Covalently functionalized layered MoS\textsubscript{2} supported Pd nanoparticles as highly active oxygen reduction electrocatalyst

Dimitrios K. Perivoliotis\textsuperscript{a,b}, Yuta Sato\textsuperscript{b}, Kazu Suenaga\textsuperscript{a} and Nikos Tagmatarchis\textsuperscript{a,\ast}

Molybdenum disulfide nanosheets covalently modified with a 1,2-dithiolane derivative were used as novel substrate for the immobilization of Pd nanoparticles (Pd\textsubscript{nm}/f-MoS\textsubscript{2}) towards the development of highly efficient hybrid electrocatalyst, namely Pd\textsubscript{nm}/f-MoS\textsubscript{2}, for the oxygen reduction in alkaline medium. The newly prepared hybrid material was thoroughly characterized through complementary techniques such as Raman and IR spectroscopy, TGA as well as HRTEM, STEM/EELS, and EDS. The Pd\textsubscript{nm}/f-MoS\textsubscript{2} nanohybrid exhibited excellent performance towards oxygen electroreduction with a positive onset potential of +0.066 V and half-wave potential of −0.116 V vs Hg/HgO, along with high current response, which are superior to those of its graphene counterpart and comparable to those of the benchmark Pd/C product. Moreover, Pd\textsubscript{nm}/f-MoS\textsubscript{2} was proved to be remarkably stable as chronoamperometric assays showed the minimum activity loss among the tested materials, clearly outperforming the commercial catalyst. The excellent performance of Pd\textsubscript{nm}/f-MoS\textsubscript{2} is attributable to (i) the high affinity of the catalytic Pd\textsubscript{nm} with the f-MoS\textsubscript{2} substrate, (ii) the absence of any capping agent for the stabilization of the Pd\textsubscript{nm} onto f-MoS\textsubscript{2}, and more importantly (iii) to the preservation of the integrity of the MoS\textsubscript{2} basal plane during the functionalization process. Last, the oxygen reduction on Pd\textsubscript{nm}/f-MoS\textsubscript{2} proceeded through the energy efficient four-electron pathway, showing great potential for the use of layered transition metal dichalcogenides in energy conversion applications, comprising fuel cells.

**Introduction**

Tailoring electrocatalysts to accelerate the sluggish kinetics of the oxygen reduction reaction (ORR) still remains a key challenge towards the commercialization of the fuel cell technology.\textsuperscript{1} In this regard, supported catalysts for the ORR have drawn much attention, since they offer not only enhanced electrocatalytic activities, but more importantly, improved durability. Notably, the efficient interactions between nanoparticle catalyst and support could modify the electronic structure of the catalyst, facilitating the oxygen adsorption and dissolution, while, at the same time, prevent nanoparticles from aggregation, contributing to long term stability.\textsuperscript{2}

Graphene, a two-dimensional (2D) sp\textsuperscript{2} hybridized carbon allotrope has been widely used as supporting material, owed to its high surface area and electrical conductivity as well as good chemical stability.\textsuperscript{3} Beyond graphene, layered transition metal dichalcogenides, abbreviated as TMDs, consist another class of 2D materials that combine the exceptional properties of graphene with remarkable intrinsic electrocatalytic activities toward key electrochemical reactions, originating from the large number of exposed prismatic edges.\textsuperscript{4,5} Actually, TMDs are atomically thick nanocrystals with MX\textsubscript{2} stoichiometry, where M refers to a transition metal atom (e.g. Mo, W, Ta) and X to a chalcogen atom (S, Se, Te).\textsuperscript{6} Among various TMDs, molybdenum disulfide (MoS\textsubscript{2}) nanosheets have received special scientific attention as it is readily accessible and chemically stable.\textsuperscript{7} Liquid phase exfoliation from the bulk material is the most effective way to obtain high quality layered MoS\textsubscript{2} on a large scale.\textsuperscript{8-11} Similar to other TMDs, MoS\textsubscript{2} is characterized by a thickness dependent semiconducting behavior and an indirect-to-direct bandgap transition occurs when its thickness decreases to a single layer.\textsuperscript{12} Moreover, MoS\textsubscript{2} monolayer presents a much lower bandgap (∼1.2 eV) than typical semiconducting materials (>3 eV)\textsuperscript{13}, while its electronic structure is closely related to the coordination of the Mo atoms. All in all, these fascinating properties offer to layered MoS\textsubscript{2} a clear advantage over graphene, rendering it attractive component for potential use in energy conversion (electrocatalysis\textsuperscript{14} and (photo)-electrocatalysis\textsuperscript{15}) and storage\textsuperscript{16-19} applications.

