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Phosphorus doped MoS₂ nanosheets supported on carbon cloths as efficient hydrogen generation electrocatalysts

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Abstract: Highly efficient and stable non-noble-metal electrocatalysts for hydrogen generation are desired for sustainable development of energy conversion and storage. Here, a facile low-temperature phosphidation process is developed for phosphorus doping into molybdenum disulfide (MoS₂) nanosheets directly synthesized on carbon cloths to function as an integrated electrode for efficient hydrogen evolution reaction. As compared with the undoped MoS₂ nanosheets, the optimal phosphorus-doped (3.3 at%) MoS₂ nanosheets exhibit the substantially lower overpotentials of 133 mV and 189 mV to drive the current densities of 20 mA cm⁻² and 100 mA cm⁻², respectively, with an impressive small Tafel slope of 67.0 mV dec⁻¹. The excellent stability in acid media also guarantees the phosphorus-doped MoS₂ nanosheet catalysts as promising candidates towards hydrogen generation for practical applications.

Introduction

In the past decades, hydrogen is not only considered as one of the most promising future clean fuel, but also regarded as an ideal carrier to store electricity generated from other renewable energy sources in large scale for practical applications.^[1-3] Particularly, water electrolysis is a simple and eco-friendly approach to simultaneously generate hydrogen and oxygen in

acidic, alkaline or neutral media.^[4] The efficiency of these hydrogen and oxygen evolutions is closely related to the selection of electrode materials, and hence, it is important to develop low-cost, highly-active and stable electrocatalysts for sustainable water splitting. At the same time, although Pt is known to be a very electrocatalytic active and stable material for hydrogen evolution reaction (HER), its high cost and scarcity greatly restrict its industrial utilizations.^[5-6] In this regard, extensive efforts have been devoted to investigate highly efficient, non-noble metal electrocatalyst materials with low overpotentials and large HER current densities. Among many promising recent candidate materials, due to the large capacities of well-known catalytically active edge sites and excellent stability, two-dimensional (2D) transition metal dichalcogenides (TMDs), such as molybdenum disulfide (MoS₂) nanosheets, have attracted substantial attentions for making electrochemical hydrogen production efficient.^[7-10]

Previously, MoS₂ was researched as a potential candidate for HER because of its low free energy of hydrogen adsorption, as demonstrated by theoretical and experimental analyses.^[11] Nevertheless, the bulk MoS₂ crystal is usually performed as the poor HER electrocatalyst due to its relatively low content of active catalytic sites and small specific surface area. In this case, many methods have been employed to enhance its quantities of electrochemical active sites and surface area since then. For example, defect engineering is a newly developed method to reconstruct the surface of MoS₂ with more edges and defects, which helps to expose more active catalytic sites of unsaturated sulfur atoms.^[12-14] On the other hand, controllable disorder engineering has also been demonstrated in oxygen-incorporated MoS₂ ultrathin nanosheets for the efficient hydrogen evolution.^[13] Furthermore, interface engineering on the surface of nanostructured MoS₂ by building a heterogeneous catalyst is also well established to increase the number of surface active sites and correspondingly to improve the catalytic properties.^[15-17] Recently, doping engineering has as well been proved as a very effective technique to create active catalytic sites on MoS₂ nanosheets. Because of the earth abundance and good stability,^[18-20] several dopants, such as phosphorus (P), carbon (C) and nitrogen (N), etc., are widely employed to dope into MoS₂ nanosheets in order to lower the energy barrier of the water-dissociation step and to facilitate the desorption of the as-formed hydroxide species to accelerate HER processes.^[12-13, 21] Specifically, Liu et al. have reported that P dopants in MoS₂ matrix can significantly enhance the HER activity by not only increasing the quantity of intrinsic basal plane active sites, but also enhancing the conductivity of the materials.^[22] Moreover, it would be extremely attractive to prepare an integrated electrode of phosphorus-doped MoS₂ on a flexible substrate to afford the large current density for practical utilizations.

