17.45 μmol.

For the reaction solution at 70 °C, $V_{EP}$ was 1.6 mL. Here $C_{70^\circ\text{C}}$ was calculated to be:

$C_{70^\circ\text{C}} = (5/2 \times 1.6 \text{ mL} \times 2 \text{ mmol/L})/10 \text{ mL} = 0.8 \text{ mmol/L}$
The volume of the reaction solution was 80 mL, so the actual $\text{H}_2\text{O}_2$ was 0.8 mmol/L $\times$ 0.08 L = 0.064 mmol = 64 μmol where the amount of H$_2$ was determined to be 457.6 μmol by the gas chromatography, corresponding to a theoretical $\text{H}_2\text{O}_2$ amount of 457.6 μmol.

**Corrosion reaction of the RP based photocatalyst with $\text{H}_2\text{O}_2$**

The corrosion reaction of RP based materials with $\text{H}_2\text{O}_2$ is a redox reaction, which can be explained by the following equation (5):

$$2\text{P} + 5\text{H}_2\text{O}_2 \rightarrow 2\text{H}_3\text{PO}_4 + 2\text{H}_2\text{O}$$

$$\Delta G = -12.5 - 120.4 - 1123.6 - 237.1 \text{ (kJ mol}^{-1}\text{)}$$

The Gibbs energy of all chemicals are listed above, and the free energy change of this reaction is calculated to be:

$$\Delta G^* = 2 \times (-1123.6) + 2 \times (-237.1) - 2 \times (-12.5) - 5 \times (-120.4) = -2094.4 \text{ kJ} \text{ mol}^{-1} < 0$$

which confirms that the corrosion of RP by $\text{H}_2\text{O}_2$ is a spontaneous chemical reaction.

**$\text{H}_2\text{O}_2$ detection by UV-vis spectroscopy**

$\text{H}_2\text{O}_2$ detection by UV-vis absorption spectroscopy was carried out using $o$-tolidine as the indicator. Typically, 1% $o$-tolidine was dissolved into 0.1 M HCl solution to perform an indicator solution. 0.5 mL of the prepared indicator was added to 2 mL of centrifugated reaction supernatant. After 2 min, the mixture was further acidified by adding 2 mL of 1 M HCl. Then a UV-vis spectrum was measured to determine the existence of $\text{H}_2\text{O}_2$ with a typical characteristic peak at 436 nm.

**DFT Calculations**

First-principle calculations were performed by using the Vienna Ab-initio Simulation Packages (VASP). The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) form was adopted for the exchange and correlation energy. The energy cutoff of the plane wave basis set was set to 400 eV. The on-site Coulomb interaction for the localized transition metal d orbitals was parametrized by $U_{\text{eff}} = U - J$ with $U_{\text{eff}} (\text{Ni}) = 6.2$ eV from linear response theory. In the calculations, Monkhorst–Pack k-points grid meshes of $3 \times 2 \times 1$ and $6 \times 4 \times 1$ were used for geometry optimization.
optimization and electronic structure calculations, respectively. A vacuum space was set to be more than 15 Å, which was used to avoid spurious interactions. The tolerance criteria for electronic and ionic relaxation were $1 \times 10^{-5}$ eV and 0.05 eV/Å, respectively. The Brillouin-zone integration was performed using a Gaussian broadening of 0.05 eV.

For the coordination number of Ni loaded on RP, we expect that Ni has a coordination number close to 6-coordination of Ni (II). However, due to the steric hindrance effect on the (001) surface, 4 coordination number was finally selected, which was the maximum coordination number on the surface. By comparing the energies of 1-coordinated and 4-coordinated Ni on the (001) surface (Fig. S19), the 4-coordinated Ni was found to be energetically favorable, where the 4-coordinated Ni was 1.01 eV in energy less than the 1-coordinated Ni.

