Synthesis of Surface Grown Pt Nanoparticles on Edge-enriched MoS₂ Porous Thin Films for Enhancing Electrochemical Performance

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Abstract

A hybrid catalyst – Pt nanocrystals deposited on the surface of MoS₂ vertically standing nanoplatelets is synthesized via chemical vapor deposition (CVD) and subsequent thermal annealing (TA) of Pt precursor. The hybrid material shows promising results as an electrocatalyst for the hydrogen evolution reaction (HER). By varying Pt synthesis condition - precursor loading and TA temperature - the deposition sites, size and morphology of Pt nanostructure can be controlled. The size effect of Pt nanoparticle on catalytic activity and sintering resistance is discussed. Results show that higher Pt loading yields better HER performance despite of smaller specific surface area; higher TA temperature delivers larger average particle size of Pt crystals and lower HER activity. Larger average size leads to fast sintering and thus poor durability of the catalyst. Based on the correlation between HER performance and growth behaviors of Pt on MoS₂ surfaces, optimization route for a highly active and stable co-catalyst can be established. The optimized Pt-MoS₂ catalyst (400 °C, 11 wt%) reported in this study possesses superior overpotential of 9 mV (close to zero), Tafel slope of 44mV/dec and moderate exchange current density of 373 $\mu\text{A}/\text{cm}^2$;

it exhibits activity degradation of 140 mV @ 20mA/cm² after 10,000 cycles. The Tafel slope indicates the combination of Volmer-Heyrovsky steps as HER mechanism in this particular hybrid catalyst system. The outstanding HER activity attributes to highly-dispersed Pt nanoparticles grown on MoS₂ basal surfaces, large MoS₂ edge density and Pt – S bonding effect induced activity improvement of MoS₂ as well as 3D porous network assisted superaerophobic surface.

Introduction

As a clean energy resource, hydrogen plays a critical role in today's society and environment.¹ An environmentally friendly approach to generate hydrogen is water splitting via electrolysis process, in which electrocatalyst is crucial for reducing the overpotential and increase current density.² Typically platinum (Pt) group metals are used at the cathode side for catalyzing hydrogen evolution reaction (HER, $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) based on their best catalytic activity towards HER and excellent corrosion resistance in acidic and alkaline environment.³ Whereas the high cost and scarcity of Pt make its use a barrier to water splitting route for mass hydrogen production.⁴⁻⁶ To reduce the cost of water electrolyzers while maintaining acceptable production of hydrogen,³ efforts have been made into (route-1) completely replacing Pt with inexpensive non-noble metal alternatives which possess high catalytic activity,³ (route-2) tailoring the morphology and microstructure of deposited Pt on its support to enhance the catalytic active surface area and (route-3) developing hybrid catalyst based on nonprecious-metal alternatives and Pt for enhanced performance at reduced Pt loading level.^{3,7-9}

Following route-1, extensive research and progress have been devoted towards discovery of inorganic catalysts in place of Pt. To date sulfides and phosphides, which usually contain transition metal cations of Mo, Co, Fe, or Ni are reported to be the most effective non-noble metal HER catalysts.⁹ The catalytic

activity reported for these newly discovered HER alternatives, however, can't be compared with Pt based catalysts.^{9,10} Taking this into consideration, optimal choice when designing advanced HER electrocatalyst still appears to base on Pt metal.^{1,7,9}

It's known that Pt electrocatalysts are mostly utilized in the form of supported particles.³ The structure of the support poses a great influence on the morphology and microstructure of Pt particles as well as bonding between metal and support materials to prevent agglomeration.⁹⁻¹² Structural modification including particle dispersion and metal-support interaction could tune the electrochemical active surface area,^{3,5,6,13} and thus enhance the catalytic activity and stability.¹⁴ This is described as aforementioned route-2. An efficient strategy is for example to reduce the size of Pt particles to (sub)-nanometer and ultimately atomic scale, which led to dramatic improvement of catalytic activity.^{7,11,15,16} Although catalyst may be deposited on a planar support, but only for low current density applications, for high current density application the Pt catalyst should be incorporated on a high surface area mesoporous or particle-based support.^{3,14} Pt-electrocatalyst supports typically are carbon-based nanomaterials which possess high surface area, conductivity and durability such as activated carbon, carbon nanofibers and carbon nanotubes.^{1,7,11,13,17} Recently two dimensional materials graphene and its analogous such as molybdenum disulfide (MoS_2) have drawn great attention as promising candidate Pt catalyst support due to extremely high surface area and superior chemical stability.^{13,14,18-22}

