COMMUNICATION

Hydrogen evolution across nano-Schottky junctions at carbon supported MoS$_2$ catalysts in biphasic liquid systems†

Peiyu Ge,$^a$ Michéal D. Scanlon,$^a$ Pekka Peljo,$^b$ Xiaojun Bian,$^c$ Heron Vubrel,$^d$
Arlene O'Neill,$^e$ Jonathan N. Coleman,$^e$ Marco Cantoni,$^f$ Xile Hu,$^b$ Kyösti Kontturi,$^b$
BaoHong Liu$^a$ and Hubert H. Girault*$^{a,d}$

Received 24th February 2012, Accepted 11th May 2012
DOI: 10.1039/c2cc31398g

The activities of a series of MoS$_2$-based hydrogen evolution catalysts were studied by biphasic reactions monitored by UV/Vis spectroscopy. Carbon supported MoS$_2$ catalysts performed best due to an abundance of catalytic edge sites and strong electronic coupling of catalyst to support.

Molybdenum disulphide (MoS$_2$) has been rigorously characterized by experimental and computational means as an alternative electrocatalyst to Pt-group metals towards the Hydrogen Evolution Reaction (HER, i.e. $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$). MoS$_2$ reduces protons at low overpotentials via under co-ordinated sulphur edge sites, while its basal planes remain catalytically inert.$^1$ The primary factors that influence electrocatalytic activity are catalyst morphology and electrical conductivity. Nanocrystalline MoS$_2$ is much more active than catalytically inert bulk MoS$_2$ due to the exposure of more reactive sulphur edge sites.$^1$ In turn, exfoliated MoS$_2$, i.e. two-dimensional MoS$_2$ nanosheets,$^2$ should also show enhanced catalytic activity due to a further increase in these sites. Recently, the syntheses of MoS$_2$ on reduced graphene oxide and MoS$_2$ on mesoporous carbon have been achieved by the groups of Dai$^3$ and Liu,$^4$ respectively. Strong chemical coupling and interactions between Mo precursors and functional groups on graphene oxide or mesoporous carbon allowed the nucleation and selective growth of highly disperse MoS$_2$ nanoparticles (NPs), free of aggregation, on both substrates.

However, in the absence of either substrate, identical experimental procedures to the original syntheses produced much larger coalesced MoS$_2$ particles. The lower overpotentials for the HER, for both electrocatalysts, were attributed to the intimate interconnections between the conductive substrates and MoS$_2$ NPs. This interaction allowed the formation of smaller and more disperse MoS$_2$ NPs, thereby unleashing an abundance of accessible catalytic edge sites, and ensuring a robust electrical coupling of MoS$_2$ to the underlying carbon supports with rapid electron transfer from the less-conducting MoS$_2$ NPs to the electrode.$^{3,4}$

The interface between two immiscible electrolyte solutions (ITIES) represents a soft platform to develop new water splitting, i.e. artificial photosynthetic, protocols.$^5$ Protons can be reduced at these defect free soft electrified interfaces to produce $\text{H}_2$ in the presence of organic reducing agents such as cobaltocene$^6$ or decamethylferrocene (DMFc)$^5,7$ in the organic phase. Previously, we have catalyzed this process by the $\text{in situ}$ reduction of metallic salts, forming adsorbed metallic NPs of Pt or Pd,$^7c$ or by adsorbing MoS$_2$ particles at the ITIES.$^{7d}$

Herein, the relative abilities of nanocrystalline MoS$_2$, exfoliated MoS$_2$, and MoS$_2$ NPs grown on either graphene or mesoporous carbon particles were investigated as hydrogen evolution catalysts (HECs) at the ITIES (for synthesis and characterisation details of each catalyst see Section S1, ESI†). The lipophilic tetraakis (pentafluorophenyl)borate anion (TB$^-$) in the aqueous phase (w) acts both as a proton pump, leading to the extraction of HTB acid to the organic phase (o), 1,2-dichloroethane (1,2-DCE), and as a potential determining ion to polarise the liquid–liquid interface.$^5$

$$\text{H}^+ + \text{TB}^- \rightarrow \text{HTB}^0 \quad (1)$$

The reaction between DMFc and aqueous protons catalyzed by MoS$_2$-based particles can be written as a proton transfer reaction followed by its reduction in the organic phase$^{5,6,d}$

$$\text{DMFc}^0 + \text{H}^+ + \text{HTB}^0 \rightarrow \text{DMFc}^{+0} + \frac{1}{2}\text{H}_2 \quad (2)$$

or as an interfacial reaction

$$\text{DMFc}^0 + \text{H}^+ + \text{HTB}^0 \rightarrow \text{DMFc}^{+0} + \frac{1}{2}\text{H}_2 \quad (3)$$