In this work, we demonstrate the successful synthesis of P-doped MoS₂ nanosheets on carbon cloths (CC) directly as an integrated electrode and then investigate the effect of

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phosphorus doping for the corresponding HER processes. The relationship between doping conditions and electrochemical catalytic properties is also clearly understood in order to achieve the high-performance catalysts based on MoS₂ nanosheets with the optimal P doping. Importantly, after treated with the optimized gas phase phosphidation, the obtained catalysts preserve their initial nanosheet morphology but present an apparent improvement in their catalytic activity with a low overpotential of 133 mV to drive the current density of 20 mA cm⁻², along with the excellent electrochemical stability. All these results have evidently revealed the technological potency of our P-doped MoS₂ nanosheets on CC as an integrated electrode for highly efficient hydrogen evolution.

Results and Discussion

Here, MoS₂ nanosheets directly supported on carbon cloths were prepared via a simple hydrothermal method, and their morphologies were studied by SEM. As shown in Figure 1a, the sheet-like morphology of MoS₂ is revealed with the size of hundreds of nanometers, while the inset image exhibits the uniform distribution of nanosheets on carbon cloths. Doping phosphorous element is then realized by using a low-temperature gas-phase phosphidation method, where NaH₂PO₂·H₂O is functioned as the phosphorous evaporation source with various time duration intervals (namely, 30, 60 and 90 minutes). Previously, Tour et al. reported the formation of mixture phase of MoS₂(1-x)P_x with enhanced catalytic properties for HER by thermally annealing mixtures of MoS₂ and red phosphorus at up to 1023 K but the nanosheet dimension and morphology are inevitably altered.^[23] In contrast to the work mentioned above, in this work, an inorganic salt of NaH₂PO₂·H₂O is employed as the phosphorous source to dope MoS₂ nanosheets at a much lower temperature of 573 K, resulting in the preservation of the nanosheet morphology. As displayed in Figure 1b and Supporting Information Figure S1a to S1d, the morphology of all P-doped MoS₂ nanosheets supported on CC and processed with different doping duration (i.e. 30, 60 and 90 minutes) is well preserved as compared to the as-prepared un-doped MoS₂ nanosheets (Figure 1a). In addition, the EDS spectra further confirm the existence of P dopants in MoS₂ nanosheets (Figure 1c). It is obvious that the P-doped MoS₂ nanosheets show a higher P doping content with a longer P doping duration. In specific, the doping concentration is determined to be 2.1 at%, 3.3 at% and 4.9 at% for the samples processed for 30 min, 60 min and 90 min of P doping, respectively. At the same time, small peaks of oxygen element with energy of ~ 0.55 KeV are observed in EDS spectra of all samples. The oxygen element may come from the adsorbed water molecules and surface hydroxide species when exposing to air, even after calcining in Ar. And for P-doped MoS₂, partial oxidation of phosphorus can also lead to the existence of oxygen element. The crystal structure and phase of the as-prepared samples are then studied by X-ray diffractometer (XRD). The corresponding XRD pattern exhibit the hexagonal structure of MoS₂, which perfectly agrees the crystal phase of

1T-molybdenite of MoS₂ (Supporting Information Figure 1e).^[24] Also, broad peaks at about 26 and 43 degrees can be ascribed to the carbon cloth as reported in the literature.^[25-26] More importantly, the thorough XRD characterization indicates that all the P-doped MoS₂ samples have the crystalline structure of 2H-MoS₂ (PDF# 37-1492),^[23-24] which is uniquely different from the un-doped MoS₂/CC sample. This conversion of crystalline structure from 1T phase to 2H phase is mainly related to the poor thermal stability of 1T-MoS₂ as well as the rapid transformation to thermodynamically stable 2H phase occurred during the low- temperature phosphidation process.^[24] All these findings demonstrate that our low-temperature P doping in MoS₂ nanosheets can preserve their morphology and lead to the effective phase transformation from 1T to 2H crystalline structures.

Figure 1. Morphology and composition of the as-prepared MoS₂ nanosheets and P-doped MoS₂ nanosheets directly synthesized on carbon cloths. (a, b) SEM images of MoS₂ nanosheets and P-doped MoS₂ nanosheets, (c) EDS spectra of MoS₂ nanosheets and P-doped MoS₂ nanosheets.

To shed light on the composition and microstructure of the as-prepared MoS₂ nanosheets and P-doped MoS₂ nanosheets, high-resolution transmission electron microscopy (HRTEM) and elemental mapping characterizations are then performed. As depicted in Figure 2a and 2b insets, MoS₂ nanosheets with the size of hundreds of nanometers are both observed for the un-

doped and P-doped samples, which are perfectly consistent with the results observed in SEM (Figure 1a & 1b). At the same time, the HRTEM images exhibit the clear and distinct interplanar spacings of 0.31 nm and 0.29 nm, corresponding to the (111) and (100) plane of un-doped 1T-MoS₂ (Figure 2a),^[27] and yield the interplanar spacings of 0.25 nm and 0.22 nm, being attributable to the (005) and (103) planes of P-doped 2H-MoS₂ (Figure 2b). All these confirm again the phase transformation of MoS₂ nanosheets from 1T to 2H structures induced by the P doping observed in XRD patterns.

Figure 2. Electron microscopy characterization of as-prepared MoS₂ nanosheets and P-doped MoS₂ nanosheets. (a, b) HRTEM images and the corresponding fast Fourier transform (FFT) of the representative MoS₂ nanosheet and P-doped MoS₂ nanosheet (3.3 at%), respectively. The insets show the low-resolution TEM images of the samples. Red circles indicate the region for the high-resolution imaging given in the main panels. (c, d, e) Scanning TEM image (inset) and corresponding EDS mapping of the P-doped MoS₂ nanosheet (3.3 at%), indicating the uniform distribution of Mo, S and P, accordingly.

Furthermore, one can also see that there are qualitatively lot more crystal defects existed in P-doped MoS₂ nanosheets as compared to the un-doped ones (Figure 2b). These additional crystal defects can be probably accredited to the elemental substitution of P into S sites in MoS₂ microstructures.^[28] Notably, based on the EDS mapping (Figure 2c to e), all constituents, including the P dopants, are uniformly distributed, indicating that the P atoms are successfully and homogeneously doped into MoS₂ without deteriorating the nanosheet morphology.

Apart from the morphology, crystallinity and composition, it is also important to assess the surface chemical states of all MoS₂ samples. In this case, X-ray photoelectron spectroscopy (XPS) is utilized to characterize any change in the surface chemical state before and after P doping in the MoS₂ nanosheets. As depicted in the P 2p spectra in Figure 3a, there is not any peak observed for the un-doped MoS₂ sample, while obvious peaks are found to be located at 133.4 eV for all P-doped MoS₂ samples. This peak is believed to be due to the surface oxidized phosphate species when P atoms are doped into the lattice of MoS₂.^[29–30] On the other hand, for the Mo 3d and S 2p spectra as shown in Figure 3b and c, there are a tiny peak at 225.6 eV as

well as strong peaks at 228.3 eV and 231.5 eV, corresponding to the Mo-S bond, Mo⁴⁺ species of Mo 3d_{5/2} and Mo 3d_{3/2},^[17] and another set of strong peaks at 161.2 eV and 162.3 eV for 2p_{3/2} and 2p_{1/2} orbitals of S²⁻ species in un-doped MoS₂, respectively.^[13, 28] After P doping, the spectra of Mo 3d and S 2p of MoS₂ are still similar to those of the un-doped one, except for the apparent shifts in their binding energies. Explicitly, the peaks of Mo 3d spectra are shifted to 226.0 eV, 228.9 eV and 232.0 eV correspondingly; while for S 2p spectra, the peaks are moved to 161.7 eV and 162.9 eV, respectively. These peak shifts may be related to the low-temperature annealing process, indicating that the elemental

Figure 3. Surface elemental analysis of as-prepared MoS₂ nanosheets and P-doped MoS₂ nanosheets. (a) P 2p bonding region, (b) Mo 3d bonding region, (c) S 2p bonding region.

substitution of P into S sites are occurred in MoS₂ crystals for the doping process. The similar peak shift phenomenon has also witnessed in previous literatures, in which the shifts in binding energies for substitutional doped MoS₂ is revealed.^[17] At the same time, this occurrence also suggests that annealing at 673 K may lead to the phase transition from 1T-MoS₂ to 2H-MoS₂, accompanied with the downshift of binding energy of Mo as

demonstrated by Xiang et al.^[31] Therefore, the changes observed for the surface chemical states of P-doped MoS₂ as compared with those of the un-doped MoS₂ have evidently demonstrated the interaction of P dopants and MoS₂ as a result of the low-temperature phosphidation process.

Besides, catalytic activity as well as durability of electrocatalysts of various P-doped MoS₂ and un-doped MoS₂ nanosheets are evaluated in acidic H₂SO₄ (0.5 M, pH = 0.6) electrolyte using a three-electrode system. Polarization curves of all catalysts are measured using the linear sweeping voltammetry (LSV) method at a scan rate of 5 mV/s. As shown in Figure 4a, to obtain an HER catalytic current density of 20 mA cm⁻², an overpotential of 170 mV is required for un-doped MoS₂ and an additional overpotential

reduced significantly to 156 mV, 133 mV and 152 mV for the doping (i.e. annealing) duration of 30 min (2.1 at%), 60 min (3.3 at%) and 90 min (4.9 at%), respectively, as compared with the un-doped one of 170 mV in order to reach the same current density of 20 mA cm⁻². Even for the higher current density of 100 mA cm⁻², a similar trend is still observed with the overpotential values of 257 mV, 227 mV, 189 mV and 217 mV for the un-doped, 2.1 at%, 3.3 at% and 4.9 at% P-doped MoS₂ nanosheet samples, correspondingly. Among all of these catalysts, 3.3 at% P-doped MoS₂ nanosheets (i.e. 60 min doping duration) exhibit the best electrochemical activity, although they consist of the semiconductor 2H phase, instead of the metallic 1T phase.

To evaluate their kinetic properties, Tafel equation is employed to describe the relationship between current and overpotential:

$$\eta = b \log (j/j_0)$$

where η is the overpotential (mV), b is the Tafel slope (mV/dec), j is the current density (mA cm⁻²) and j_0 is the exchange current density (mA cm⁻²).^[34] As extracted from Figure 4a, after iR correction, the Tafel slope of 3.3 at% P-doped MoS₂ (60 min doping duration) is found to be 67.0 mV/dec, which is smaller

than the ones of 2.1 at% P-doped nanosheet (77.6 mV/dec), 4.9 at% P-doped nanosheets (71.1 mV/dec), undoped nanosheet (102.9 mV/dec) and annealed control sample (138.9 mV/dec). Based on the Tafel slope without iR correction (shown in Supporting Information Figure S2), MoS₂ nanosheets treated with an optimal P doping of 60 min also show the superior electrochemical HER activity. It is obvious that an optimal P doping (i.e. 3.3 at%) is needed to enhance the number of active catalytic sites and to improve the conductivity in order to achieve the superior electrochemical HER activity of MoS₂ nanosheets directly synthesized on carbon cloths as an integrated electrode system. As shown in Supporting Information Table S1, by using the adopted simple low temperature annealing process, HER performance of the as-prepared P-MoS₂ nanosheets on CC is similar to the other researches.^[13, 17, 35-37] To further study the difference in their intrinsic properties, the electrochemical active surface area (ECSA) established from the electrochemical double-layer capacitance of the catalyst surface is as well utilized to compare the difference in catalytic active sites.^[38] Because ECSA is proportional to the electrochemical double-layer capacitance (C_{dl}) in the non-Faradaic potential region, herein, cyclic voltammogram (CV) curves with various scan rates are measured to calculate the C_{dl} values. CV curves of un-doped MoS₂ and P-doped (3.3 at%) MoS₂ nanosheets are then scanned with the rate of 10, 20, 30, 40 and 50 mV/s and compiled in Supporting Information Figure S3. The extracted C_{dl} values of un-doped MoS₂ and P-doped (3.3 at%) MoS₂ samples are found to be 7.0 and 17.6 mF cm⁻², respectively (Figure 4c), illustrating that the P doping can indeed result in more active sites for the more efficient catalytic hydrogen generation. Furthermore, the catalytic activity normalized to ECSA is also given in Supporting Information Figure S4, suggesting the better intrinsic activity of P-doped (3.3 at%) MoS₂ nanosheets, as compared with it of un-doped MoS₂.