As a prototype compound of a two-dimensional layered transition-metal dichalcogenides (TMDs),¹⁹ MoS_2 has received great attention due to its many interesting properties and thus application in the fields of lubrications,²³⁻²⁶ transistors,²⁷⁻²⁹ catalysis and batteries.³⁰⁻³⁴ Especially, nanostructured MoS_2 , has been intensified to be employed as HER electrocatalyst.^{1,14,35} Both theoretical and experimental investigations proved that the edge sites of monolayer MoS_2 are catalytic active,³⁶ therefore edge exposed nanostructure design is effective in increasing the total number of active sites of the MoS_2 catalysts and device-orientated

catalytic performances.^{37–39,57} Previously we have reported that edge enriched MoS₂ nanoplatelets can be synthesized via one-step chemical vapour deposition (CVD) method with real surface area to geometric area ratio (as high as ~ 340), 3D open framework and superaerophobic surface.⁴⁰ This led us to construct a functional composite by synthesizing Pt nanoparticles on 2D MoS₂. This novel structure will not only enhance the intrinsic properties of individual materials but also trigger synergetic effect by bringing enhanced properties and functions. (route-3)^{3,6,19,58,59} Firstly, such morphology, consisting of vertically standing platelets to maximally expose edges and vast amount of catalytic inert basal surfaces, appears promising to be utilized as scaffold for well-dispersed Pt nanoparticle surface growth,¹⁴ which is consequently beneficial for electrochemical active surface area and sintering stability of metal particles. Secondly, unlikely carbon-material based supports that are catalytic inert, the Pt synthesis scaffold MoS₂ as an effective 2D electrocatalyst itself, will act not only structurally as Pt growth template but also provide additional catalytic active edges for the HER. Thirdly, it's found that single heteroatom doping is capable of enhancing the activity of the surface S atoms; metal clusters can facilitate electron transfer to the 2D crystals and thus modify the surface electronic structure and enhance reactivity of MoS₂.⁴¹ In previous studies utilization of MoS₂ nanosheets as substrate has been found to reduce Pt loading and obtain higher catalytic activity.^{14,21,22,42} For example, electrochemical exfoliated MoS₂ monolayer decorated with Pt particles was reported with high catalytic activity at reduced Pt loading but the electrochemical exfoliation requiring Li-battery system has introduced process complexity; moreover MoS₂ monolayer used in this study lacked porous 3D architecture for the size and surface area control of the Pt particles.²² Pt nanospheres on few-layer MoS₂ have been prepared via hydrothermal route but the thickness of MoS₂ can't be controlled, therefore lack of transferrable guidelines to other materials system.⁴²

Herein, we develop a facile and scalable synthesis approach to prepare Pt- MoS₂ hybrid catalyst system directly on glassy carbon electrode via CVD and subsequently thermal annealing (TA) method. Our

strategy was to utilize the vertical standing MoS₂ nanoplatelets with high surface area as scaffold to grow Pt nanocrystals mainly on the basal planes to achieve high dispersion of nanoparticles, which promoted electrocatalytic active surface area and sintering resistance of Pt crystals. Moreover, the MoS₂ nanoplatelets themselves exposed large number of catalytic active edge sites, contributing to the overall activity of the hybrid catalyst. The morphology, crystal structure and chemical composition were studied using scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray (EDX) analysis. Electrocatalytic performance of the as-received hybrid catalysts was investigated in acidic solution via linear sweep voltammetry (LSV) and cycling test. The growth behavior of Pt nanocrystals and HER activity as well as stability of Pt- MoS₂ were correlated with different Pt loading levels and TA temperatures. Our study has provided a facile and scalable strategy for Pt metal nanocrystals synthesis with controllable size and morphology on the surface of edge-enriched 3D porous MoS₂ film, to construct a novel functional materials system that has shown promising as HER electrocatalyst.

Results and Discussion

Figure 1. Morphological and microstructural characterization of supported Pt nanocrystals on CVD synthesized vertically-standing MoS₂ nanoplatelets. (a) Schematic illustration of two-stage process of drop coating - thermal annealing (TA) to realize dispersive Pt nanoparticles growth onto edge-exposed MoS₂ nanoplatelet. SEM images showing surface morphology of (b) CVD pristine MoS₂ and (e) Pt decorated MoS₂ (Pt - MoS₂), proving vertically alignment of nanoplatelets was perfectly preserved after TA process. Microstructure determination using TEM imaging of (c and d) pristine MoS₂ and (f and g) Pt-MoS₂ hybrid catalyst.

The porous 3D thin film of Pt nanoparticles grown on edge exposed MoS₂, to be used as electrocatalyst towards hydrogen evolution, was produced via a two-step process: (1) synthesis of support/host catalyst material MoS₂ and (2) formation of dispersive Pt decoration crystals via TA approach. As reported in our

previous work,⁴⁰ the MoS₂ porous thin film consisting of vertically-aligned nanoplatelets was synthesized via one-pot CVD method directly on glassy carbon substrate in order to be employed as working electrode in the subsequent three – electrode electrochemical measurement. Then the as-grown CVD MoS₂ was treated by TA approach as illustrated in Figure 1a for decoration of Pt nanoparticles: (2-1) drop coating of 10 μ L sonicated H₂PtCl₆·6H₂O in ethanol (H₂PtCl₆·6H₂O:ethanol of 0.1, 1 and 10 mM) onto CVD MoS₂ thin film and natural air dry, followed by (2-2) thermal annealing in H₂/Ar gas at 400, 500 and 600 °C for 20, 40 and 80 mins for the Pt nanocrystals to nucleate and grow on basal surfaces and edges of MoS₂. The as-prepared Pt-MoS₂ was then carefully characterized by SEM, TEM and EDX to investigate its morphology, microstructure and elemental composition.