The concentrations of DMFc$^+$ formed during biphasic reactions in the presence and absence of different MoS$_2$-based
MoS2-based particles to act as HECs were further corroborated by monitoring changes in the UV/Vis absorbance ($S_{max} = 779$ nm) for DMFc$^+$. Fits (dotted lines) were obtained from the calculated rate constants ($k$/$s^{-1}$, see Table 1). On the left, a photograph of the two-phase reaction after 30 minutes stirring in an UV/Vis quartz cuvette sealed with a Teflon cap. The clear aqueous phase contains 10 mM LiTB and 100 mM HCl with 0.25 mM of MoS2 particles visible at the interface; the green 1,2-DCE phase contains 2.5 mM DMFc$^+$ post reaction.

Catalysts (0.25 mM) were monitored by observing changes of the UV/Vis absorbance at 779 nm (Fig. 1, for experimental details see Section S2, ESI†). The maximum stoichiometric amount of DMFc$^+$ (2.5 mM) limited by the initial DMFc concentration (2.5 mM) was attained after 1800 s in the presence of each catalyst. Slower kinetics in the absence of catalyst preclude the reaction from proceeding to completion during this time-frame. The reaction was found to be 1st order with respect to DMFc (Fig. S2, ESI†). The rate constants (Table 1) were calculated by fitting (Section S2, ESI†).

MoS2 on mesoporous carbon particles were found to be the best catalyst for H2 evolution, increasing the rate of reaction by a factor of 170. MoS2 on graphene particles showed a 40 times increase in reaction rate, and exfoliated MoS2 was slightly more effective compared to nanocrystalline MoS2. These trends in the relative performances of each of the MoS2-based particles act as HECs were further corroborated by cyclic voltammetry (CV) studies at a potentiostatically polarised ITIES. For experimental details and a thorough discussion of the ion-transfer events refer to Section S3 (ESI†).

An increased abundance of exposed negatively charged sulphur edge atoms, as discussed, is expected on moving from nanocrystalline to exfoliated MoS2 and on modifying the surfaces of graphene and mesoporous carbon particles with disperse islands of MoS2. Directly measuring the surface charge of a particle for real systems is not possible. Instead, the zeta (ζ)-potential, $i.e.$ the electrostatic potential difference between an average point at the hydrodynamic shear plane and the bulk liquid, may be probed and represents a measure of the surface charge.8 Herein, the ζ-potential represents a useful qualitative probe to verify the relative abundances of sulphur edge sites for each electrocatalyst. The ζ-potential of each of the MoS2-based catalysts was analysed using a Nano ZS Zetasizer (Malvern Instruments, U.K.) with irradiation ($\lambda = 633$ nm) from a He–Ne laser (Fig. 2, for experimental details and additional discussion see Section S4, ESI†). Substantial negative surface charges at pHs < 7 and shifts of the isoelectric points (pI$s$) below pH 2 were observed, on moving from nanocrystalline (pI $\approx 3.1$)8 to exfoliated MoS2 and on modifying the surfaces of graphene and mesoporous carbon particles with disperse islands of MoS2 (for ζ-potentials of the control materials, see Fig. S5, ESI†). More negative ζ-potentials over the pH range 2.5 to 11 for MoS2 NPs grown on mesoporous carbon rather than on graphene particles infer the presence of more MoS2 sulphur edge sites on mesoporous carbon, correlating with its superior rate of reaction as seen in Fig. 1.

A reaction scheme outlining the biphasic mechanism of proton reduction by DMFc in 1,2-DCE under anaerobic conditions, with carbon supported MoS2 catalysts present either at the interface or in the bulk, is illustrated in Scheme 1 (see Section S5 (ESI†) for band calculations, redox potentials, etc.). An interfacial Galvani potential difference ($\Delta V_{G}$) is established due to the distribution of the lipophilic anion, TB$^-$. Consequently, protons are pumped across the interface and, in the presence of an MoS2 species, are adsorbed at catalytic sulphur edge sites (denoted here as #). When the semiconductor MoS2 is in contact with graphene (or, indeed, mesoporous carbon) an insulated nano-Schottky junction is formed, as highlighted in Scheme 1. For MoS2 on graphene particles, electrons are transferred from graphene to the semiconductor until the Fermi levels are equalised. On transfer of