At the same time, stability is another momentous parameter to evaluate the performance of HER electrocatalysts. The chronopotentiometry technique is adopted to examine the

Figure 4. Electrochemical properties of both MoS₂ nanosheets and P-doped MoS₂ nanosheets. (a) Polarization curves of as-synthesized MoS₂ nanosheets, P-doped MoS₂ nanosheets with various doping durations (30, 60, and 90 minutes), and simply annealed MoS₂ nanosheets in 0.5 M H₂SO₄ solution, (b) Tafel slopes derived from (a), (c) The plots of capacitive current densities as a function of scan rates for as-synthesized MoS₂ nanosheets and P-doped MoS₂ nanosheets with the doping duration of 60 minutes, (d) Polarization curves of P-doped MoS₂ nanosheets with the doping duration of 60 minutes before and after stability tests. Inset shows the stability test of P-doped MoS₂ nanosheets with the doping duration of 60 minutes and a fixed current density of 20 mA cm⁻².

of 200 mV is needed for simply annealed MoS₂ (60 min) in Ar, serving as the control sample without any P doping for the consistent study here. Based on the discussion XRD results (Supporting Formation Figure S1e), there is a crystalline phase transformation of MoS₂ from 1T to 2H structures during low-temperature phosphidation process. Since the metallic 1T phase MoS₂ nanosheets was demonstrated with the better electrocatalytic performance than the semiconductor 2H phase sample due to electrochemical oxidation of the edges of 2H phase nanosheets, leading to a dramatic reduction in their catalytic activities,^[32-33] it perfectly explains the degradation in overpotential of the annealed control sample. However, when P doping is performed along with the annealing process, the overpotential of all P-doped MoS₂ nanosheet samples are

overpotential stability with a fixed current density of 20 mA cm^{-2} . The stable overpotentials (135 mV, without iR corrections) with insignificant fluctuations are observed to maintain the current density of 20 mA cm^{-2} in acidic solutions over 10 hours for the P-doped (3.3 at%) MoS_2 nanosheets as illustrated in the set of Figure 4d. After long-term durability tests, the P-doped MoS_2 nanosheets preserve the excellent performances in activity with negligible loss of the current density, which further certifies their superior catalytic durability in acidic media. In general, the HER activity of MoS_2 nanosheets based on their exposed edges and catalytic sites would easily reach the limitation owing to the poor inter-particle (or inter-domain) electron transport for the insufficient conductivity.^[9, 12] Therefore, chemical doping is widely considered as an effective approach to improve the HER activity of their inert basal plane sites in MoS_2 as well as to increase the intrinsic electrical conductivity.^[12, 21–22] In this work, as demonstrated by XPS (Figure 3), the S constituents has been partially replaced by P atoms in the MoS_2 crystal. Evidently, this substitution would induce more active unsaturated sites and defects in MoS_2 microstructures, resulting in the better catalytic property for hydrogen generation. The increased activity may be related to the modified electronic structure of P-doped MoS_2 . A smaller band gap is observed as compared with pristine MoS_2 after doping P, resulting in the lower adsorption free energy of hydrogen, as previous literatures demonstrated.^[22, 23] However, with the increase of P content, the electrocatalytic performance of MoS_2 nanosheets (e.g. 4.9 at% P-doped sample with 90 min doping duration) becomes degraded, which may be contributed to the conducting behavior switch of MoS_2 by increasing the content of intercalated P in MoS_2 , leading in a ruined conductance during the process of hydrogen generation. Also, for the longer annealing time, the re-structure of P-doped MoS_2 may be benefited to further improve the crystallinity with less active site and defects. However, the detailed reason for electrocatalytic performance degradation of highly doped (4.9 at%) P- MoS_2 is complex and requires more thorough studies in the near future. Anyway, all these findings have clearly confirmed the favorable effect of P-doped MoS_2 nanosheets directly synthesized on carbon cloths as an attractive integrated electrode with the superior catalytic properties for hydrogen generation.

Conclusions

In summary, a facile post-growth phosphorus doping into MoS_2 nanosheets directly synthesized on carbon cloths is successfully developed by utilizing low-temperature phosphidation. Phosphorus doping is found to change the surface chemical states of MoS_2 nanosheets, increasing their surface catalytic sites and facilitating the better conductivity. The effect of different doping content and annealing durations are also investigated. The optimal phosphorus doped (3.3 at%) MoS_2 nanosheets exhibit the substantially improved catalytic activity for HER with a low overpotential of 133 mV to drive the current density of 20 mA cm^{-2} and a small Tafel slope of 67.0 mV/dec, as compared with the un-doped MoS_2 nanosheets. All these

demonstrate the technological potency of our phosphidation approach to modify MoS_2 nanosheets to improve their catalytic properties for hydrogen generation.