Figure 1b is the SEM image depicting the CVD as-grown pristine MoS₂ consisting of vertical standing platelets with size of less than 1 μ m. The microstructure of those MoS₂ flakes was examined and detailed by TEM images in Figure 1c-d, where the smooth and clean horizontal aligned triangular domain and vertically standing multilayers of MoS₂ can be clearly observed. From SEM image in Figure 1e, it can be found the as-received Pt decorated MoS₂ exhibits comparable morphology of vertically-standing platelets to its CVD as-grown counterpart. It's been studied that the energy of edge is higher than the terrace surface. However, we have successfully synthesized the edge exposed morphology using CVD method. A kinetic growth mechanism for this morphology has been suggested by other work.^{60,61} Moreover, such edge termination is proven to be robust enough to survive the thermal annealing process under reducing atmosphere. That ensures the resultant Pt-MoS₂ hybrid catalysts will maintain the high MoS₂ edge density; and also benefit from its high real surface area of active edges and superaerophobic surface structure resulted from the edge-exposing morphology.

Figure 2 (a) ADF-STEM image of a Pt nanocrystal attached on the MoS₂ horizontal oriented flakes, with interlayer spacing $d_{(111)Pt}$ of 0.24 nm. (b) Power spectrum calculated from (a). (c) FFT of entire image in (a), with reflexes from MoS₂ and Pt labeled.

ADF-STEM images and its corresponding FFT of the resultant Pt nanocrystal decorated MoS₂ catalyst are shown in Figure 2, which confirms good crystallinity of the Pt-MoS₂. The black lines measuring the interlayer spacing of 0.24 nm corresponds to lattice spacing of Pt nanocrystal in the (111) direction, slightly larger than what has been reported to be 0.23 nm.⁴³ It confirms the nanocrystals synthesized on MoS₂ via aforementioned TA approach to be Pt. The lattice expansion of 6% compared to bulk Pt (0.2265 nm) implies the possible strain effect of the MoS₂ template on the growth of Pt nanocrystal. FFT analysis of the entire image of Figure 2a is recorded in Figure 2b. {100} and {110} represent zigzag and armchair orientations of MoS₂, respectively. The crystal structure of Pt nanocrystals at different loadings and TA temperatures are summarized in Figure S1-2, with the interlayer spacing 0.23nm indicating $d_{(111)Pt}$.

Figure 3. The influence of Pt metal loading on growth sites, particle density and size distribution of as-formed Pt nanocrystals on MoS₂. Low resolution TEM images, intermediate resolution TEM images, high resolution ADF-STEM images of as-prepared Pt-MoS₂ catalyst and Pt nanoparticle size histograms at Pt wt% of (a-d) 0.11 wt%, (e-h) 1.1 wt% and (i-l) 11 wt%. (Pt loading was controlled via tuning precursor concentration at 0.1 mM, 1mM and 10 mM; the volume of drop coated precursor solution was kept constant at 10 μ L).

In order to investigate the growth behavior and mechanisms of Pt nanocrystals on MoS₂, the TA process was carried out by tuning Pt precursor loading, annealing temperature and time. These factors are believed to have profound influence on the number and mobility of Pt species, size distribution as well as specific surface area of as-formed Pt nanoparticles, and thus catalytic property of the resultant hybrid catalyst.

Table 1. Elemental composition, Pt wt% and equivalent Pt loading on glassy carbon working electrode in the Pt-MoS₂ hybrid catalyst system determined by EDX at different precursor concentrations.

H ₂ PtCl ₆ ·6H ₂ O:ethanol (mM)	n _{Pt:Mo}	Pt wt%	Pt loading (μ g/cm ²)
10	0.1	11 wt%	13
1	0.01	1.1 wt%	1.3
0.1	0.001	0.11 wt%	0.13

The volume of Pt precursor drop coated onto MoS₂ before TA and geometric area of the glassy carbon electrode were kept constant at 10 μ L and 1.5 cm².

The effect of Pt loading on growth sites and size distribution of Pt nanoparticles is shown in Figure 3. 10 μ L of H₂PtCl₆·6H₂O:ethanol at 10 mM, 1mM and 0.1 mM were employed for TA synthesis of Pt nanocrystals. EDX analysis was utilized to quantitatively characterize the corresponding elemental ratio of Pt to Mo of the resultant hybrid catalysts. (See details in Table S1 on EDX quantitative elemental analysis of the as-received Pt- MoS₂; Figure S3 on the EDX spectrum of Pt-MoS₂). In the as-prepared Pt-

MoS₂ system, $n_{\text{Pt:Mo}}$ was measured to be 0.1, 0.01 and 0.001, resulting in corresponding Pt wt% of 11 wt%, 1.1 wt% and 0.11 wt% and Pt loading of 13 $\mu\text{g}/\text{cm}^2$, 1.3 $\mu\text{g}/\text{cm}^2$ and 0.13 $\mu\text{g}/\text{cm}^2$, respectively.

