Electronic Supporting Information

Materials

Ammonium molybdate (AM) and sulfur (Sisco Research laboratories), Dopamine hydrochloride (DA) and Tris(hydroxymethyl)aminomethane (Alfa Aesar), N, N’-dimethylformamide (Merck) were used as received. All aqueous solution was prepared using MilliQ (18.2MΩ cm).

Infrared spectroscopy for the samples was done on a Bruker Tensor 27 FT-IR spectrometer. X-ray diffraction patterns were recorded using a Bruker D8 Advance X-ray diffractometer with a Cu Kα radiation (λ = 1.5418 Å). Surface morphology was studied using Field Emission Scanning Electron Microscope (Zeiss supra 55VP). TEM characterizations were done by TECHNAI G20 microscope functioning at 200 kV accelerating voltage and samples were prepared on carbon coated copper grid. X-ray photo electron spectroscopy was performed using SPECS, Phoibos 100 MCD Analyzer with pass energy of 20 eV (Al Kα anode (1486.6eV)) in ultrahigh vacuum (5×10⁻¹⁰mbar). Diffused reflectance spectra were recorded using V-670 spectrophotometer (Jasco). UV-Vis spectroscopy was performed with Cary 60 (Agilent technologies). Cyclic voltammetric experiments were performed on a BASi100 workstation.

Synthesis of MoS$_2$@S-C$_{\text{PDA}}$, MoS$_2$ and S-C$_{\text{PDA}}$:

DA and AM (2:1) was dissolved in Tris buffer solution (~ pH 8.5). The colorless solution turned yellow indicating the formation of dopamine-molybdate complex; the solution was kept aside for 12 h for complete polymerization. The composite was then pyrolyzed in a tube furnace for 5 h in the presence of elemental sulfur under flowing Ar. The resultant black solid product (MoS$_2$@S-C$_{\text{PDA}}$) was stored in desiccator. Similar procedure was followed for the synthesis of S-C$_{\text{PDA}}$ and MoS$_2$ without ammonium molybdate and dopamine respectively.

Electrochemical Characterization:

A three-electrode cell with Ag/AgCl as reference electrode and a Pt foil as the counter electrode was used. The glassy carbon disk electrode was modified with the S-C$_{\text{PDA}}$, MoS$_2$ and MoS$_2$@S-C$_{\text{PDA}}$ and employed for studying the hydrogen evolution reaction. Prior to modification, the glassy carbon electrode was well-polished with 1, 0.3 and 0.05 micron-sized
alumina powder and sonicated for about 5 minutes. 3 mg of S-C$_{PDA}$, MoS$_2$ and MoS$_2$@S-C$_{PDA}$
samples were well dispersed in 200µL DMF solvent and sonicated for 0.5 h. The dispersed
solution was drop casted each on separate glassy carbon disk electrodes followed by overnight
drying and employed for testing the hydrogen evolution. Electrochemical impedance
spectroscopy (EIS) was performed in 0.5 M H$_2$SO$_4$ using PAR potentiostat with a frequency
range of 1 to 50 MHz.
FT-IR spectroscopy was used to evaluate the complex formation between dopamine (DA) and (NH$_4$)$_2$MoO$_4$ (AM). The spectrum of DA shows vibrations of characteristic $\nu$(N–H), $\nu$(N–H), $\delta$(C=C), and $\nu$(C=N), $\nu$(C-O) at 3344, 1606, 1501, 1280 and 1190 cm$^{-1}$ respectively. As expected AM shows its characteristic peaks of $\nu$(Mo-O), $\delta$(Mo-O) at 914, 658 cm$^{-1}$ respectively. Additionally, the appearance of $\nu$(N-H), $\delta$(N-H) stretching frequencies at 3185 and 1412 cm$^{-1}$ confirms the presence of ammonium ions in AM. The complex formation between DA and AM was confirmed by the presence of characteristic vibrations, **viz.,** $\nu$(N–H), $\nu$(N–H), $\delta$(C=C),$\nu$(Mo-O), $\delta$(Mo-O) with a blue-shift indicating the complex formation occurring *via* hydrogen bonding or electrostatic interactions between molecules.
Figure S2: XRD of S-C\textsubscript{PDA}.
Figure S3: Raman spectrum of MoS$_2@$S-C$_{PDA}$ and MoS$_2$
Figure S4: FTIR spectrum of MoS$_2$@S-C$_{PDA}$, MoS$_2$ and S-C$_{PDA}$
Figure S5: High resolution XPS ($S_{2p}$) of MoS$_2@$S-C$_{pDA}$ and MoS$_2$
Figure S6: Tauc plot of MoS$_2$@S-C$_{\text{PDA}}$ and MoS$_2$ using the data obtained from diffuse reflectance spectra
Figure S7: UV-visible spectra of MoS$_2$@S-C$_{PDA}$ and MoS$_2$
Figure S8: Stability studies on MoS$_2$@S-C$_{PDA}$ modified electrodes towards HER.
Electrolyte: 0.5 M H$_2$SO$_4$, Scan rate: 50 mV/s
<table>
<thead>
<tr>
<th>Materials</th>
<th>Onset potential (mV)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>Exchange current density ($J_o$) (mA/cm$^2$)</th>
<th>$\eta$@10mA/cm$^2$ (mV)</th>
<th>$j$@200mV (mA cm$^{-2}$)</th>
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References: