Electronic Supplementary Information

Nano-Tungsten Carbide Decorated Graphene as Co-catalyst for Enhanced Hydrogen Evolution on Molybdenum Disulfide

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Experimental details

Synthesis of nano-WC: For a typical synthesis of nano-WC, a certain amount (50-80 mg) of as-prepared WO₃ nanorods as mentioned in our previous paper¹ was transferred into a tube furnace for reduction-carburization. The whole system was first purged with argon gas to completely remove any air before heating. The argon gas
was then switched off and a mixture of CH\(_4\) (20 mL min\(^{-1}\)) and H\(_2\) (80 mL min\(^{-1}\)) was fed to the furnace. In the meantime, the furnace was first heated to 600 °C with a ramp rate of 5 °C min\(^{-1}\) and then to 800 °C at a rate of 2 °C min\(^{-1}\) and kept at this temperature for 3h. After that, the furnace was cooled down to a temperature of 700 °C. The supply of the carburizing agent was switched off and argon was used to purge the furnace again. The furnace was further cooled down to room temperature.

*Synthesis of Graphene oxide (GO):* Graphene oxide (GO) was synthesized from natural graphite powder by a modified Hummers’ method.

*Synthesis of the nano-WC/GO hybrids:* Hybrid of WC/GO was obtained by adding as-prepared nano-WC to GO dispersed in 15 mL of Dimethylformamide (DMF)/H\(_2\)O (10:1) mixture. The mixture was sonicated in ice water bath for accumulated 30 min in a program of 1s on 1s off and then stirred at room temperature overnight. In order to investigate the effect of WC content in the WC/GO hybrid co-catalyst on the electrocatalytic hydrogen evolution activity of MoS\(_2\), the weight percentages of WC to GO were varied from 0 to 100 (0, 20, 25, 33.3 and 100 wt%) by varying the weight of nano-WC, the resulting samples were labeled as \(x\)W(100-\(x\))G, where W and G refer to WC and graphene, respectively, and \(x = 0, 20, 25, 33.3\) and 100, respectively.

*Synthesis of layered-MoS\(_2\)/WC/RGO composite:* The composite samples were synthesized by a solvothermal method. (NH\(_4\))\(_2\)MoS\(_4\) was used as the MoS\(_2\) source and was added to the 15 mL thoroughly mixed WC/GO hybrid GO. The mixture was sonicated at room temperature for approximately 20 min until a clear and
homogeneous solution was achieved. Then, 0.2 ml of \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \) was added and this obtained solution mixture was further sonicated for 10 min before transferred to a 50 mL Teflon-lined autoclave with a Teflon liner and kept at 210 °C for 18 h. The resulting precipitate was collected, washed thoroughly with distilled water followed by a rinse in ethanol, and then dried at 60 °C for 12 h. Similarly, a series of the MoS\(_2\)/WC/RGO composites were prepared by using the \( x\text{W}(100-x)\text{G} \) as co-catalyst under the same conditions but replacing 25W75G with \( x\text{W}(100-x)\text{G} \). Blank MoS\(_2\) was also prepared following the same procedure as above except for the first addition of WC/GO hybrid co-catalyst. The detailed data are listed in Table S1. Moreover, in order to further investigate the content effect of the WC/RGO (25W75G) co-catalyst on the electrocatalytic hydrogen evolution activity of MoS\(_2\), the weight ratio of 25W75G/MoS\(_2\) was changed from 15wt % to 50wt % by varying the amount of 25W75G (see Table S2). For the purpose of comparison, 30%-25W75G/MoS\(_2\) mixture was prepared by simple mechanical mixing of the pristine MoS\(_2\) and 30 wt% of 25W75G without the solvothermal process.