Electron microscopy images at different magnifications along with particle size histograms are summarized for each loading to demonstrate the growth sites and size distribution of the as-prepared Pt nanocrystals on the surface of MoS₂ platelet. It can be seen from TEM and ADF-STEM images of as-prepared Pt-MoS₂ in Figure 3a-k, when Pt wt% increases from 0.11 wt% to 11 wt%, the density of Pt nanocrystals formed on MoS₂ surface increases accordingly, which is resulted from increased number of Pt atoms available to form crystals at elevated metal loading. Apart from larger quantity of as-formed Pt nanocrystals, the distribution of those Pt crystals changed notably as well. Previous work suggested that defects act as the nucleation sites to strongly bind the Pt crystals.²⁰ Also, both edges and basal surfaces contain a certain number of defects. The defectiveness of edges is higher than that of the basal planes due to being exposed to the environment, where moisture, oxygen and reducing agents can disturb the crystallinity and form defects. Therefore, we firstly observe pure edge decoration when there is only a small amount of Pt loaded (0.11 wt% as in Figure 3a-c), the Pt atoms tend to be more strongly hindered by the more defective edges and form particles. At increased loading of 1.1 wt% (Figure 3e-g), both edges and basal surfaces have seen an increase in population of decorated Pt particles, where the Pt crystals continue to nucleate at defect sites of edges until edge defects have been fully occupied, then start to form on the basal surface defects. At high Pt loading of 11 wt% as seen in Figure 3i-k, the Pt nanocrystals are formed uniformly across the surface of MoS₂. Another explanation can be that, before Pt crystals are formed during TA process, drop coating and drying process of the Pt precursor are likely to form clusters and the as-formed clusters cover the MoS₂ surface unevenly and primarily on the more defective edges sites rather than basal planes; then in the following TA process, under identical TA temperature/time where Pt atoms are supposed to possess the same mobility, the distribution manner determined in the

precursor coating process will remain in the final growth product. High resolution ADF-STEM images in Figure 3c, g and k demonstrate TA synthesis method applied in this study yields only surface cluster growth of Pt atoms in the form of nanocrystals with size 2-3 nm and no solid evidence of atomic level Pt doping. The size distributions of the Pt nanocrystals are measured and summarized in the histograms in Figure 3d, h and l. It's found that the higher Pt loading delivers larger average nanoparticle size. These results reveal that by tuning Pt loading, the size and growth sites of Pt nanocrystals on MoS₂ can be controlled.

In order to systematically investigate the effect of synthesis conditions on the average size and specific surface area of the Pt nanostructure. Determination of particle diameter and real surface area of the nanoparticles grown at various loadings and TA temperatures was performed based on TEM images.⁴⁴⁻⁴⁶ The number averaged (d_n) and surface averaged (d_s) particle diameters are calculated by

$$d_n = \frac{\sum n_i d_i}{\sum n_i} \quad (1)$$

$$d_s = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad (2)$$

In its simplest version the specific surface area can be calculated according to the following equation:

$$A = \frac{6}{\rho d_s} \times 10^3 \quad (3)$$

where ρ is the density of Pt metal (21.4 g/cm³) and the resultant A is in m²/g_{Pt}. Here d_s is better than d_n for calculation of specific surface area A. The calculated results are summarized in Table 2. We can be assured that the as-calculated specific surface area in relation with average particle size is in good agreement with values from previous studies on Pt nanoparticles synthesized on carbon support.^{20,44-46}

Table 2. Number averaged (d_n) and surface averaged (d_s) particle size determined from TEM imaging analysis, and specific surface area (A) calculated from d_s .

Sample	d_n (nm)	d_s (nm)	A (m^2/g_{Pt})
0.11 wt%, 400 °C	2.1 ± 0.4	2.3	124
1.1 wt%, 400 °C	2.4 ± 0.9	3.2	88
11 wt%, 400 °C	2.9 ± 1.1	3.8	74
0.11 wt%, 500 °C	1.6 ± 0.8	2.4	117
1.1 wt%, 500 °C	2.6 ± 0.8	3.2	87
11 wt%, 500 °C	3.5 ± 1.7	5.2	54

Figure 4. The effect of Pt loading and TA temperature on average size and specific surface area of Pt nanocrystals grown on MoS₂ nanoplatelets. (a and b) Pt nanoparticle size distribution histograms under 400 °C and 500 °C, respectively. (c) Number averaged size d_n , (d) surface averaged size d_s and (e) specific surface area A calculated from d_s of Pt nanocrystals at different loadings and TA temperatures.