Table 1 Calculated apparent rate constants ($k$/s$^{-1}$) for the biphasic reaction, and the rate constant relative to the experiment without any catalyst ($k/k_{no\,catalyst}$)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$k$/s$^{-1}$</th>
<th>$k/k_{no,catalyst}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No catalyst</td>
<td>0.00021</td>
<td>1</td>
</tr>
<tr>
<td>Nanocrystalline MoS2</td>
<td>0.0030</td>
<td>14</td>
</tr>
<tr>
<td>Exfoliated MoS2</td>
<td>0.0039</td>
<td>19</td>
</tr>
<tr>
<td>MoS2 on graphene</td>
<td>0.0080</td>
<td>38</td>
</tr>
<tr>
<td>MoS2 on mesoporous carbon</td>
<td>0.036</td>
<td>171</td>
</tr>
</tbody>
</table>

Fig. 1 Kinetics of the hydrogen evolution reaction (HER), in the absence and presence of each of the MoS2-based catalysts, as followed by monitoring changes in the UV/Vis absorbance ($S_{max} = 779$ nm) for DMFc$^+$. Fits (dotted lines) were obtained from the calculated rate constants ($k$/s$^{-1}$, see Table 1). On the left, a photograph of the two-phase reaction after 30 minutes stirring in an UV/Vis quartz cuvette sealed with a Teflon cap. The clear aqueous phase contains 10 mM LiTB and 100 mM HCl with 0.25 mM of MoS2 particles visible at the interface; the green 1,2-DCE phase contains 2.5 mM DMFc$^+$ post reaction.

Fig. 2 Zeta (ζ)-potentials (mV) of nanocrystalline MoS2, exfoliated MoS2, MoS2 on graphene and MoS2 on mesoporous carbon as a function of pH in aqueous dispersions at concentrations of 0.7-1 mg per 5 ml.
an electron from graphene to MoS\(_2\), the Fermi level of graphene is lowered. Inversely, since MoS\(_2\) becomes negatively charged, the Fermi level moves up. Band bending occurs as a result of the excess negative charge transferring from graphene to MoS\(_2\). DMFc is insoluble in the aqueous phase and electron injection can be considered to take place exclusively in 1,2-DCE. Electrons are injected from DMFc to a state in graphene close to the Fermi level. The aqueous and organic phases are coloured blue and red, respectively.

as many multilayers clumped together as particles and not as individual single-layer flakes. The conductive carbon supports increase the HER rate in multiple ways. Firstly, these supports act as nucleation sites for the formation of small and highly dispersed MoS\(_2\) NPs, thus massively increasing the abundance of catalytic edge sites in comparison to nanocrystalline MoS\(_2\) freely grown in solution.\(^{7,4}\) Secondly, their conductive nature allow electron injection from DMFc to occur at any point on the hybrid catalyst, i.e. not specifically at the MoS\(_2\) edge sites, increasing the cross-section of reaction between DMFc and the catalyst and hence also the reaction rate. The sizable increase in rate for MoS\(_2\) on mesoporous carbon particles over its graphene analogue suggests that the very large specific surface area of mesoporous carbon allows huge loadings of small, highly dispersed MoS\(_2\) NPs (hence more catalytic edge sites) than possible on the surface of comparatively flat graphene.

In conclusion, MoS\(_2\) NPs nucleated and grown on carbon supports, in particular mesoporous carbon, act as superior electrocatalysts towards the HER. Their catalysis of the biphasic reduction of protons at the liquid–liquid interface offers new opportunities in energy research towards the development of artificial photosynthetic systems.

This work was financially supported by the SNF program “Solar fuels”. The work in LSCI is supported by an ERC starting grant under the European Community’s 7th Framework Programme (FP7 2007-2013) ERC Grant agreement no. 257096. P.P. and K.K. acknowledge financial support from the Academy of Finland (Grant No. 133261).

Notes and references

Scheme 1  Biphasic mechanism of proton reduction to molecular hydrogen in the presence of MoS\(_2\) on graphene catalyst. \(\Delta \phi\) is the interfacial Galvani potential difference established by distribution of the lipophilic anion, TB\(^-\). VB and CB are the valence and conduction bands of MoS\(_2\), respectively, \(E_f\) is the Fermi level of MoS\(_2\) and \(\phi\) is the work function of graphene. The aqueous and organic phases are coloured blue and red, respectively.