**Characterization:** All transmission electron microscopy (TEM), high-resolution (HR)TEM images and element mapping were taken from JEOL JEM 2100F, while the field emission scanning electron microscopy (FESEM) images and energy-dispersive X-ray spectroscopy (EDX) spectra were taken on a JEOL JSM 6700F. XRD analysis of different samples was carried out on a X-ray diffractometer (Bruker AXS D8, Cu K\( \lambda \), \( \lambda = 1.5406 \) Å, 40 kV and 20 mA). Raman spectra were collected via a Renishaw Ramanscope in the backscattering configuration using 514
nm (2.41 eV) laser wavelengths over five random spots on the powers. X-ray photoelectron spectroscopy (XPS) spectrum was measured on a VG Escalab 250 spectrometer equipped with an Al anode (Al Kα = 1846.6 eV). The specific surface area and pore size distribution of the samples were evaluated in Autolab-6B (Quantachrome Instruments) using the liquid nitrogen adsorption/desorption method. All the samples were degassed at 120 °C for 2 hours before the measurements. The BET surface area was determined using adsorption data in the relative pressure \((P/P_0)\) range of 0.05-0.25. The desorption branch was used to determine the pore size distribution \(\text{via}\) the Barret-Joyner-Halender (BJH) method. The nitrogen adsorption volume at the relative pressure \((P/P_0)\) of 0.95 was used to determine the single-point pore volume and the average pore size. Thermo gravimetric analysis (TGA) and the derived differential thermogravimetric (DTA) experiments were conducted on a PerkinElmer Diamond TG/DTA equipment. The sample was first kept at 100 °C for 30 min to remove moisture and then was heated up to 1000 °C under high purity air flow (50 sccm) in a ramp of 10 °C/min while its weight was monitored. Atomic force microscope (AFM) with a MPF3D microscope from Asylum Research was used in this paper.

**Electrochemical measurements:** All electrochemical measurements were conducted on an Autolab PGSTAT302 potentiostat (Eco Chemie, Netherlands) in a three-electrode cell at room temperature. A Pt foil (4.0 cm²) and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The working electrode was prepared on a glass carbon (GC) disk as the substrate.
Typically, a mixture containing 2.0 mg catalyst, 2.5 mL ethanol and 0.5 mL Nafion solution (0.05 wt%, Gashub) was ultrasonicated for 15 min to obtain a well-dispersed ink. Then 20 μl of the catalyst ink (containing 13 μg of catalyst) was loaded onto a glassy carbon electrode of 4 mm in diameter (loading ~ 0.104 mg/cm²). The presented current density refers to the geometric surface area of the glass carbon electrode. Linear sweep voltammetry with scan rate of 5 mV s⁻¹ was conducted in 0.5 M H₂SO₄. The working electrodes were mounted at a rotating disc electrode with a rotating rate of 1000 rpm during the test. In all experiments, the electrolyte solutions were purged with N₂ for 15 min prior to the experiments in order to remove oxygen. During the measurements, the headspace of the electrochemical cell was continuously purged with N₂. AC impedance measurements were carried out in the same configuration at η = 0.15 V from 10⁵-0.02 Hz with an AC voltage of 5 mV. Commercial Pt/C (20 wt %) from E-TEK was measured as received. All the potentials reported in our manuscript were referenced to a reversible hydrogen electrode (RHE) by adding a value of (0.241+0.059 pH) V.
Table S1. Effects of WC/RGO co-catalyst content in the MoS$_2$/WC/RGO electrocatalysts on the HER activity according to polarization measurements.

<table>
<thead>
<tr>
<th>Sample[a]</th>
<th>Composition</th>
<th>Tafel slope [mV/decade][b]</th>
<th>Onset potential [V][c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100M/0(W-G)</td>
<td>100MoS$_2$+0(WC/RGO)</td>
<td>106</td>
<td>-0.14</td>
</tr>
<tr>
<td>85M/15(W-G)</td>
<td>85MoS$_2$+15(WC/RGO)</td>
<td>74</td>
<td>-0.13</td>
</tr>
<tr>
<td>80M/20(W-G)</td>
<td>80MoS$_2$+20(WC/RGO)</td>
<td>78</td>
<td>-0.13</td>
</tr>
<tr>
<td>70M/30(W-G)</td>
<td>70MoS$_2$+30(WC/RGO)</td>
<td>41</td>
<td>-0.11</td>
</tr>
<tr>
<td>60M/40(W-G)</td>
<td>60MoS$_2$+40(WC/RGO)</td>
<td>60</td>
<td>-0.15</td>
</tr>
<tr>
<td>50M/50(W-G)</td>
<td>50MoS$_2$+50(WC/RGO)</td>
<td>51</td>
<td>-0.16</td>
</tr>
</tbody>
</table>

[a] W-G samples contains 25%WC and 75% of RGO in the co-catalyst.

[b] Calculated from the linear portion of the plot in the potential range of 150 mV-200 mV.

[c] The onset potential at which the hydrogen evolution occurred measured versus RHE.

Table S2. Effects of WC/RGO weight ratio on the HER activity according to polarization measurements.