Likewise to graphene, in order to fully exploit the intriguing properties of layered TMDs, their chemical functionalization is an absolute necessity.\textsuperscript{20} Needless to mention, introduction of functional groups on their surface could not only solve the problem of their limited solubility in common solvents and restacking of nanosheets, but also allows the design of entirely new hybrid materials. Markedly, the covalent attachment of the appropriate organic moieties on MoS\textsubscript{2} sheets surface render them ideal platforms for the immobilization of various catalytic nanoparticles by effectively tuning the interfacial interactions and hence leading to hybrids with increased electrocatalytic activity and excellent durability. Up to date, diverse methodologies have been developed towards the covalent functionalization of layered MoS\textsubscript{2}\textsuperscript{21}, comprising the reaction with electrophiles e.g. organoiodides and aryl diazonium salts\textsuperscript{22} and organic thiols\textsuperscript{23}. In the latter case, a Mo-S bond is formed between an unsaturated molybdenum atom in the MoS\textsubscript{2} and a sulfur atom in the organic functional group. Interestingly, unsaturated Mo atoms are dominant at the edges of the MoS\textsubscript{2} nanosheets, where structural defects (S-vacancies) have been naturally introduced during the exfoliation process.\textsuperscript{8} Therefore, the MoS\textsubscript{2} basal plane remains intact and hence its exceptional properties, which are essential when considering the design of highly performance electrocatalysts, are preserved. However, a
major drawback of this approach is related to the possible conversion of thiols into the corresponding disulfides—a reaction that activated by the presence of MoS₂. Based on that, an alternative route employing 1,2-dithiolanes as robust thiol groups to react with exfoliated MoS₂ sheets has been recently developed.

Regardless of the huge potential of MoS₂ as catalyst substrate, only few reports have been published employing MoS₂ sheets as supporting material for metal-based catalytic nanomaterials towards ORR. Actually, the main bottlenecks that keep MoS₂ behind the scenes are related to their low conductivity and the poor dispersity and the homogeneity of the resulting hybrids. Therefore, developing efficient synergistic interactions between MoS₂ sheets and noble metal nanoparticles is essential to overcome these limitations. To this end, diverse methodologies e.g. epitaxial growth, physical mixing, sonochemical approach, have been involved for the preparation of such hybrid materials aiming at the optimization of the ORR performance of the supported catalysts. Despite of the advancements that have been made in the field, the ORR performance of the reported hybrids still needs improvement to compete the benchmark catalysts. In the same context, the surface functionalization of MoS₂ sheets could tune the intra-hybrid interactions, and hence significantly boost the performance of the hybrid electrocatalysts. However, to the best of our knowledge, the use of modified layered MoS₂ as ORR catalyst substrate has not been reported yet.

The present work goes beyond the current state-of-the-art by employing covalent functionalized MoS₂ nanosheets with a 1,2-dithiolane derivative (f-MoS₂), featuring free amino groups, as substrate for immobilization of Pd nanoparticles (PdNPs). The obtained hybrid, abbreviated as PdNPs/f-MoS₂, was examined as electrocatalyst for the ORR in alkaline conditions and its performance was further compared with that of its counterpart based on functionalized graphene (f-G), abbreviated as PdNPs/f-G. The results clearly demonstrated an overall improved performance of PdNPs/f-MoS₂ over that of PdNPs/f-G, highlighting the benefits of using the TMD-based substrate. The exceptional ORR activity and stability of PdNPs/f-MoS₂ was ascribed to (i) the high affinity of the PdNPs with the f-MoS₂ substrate, (ii) the absence of any capping agent for the stabilization of PdNPs onto f-MoS₂ and more importantly (iii) to the preservation of the integrity of the MoS₂ basal plane during the functionalization process. Markedly, the latter explains to rage extent why PdNPs/f-MoS₂ outperforms the graphene-based PdNPs/f-G electrocatalyst as in that case the covalent functionalization induces damage to the graphene lattice leading to the deterioration of its inherent properties. General speaking, the latter consists the main obstacle in using covalently functionalized graphene as component in electrocatalytic applications and thus the current research on graphene-based electrocatalysts has been focused on the non-covalently modified as well as the doped graphene. This work proposes the use of covalently edge-functionalized MoS₂ nanosheets as platforms for the fabrication of the next generation of hybrid electrocatalysts, paving the way for their further use in real energy conversion applications.

