Supplementary information

Amorphous molybdenum sulfide quantum dots: an efficient hydrogen evolution electrocatalyst in neutral medium

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Table-S1: Comparison of onset potentials for different MoS$_2$ based nano materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>Onset Potential (mV)</th>
<th>Tafel Slope (mv/dec)</th>
<th>References</th>
<th>Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Mo-S nano sheets on carbon fiber cloth</td>
<td>132</td>
<td>85.3</td>
<td><em>Science Advances</em>, DOI: 10.1126/sciadv.1500259</td>
<td>pH 7</td>
</tr>
<tr>
<td>Amorphous MoS$_x$ on carbon fiber</td>
<td>205</td>
<td>46</td>
<td><em>Energy Environ. Sci.</em> 2012, 5, 6136–6144.</td>
<td>0.5 M H$_2$SO$_4$</td>
</tr>
<tr>
<td>Amorphous MoS$_x$/Graphene/Ni-foam</td>
<td>109</td>
<td>42.8</td>
<td><em>Chem. Commun.</em>, 2015, 51, 6293–6296.</td>
<td>0.5 M H$_2$SO$_4$</td>
</tr>
<tr>
<td>Monolayer MoS$_2$ quantum dots</td>
<td>120</td>
<td>69</td>
<td><em>RSC Adv.</em>, 2015, 5, 97696–97701</td>
<td>0.5 M H$_2$SO$_4$</td>
</tr>
<tr>
<td>Monolayer MoS$_2$ /WS$_2$ composite Quantum Dots</td>
<td>120</td>
<td>69-75</td>
<td>Adv. Funct. Mater. 2015, 25, 1127–1136</td>
<td>0.5 M H$_2$SO$_4$</td>
</tr>
<tr>
<td>MoS$_2$ quantum dot decorated RGO</td>
<td>64</td>
<td>63</td>
<td>J. Mater. Chem. A, 2015, 3, 21772</td>
<td>0.5 M H$_2$SO$_4$</td>
</tr>
<tr>
<td>Tungsten Phosphide Submicroparticles</td>
<td>54</td>
<td>57</td>
<td>ACS Catal. 2015, 5, 145149</td>
<td>pH 7</td>
</tr>
<tr>
<td>Tungsten Phosphide Nanorod</td>
<td>100</td>
<td>125</td>
<td>ACS Appl. Mater. Interfaces 2014, 6, 21874</td>
<td>pH 7</td>
</tr>
<tr>
<td>Amorphous MoS$_x$ quantum dots</td>
<td>65</td>
<td>73.9</td>
<td>Present work</td>
<td>pH 7</td>
</tr>
</tbody>
</table>
Table-S2: Comparison of exchange current density ($j_0$) values

<table>
<thead>
<tr>
<th>Material</th>
<th>$j_0$ (μA/cm$^2$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active edge MoS2</td>
<td>7.9</td>
<td><em>Science</em>, 2007, 317, 100–102</td>
</tr>
<tr>
<td>S-rich MoS$_2$</td>
<td>0.4</td>
<td><em>J. Mater. Chem. A</em>, 2015, 3, 15927-15934</td>
</tr>
<tr>
<td>MoS$_3$ on glassy carbon</td>
<td>0.89</td>
<td><em>Chem. Sci.</em>, 2012, 3, 2515-2525</td>
</tr>
<tr>
<td>Amorphous MoS$_x$ quantum dots</td>
<td>8.71</td>
<td>Present work</td>
</tr>
</tbody>
</table>

**Photoluminescence Study of quantum dots:**

To establish the quantum dot behavior, we have measured the fluorescence property of these MoS$_x$ nano particles. It shows quite weak blue photo luminescence (PL) spectra at ~ 430 nm when excited at 360 nm wavelength. As the nano particle is amorphous in nature it gives very weak PL compared to crystalline MoS$_x$ nanoparticles as shown in Fig S1. The most striking feature of quantum dots is that they show excitation dependent PL property due to splitting of the energy band gap$^{1-4}$ and our material also shows such excitation dependent photoluminescence behavior as shown in Fig. S2. With the increase in excitation wavelength the peak position is gradually red shifted. It is noted that the band gap of monolayer MoS$_2$ is ~ 1.9 eV (direct band
gap), whereas it is found to be ~ 2.9 eV for our material. Therefore, a huge blue shift (~ 1 eV) and splitting of energy levels giving rise to excitation dependent PL confirming the quantum confinement of the electronic wave functions in the as synthesized material. This strongly resembles the quantum dot behavior of our MoS$_x$ nano particles.