<table>
<thead>
<tr>
<th>Sample[a]</th>
<th>Composition</th>
<th>Tafel slope [mV/decade][b]</th>
<th>Onset potential [V][c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>M/0W-100G</td>
<td>MoS$_2$+RGO</td>
<td>47</td>
<td>-0.13</td>
</tr>
<tr>
<td>M/33.3W-66.7G</td>
<td>MoS$_2$+33.3WC-66.7RGO</td>
<td>47</td>
<td>-0.12</td>
</tr>
<tr>
<td>M/25W-75G</td>
<td>MoS$_2$+25WC-75RGO</td>
<td>41</td>
<td>-0.11</td>
</tr>
<tr>
<td>M/20W-80G</td>
<td>MoS$_2$+20WC-80RGO</td>
<td>45</td>
<td>-0.13</td>
</tr>
<tr>
<td>M/100W-0G</td>
<td>MoS$_2$+WC</td>
<td>54</td>
<td>-0.12</td>
</tr>
</tbody>
</table>

[a] All composite samples contain 70% of MoS$_2$ and 30% of co-catalyst in the composite electrocatalyst.

[b] Calculated from the linear portion of the plot in the potential range of 150 mV-200 mV.

[c] The onset potential at which the hydrogen evolution occurred measured versus RHE.
Figure S1. FESEM images (a), XRD pattern (b), XPS W4f spectra (c) and TGA-DSC (d) of the nano-WC obtained in the CH₄/H₂ mixtures at 800 °C for 3h.

The as-prepared WC nanoparticles exhibits an interesting string-like morphology with average size of 35 nm. XRD pattern demonstrated the material was a hexagonal WC (PDF # 25-1047. From XPS spectrum, the W4f7/2 and the W4f5/2 peaks corresponding to the binding energy of 31.6 and 33.7eV are assigned to the tungsten carbide.² It also demonstrates the oxygen-modified W on the particle’s surface at 35.7 and 37.2 eV which could come from the thin WOₓ film that was formed in air at nanometer level, which is hardly detectable by XRD.³ TG analysis of the nano-WC under air shows that there is a very slight weight loss (~0.5%) during the heating range of 150-500°C, which could be from undesirable amorphorous carbon. Beyond
this temperature range, an obvious weight increase caused by the oxidation of WC is observed from 500-600°C, which is consistent with the reported fact that oxidation of WC starts at 500–600 °C. The above results could indicate the relatively high purity of the nano-WC precursor.

Figure S2. AFM image (a), Raman spectrum (b) and XRD pattern (c) of the prepared graphene oxide sheets as starting material.
Figure S3. Schematic illustration of the synthesis of MoS$_2$/WC/RGO composite.
**Figure S4.** TEM image of the selected area of the MoS$_2$/WC/RGO composite for element mapping.
Figure S5. Raman spectra of self-prepared WC and commercial WC. The characteristic peaks of the as-prepared WC are consistent with the commercial one.
Figure S6. High-resolution XPS spectra of MoS$_2$/WC/RGO composites. (a) C 1s, (b) S2p and (c) W 4f spectrum.
Figure S7. N\textsubscript{2} adsorption/desorption isotherms and the corresponding BJH pore-size distribution (inset) of nano-WC. The pore diameter distribution was determined from the desorption branch.
Figure S8. FESEM images and EDS spectra of MoS$_2$/WC/RGO composites (70M/30(W-G)) (a, c) and MoS$_2$/RGO hybrid (70M/30G) (b, d), respectively.
**Figure S9.** FESEM images of (a) nano-WC/RGO, (b) MoS$_2$/nano-WC hybrid.

Control experiment was also conducted in the absence of RGO by following the exactly same procedure, which resulted in the aggregation of MoS$_2$ particles and WC particles in separate regions (Figure S9b) and low activities and low activities.
Figure S10. The Tafel plot of 70M/30(W-G) in the region of low current densities.

The onset potential for HER was read from the semi-log (Tafel) plot. For example, the semi-log plot of 70M/30(W-G) in the region of low current densities as displayed in Fig.S8 shows a linear relationship below -0.11V but stars to deviate above -0.10V. Therefore, -0.11 was chosen as the onset potential for 70M/30(W-G). The same method was applied on determining the overpotential for other samples.\(^5\)
**Figure S11.** (a) FESEM image of the MoS$_2$ (70%) particles physically mixed with WC/RGO (30%) and (b) the corresponding polarization curve.
Figure S12. Polarization curve of (a) MoS$_2$/WC/RGO composites with different WC/RGO ratio in the WC/RGO co-catalyst and (b) nano-WC (MoS$_2$ was used as a reference).

References