Results and discussion

Preparation. The preparation of PdNPs/f-MoS₂ and PdNPs/f-G hybrids is illustrated in Scheme 1. First, MoS₂ and graphene sheets were covalently functionalized with organic moieties bearing free amino groups to enable the attachment of the PdNPs on their surface. As for MoS₂, exfoliated MoS₂ nanosheets (exf-MoS₂) were obtained upon chlorosulfonic acid treatment of the bulk material and modified with the 1,2-dithiolane N-tert-butoxycarbonyl (BOC) derivative. Notably, the latter reaction is based on the high binding affinity of 1,2-dithiolane component for the Mo atoms that located at the edges of MoS₂, where sulfur vacancy sites were introduced during the exfoliation process. On the other hand, graphite was oxidized to graphene oxide (GO) and the GO functionalization was realized upon (i) activation of the carboxylic acid groups by acyl chloride followed by the condensation reaction with BOC-2,2’-(ethylenedioxy)bis-ethylamine and (ii) the ring-opening reaction of the epoxy groups present on the graphene lattice by the nucleophilic attack of the BOC-2,2’-(ethylenedioxy)bis-ethylamine, yielding covalently functionalized graphene sheets at both edges and basal plane simultaneously. Importantly, in both MoS₂ and graphene modified nanosheets, the attached amine species were masked with the BOC-protecting group, which was effectively cleaved after acidic treatment, yielding the amino functionalized MoS₂ and graphene materials, respectively (Scheme 1). Afterwards, a modified polyol method was employed for the in-situ synthesis and immobilization of PdNPs onto f-MoS₂ and f-G substrates towards the realization of PdNPs/f-MoS₂ and PdNPs/f-G hybrids. At this point, it is worth noting that the free amino groups serve as anchoring sites for metal-ion nucleation and subsequent nanoparticle growth, stabilizing effectively the in-situ formed nanoparticles without using any additional capping agent, which significantly impair their electrocatalytic activity.
Scheme 1. Illustrative scheme for the preparation protocol of (A) PdNPs/f-MoS$_2$ and (B) PdNPs/f-G hybrids.
Characterization. Direct proof for the formation of f-MoS$_2$ was given by complementary characterization tools. In this context, the ATR-IR spectrum of the BOC-modified MoS$_2$ is governed by bands in the 2840–2960 cm$^{-1}$ range owing to the alkyl chain C-H vibration modes, while two discrete bands at 1645 and 1707 cm$^{-1}$ attributed to carbonyl amide and BOC units, respectively, are also present (Figure 1, panel A). Interestingly, the band of the latter is absent in the ATR-IR spectrum of f-MoS$_2$, indicating the successful BOC deprotection process. Moreover, a band at 3225 cm$^{-1}$ owed to the N-H stretch can be observed at the ATR-IR spectrum of f-MoS$_2$, further proving the presence of the free amine group on the MoS$_2$ surface. Next, Raman analysis of f-MoS$_2$ and exf-MoS$_2$ sheets further confirmed the accomplishment of MoS$_2$ covalent functionalization (Figure 1, panel B). Upon excitation at 633 nm, which produces resonance Raman enhancement of the first and second order vibrational modes, both exf-MoS$_2$ and f-MoS$_2$ Raman spectra clearly revealed four dominant Raman bands, namely, A$_{1g}$, E$_{2g}$, A$_{1g}$ and 2LA(M) at 177, 378, 405 and 450 cm$^{-1}$, respectively. The E$_{2g}$ and A$_{1g}$ modes derive from the in-plane and out-of-plane vibrations within the S-Mo-S layer, while the 2LA(M) vibration mode is closely related to the S vacancies. Therefore, the intensity ratio of 2LA(M) to A$_{1g}$ is commonly used as an indicator to quantify the functionalization degree in layered MoS$_2$ materials. Here, the 2LA(M)/A$_{1g}$ value was found decreased for the f-MoS$_2$, implying to the elimination of S vacancies due to the functionalization process. The latter observation was further confirmed through complementary Raman mapping assays, revealing an average intensity ratio 2LA(M)/A$_{1g}$ of 0.75 for the f-MoS$_2$ versus 1.35 for the exfoliated MoS$_2$ sheets, as presented in panels C and D of Figure 1. Please note, that we have performed various mappings in both exf-MoS$_2$ and f-MoS$_2$ materials (5 mappings with 121 acquisition points each) and we here present a representative one close to the total average. It is worth also mentioning that no significant changes on the f-MoS$_2$ Raman spectrum are observed after the immobilization of the Pd$_{n_{\text{NPs}}}$, suggesting that no structural alterations occurred during the synthesis of the hybrid material (Figure S1). Last, the functionalization degree was quantified by the means of thermogravimetric analysis (TGA). Given that exf-MoS$_2$ sheets are thermally stable up to 900$^\circ$C, the weight loss (around 6%) observed in the temperature range 200-500$^\circ$C for the f-MoS$_2$ (Figure 1, panel E) is ascribed to the thermal decomposition of the covalently grafted organic functionalities onto f-MoS$_2$. Based on these data, the loading of the organic material was calculated to be 186 $\mu$mol/g.

