Photo-enhanced electrocatalysis of sea-urchin shaped Ni$_3$(VO$_4$)$_2$ for hydrogen evolution reaction

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S1 Morphological evolution of the as-prepared Ni$_3$(VO$_4$)$_2$ with reaction times
S2 Comparison of the morphology and electrocatalytic HER activity of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$ and Ni$_x$V$_{1-x}$ materials
S3 Experiments of the stability of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$ in HER electrocatalysis
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S1 Morphological evolution of the as-prepared Ni$_3$(VO$_4$)$_2$ with reaction times

**Figure S1** Morphological evolution of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$ prepared at 200 ºC at different reaction times: 0 h (a), 0.5 h (b), 1 h (c), 2 h (d), 4 h (e), 8 h (f), 12h (g), and 18 h (h).
Here, sea-urchin shaped Ni₃(VO₄)₂ was successfully synthesized through a simple approach employing temperature (200 °C) reaction of Ni(NO₃)₂·6H₂O, NH₄VO₃, and DTAB in homogeneous solution of ethanediol and H₂O. The formation process of sea-urchin structure is schematically illustrated in Fig. S2. In the initial stages, a large number of intermediate nuclei were formed the solvothermal treatment in a short time (Fig. S1a-c) and aggregated to large spheres (Fig. S1d) through the reaction between Ni(NO₃)₂, NH₄VO₃ and DTAB in a homogeneous solution. Then, slow crystal growth followed: nanoflakes were grown on the surfaces due to their propensity for two-dimensional growth (Fig. S1e, f). The nanoflakes located on the outside surface would serve as starting points for the subsequent crystallization process (Fig. S1g), and then an interior cavity and an inner core were gradually formed via a core evacuation process due to higher surface energies (Fig. S1h).¹⁻³
**Figure S3** Morphology of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$. a, c) SEM images of the as-synthesized specimen. b, d) TEM images of the as-synthesized specimen.

**Figure S4** EDS spectrum of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$.

**Table S1.** EDS elements analyze of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
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<tbody>
<tr>
<td>O K</td>
<td>34.53</td>
<td>64.68</td>
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<tr>
<td>V K</td>
<td>24.17</td>
<td>14.22</td>
</tr>
<tr>
<td>Ni K</td>
<td>41.30</td>
<td>21.09</td>
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<td>Totals</td>
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<td></td>
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</table>
There are nickel (Ni), vanadium (V) and oxygen (O) elements in the EDS spectrum of Ni$_3$(VO$_4$)$_2$ (Figure S4). The atomic ratio of nickel and vanadium is nearly 3:2. The atomic content of oxygen is a little larger than theoretical value. We conclude that the small amount of redundant oxygen may be introduced from the residual surfactant (DTAB) in the preparation process. The peak beside O peak belongs to C, which is due to the use of carbon tape as the substrate in testing process.

Figure S5 The XPS survey spectrum of Ni$_3$(VO$_4$)$_2$ catalysts.
Comparison of the morphology and electrocatalytic HER activity of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$ and Ni$_x$V$_{1-x}$ materials

Figure S6 (a) BET surface area of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$ and Ni$_x$V$_{1-x}$ materials (Ni$_{0.9}$V$_{0.1}$, Ni$_{0.8}$V$_{0.2}$, Ni$_{0.7}$V$_{0.3}$ and Ni$_{0.5}$V$_{0.5}$). (b) The corresponding pore size distribution of the as-synthesized specimen above.

Figure S7 (a) XRD patterns of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$ and Ni$_x$V$_{1-x}$ materials (Ni$_{0.9}$V$_{0.1}$, Ni$_{0.8}$V$_{0.2}$ and Ni$_{0.7}$V$_{0.3}$). (b) The corresponding enlarged drawing of a.

The excessive nickel transfer to Ni(OH)$_2$ in the Ni$_x$V$_{1-x}$ materials (Ni$_{0.9}$V$_{0.1}$, Ni$_{0.8}$V$_{0.2}$ and Ni$_{0.7}$V$_{0.3}$). As is shown in Figure S7 a-b, the characteristic peaks of Ni(OH)$_2$ at 18.3° which covered one of the diffraction peaks of Ni$_3$(VO$_4$)$_2$ at 19.0° are attenuated with the decrease of excessive nickel. Once again these results confirm that optimizing the initial raw material proportion of nickel and vanadium (3:2) gives rise to the formation of single Ni$_3$(VO$_4$)$_2$ without any impurities.
Table S2. ICP analyze of Ni$_3$(VO$_4$)$_2$ and Ni$_x$V$_{1-x}$ materials

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ni(58.70) ppm</th>
<th>V(50.94) ppm</th>
<th>The ratio of elements $^a$ (%)</th>
<th>The theoretical ratio of elements (%) $^a$</th>
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</thead>
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<tr>
<td>Ni$<em>{0.9}$V$</em>{0.1}$</td>
<td>75.72</td>
<td>7.44</td>
<td>8.834</td>
<td>9.000</td>
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<td>Ni$<em>{0.8}$V$</em>{0.2}$</td>
<td>53.14</td>
<td>11.97</td>
<td>3.852</td>
<td>4.000</td>
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<tr>
<td>Ni$<em>{0.7}$V$</em>{0.3}$</td>
<td>58.51</td>
<td>20.70</td>
<td>2.453</td>
<td>2.333</td>
</tr>
<tr>
<td>Ni$_3$(VO$_4$)$_2$</td>
<td>62.32</td>
<td>36.84</td>
<td>1.468</td>
<td>1.500</td>
</tr>
<tr>
<td>Ni$<em>{0.5}$V$</em>{0.5}$</td>
<td>47.09</td>
<td>40.99</td>
<td>0.997</td>
<td>1.000</td>
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<tr>
<td>Ni$<em>{0.4}$V$</em>{0.6}$</td>
<td>52.66</td>
<td>66.71</td>
<td>0.685</td>
<td>0.667</td>
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</table>

$^a$The ratio of elements = mole number of nickel / mole number of vanadium.

Figure S8 SEM images of Ni$_{0.9}$V$_{0.1}$ (a), Ni$_{0.8}$V$_{0.2}$ (b), Ni$_{0.7}$V$_{0.3}$ (c), Ni$_3$(VO$_4$)$_2$ (d), Ni$_{0.5}$V$_{0.5}$ (e) and Ni$_{0.4}$V$_{0.6}$ (f).
Figure S9  Polarization curves of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$, the Ni$_x$V$_{1-x}$ materials of lower Ni ratios (x means ratios of nickel) with a scan rate of 0.5 mV s$^{-1}$ in 0.5 M H$_2$SO$_4$.

Figure S10  Tafel plots of Ni$_{0.3}$V$_{0.7}$, Ni$_{0.2}$V$_{0.8}$ and Ni$_{0.1}$V$_{0.9}$ derived from Figure S9.

The polarization curves show the overpotentials needed for Ni$_{0.3}$V$_{0.7}$, Ni$_{0.2}$V$_{0.8}$ and Ni$_{0.1}$V$_{0.9}$ to achieve a catalytic current density of 10 mA cm$^{-2}$ are 277, 309 and 318 mV versus RHE, respectively (Fig. S9). As shown in Fig. S10, the Tafel slope of Ni$_{0.3}$V$_{0.7}$, Ni$_{0.2}$V$_{0.8}$ and Ni$_{0.1}$V$_{0.9}$ are ~200 mV/decade, ~211 mV/decade and 215 mV/decade, respectively.
Figure S11  a) UV-vis DRS on Ni$_3$(VO$_4$)$_2$ and samples of lower Ni ratios. b-f) The comparison of the polarization curves of Ni$_{0.5}$V$_{0.5}$, Ni$_{0.4}$V$_{0.6}$, Ni$_{0.3}$V$_{0.7}$, Ni$_{0.2}$V$_{0.8}$ and Ni$_{0.1}$V$_{0.9}$ before and after visible light irradiation.

The results of the UV-vis diffuse reflectance spectroscopy (UV-vis DRS) on Ni$_3$(VO$_4$)$_2$ and samples of lower Ni ratios are shown in Fig. S11a. It can be observed in Fig. S13a that the samples of the samples of lower Ni ratios (Ni$_{0.5}$V$_{0.5}$, Ni$_{0.4}$V$_{0.6}$, Ni$_{0.3}$V$_{0.7}$, Ni$_{0.2}$V$_{0.8}$ and Ni$_{0.1}$V$_{0.9}$) all act out very weak or even no visible light absorption. Besides, in the catalytic system above, there is no enhancement of the electrocatalytic HER activity under visible light irradiation (Fig. S11 b-f).
S3 Experiments of the stability of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$ in HER electrocatalysis

**Figure S12** Time-dependent current density curve under static overpotential of 120 mV. The measurement was conducted in 0.5 M H$_2$SO$_4$.

**Figure S13** SEM images of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$ before (a) and after (b) the stability test.
**Figure S14** XRD patterns of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$ before and after the PEC stability test.