**Fig. S1:** Comparison of PL spectra between crystalline and amorphous MoS$_x$ quantum dots

**Fig. S2:** Excitation dependent PL spectra of amorphous MoS$_x$ quantum dots
HER study of MoS$_x$ quantum dots in different medium:

*In 0.5 M $H_2SO_4$ medium:*

![Graph showing HER activity in acidic condition](image1)

**Fig. S3:** HER activity in acidic condition

*In 1 N NaOH medium:*

![Graph showing HER activity in basic condition](image2)

**Fig. S4:** HER activity in basic condition
Determination of TON and TOF:

Turn over frequency is determined from the double layer capacitance \((C_{dl})\) of the MoS\(_x\) film modified ITO electrode. \(C_{dl}\) could easily be determined from the current density of the modified electrode where no faradaic current is observed. The difference between the anodic and cathodic current at 0.08 V vs RHE is plotted against scan rate as shown in **Fig. S3**. From the slope of this linear fit the double layer capacitance of the modified electrode is easily determined to be \(\sim 765 \mu F/cm^2\). The area-averaged capacitance depends on the electrode materials. The TOF has been determined from the double layer capacitance of the MoS\(_x\) surface \((C_{dl} = 765 \mu F/cm^2)\) and charge consumed \((22.18 \text{ C})\) which is converted to the number of electrons passes through the electrode per second.\(^5\) The total charge consumed during bulk electrolysis at particular time consumption is taken from **Fig. S4**. The number of electrons could be converted to number of hydrogen per second dividing it by 2, as each molecule of hydrogen generation involves \(2e^-\). Using these results, the TON has been determined to be \(1.13 \times 10^4\) and TOF is \(2.83 \text{ s}^{-1}\) at 480 mV overpotential.

![Image](image_url)

**Fig. S5**: Plot of difference between cathodic and anodic current against scan rate.
Fig. S6: Consumption of charge at particular time interval during bulk electrolysis.

Tafel plot at lower over potential:

Fig. S7: Tafel plot of MoS$_x$ quantum dots in pH 7 at lower over potential region.
**LSV experiment on bare ITO plate:**

![Graph showing LSV experiment over bare ITO coated PET plate at pH7.](image)

**Fig. S8:** LSV experiment over bare ITO coated PET plate at pH7.

**Faradaic Efficiency calculation:**

No of moles of H$_2$ produced during bulk electrolysis = $8 \times 10^{-4}$

Charge consumed = 22.18 C

F. E (%) = \[
\frac{100 \times \text{H}_2 \text{ produced (mol)} \times 2 \times 96500}{\text{Charge consumed (C)}}
\]

= \sim 70\%
Study of amorphous MoS$_x$ quantum dots film after HER experiment:

*Morphological study:*

Fig. S9: SEM images of MoS$_x$ quantum dots (a) before and after HER experiment.

*Structural study:*

Fig. S10: XPS profile of S 2p in MoS$_x$ quantum dots (a) before and (b) after HER.
Electrochemical measurements with amorphous MoS$_x$ quantum dots on Cu foil:

We have also carried out electrochemical measurements with MoS$_x$ quantum dots on Cu foil. It shows similar HER activity compared to ITO coated PET substrate. It also shows 65 mV onsets potential during HER at pH 7.

![Polarization curve of amorphous MoS$_x$ quantum dots on Cu foil substrate.](image)

**Fig. S11:** Polarization curve of amorphous MoS$_x$ quantum dots on Cu foil substrate.

Nyquist plots of amorphous MoS$_x$ quantum dots on Cu foil substrate:

To decrease the $R_{ct}$ value of the material, we have drop casted this material on Cu foil as it is more conducting substrate. The nature of plot is quite similar compared to our previous results with ITO coated PET substrate as shown in **Fig. S5**. Here, the material shows low charge transfer resistance ($R_{ct}$) of 283 $\Omega$ at 70 mV overpotential. With increasing bias it drastically decreases to 30 $\Omega$ at 570 mV overpotential. As the Cu foil is more conducting than PET substrate, electron transfer rate during the HER is quite fast compared to PET, resulting such low $R_{ct}$ value. But the major drawback for this substrate is its non-flexibility to use. In recent times, as most of the people are trying to design some flexible electrodes for HER process, it is quite challenging to
use Cu foil as substrate. To avoid this, we have used ITO coated PET substrate as an electrode in spite of its slightly higher $R_{ct}$ value (604 $\Omega$) during HER.

**Fig. S12:** Nyquist plot of MoS$_x$ quantum dots on Cu foil substrate.

Characterization of amorphous MoS$_x$ nanoparticles with larger particle size:

*XRD study:*

**Fig. S13:** XRD patterns of amorphous MoS$_x$ nanoparticles.
**XPS study:**

![XPS spectra of S 2p of amorphous MoS\textsubscript{x} nanoparticles.](image1)

**Fig. S14:** XPS spectra of S 2p of amorphous MoS\textsubscript{x} nanoparticles.

**Raman study:**

![Raman spectra of amorphous MoS\textsubscript{x} nanoparticles.](image2)

**Fig. S15:** Raman spectra of amorphous MoS\textsubscript{x} nanoparticles.
Stability curve of MoS$_x$ nano particle during bulk electrolysis:

![Graph showing stability curve]

**Fig. S16:** Durability test of MoS$_x$ nano particles during bulk electrolysis at pH 7.

**References:**