Concerning f-G, ATR-IR assays provided spectroscopic proof for the success of the functionalization (Figure S2, panel A). In short, although the IR spectrum of GO is governed by bands centered at 1720 cm$^{-1}$ (carbonyl C=O), the BOC-functionalized graphene material manifests a different and broad band at 1708 cm$^{-1}$ due to the BOC protecting groups and the carbonyl amide formed. Moreover, strong vibration bands are recorded in the region 2840–2960 cm$^{-1}$ (C-H stretching and bending) and 3225 cm$^{-1}$ (N-H stretching), further proving the attachment of the organic moiety onto graphene nanosheets. Notably, at the IR spectrum of f-G, in which free amine functionalities are present, the band related to the BOC unit was disappeared, while a pronounced peak at 1655 cm$^{-1}$ derived from the carbonyl amide is present. The epoxy group ring-opening reaction is also confirmed via ATR-IR measurements, as the bands assigned to the C-O-C vibrations (at 1200 – 1250 cm$^{-1}$) that observed at the GO spectrum are absent in both BOC-G and f-G materials. Raman spectroscopy was employed to estimate the disorder degree in f-G (Figure S2, panels B-D) through the evaluation of the relative intensity of the defect activated D-band at around 1350 cm$^{-1}$. Briefly, the D/G intensity ratio for f-G was found to be close to 1.0, witnessing its defective nature. Notably, the presence of sp$^2$ hybridized carbon atoms is mainly related to the introduction of the oxygen containing groups (the D/G intensity ratio for GO is around to 0.90) which are essential for the further graphene functionalization. It was also demonstrated (Figure S3) that the in-situ synthesis and immobilization of Pd$_{n_{\text{NPs}}}$ was not affected the graphene structure. Last, the loading of the organic functionalities was determined through TGA (Figure S2, panel E) and it was found to be 840 $\mu$mol/g, being considerably higher than that registered for the f-MoS$_2$ material, as
The surface morphology of Pd$_{NPs}$/f-MoS$_2$ and Pd$_{NPs}$/f-G hybrids was thoroughly investigated via high-resolution and annular dark-field scanning transmission electron microscopy (HRTEM and ADF-STEM, respectively) whereas their elemental composition was probed by energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS) chemical mapping. HRTEM images of Pd$_{NPs}$/f-MoS$_2$ and Pd$_{NPs}$/f-G ensembles (Figure 2, panels A and D) revealed a uniform distribution of Pd$_{NPs}$ onto f-MoS$_2$ and f-G, respectively, as only few agglomerations are observed. Actually, the free amino groups possess high affinity with Pd$_{NPs}$, stabilizing them effectively on f-MoS$_2$ and f-G substrates.\textsuperscript{34} Interestingly, focusing on the Pd$_{NPs}$/f-MoS$_2$ HRTEM image, the presence of a few overlapping MoS$_2$ monolayers is observed while the Pd$_{NPs}$ are mainly located at the edges, contrasting the case of Pd$_{NPs}$/f-G hybrid in which the Pd$_{NPs}$ can be found on the entire f-G surface. This finding is in good agreement with the hypothesis that the covalent modification of MoS$_2$ sheets with 1,2-dithiolane derivatives takes place only at their edges. Next, higher magnification ADF-STEM images revealed that the average size of the Pd$_{NPs}$ is 2-3 nm for both hybrid materials (Figure 2, panels B and E), while at the same time EDS and EELS elemental analysis (Figure 2, panels C and F) confirmed the existence of Mo, S and Pd for the Pd$_{NPs}$/f-MoS$_2$ as well as the presence of C and Pd for the Pd$_{NPs}$/f-G hybrid.

Electrocatalytic performance toward ORR. To explore the ORR performance of Pd$_{NPs}$/f-MoS$_2$ and Pd$_{NPs}$/f-G electrocatalysts, linear sweep voltammetry (LSV) measurements on rotating ring–disk electrode (RRDE) were carried out in O$_2$-saturated 0.1 M KOH electrolyte at a rotation rate of 1600 rpm. As control, the performance towards ORR of the benchmark Pd/C catalyst was also recorded. As can be seen in Figure 3, the Pd$_{NPs}$/f-MoS$_2$ hybrid presented by far improved ORR activity, clearly outperforming its counterpart based on graphene. Indeed, the ORR onset and half-wave potential values of Pd$_{NPs}$/f-MoS$_2$ were determined to be +66 and -116 mV (vs Hg/HgO), respectively, being more positive by 50 mV when compared with those recorded for the Pd$_{NPs}$/f-G hybrid. In addition, the diffusion-limited current density ($i$) for Pd$_{NPs}$/f-MoS$_2$ reached at 5.70 mA cm$^{-2}$, whereas its kinetic current density ($j$) was found to be 2.65 mA cm$^{-2}$ at -60 mV (vs Hg/HgO). Notably, these values are 46% and 4.5 times higher over those of Pd$_{NPs}$/f-G. Next, the ORR activity of Pd$_{NPs}$/f-MoS$_2$ was further compared with that of the state-of-the-art catalyst, displaying analogous or enhanced performance, especially in terms of onset potential and kinetic current density. Needless to mention, Pd$_{NPs}$/f-MoS$_2$ manifested a more positive onset potential by 53 mV along with a 32.5% greater kinetic current density value at -60 mV (vs Hg/HgO).