**Figure S15** TEM and HR-TEM images of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$ before (a, c, e) and after (b, d, f) the PEC stability test.
**Figure S16** a) The XPS survey spectrum of Ni$_3$(VO$_4$)$_2$ after PEC test. High-resolution XPS spectrum of Ni 2p region b), V 2p region c), and O 1s region d).

**Figure S17** High-resolution XPS spectrum of Ni 2p region a), V 2p region b) of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$ before and after the PEC stability test.
Figure S18 EDS spectrum of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$ after the stability test.

Table S3. EDS elements analyze of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$ after the stability test.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
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<tbody>
<tr>
<td>O K</td>
<td>38.66</td>
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<td>V K</td>
<td>23.01</td>
<td>12.82</td>
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<tr>
<td>Ni K</td>
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<td>Totals</td>
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</tr>
</tbody>
</table>

Figure S19 The comparison of the element weight ratio of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$ before and after the stability test.
Figure S13 compares the SEM images of the sea-urchin shaped Ni$_3$(VO$_4$)$_2$ before and after stability test of photo-enhanced HER electrocatalysis. There are only tiny changes in the morphology of the structure, which may attribute to some strain relaxation of the thin nanoflakes on the spherical surface or the oxidation of Ni$_3$(VO$_4$)$_2$ during the HER process.$^5$ Fig. S14 exhibits XRD patterns of sea-urchin shaped Ni$_3$(VO$_4$)$_2$ before and after PEC stability test, tiny change can be found, which further confirms the chemical stability of catalyst. In addition to the SEM images, the structural stability is further supported by TEM (Fig. S15). Fig. S15 a-d illustrate that the main morphology was nicely maintained which is consistent with the SEM results. It's worth mentioning that the sea-urchin shaped sphere somewhat agglomerated and adhesion between the spheres appeared after PEC stability test. Although the nanoflakes on the surface slightly crimped, the lattice fringes with interplanar distances maintain in ~0.249 nm corresponding to the (122) planes of Ni$_3$(VO$_4$)$_2$ (Fig. S17 e-f).$^6,7$ As is shown in Figure S19, the major elements do not illustrate particular changes. Beside the oxidation of catalysts, the residual Nafion being used in HER electrocatalysis test may also produce the incremental oxygen.
S4 Photoelectrochemical properties of catalysts

**Figure S20** Time-dependent photocurrent responses curve under open circuit potential with/without visible light irradiation.

![Time-dependent photocurrent responses curve](image)

**Figure S21** (a) Photocurrent responses of Ni$_{0.9}$V$_{0.1}$, Ni$_{0.8}$V$_{0.2}$ and Ni$_{0.7}$V$_{0.3}$ in 0.5 M Na$_2$SO$_4$ solution under visible light irradiation. (b) Photo-generated current-time curve of Ni$_{0.9}$V$_{0.1}$ within a small range scale.

As a proof-of-concept application, the FTO photoanode of PEC cell was used to examine the photocurrent characteristics. Figure S20 illustrate the photo-generated current-time curves, where the black and red lines represent the current density in the dark and under illumination, respectively. The enhanced photocurrent could be seen at any external potentials, indicating the effective photoresponse ability. For a distinct
comparison, the photo-generated current-time curves of Ni\textsubscript{0.9}V\textsubscript{0.1} within a small range scale was shown in Fig. S21b. Almost no photocurrent response of is detected on bare FTO substrate, excluding the contribution from FTO.

![Image](image.png)

**Figure S22** Nyquist plots of the sea-urchin shaped Ni\textsubscript{3}(VO\textsubscript{4})\textsubscript{2} and Ni\textsubscript{x}V\textsubscript{1-x} materials (Ni\textsubscript{0.9}V\textsubscript{0.1}, Ni\textsubscript{0.8}V\textsubscript{0.2} and Ni\textsubscript{0.7}V\textsubscript{0.3}) before and after visible light irradiation.

As is shown in Figure S22, all the catalysts display a lower charge transfer resistance (Rct) after light irradiation than before, and the Ni\textsubscript{3}(VO\textsubscript{4})\textsubscript{2} catalyst reveal lower faradaic impedance than other catalysts. The small Rct value observed for the Ni\textsubscript{3}(VO\textsubscript{4})\textsubscript{2} after light irradiation implies good electron transfer ability,\textsuperscript{8} suggesting the composite is indeed a highly efficient photoresponse electrocatalyst in the hydrogen evolution reaction.

**Reference**

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