The above investigation on Pt loading were carried out at 500 °C as well. The microstructure study by TEM images are shown in supporting information Figure S4. The effect of Pt loading on density and size distribution of the as-formed Pt nanoparticles under 500 °C is in consistence with 400 °C batch (Figure 4b): Pt particle size rises with Pt content increasing in the hybrid materials system. Moreover, from Figure 4d it's found that at the same Pt loading, higher TA temperature delivers larger average particle size. Standard deviation of d_n increases as particle size becomes larger, which is consistent with previous studies.⁴⁴ It's worth noting that both higher loading and higher annealing temperature can increase the average particle size and subsequently decrease specific surface area as seen in Figure 4d and e, which significantly influences the number of accessible active sites per mass of Pt as well as the sintering resistance during long term operation. TA temperature doesn't appear to exert a dramatic influence on Pt growth sites (comparing Figure S4 with Figure 3) that 0.11 wt% Pt loading always leads to Pt nanoparticle growth on the edges of MoS₂ flakes and 11 wt% always results in even distributed growth of Pt particles across the MoS₂ surface.

Figure 5. Electrocatalytic activity towards HER of the as-prepared Pt-MoS₂ catalysts as a function of Pt loading: (a) Cathodic polarization curves at scan rate 1 mV/s and (b) Tafel plots of as-received Pt-MoS₂ catalysts (values normalized by geometric area) at different Pt loadings (TA: 400 °C, 40 min) compared to pristine MoS₂. (c) Comparison of HER catalytic activities of MoS₂, H₂ annealed Pt-MoS₂ and Ar annealed Pt-MoS₂ catalysts; revealing the contribution of pure Pt, MoS₂ and H₂ to the electrocatalytic activity in the present Pt-MoS₂ catalyst. (d-f) Onset potential, exchange current density and Tafel slope of the Pt-MoS₂ hybrid catalysts as a function of Pt wt%.

In order to understand the effect of Pt loading and TA temperature induced structure and morphology change on electrocatalytic property of the as-received hybrid catalyst. Electrochemical test of linear sweep voltammetry (LSV) and cycling treatment as described in experimental section were conducted in order to demonstrate the HER electrocatalytic performances of the as-received Pt-MoS₂ hybrid catalysts with 0.11 wt% ~ 11 wt% Pt loading annealed at 400 °C and 500 °C. As indicated in the experimental section, the catalysts are produced directly on glassy carbon working electrode through CVD and TA process; no additional transfer process is needed, which ensures the materials being electrochemically tested are

purely as-received. Cathodic polarization curves are recorded at scan rate of 1 mV/s in a typical three-electrode electrochemical cell with 0.5 M H₂SO₄ solution. Tafel slope and exchange current density are determined by fitting the linear portion of the Tafel plot at low cathodic current to the Tafel equation ($\eta = b \log |j| + a$, where j is the current density and b is the Tafel slope). Onset potential is obtained from Tafel plot by identifying the point where linear relationship $\eta = b \log |j| + a$ starts to deviate. Tafel slope suggests the rate limiting step in the HER mechanisms. In the acid media, the corresponding Tafel slope values for Volmer (adsorption of H⁺ on catalyst active sites to form H_{ad}), Heyrovsky (electrochemical desorption of hydrogen from the active sites $H_{ad} + H^+ + e^- \rightarrow H_2$), and Tafel (combination reaction $H_{ad} + H_{ad} \rightarrow H_2$) of water splitting are 120, 40, and 30 mV/dec, respectively.

Figure 5 shows the influence of Pt loading on the HER activity in the hybrid Pt-MoS₂ catalyst system at the same TA temperature. Firstly, as seen from the polarization curves in Figure 5a, the amount of deposited Pt nanoparticles on the MoS₂ platelets exerts a proportional effect on the HER activity (as indicated by the grey arrow). Although as discussed in Figure 4 that higher Pt loading leads to slightly larger average particle size (2.9 nm vs. 2 nm), since Pt has extremely high catalytic activity towards hydrogen evolution reaction, higher Pt content always leads to earlier onset of hydrogen evolution and larger amount of produced hydrogen gas (corresponding current density at given overpotential). Thus, in this case, size effect of Pt nanoparticle on catalytic activity can be neglected and discussion will be focusing on the bonding effect of Pt and MoS₂ with different Pt contents. The electrocatalytic metrics of the Pt-MoS₂ co-catalysts are determined via methods described above and plotted in Figure 5d-f. Detailed values can be found in Table S2. It can be seen that with Pt content increasing, the hybrid catalyst exhibits increased exchange current density (Figure 5e), decreased onset potential Figure 5d) and Tafel slope (Figure 5f).