Overall, the ORR performance of the tested catalysts was in the order of Pd$_{NPs}$/f-MoS$_2$ > Pd/C > Pd$_{NPs}$/f-G. Interestingly, a consistent result was also obtained through durability experiments, in which chronoamperometric assays of Pd$_{NPs}$/f-MoS$_2$, Pd$_{NPs}$/f-G as well as Pd/C were performed at a constant applied potential of -0.45 V (vs Hg/HgO) for 10,000 s and rotation speed of 1600 rpm. As shown in panel B of Figure 3, the current response of Pd$_{NPs}$/f-MoS$_2$ retained 86% of its initial value, whereas an activity loss of 31.8 and 29.7 was recorded for Pd$_{NPs}$/f-G and Pd/C, respectively. Next, the LSV profiles for all tested materials after 10,000 s of chronoamperometric assays were recorded in O$_2$-saturated 0.1 M KOH electrolyte at a rotation rate of 1600 rpm (panel A of Figure 3). The results clearly demonstrate that the Pd$_{NPs}$/f-MoS$_2$ electrocatalyst is remarkably stable, being in total agreement with the chronoamperometric experiments. Needless to say, after 10,000 s, Pd$_{NPs}$/f-MoS$_2$ presented less than 10% decrease in its initial diffusion-limited and kinetic current density values, while its half-wave potential value remained almost unchanged. On the other hand, the Pd$_{NPs}$/f-G material experienced a significant loss of its initial performance (23 and 40 % decrease in diffusion-limited and kinetic current density values, respectively, as well as 26 mV negative shift in half-wave potential value). Last but not least, after 10,000 s, the MoS$_2$ based electrocatalyst continues to outperform the commercial Pd/C catalyst by manifesting almost 1.5 and 3.5 times greater diffusion-limited and kinetic current density values, respectively. Interestingly, the observed activity loss after the chronoamperometric assays is mainly attributable to the reduction of the electrochemical active surface area (EASA) of each hybrid electrocatalyst owing to the possible agglomeration of the metal nanoparticles during the chronoamperometric experiment. Given the fact that the EASA is closely related to capacitance\textsuperscript{42-44}, the capacitance values for Pd$_{NPs}$/f-MoS$_2$ and Pd$_{NPs}$/f-G hybrids as well as the Pd/C were calculated by integrating the graph-area derived by cyclic voltammograms obtained at the “double layer region”, according Equation 6, before and after the chronoamperometric assays.\textsuperscript{42} Particularly, it was found that the capacitance value of Pd$_{NPs}$/f-MoS$_2$ decreased only by 13.8 % while the same value for the Pd$_{NPs}$/f-G and Pd/C was 43 and 31.5 %, respectively (Figure S4). Based on these data, the superior...
stability of PdNPs/f-MoS\textsubscript{2} is well justified, as it presents the minimum EASA loss, implying the minimum agglomeration.

To elucidate the reaction kinetics, hydrodynamic voltammetry experiments were conducted by altering the electrode’s rotation speed. The related ORR polarization curves for Pd\textsubscript{np}/f-MoS\subscript{2} and Pd\textsubscript{np}/f-G obtained at different rotation rates between 400 and 3600 rpm are presented in panel A of Figure 4 and panel A of Figure S5, respectively, showing the typical increase in current with the increase of the rotation speed due to the shortening of diffusion layer at high speeds. Next, the corresponding Koutecky-Levich (K-L) plots (Figure 4 panel B and Figure S5 panel B) were constructed at different potential based on the inverse of current density (j\textsuperscript{-1}) against the inverse of the square root of the rotation rate (ω\textsuperscript{-1/2}). As can be seen, these plots presented good linearity, implying first order reaction kinetics towards the dissolved O\textsubscript{2} concentration. All measurements were conducted in O\textsubscript{2}-saturated 0.1 M KOH electrolyte, and the corresponding electrocatalysts LSVs were recorded at a scan rate of 5 mV s\textsuperscript{-1}. In all graphs the current densities are normalized to the geometric electrode area.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure3.png}
\caption{(A) LSV ORR polarization curves obtained at a rotation speed of 1600 rpm for Pd\textsubscript{np}/f-MoS\subscript{2} and Pd\textsubscript{np}/f-G before and after 10,000 sec of chronoamperometric assays as compared to that due to Pd/C; (B) ORR chronoamperometric response for all materials at −0.45 V (vs Hg/HgO) for 10,000 s and (C, D) corresponding diffusion limited and kinetic current density values. All measurements were conducted in O\textsubscript{2}-saturated 0.1 M KOH electrolyte, and the corresponding electrocatalysts LSVs were recorded at a scan rate of 5 mV s\textsuperscript{-1}. In all graphs the current densities are normalized to the geometric electrode area.}
\end{figure}

In this regard, the electron transfer number per oxygen molecule (n) was estimated and it was found to be 3.6 – 4.0 and 3.4 – 3.6 for Pd\textsubscript{np}/f-MoS\subscript{2} and Pd\textsubscript{np}/f-G, respectively. Such n value clearly suggests a four electron selectivity for the MoS\textsubscript{2} based ensemble, in which oxygen reduced directly into water. Last, for comparison reasons, the electrocatalytic properties of the f-MoS\textsubscript{2} substrate have been also investigated (Figure S6). Briefly, f-MoS\textsubscript{2} was found to present a substantial intrinsic oxygen reduction activity, mainly proceed ed through the two-electron pathway (n=2.1 – 2.3).

The RRDE approach was applied to further scrutinize the ORR kinetics of Pd\textsubscript{np}/f-MoS\subscript{2} and Pd\textsubscript{np}/f-G hybrids (Figure 4, panel C and Figure S5, panel C, respectively). Markedly, the recorded ring current corresponds to the amount of hydrogen peroxide intermediate produced at the disk electrode during ORR, providing us not only a more accurate way to calculate the n value, but also a reliable method to estimate the percentage (%) of produced H\textsubscript{2}O\textsubscript{2}.\textsuperscript{45} In this regard, the electron transfer
number and the H$_2$O$_2$ yield for Pd$_{NPs}$/f-MoS$_2$ in the potential range from 0.2 to 0.5 V (vs Hg/HgO) was recognized to be 3.6 and 20%, suggesting that the oxygen reduction was mostly proceeded through the four electron transfer route and the main product was the water. In general, the four-electron pathway is considered as more efficient and it is highly preferred in energy conversion applications. On the other hand, in the case of Pd$_{NPs}$/f-G the two-electron and the four-electron pathways coexist as the n and % H$_2$O$_2$ were calculated to be 3.1 and 47%, respectively. Markedly, these results are consistent with those extracted through the K-L method.