Experimental Section

Nanosheet synthesis

Carbon cloths were washed with 10% HCl, ethanol and distilled water with ultrasonication sequentially, and then dried in air. MoS_2 nanosheets supported on carbon cloths (MoS_2/CC) were then prepared using an as-reported hydrothermal method with some modification.^[39] In detail, a piece of carbon cloth (1 cm by 3 cm) was immersed into 15 ml of transparent solution, containing 0.5 mmol of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and 1 mmol of $\text{CS}(\text{NH}_2)_2$. Next, the mixture was sealed in a Teflon-lined autoclave and heated at 373 K for 20 hours. After cooling to room temperature, the obtained MoS_2 nanosheets supported on carbon cloths were washed with distilled water and ethanol alternatively for several times and then dried at 333 K overnight. By carefully measuring the mass of carbon cloth before and after synthesizing MoS_2 , the loading mass density is calculated to be 2.8 mg cm^{-2} .

To prepare P-doped MoS_2 nanosheets, a low-temperature phosphidation method using $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ as the phosphorous source was performed. Typically, 300 mg of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ and the obtained MoS_2/CC sample were placed in the upstream and downstream of a quartz furnace tube, respectively. The sample was then annealed at 673 K for 60 minutes with a temperature ramping of 10 K/min under the Argon (Ar) flow of 100 sccm. After cooling to room temperature with the continuous Ar purge, the P-doped MoS_2/CC catalysts were obtained. In order to study the effect of different annealing times on the catalytic property, the as-synthesized MoS_2 was treated under the identical process conditions for 30 and 90 minutes, respectively.

Materials characterization

Surface morphologies of the obtained samples were examined using scanning electron microscope (SEM, FEI Company, Oregon, USA/Philips XL30, Philips Electronics, Amsterdam, Netherlands). Crystal structures were determined by collecting XRD pattern on a Philips powder diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) and imaging with a high-resolution TEM (HRTEM, JEOL 2100F, JEOL Co., Ltd., Tokyo, Japan). Elemental mappings were then performed using an energy dispersive x-ray (EDS) detector attached to a JEOL 2100F, and the chemical composition of the samples was measured. The chemical state of the as-prepared MoS_2 and P-doped MoS_2 nanosheets were examined by X-ray photoelectron spectroscopy (ULVAC-PHI5802). For the TEM studies, the nanosheets were first suspended in ethanol solution by ultrasonication and then drop-casted onto the grid for the subsequent characterization.

Electrochemical measurement

All the electrochemical tests were performed on a Gamry G300 electrochemical workstation (Gamry Instruments, USA). A setup of three-electrode system was employed to measure the electrochemical activity and stability of P-doped MoS_2/CC , where the electrocatalysts, saturated calomel electrode (SCE) and Ti plate functioned as working electrode, reference electrode and counter electrode, respectively. The geometrical active area of P-doped MoS_2/CC was defined by the silicon rubber for immersing into electrolytes. Linear sweeping voltammetry (LSV) curves

were measured with a scan rate of 5 mV/s in 0.5 M H₂SO₄ solution (pH=0.6) for HER at room temperature. The HER stability tests were also performed using chronopotentiometry in the basic solution. The potential scale with respect to reverse hydrogen electrode (RHE) was corrected by the Nernst equation, where $E_{\text{vs RHE}} = E_{\text{vs SCE}} + 0.0592 \times \text{pH} + 0.242 \text{ V}$. The iR corrections in polarization curves were performed using the current interrupt method provided by the Gamry G300 workstation.

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

A facile low-temperature phosphidation process is developed for phosphorus doping into molybdenum disulfide (MoS_2) nanosheets directly synthesized on carbon cloths to function as an integrated electrode, in which they are capable to catalyze hydrogen evolution with the activity and stability comparable to those of state-of-the-art precious catalysts.

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Page No. – Page No.

Phosphorus doped MoS_2
nanosheets supported on carbon
cloths as efficient hydrogen
generation electrocatalysts