Supporting Informations

Sulphur edge and vacancy assisted nitrogen-phosphorus co-doped exfoliated tungsten disulfide: a superior electrocatalyst in hydrogen evolution reaction

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S1
Room temperature XRD analysis is carried out on Philip Holland instrument using cu kα radiation (150.1 nm) at scan rate of 5°/min in the range of 5-90°. FT-IR analysis is carried out on Perkin Elmer instrument from 400-4000 cm⁻¹ by KBR disc. The morphology of the samples were characterized by field emission scanning electron microscopy (FESEM) on Carl Zeiss operating at 20 kV respectively. TEM images were recorded on a TECNAI G2 SEI (Netherland) operating at 200 kV and Gatan multipole charge-coupled device (CCD) camera. The samples for this purpose were prepared as droplet on carbon-coated copper grids and left for drying overnight in vacuum. HRTEM was investigated by JEOL-JEM 2100, Japan, operating at an accelerating voltage of 200 kV and beam current 116 mA with lanthanum hexaboride target. The gas sorption experiment was carried out using a Micromeritics 3Flex instrument. 20–25 mg of sample was taken in a 6 mm sample holder without rod. The samples were degassed at 90 °C for 2 h prior to the experiment. Ultraviolet-visible (UV-vis) absorption spectrum of samples was performed on Varian Cary 5000 UV-Visible spectrophotometer. The XPS experiments were recorded in an ultra-high vacuum (UHV) system with the surface analysis system (ESCALAB 250Xi, Thermo Fisher Scientific, Waltham, MA) at the room temperature base pressure of the analysis chamber during the measurements was kept lower than 1.0 × 10⁻⁹ mbar. For XPS Al Kα radiation (hv = 1486.6 eV) from a monochromatized X-
ray source. Atomic force microscopy (AFM) was performed on a scanning probe microscope (SPM), Model Multiview-1000. Commercial Hitachi Fluorescence spectrophotometer (model no. F-7000) is used for PL measurement. EPR spectra were recorded on Bruker ELEXSYS 580. STEM-HADDF image were taken on FEG-HIGH RESOLUTION-CRYO-ANALYTICAL TEM machine.( Model number -JEM 2100F). All electrochemical work is carried on a CHI 7086E electrochemical workstation (CHI instruments Inc.). The density of state (DOS) and partial density of states (PDOS) of WS\textsubscript{2} and PNEWS\textsubscript{2} were calculated by using the Wien2k package with the self-consistent full potential linearized-augmented plane wave (F-LAPW) \textsuperscript{1} method comprising of generalized gradient approximation. within Density functional theory (DFT employed to calculate the band and density of state (DOS) of sample of WS\textsubscript{2} and 1T-PNEWS\textsubscript{2}. 
Fig. S2 XRD of WN$_{12}$. 
Fig. S3 Raman spectra of a) $\text{WN}_{12}$ b) PMMA-$\text{WN}_{12}$. 
Fig. S4 IR spectra of a) WS₂, EWS₂, WN₁₂, NEWS₂ and PNEWS₂ b) PMMA-WN₁₂.
Fig. S4 shows FT-IR spectra of bulk WS$_2$, EWS$_2$, NEWS$_2$, PNEWS$_2$ in the range of 400-4000 cm$^{-1}$. A common peak appeared is at ~ 578 cm$^{-1}$ corresponding to metal (W)-sulfur (S) bond in all samples.\textsuperscript{2} WN$_{12}$ showed appearance of peaks at ~ 3407, 2950, 1650, 1225 cm$^{-1}$ corresponding to –NH$_2$ strech, -CH$_2$ asymmetric strch, C=C strech and =C-H bending vibration respectively.\textsuperscript{3} The presence of peaks corresponding to N-H stretching (3452 cm$^{-1}$) and alkyl C-H stretching frequency (2850 cm$^{-1}$) confirmed presence of oleyl amine in WN$_{12}$.\textsuperscript{3} The spectra of WN$_{12}$ film deposited on PMMA consist of peaks corresponding to =CH bending (1471 cm$^{-1}$), keto group (1730 cm$^{-1}$).\textsuperscript{4} In contrast, these peaks disappeared in NEWS$_2$ and PNEWS$_2$ indicating successful expulsion of PMMA and oleyl amine on washing with acetone and toluene washing respectively.
Fig. S5 (a) XPS spectrum of PNEWS$_2$ and WS$_2$. (b) S2P intensity of PNEWS$_2$ and WS$_2$. 
Fig. S6 XPS of PNEWS$_2$. 
Fig. S7  a) FESEM image EWS₂, b) FESEM image of NEWS₂, c) FESEM image of PNEWS₂.
Fig. S8 FE-SEM image of a) WS₂, b) WN₁₂.
Fig. S9 a) EDS pattern of PNEWS\textsubscript{2} and b) Mapping image of PNEWS\textsubscript{2}.
Fig. S10 HAADF–STEM (a) bright and (b) dark field image of PNEWS$_2$
Fig. S11  a) HRTEM Image of PMMA-WN$_{12}$, b) SAED pattern of PMMA-WN$_{12}$,(By HRTEM analysis), c) SAED pattern of NEWS$_2$ and d) PNEWS$_2$ by TEM analysis. (e) NEWS$_2$ shows summary of d$_{100}$ spacing.(f) PNEWS$_2$ shows summary of d$_{100}$ spacing).
Fig. S12 Lifetime of different catalysts
Fig. S13 AFM image and height-length profile of a) PNEWS₂ b) NEWS₂ and c) EWS₂.
Fig. S14 UV spectrum of PNEWS$_2$.

Fig. S15 PL Spectra of PNEWS$_2$. 
Fig. S16 represent N$_2$ adsorption–desorption isotherms and pore size distribution in forming a network of mesopore associate with micro pores. Further, it is noted that PNEWS$_2$ exhibited significantly higher specific surface area (220 m$^2$g$^{-1}$) compared to NEWS$_2$ (54.5 m$^2$g$^{-1}$) and EWS$_2$ (45.9 m$^2$g$^{-1}$). The enhanced surface area and pore volume of PNEWS$_2$ could be ascribed to expulsion of PH$_3$ gas leading to the further exfoliation of PNEWS$_2$. Such significantly higher specific surface area and porosity of PNEWS$_2$ is likely to provide abundant exposed edges as well as catalytic sites for HER.

Fig. S16 a) N$_2$ adsorption–desorption isotherms and b) Pore size distribution in PNEWS$_2$, NEWS$_2$, EWS$_2$. 
**Fig. S17** a) LSV of catalysts EWS$_2$, NEWS$_2$ and PNEWS$_2$ at 1mV/ sec and its b) corresponding Tafel slope in 0.5molar H$_2$SO$_4$. 
Fig. S18 Cyclic voltammograms of PNEWS$_2$ measured at different scan rate.

Fig. S19 Cyclic voltammograms of NEWS$_2$, measured at different scan rate.

Fig. S20 Cyclic voltammograms of EWS$_2$, measured at different scan rate.
Fig. S21 (a) CV of Pt/C (10 wt%) at (20-80) mVs\(^{-1}\) scan rate and its (b) corresponding double layer capacitance.

Fig. S22 Accounting graphite as counter electrode (a) Total current density (J) vs Potential curve of catalyst in 0.5 M H\(_2\)SO\(_4\). (b) Tafel slope of catalysts in 0.5 Molar H\(_2\)SO\(_4\). (c) Nyquist plot of catalysts.
Fig. S23 Variation of current density versus potential of at different catalyst loadings. a) PNEWS$_2$ b) NEWS$_2$ c) EWS$_2$.

Fig. S23 show variation of current density versus potential of PNEWS$_2$ at different catalyst loadings. It is noted that current density increase linearly with mass loadings of PNEWS$_2$. This clearly suggest that increased roughness factor (RF) could account for enhanced HER due to the presence of more number active sites accessible to perform the catalysis.$^6$,$^7$
**Fig. S24** Cyclic voltammograms of EWS$_2$, NEWS$_2$ and PNEWS$_2$ (Scan rate: 50 mV s$^{-1}$).

**Fig. S25** CV of EWS$_2$, NEWS$_2$ and PNEWS$_2$ after 1000 cycle

**Fig. S26** PNEWS$_2$ shows 15 hour i-t test at -0.74 V.
**Fig. S27** Elemental mapping image of catalyst PNEWS\textsubscript{2} after 15 hour electrocatalysis.
Fig. S28 After 15 hour electrocatalysis of catalyst PNEWS<sub>2</sub> a) XPS b) XRD c) TEM d) EDS
Fig. S29 Raman spectra after 10 hour electrocatalysis of catalyst PNEWS₂.