The calculation of free energy for H adsorption, $\Delta G^*_H$, in the HER process is defined as equation (6): \[ \Delta G^*_H = \Delta E_H + \Delta ZPE - T\Delta S \] where $\Delta E_H$ can be calculated by taking the isolated H$_2$ as a reference state, as shown in equation (7):
\[ \Delta E_H = E^* - E^* - 1/2E_{H2} \] The HPER process has 3 steps in neutral media, as shown in equations (8)-(10):
\[ * + H_2O \rightarrow *OH_2 \] \[ *OH_2 \rightarrow *OH + H^+ + e^- \] \[ *OH + H_2O \rightarrow * + H_2O_2 + H^+ + e^- \] In the above equations (6)-(10), the star (*) represents the catalyst and *S represents the substrate S adsorbed onto the catalytic site *.

The free energy of each step was then calculated with equation (11):
\[ \Delta G = \Delta E + \Delta ZPE - T\Delta S \] where $E$ is the calculated DFT electronic energy, ZPE is the zero-point energy contribution, and $S$ is the entropic contribution. Both ZPE and $S$ are calculated based on the molecular vibration analysis at $T = 300$ K.
Figure S1. (a) N$_2$ adsorption-desorption isotherms and (b) the corresponding pore size distribution curves of various samples.

| Sample | BET surface area (m$^2$ g$^{-1}$) | Mean pore diameter (nm) | Pore volume (cm$^3$ g$^{-1}$) |
|--------|----------------------------------|-------------------------|--------------------------------|
| RP     | 0.75                             | None                    | None                           |
| Ni-RP  | 0.61                             | None                    | None                           |
| HRP    | 13.39                            | 5.52                    | 0.093                          |
| Ni-HRP | 8.96                             | 8.21                    | 0.056                          |
Figure S2. TEM and corresponding SAED analysis of RP, HRP, and Ni-HRP, demonstrating amorphous structures.
Figure S3. HAADF-STEM images of Ni-HRP. The bright spots are assigned to single-atom Ni sites.
Figure S4. (a) TEM, (b) HRTEM, and (c) STEM images of Ni-RP. Elemental mapping images of (d) Ni and (e) P in Ni-RP.

Figure S5. XPS analysis of P in Ni-HRP, HRP, and RP. All samples exhibited the typical P 2p peaks at 130.0 (P 2p_{3/2}) and 130.8 eV (P 2p_{1/2}) of P⁰. The broad peaks at 134.5, 134.0, and 133.9 eV of Ni-HRP, HRP, and RP are ascribed to the oxidation states of phosphorus.
Figure S6. H₂ evolution amount of Ni-HRP with different photodeposition times of Ni species and the contrast sample Ni-RP with Ni nanoparticles under visible light irradiation (λ > 430 nm) at 30 °C. All Ni-HRP samples exhibited enhanced hydrogen evolution rates than Ni-RP, verifying the important role of single-atom dual-function Ni sites.

Figure S7. H₂ evolution rate of different Ni-HRP samples using varied amounts of NiCl₂·6H₂O precursor in the preparation process. The hydrogen evolution was carried out under visible light irradiation (λ > 430 nm) at 30 °C.
Figure S8. Arrhenius plots to determine the activation energy for hydrogen evolution using Ni-RP and Ni-HRP.

Figure S9. Long-term H₂ evolution tests of Ni-HRP for (a) 48-h at 30 °C and (b) 16-h at 70 °C.
Figure S10. XRD patterns of Ni-HRP before and after photocatalytic reaction at 30 and 70 °C.

Figure S11. XPS Spectra of Ni 2p for Ni-HRP before and after photocatalytic reaction at 30 °C and 70 °C.
Figure S12. TEM images of Ni-HRP before and after photocatalytic reaction at 30 °C and 70 °C.
Figure S13. Rotating ring-disk electrode (RRDE) I-t curves to test electron transfer number of Ni-HRP (I_d: disk current; I_r: ring current).

Figure S14. I-t curves measured by the rotating ring-disk electrode (RRDE) at 1600 rpm at 1.5 V vs. RHE in various electrolytes to detect H_2O_2. When the solution after the photocatalytic reaction was used as the electrolyte (red line), the current was higher than that in pure water (black line), which could be attributed to the detection of O_2 at the platinum disk electrode, where O_2 came from the decomposition of H_2O_2 in the reaction solution. After MnO_2 was added (blue line) to the solution, H_2O_2 could be decomposed, resulting in a significantly decreased current.
Figure S15. Digital photographs of 40 mg of (a) HRP and (b) Ni-HRP in 80 mL of aqueous solution with 10 mmol of H$_2$O$_2$. The whole process was conducted in the dark, except when taking pictures. The solution became transparent after stirring for 5 h, indicating the corrosion of HRP and Ni-HRP with H$_2$O$_2$. No H$_2$ or O$_2$ was detected during the process.