The onset overpotential reveals the energy barrier for the catalyst surface to be activated to mediate HER. There's an obvious onset overpotential shift from MoS₂ and 0.11 wt% Pt-MoS₂, which implies the possible change of nature of catalytic site. According to previous study on Pt nanoparticles/MoS₂ nanosheets/carbon fiber hybrid system, characteristic peak of S2p shift from X-ray photoelectron spectroscopic (XPS) measurements suggested the bonding effect between Pt and S and the accordingly changed electronic state density of S can enhance catalytic activity of the exposed Mo (catalytically active sites in MoS₂).¹ It's worth noticing that the onset overpotential at this point (0.11 wt%) is still much worse than Pt (~ 0 mV) indicates that at such loading level Pt hasn't yet come to play a dominant role in the catalytic process. Whereas when Pt loading further increases from 0.11 wt% to 0.55 wt% and 1.1 wt%, the onset overpotential is seen to continue shifting but not as largely as the one from MoS₂ to 0.11 wt% (Figure 5a and d). This phenomenon suggests that in the loading range of 0.11 wt% ~ 1.1 wt%, as Pt content increasing, the Pt and S bonding effect continues to enhance the activity of Mo and thus decrease activation energy of HER. Also the contribution of loaded Pt particles on catalytic activity is worth mentioning as the onset overpotential is moving towards the range of Pt/C catalyst (13 mV). Finally, when Pt content reaches 11 wt%, the activation energy for active sites in this system shifted down to 9 mV, which is better than pure Pt/C (13 mV). The possible reason for the better activity is the dual enhancement – highly dispersed Pt particles providing high specific surface area as well as the synergistic effect from the Pt and S bond that leads to the intrinsic improvement of Mo sites of MoS₂.

The Tafel plots of the as-received composites are depicted in Figure 5b in accordance with Figure 5f. Tafel slope decreases from 166 to 44 mV/dec after Pt loading (11 wt%). It indicates in Pt-MoS₂ system, hydrogen desorption is the rate determining step and HER proceeds through combination of Vomer-Heyrovsky and Volmer-Tafel mechanism; whereas hydrogen adsorption (Volmer reaction) is the rate determining step in pure MoS₂. It's therefore revealed that Pt contributes dominantly to the HER activity

despite only 11 wt% content in the hybrid system. The increased exchange current density normalized by the electrode area reflects the improved device performance of the Pt-MoS₂ as Pt content rises.

In order to elucidate the role of H₂ in TA process and HER activity of Pt-MoS₂, control experiment was conducted by annealing the sample with Ar. It can be seen from the TEM images in Figure S5 that a much smaller amount of Pt particles are formed on the MoS₂ flakes under Ar (compared to H₂ annealing in Figure S4 at the same precursor concentration, TA temperature and time), which reveals H₂ ensures effective reduction of Pt precursor and promotes Pt nanocrystal formation at the designated reaction temperature and time. The improvement of H₂ annealed sample over Ar annealed sample resulted mainly from thorough reducing and formation of Pt particles. H₂ induced catalytic activity improvement of MoS₂ can be excluded. The activity loss of pure MoS₂ subject to the same annealing process can be explained by eliminated defects and increased crystallinity when annealed. (Details can be found in supporting information) Similarly, pure Pt synthesized directly on glassy carbon substrate by the same annealing procedure was tested for HER (Figure S8). It's found that pure Pt exhibits lower activity than the Pt-MoS₂ composite, as well as current fluctuation. This result indicates MoS₂ acts as both superaerophobic scaffold and catalytic active material.

The HER catalytic parameters of supported Pt catalysts from literature are summarized in Table S3. It can be seen that our optimized Pt-MoS₂ (11 wt%, 400 °C) catalyst possesses outstanding onset potential of 9 mV, which is amongst the best to our best knowledge (2.7 ~ 188 mV).^{1,2,6,11,47-54} The Tafel slope fits well with reported Pt-supported catalyst (27 ~ 85 mV/dec).^{1,2,6,11,17,22,47-49,51-55} The exchange current density of the Pt-MoS₂ is moderate compared to previous values (6.27 ~ 4420 $\mu\text{A}/\text{cm}^2$),^{2,10,11,17,47,48,51,53,55} mainly arising from the semi-conductive nature of the MoS₂, which doesn't facilitate an excellent charge transfer rate.

Figure 6. Influence of TA temperature on electrocatalytic activity and durability towards HER of the as-prepared Pt-MoS₂ catalysts: (a) cathodic polarization curves at scan rate 1 mV/s of as-received Pt-MoS₂ catalysts on glassy carbon for different Pt wt% at 400 °C and 500 °C. (b) Influence of TA temperature on electrocatalytic stability of Pt-MoS₂ catalysts. (c) Degradation analysis of Pt-MoS₂: overpotential increase (@ current density of 20mA/cm²) after stability test under different Pt loadings and TA temperatures.

The HER activity of Pt-MoS₂ at TA temperatures of 400 °C and 500 °C is shown in Figure 6a. At 500 °C, the catalytic activity increases with increased Pt loading similarly to 400 °C. It should be also noticed that at the same Pt loading, the 400 °C Pt-MoS₂ always outperforms the 500 °C Pt-MoS₂ catalysts. This is due to the size effect that higher TA temperature leads to larger average Pt particle size and smaller specific surface area (as discussed in Figure 4). Therefore at the same Pt content, higher annealing temperature results in fewer Pt surface active sites for HER.