Next, to gain insight into the rate-determining step involved in the oxygen electroreduction, the mass transfer corrected Tafel plots for all tested catalysts were constructed. As shown in Figure 5, at the low current density region (region I) the Pd$_{NPs}$/f-MoS$_2$ and Pd$_{NPs}$/f-G hybrids exhibited a slope of -40 and -70 mV dec$^{-1}$, respectively, which are roughly close to that of Pd/C (-46 mV dec$^{-1}$). Actually, a Tafel slope near to -60 mV dec$^{-1}$ in this region is indicative that the reaction rate is governed by the surface oxide coverage (Temkin adsorption mechanism). In the high current density region (region II), a Tafel slope value of -180 mV dec$^{-1}$ was recorded for both Pd$_{NPs}$/f-MoS$_2$ and Pd$_{NPs}$/f-G, whereas the corresponding value for the commercial catalyst was found to be -112 mV dec$^{-1}$. The higher Tafel value in the region II is ascribed to a switch in the oxygen reduction mechanism since at these potentials the significant oxide coverage ceases to exist. In more depth, a slope close to -120 mV dec$^{-1}$ indicates that ORR is limited by the transfer of the first electron to the oxygen molecule (Langmuir adsorption) while for a value around to -200 mV dec$^{-1}$, the adsorption of molecular oxygen has been proposed as the rate-determining step. Therefore, the abovementioned results suggest a different rate-determining step at the region II for the hybrid materials and the benchmark Pd/C catalyst.

| Table 1 | summarizes the electrochemical performance towards ORR for all tested materials. Overall, it can be deduced that the Pd$_{NPs}$ immobilized onto MoS$_2$ sheets covalently functionalized with free amino groups (Pd$_{NPs}$/f-MoS$_2$) manifested improved electrocatalytic activity and stability as |

![Figure 5. Tafel plot for the Pd$_{NPs}$/f-MoS$_2$ and Pd$_{NPs}$/f-G hybrid electrocatalyst as compared to those due to Pd/C. Data derived from Figure 3A.](image-url)
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Improves its ORR activity by providing more active sites on the nanoparticles surface. An overview of the recently developed hybrid ORR electrocatalysts based on Pd nanoparticles and MoS2 nanosheets is provided in Table S1. For instance, Pd nanoparticles were formed and in-situ immobilized on exfoliated MoS2 via a sonochemical method. The obtained Pd/MoS2 hybrid exhibited an onset potential of -100 mV vs SCE along with a diffusion-limited current density of 5.20 mA cm⁻² in alkaline medium. Furthermore, the hybrid electrocatalyst outperformed the commercial one in terms of long-term stability. In a more recent work, a hybrid material based on palladium sulfide (PdS) nanoparticles supported on MoS2/N-doped graphene heterostructure (PdS-MoS2/N-G) has been developed through a two-step thermolysis process while its ORR performance was examined in alkaline conditions. Markedly, the hybrid catalyst demonstrated more positive onset and half-wave potential values (-146 and -214 mV vs SCE, respectively) as well as greater diffusion limited current density (4.1 mA cm⁻²) than that of MoS2/N-G and PdS/N-G references, despite failing to surpass the commercial Pt/C catalyst. Based on these data, the current Pd nanoparticles/f-MoS2 hybrid is ranked among the top TMD-supported ORR electrocatalysts reported in the literature.

Table 1. ORR electrochemical parameters for Pd nanoparticles supported on MoS2 nanosheets (f-MoS2) and Pd nanoparticles/f-G as compared to Pd/C and f-MoS2.

| Catalyst | Onset potential (mV vs Hg/HgO) | Half-wave potential (mV vs Hg/HgO) | Diffusion-limited current density (mA cm⁻²) | Kinetic current density (mA cm⁻²) | Tafel slopes | n_CCL | n_BEC | H₂O₂ yield (%) |
|----------|--------------------------------|-----------------------------------|------------------------------------------|----------------------------------|---------------|-------|-------|----------------|
| Pd nanoparticles/f-MoS2 | +66 | -116 | 5.70 | 2.65 | -40/-180 | 3.6 - 4.0 | 3.6 | 20 |
| Pd nanoparticles/f-MoS2 after | +52 | -120 | 5.20 | 2.40 | - | - | - |
| Pd nanoparticles/f-G | +15 | -168 | 3.90 | 0.58 | -70/-175 | 3.4 - 3.6 | 3.1 | 47 |
| Pd nanoparticles/f-G after | 0 | -194 | 3.00 | 0.35 | - | - | - |
| f-MoS2 | -236 | -360 | 1.47 | 0.00 | - | 2.1 - 2.3 | - |
| Pd/C | +13 | -93 | 5.40 | 2.00 | -46/-112 | 3.8 - 4.0 | 3.8 | <10 |
| Pd/C after | -11 | -135 | 3.70 | 0.69 | - | - | - |

a At 1600 rpm rotation rate (at -0.50 V vs Hg/HgO).

b Calculated at -60 mV vs Hg/HgO by K-L equation.
c After 10,000 sec of chronoamperometric experiment.

d Experimental Section

Materials. All chemicals and solvents were purchased from Aldrich and used without further purification unless otherwise stated.