Fig. S30 IR spectra of catalyst PNEWS₂ before and after electrocatalysis.
Fig. S31 Impedence spectra of PNEWS$_2$ at -100, -140 and -150 mV potential.
Fig. S32. a) Impedance versus frequency plots and b) Phase versus frequency plots of PNEWS$_2$ at -100, -140 and -150 mV.
**Table S1.** Comparative performance of different electrocatalysts on HER.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Onset-potential (mV)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>Current density (mA cm$^{-2}$)</th>
<th>Overpotential (mV)</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>WS$_2$@heteroatom doped graphene film</td>
<td>-</td>
<td>52.7</td>
<td>10</td>
<td>125</td>
<td>8</td>
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<tr>
<td>C$_3$N$_4$@NG</td>
<td>-</td>
<td>51.5</td>
<td>10</td>
<td>240</td>
<td>9</td>
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<tr>
<td>MoS$_2$ nanoparticles</td>
<td>90</td>
<td>69</td>
<td>-</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>MoS$_2$ nanolayers</td>
<td>90</td>
<td>53</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>MoS$_2$ formed on mesoporous graphene</td>
<td>-</td>
<td>85</td>
<td>10</td>
<td>200</td>
<td>11</td>
</tr>
<tr>
<td>Co=CoO/N-doped carbon hybrids</td>
<td>85</td>
<td>115</td>
<td>10</td>
<td>235</td>
<td>12</td>
</tr>
<tr>
<td>WS$_2$/rGO</td>
<td>73</td>
<td>73</td>
<td>10</td>
<td>229</td>
<td>13</td>
</tr>
<tr>
<td>CoP/rGO</td>
<td>13</td>
<td>50</td>
<td>10</td>
<td>105</td>
<td>14</td>
</tr>
<tr>
<td>WS$<em>{2(1-x)}$P$</em>{2x}$</td>
<td>-</td>
<td>71</td>
<td>10</td>
<td>98</td>
<td>15</td>
</tr>
<tr>
<td>er-WS$_2$-Pt</td>
<td>-</td>
<td>27</td>
<td>10</td>
<td>30</td>
<td>16</td>
</tr>
<tr>
<td>Exfoliated WS$_2$ Nanodots</td>
<td>90</td>
<td>51</td>
<td>-</td>
<td>-</td>
<td>17</td>
</tr>
<tr>
<td>3D WS$_2$ Nanolayers@Heteroatom-Doped Graphene Films</td>
<td>-</td>
<td>52.7</td>
<td>10</td>
<td>125</td>
<td>18</td>
</tr>
<tr>
<td>PNEWS$_2$</td>
<td><strong>11</strong></td>
<td><strong>35</strong></td>
<td><strong>10</strong></td>
<td><strong>59</strong></td>
<td><strong>This work</strong></td>
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</table>

This work
Table S2. Summary of HER performance with catalyst loading.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst loading</th>
<th>Current density (mA/cm²)</th>
<th>Overpotential (mV)</th>
<th>Tafel slope (mV decade⁻¹)</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>Exfoliated WS₂</td>
<td>0.1-0.2 μg cm⁻²</td>
<td>10</td>
<td>80-100</td>
<td>60</td>
<td>20</td>
</tr>
<tr>
<td>CoMoSₓ</td>
<td>50 μg cm⁻²</td>
<td>5</td>
<td>207</td>
<td>-</td>
<td>21</td>
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<tr>
<td>WO₃₀</td>
<td>0.285 mg cm⁻²</td>
<td>10</td>
<td>70</td>
<td>50</td>
<td>22</td>
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<tr>
<td>Edge terminated MoS₂</td>
<td>0.28 mg cm⁻²</td>
<td>10</td>
<td>150</td>
<td>49</td>
<td>23</td>
</tr>
<tr>
<td>Pt-MoS₂</td>
<td>75 μg cm⁻²</td>
<td>10</td>
<td>53</td>
<td>40</td>
<td>24</td>
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<tr>
<td>Co-NG</td>
<td>0.285 mg cm⁻²</td>
<td>0.3</td>
<td>30</td>
<td>82</td>
<td>25</td>
</tr>
<tr>
<td>MoP₂ nanosheet</td>
<td>7.80 mg cm⁻²</td>
<td>10</td>
<td>58</td>
<td>34.6</td>
<td>26</td>
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<tr>
<td>P-W₂C@N</td>
<td>3.50 mg cm⁻²</td>
<td>10</td>
<td>89</td>
<td>53</td>
<td>27</td>
</tr>
<tr>
<td>NiCo₂Px Nanowires</td>
<td>5.90 mg cm⁻²</td>
<td>10</td>
<td>104</td>
<td>59.6</td>
<td>28</td>
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<tr>
<td>PNEWS₂</td>
<td>1.4 mg cm⁻²</td>
<td>10</td>
<td>59</td>
<td>35</td>
<td>This work</td>
</tr>
</tbody>
</table>

Reference

18. X. Zhao, X. Ma, J. Sun, D. Li and X. Yang, ACS Nano, 2016, 10, 2159-2166.