Durability is important when it comes to practical application aspects. The Pt-MoS₂ cocatalysts were subjected to stability treatment in acidic solution via linear sweep voltammetry with a fast scan rate of 100 mV/s for 10,000 cycles in order to simulate the working condition of practical water-splitting devices. The cathodic polarization curves and TEM images were recorded in Figure 6b-c and Figure 7, to monitor functional and microstructural changes before and after stability test, if there are any. It can be seen from polarization curves of the catalysts before and after 10,000 cycles in Figure 6b, at each Pt content, 500 °C samples always exhibit better stability of cathodic current density than 400 °C samples. In order to

evaluate the degradation extent of the catalysts, the increase of overpotential required to reach a certain current density ($20\text{mA}/\text{cm}^2$) are extracted and summarized in Figure 6c. It demonstrates that at the same Pt loading, higher TA temperature leads to smaller degradation; at the same TA temperature, higher Pt loading leads to smaller degradation. The degradation of nanoparticle catalyst is mainly caused by:

- (1) Nanoparticle sintering by Ostwald ripening (dissolution of metal atoms and recrystallization) or/and aggregation (thermal motion of particles);^{12,56}
- (2) Detachment of the nanoparticles from the support/electrode;
- (3) Corrosion of the support materials, in this case MoS_2 .

Figure 7. Structural degradation analysis of Pt-MoS₂ catalysts post 10,000 cycles. TEM images and Pt nanocrystal size histogram before and after stability test of the Pt-MoS₂ catalyst received at TA temperature of (a-c) 400 °C and (d-f) 500 °C. (g) Number averaged particle size and (h) specific surface area degradation analysis before and after 10,000 cycles. (11 wt% Pt)

In order to understand the degradation determining factors and optimize further catalyst design, the microstructure of the post-cycled catalysts was studied by TEM microstructural analysis. Corresponding

TEM images, Pt nanocrystal size and specific surface area histograms are shown in Figure 7. In good alignment with the degradation of HER activity, the average nanoparticle size increased from 2.9 nm to 6.2 nm and specific surface area from 74 m²/g to 20 m²/g after cycling with the 400 °C sample; average particle size and specific surface area of the 500 °C sample, on the other hand, stayed almost unaffected after 10,000 cycles. Firstly, as we discussed before, the as-received 400 °C sample possesses smaller average Pt particle size compared to the 500 °C sample and thus higher mobility. Secondly, lower TA temperature facilitates weaker bonding of Pt and Mo atoms, which will increase the migration and aggregation of Pt nanoparticles. Thirdly, lower TA temperature resulted weaker Pt-Mo bond tend to accelerate detachment of the Pt nanoparticles from its support/electrode. Due to the above three reasons, the 400 °C sample undergoes a faster sintering process than the 500 °C sample. The higher loaded samples (11 wt%) are employed for the investigation for better TEM visualization due to higher density and larger particle size. TEM images of lower Pt content samples (0.11 wt%) are shown in Figure S6.

Conclusion

In this work, we have demonstrated that an advanced hybrid catalyst of highly dispersive Pt nanocrystal grown on MoS₂ edge exposed nanoplatelet has been produced via CVD – TA method. The size distribution and specific surface area of Pt nanocrystals on MoS₂ was successfully controlled by tuning Pt loading and TA parameters. It's found that when Pt wt% decreases from 11% to 0.11%, the number of Pt nanocrystals formed on MoS₂ surface decreased accordingly; the nanoparticle distribution became less uniform across the surface of MoS₂; the average size of nanocrystals decreased and specific surface area increased. At the same Pt loading, higher TA temperature delivers larger average particle size and lower specific surface area. Our study demonstrated that the higher TA temperature induced larger Pt particle size have a smaller initial HER activity but better long term durability, due to that lower migration ability of larger particles and thus higher sintering resistance. In this hybrid catalyst system, MoS₂ contributes both functionally (i.e.

catalytic activity benefitting from vertical alignment enhanced high edge density) and structurally (i.e. construct as porous and superaerophobic scaffold for Pt nanocrystal to deposit). The Pt-MoS₂ shows potential as good HER catalyst for the three following reasons: firstly, 3D MoS₂ support promote highly dispersive Pt nanoparticle growth; secondly, MoS₂ itself contributes to HER activity by providing active edge sites; thirdly, the Pt and S bonding effect leads to possible enhanced activity of the active Mo sites. Our work provides a new idea for optimization of microstructure and electrocatalytic functionalization in Pt-MoS₂ hybrid catalyst system and provided sensible route to increase the commercial viability of water electrolysis application.

Experimental Methods

Synthesis of edge exposed MoS₂ nanoplatelets. The edge-exposed MoS₂ thin film was synthesized by chemical vapor deposition (CVD) method directly on glassy carbon substrates using 500 mg of molybdenum (VI) oxide (MoO₃) powder ($\geq 99.5\%$ Sigma-Aldrich) powder and 600 mg sulfur powder ($\geq 99.5\%$, Sigma-Aldrich). Two-furnace double-quartz tube system was applied to separately control the temperatures of MoO₃ and S. Glassy carbon substrates were placed vertically into the center of inner quartz tube. Argon was used to protect the system from oxygen and carry sulfur vapor from the upstream of the low-temperature tube for reaction. In order to achieve edge terminated surface structure, the temperatures for S, MoO₃ and glassy carbon substrates were set at 180 °C, ~ 380 °C and 800 °C. Growth stage lasted 60 mins under 50 s.c.c.m. of Ar gas.