Preparation of functionalized MoS2 (f-MoS2). First, a chlorosulfonic acid assisted method was applied for the MoS2 exfoliation from the bulk in the form of semiconducting nanosheets. Next, the covalent functionalization of MoS2 sheets was achieved by employing 1,2-dithiolane units bearing an ethylene glycol alkyl chain terminated to a butoxycarbonyl (BOC)-protected amine. In short, exfoliated MoS2 (25 mg) and 1,2-dithiolane derivative (30 mg) were dissolved in N,N-dimethylformamide (15 mL) and the reaction mixture was heated at 70°C under stirring for 3 days. After that period, the mixture was filtered through a PTFE membrane filter (0.2 µm pore size) and the solid residue extensively washed with dichloromethane. To cleave the BOC protecting group, the BOC modified MoS2 nanosheets (20 mg) were redispersed in dichloromethane and treated with gaseous HCl. Finally, the reaction mixture was left under stirring overnight, filtered through a PTFE membrane (0.2 µm pore size), washed with dichloromethane and neutralized with triethylamine to yield the amino functionalized MoS2 sheets (f-MoS2).
Preparation of functionalized graphene (f-G). Graphene oxide (GO) was prepared following a modified Hummers method. Briefly, graphite powder was mixed with concentrated sulfuric acid, sodium nitrate and potassium permanganate to obtain brownish slurry and the mixture was heated at 50°C for 24 h. The suspension was diluted with water and hydrogen peroxide was added to get a higher oxidation degree. GO was finally obtained after washing with distilled water, upon the pH value became neutral. To prepare amino functionalized graphene (f-G), first, GO (20 mg) was activated by treatment with thionyl chloride (7 mL) at 66°C for overnight under inert atmosphere. Next, the excess thionyl chloride was evaporated under reduced pressure and the remaining solid was carefully washed with dry tetrahydrofuran under nitrogen. The as-produced acyl-chlorinated graphene was dispersed in dry tetrahydrofuran (10 mL) followed by the addition of N-tert-butoxy carbonyl-2,2’-(ethylenedioxy)bis-ethylamine (300 mg) dissolved in dry tetrahydrofuran (5 mL). The reaction mixture was refluxed for 3 days. The resulting suspension was filtered over a PTFE membrane filter (0.2 μm pore size) and the filtrate extensively washed with dichloromethane to remove organic residues before dried under vacuum. Afterwards, the material was dispersed in dry dichloromethane and treated with gaseous HCl overnight to cleave the N-tert-butoxy carbonyl moieties. Finally, the reaction mixture filtered through a PTFE membrane (0.2 μm pore size), washed with dichloromethane and was neutralized with triethylamine to yield the amino functionalized graphene sheets (f-G).

Physical characterization. Scanning transmission electron microscopy (STEM) combined with EDS and electron energy-loss spectroscopy (EELS) were performed using a JEOL JEM-2100F microscope equipped with a couple of JEOL Centurio EDS detectors and a Gatan Quantum electron spectrometer at an electron acceleration voltage of 60 kV. EELS chemical map of Pd was obtained by measuring its M_{4,5,6} edge signals at each point of a scanned area. Infrared (IR) spectra were acquired on a Fourier transform IR spectrometer (Equinox 55 from Bruker Optics) equipped with a single reflection diamond ATR accessory (DuraSamp1IR II by SensIR Technologies). Raman measurements were performed with a Renishaw confocal spectrometer at 633 nm. The thermogravimetric analysis (TGA) was carried out using a TGA Q500 V20.2 Build 27 instrument by TA under a nitrogen inert atmosphere.

Catalyst preparation and deposition onto the working electrode. To prepare the catalyst ink, 4.0 mg of the hybrid catalytic powder were dispersed in a mixture of solvents (1 mL) containing water, isopropanol, and 5% Nafion (w/v/v=4:1:0.02) and sonicated for 15 min. The working electrode was first cleaned through polishing by 6, 3 and 1 mm diamond pastes, rinsed with deionized water, and sonicated in double-distilled water. Then, 0.5 μL aliquots of the catalyst ink were casted on the electrode surface and dried at room temperature.

Electrochemical testing and calculations. All the electrochemical measurements were carried out using an Autolab PGSTAT128 N potentiostat/galvanostat equipped with a dual mode bipotentiostat (BA module). The working electrode (Autolab RRDE electrode tips) consisted of a Teflon-embedded glassy carbon (GC) disk/Pt ring rotating assembly (5mm electrode disk diameter, 375 μm electrode gap, collection efficiency N=0.249). As counter electrode, a platinum wire was used and as reference an Hg/HgO (0.1 M KOH) electrode was placed into Luggin capillary. The ORR measurements were realized at room temperature in O2-saturated aqueous 0.1 M KOH electrolyte. Linear sweep voltammety (LSV) measurements on disk electrode were conducted from -0.8 to +0.2 V vs Hg/HgO at different rotation rates with a scan rate of 5 mV s\(^{-1}\). At the ring, the potential was fixed at +1.0 V vs Hg/HgO and the current response was recorded. Chronoamperometric measurements for all materials were probed at -0.40 V vs Hg/HgO at a rotation rate of 1,600 rpm for 10,000 s.