Figure S16. UV-vis spectra of 100 $\mu$L of H$_2$O$_2$ in 80 mL of water using O-Tolidine as the indicator. The indicator peak at 436 nm confirmed the existence of H$_2$O$_2$ in the mixed aqueous solution (black line). Then 40 mg of Ni-HRP was added to the solution under magnetic stirring. The peak disappeared after 10 min (red line) and 20 min (pink line), which verified the corrosion of the photocatalyst by H$_2$O$_2$.\cite{S4}
Figure S17. Oxygen evolution tests of 1 ml of H$_2$O$_2$ in 50 mL of deionized water. After 1 mg of MnO$_2$ was added to the solution, the oxygen amount was quickly increased and then reached around 110 µmol (black line). Clearly, after 1 mg of MnO$_2$ and 1 mg of Ni-HRP were simultaneously added, the total oxygen amount was significantly decreased compared to only MnO$_2$ added. This result further proved the non-negligible corrosion of the Ni-HRP photocatalyst by H$_2$O$_2$.

Figure S18. Comparison of 40 mg of Ni-HRP in 80 mL of aqueous solution with (A) 20 or (B) 500 µmol of H$_2$O$_2$. To simulate the corrosion process during the photocatalytic reaction, 40 mg of Ni-HRP were respectively dispersed into 80 mL of aqueous solution with 20 or 500 µmol of H$_2$O$_2$ to form suspension A or suspension B. After stirring for 24 h, the color of suspension A didn’t change, but the color of suspension B became much lighter. This phenomenon indicated that the corrosion of Ni-HRP was dependent on the H$_2$O$_2$ concentration.
Figure S19. The configurations of 1-coordinated (left) and 4-coordinated (right) Ni on the (001) surface of red phosphorus. The 4-coordinated Ni was found to be energetically favorable, where the 4-coordinated Ni was 1.01 eV lower in energy than the 1-coordinated Ni (P: red, Ni: green).

Figure S20. Diagram of the suggested photocatalytic process of Ni-HRP.
Table S2. Comparison of apparent quantum efficiencies (AQEs) for hydrogen production over non-metal phosphorus or carbon nitride-based photocatalysts from pure water.

| Photocatalyst                     | AQE (%) at 420 nm | Ref.    |
|-----------------------------------|-------------------|---------|
| Ni-HRP                           | 8.9               | This work |
| Z-scheme CNN/BDCNN                | 11.76             | S11     |
| RP@CoP/CZS                        | 6.4               | S12     |
| PCN@HP                            | 3.59              | S13     |
| C Dots-C3N4                       | 16                | S14     |
| Co1-phosphide/PCN                 | 3.6               | S15     |
| C3N4/MnO2                         | 3.82              | S16     |
| BP/RP quantum dots                | 1.53              | S17     |
| BP/RP hetero-phase junction       | 1.21              | S18     |
| (C
\text{ring})\text{-C}_3\text{N}_4 | 5.0               | S19     |
| Pt-CoP/P-CNS                       | 6.8               | S20     |
| Z-scheme WO\text{3 H}_2\text{O/g-C}_3\text{N}_4 | 6.2 | S21 |
Table S3. Fitted values in the equivalent circuit for the Nyquist impedance plots of prepared samples.

| Electrode | $R_s$ (Ω) | $R_{rec}$ (Ω) | $R_{ct}$ (Ω) | CPE1 ($\times 10^{-5}$ F) | CPE2 ($\times 10^{-5}$ F) |
|-----------|-----------|---------------|---------------|--------------------------|--------------------------|
| RP        | 6.314     | 159.6         | 343.4         | 8.447                    | 4.290                    |
| Ni-RP     | 4.650     | 103.9         | 198.3         | 7.624                    | 3.175                    |
| HRP       | 6.028     | 147.4         | 306.5         | 8.115                    | 3.967                    |
| Ni-HRP    | 3.269     | 82.61         | 165.4         | 7.162                    | 1.645                    |

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