Synthesis of Pt nanocrystals on MoS₂ edge terminated nanoplatelets on glassy carbon electrode. The CVD as grown MoS₂ edge exposed thin film on glassy carbon electrode was drop casted with 10 μ L of 0.1 ~ 10 mM H₂PtCl₆·6H₂O - ethanol (Sigma-Aldrich) solution, then allowed to evaporate in air at room temperature for 10 mins. The resulted H₂PtCl₆ coated MoS₂ sample was subsequently placed into the tube furnace and heated up to 400 ~ 600 °C for 40 mins under H₂ flow (20% in argon, 100 s.c.c.m.), to

decompose H_2PtCl_6 to Pt. After annealing, the sample was naturally cooled down to room temperature under the protection of argon gas.

Synthesis of Pt nanocrystals directly on glassy carbon electrode. The Pt nanoparticles on glassy carbon electrode was prepared with identical drop casting and TA procedure as described above directly on the bare glassy carbon substrate, as opposed to glassy carbon with CVD pre-grown MoS_2 .

Characterization. Surface morphology and microstructure were analyzed by scanning electron microscopy (SEM), (aberration-corrected) transmission electron microscope ((AC-)TEM) and scanning transmission electron microscope (STEM) techniques, respectively. SEM characterization was carried out on Hitachi S-4300 with an accelerating voltage of 3.0 kV. TEM samples were prepared by gently rubbing the TEM grid across the surface of the MoS_2 thin film to mechanical exfoliate flakes and promote their adhesion to the lacey carbon TEM grid. Low magnification TEM was performed using a JEOL JEM-2100 with an accelerating voltage of 200 kV and AC-TEM was performed using Oxford's JEOL JEM-2200MCO FEGTEM with a CEOS image corrector and operated at an accelerating voltage of 80 kV. Room-temperature ADF-STEM imaging was conducted using an aberration-corrected JEOL ARM200CF STEM equipped with CEOS corrector operated at an accelerating voltage of 60kV.

Electrochemical studies. Electrochemical testing was performed in 0.5 M H_2SO_4 Ar-purged solution using a three-electrode setup for measurement of electrocatalytic activities towards HER, with Ag/AgCl / KCl (3M) as reference electrode ($E(\text{RHE}) = E(\text{Ag/AgCl / KCl (3M)}) + 0.21 - 0.059 \cdot \text{pH}$), and an activated carbon counter electrode. A 1 mm thick glassy carbon plate (Sigma-Aldrich Company Ltd.) containing the as-received Pt nanocrystal decorated edge-exposed MoS_2 films was used as the working electrode. The effective area ($0.5 \text{ cm} \times 0.5 \text{ cm}$) of the working electrode was defined by applying electrochemically inert pure polytetrafluoroethylene (PTFE) tape. A metal clip was used to connect the working electrode with an external circuit. Linear sweep voltammetry (abbrev. LSV, scan rate of 1 mV/s) under quasi-equilibrium

conditions were recorded by a Biologic VMP3 potentiostat. 10,000 LSV scans was conducted at 100 mV/s to investigate the long term stability. The Electrochemical Impedance Spectroscopy (abbrev. EIS) was carried out from 200000 to 1 Hz with an amplitude of 10 mV.

Supporting Information

High resolution TEM images of Pt nanoparticles deposited on MoS₂ for precursor at various precursor loadings; High resolution TEM images of Pt nanoparticles deposited on MoS₂ for precursor at various thermal annealing temperatures; EDX quantitative elemental analysis based composition determination of Pt-MoS₂ catalyst synthesized with 10 mM H₂PtCl₆·6H₂O:ethanol, annealed at 400 °C for 40 mins; EDX spectrum of Pt-MoS₂ catalyst synthesized with 10 mM H₂PtCl₆·6H₂O:ethanol, annealed at 400 °C for 40 mins; TEM images of Pt-MoS₂ at Pt wt% of 11 wt%, 1.1 wt% and 0.11 wt% at TA temperature of 500 °C for 40 mins; Summary of Pt-MoS₂ catalytic activity (onset potential, Tafel slope and exchange current density) for electrochemical water splitting process; TEM image of Pt precursor coated MoS₂ thermal annealed in pure Ar gas; Summary of literature catalytic parameters towards HER of Pt supported catalysts; TEM images of the Pt-MoS₂ before and after 10,000 cycling treatment (0.11 wt% Pt, TA 500 °C); SEM and TEM images revealing the morphology and structure of the CVD MoS₂ thin film; Comparison of HER activity of Pt-MoS₂ with pure MoS₂ and pure Pt catalyst (Pt loading was kept the same at 0.11 wt%); thermal annealing of pure MoS₂ under the same condition as of Pt precursor coated MoS₂.

Acknowledgements

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