The kinetic current densities (j_k) were calculated using the Koutecky–Levich (K–L) equation:

\[
\frac{1}{j_k} = \frac{1}{j_d} + \frac{1}{j_h}
\]  

(1)

where j and j_h are the experimentally measured and the diffusion-limited current density, respectively. The number of electrons transferred in the reduction of one O\(_2\) molecule (n) can be determined by modifying the K-L equation as follows:

\[
\frac{1}{j_k} = \frac{1}{j_d} + \frac{1}{j_h} = 1/ B \omega^{1/2} + 1/j_h
\]  

(2)

where ω is the angular velocity and B is the K–L slope given by the following equation:

\[
B = 0.209 F D_0 O_2^{1/2} n^{1/6}
\]  

(3)

Here, n is the electron transfer number, F is the Faraday constant (F = 96485 C/mol), D_0 is the diffusion coefficient of O\(_2\) (D_0 = 1.9 × 10\(^{-5}\) cm\(^2\) s\(^{-1}\)), v is the kinematic viscosity of the solution (ν = 0.01 cm\(^2\) s\(^{-1}\)), and C_0 is the concentration of dissolved O\(_2\) in the solution (C_0 = 1.2 × 10\(^{-6}\) mol cm\(^{-3}\)). The constant of 0.2 is adopted when the rotation speed is expressed in revolutions per minute (rpm). Tafel plots (potential vs log(j/j_h)) were calculated in the mixed kinetic–diffusion region at a single electrode rotation rate (ω = 1600 rpm).

Based on the RRDE data, the n value and the percentage (%) of produced H\(_2\)O\(_2\) can be determined by the following equations:

\[
n = \frac{4 I_{disk} / (I_{disk} + I_{ring})}{N}
\]  

(4)
%H₂O = (200 I_{disk}/N) / (I_{disk}+I_{ring}/N)  \tag{5}

where \(I_{disk}\) is the current of the disk electrode, \(I_{ring}\) is the current of the ring electrode, and \(N\) is the collection efficiency of the Pt ring, which was provided as 0.249 by the manufacturer.

The capacitance values were calculated from the CV curves obtained in N₂-saturated aqueous 0.1 M KOH according to the equation 6:

\[
C = \frac{\int \text{d}V}{\Delta V \cdot v}
\tag{6}
\]

where \(C\) (F) is the specific capacitance; \(\int \text{d}V\) (C) is the integrated area of CV curve; \(\Delta V\) (V) is the potential window and \(v\) is the scan rate (V/s).

**Conclusions**

In summary, the fabrication of a novel hybrid ORR electrocatalyst based on covalently functionalized MoS₂ nanosheets bearing free amino moieties and Pd nanoparticles, Pd\(_{\text{NPs}}\)/MoS\(_{2}\), through a simple procedure was accomplished. For comparison, an analogous catalyst based on modified graphene, Pd\(_{\text{NPs}}\)/G, was also obtained. Complementary spectroscopic techniques and thermogravimetric analysis confirmed and quantified the covalent attachment of the organic functionalities onto MoS\(_{2}\) and graphene. TEM imaging along with EDS/EELS elemental analysis revealed the immobilization of 2-3 nm Pd\(_{\text{NPs}}\) onto both 2D substrates while the presence of agglomerations was not observed. The preservation of the MoS\(_{2}\) intrinsic properties during the functionalization process allowed us, contrasting graphene, to fully exploit the benefits of the covalent modification, leading to improved electrocatalytic activities and stability toward ORR in alkaline medium for the Pd\(_{\text{NPs}}\)/MoS\(_{2}\) hybrid, outperforming not only its graphene based counterpart but also the benchmark Pd/C catalyst. In more detail, the onset potential value for the Pd\(_{\text{NPs}}\)/MoS\(_{2}\) was found to be approximately 50 mV more positive than that of the Pd\(_{\text{NPs}}\)/G and Pd/C, whereas, with a kinetic current density value of 2.65 mA cm\(^{-2}\), the MoS\(_{2}\) based electrocatalyst possesses a 4.5-fold and by 46% greater activity over that registered for the graphene based and the commercial catalyst, respectively. Furthermore, Pd\(_{\text{NPs}}\)/MoS\(_{2}\) proved to be remarkably stable, exhibiting the lowest activity loss (~16%) after 10,000 s, among the tested electrocatalysts. A detailed analysis of the reaction kinetics suggested that the reduction of oxygen on the Pd\(_{\text{NPs}}\)/MoS\(_{2}\) hybrid abided mainly by the direct four-electron route, with a low H\(_2\)O\(_2\) yield. All in all, these findings pave the way for future designs of high-performance TMD-based ORR electrocatalysts.

**Conflicts of interest**

There are no conflicts to declare.

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The excellent performance of Pd/NPs/MoS$_2$ toward electrocatalytic ORR is presented.