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Preparation of Mo-S-P electrocatalytic films by pulsed laser ablation of MoS₂/P composite target for effective hydrogen production

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Abstract. The results of structural and electrochemical studies of thin Mo-S-P films obtained by pulsed laser deposition at various conditions from a target made of mixture of MoS₂ and P powders are presented. For variation of S/P ratio and modification structure of the catalytic films, the deposition of the laser plume was conducted in vacuum, in Ar and H₂S gas. The highest electrocatalytic properties for activating the hydrogen evolution reaction in an acid solution were found for composite amorphous/nanocrystalline MoS₆P/nc-Mo films. In the chemical state of S 2p, the high binding energy dominated. The doping of the films with phosphorus increased the efficiency of the reaction compared with that of MoS_x/nc-Mo films. The analysis of the synergistic effect of phosphorus on the performance of amorphous MoS_xP_y films in H₂ evolution was carried out using the density functional theory.

1. Introduction

One of the most acute problems of hydrogen/alternative energy is the problem of obtaining hydrogen by water splitting. An important aspect of this problem is to develop and obtain sufficiently cheap and efficient catalytic materials that can be used instead of expensive platinum. Recently, a number of promising nanomaterials have emerged (such as transition metal dichalcogenides/phosphites/carbides/nitrides, graphitic carbon nitride, and MXenes etc.) which are close to platinum in terms of the efficiency of activating the reaction of hydrogen evolution (HER) [1].

Amorphous chalcogenides of transition metals, in particular MoS_x, are among the most promising (photo) electrocatalysts for hydrogen production [2]. The catalytic properties of amorphous MoS_x films largely depend on their composition (sulfur content, $x=S/Mo$), morphology, and local structure. The use of pulsed laser deposition allows us to flexibly adjust the important characteristics of these films and achieve high-quality catalytic properties in HER [3-5]. However, by now there is a certain limit to the effectiveness of electrocatalysis when using homogeneous amorphous MoS_x films. Therefore, there is a problem of finding new ways to improve the electrocatalytic properties of these films. One of the most effective methods is to implement a synergistic effect from interaction with other nanomaterials, including in a nanocomposite catalyst containing various nanophases (clusters) based on transition metal chalcogenides/phosphides [6]. The aim of the work was to study the possibility of modifying MoS_x electrocatalysts formed by pulsed laser deposition and improving their properties by forming P-containing nanophases or clusters.



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2. Materials and methods

The target for pulsed laser ablation was made by pressing molybdenum disulphide (MoS_2) and red phosphorus (P) powders. Ablation of the target was performed by Nd:YAG laser. The duration of the laser pulse was 14 ns, the radiation wavelength was 1064 nm, and the pulse energy in the pulse did not exceed 14 mJ. The conditions for ablation of the MoS_2/P target, as well as the conditions for scattering/deposition of the laser plume were chosen similar to the conditions for obtaining $\text{MoS}_{x-2+\delta}/\text{nc-Mo}$ films by the on-axis PLD method from the MoS_2 target [3]. This made it possible to compare the catalytic properties of Mo-S-P films with the properties of $\text{MoS}_{x-2+\delta}/\text{nc-Mo}$ films at the same catalyst loading, which was achieved during an ablation time of 4 min.

Mo-S-P films were deposited on glassy carbon plates at 22°C. The film deposition chamber was pumped out by a vacuum pump to a pressure of $\sim 10^{-4}$ Pa. In some cases, an inert gas (Ar) up to a pressure of 8 Pa was injected into the chamber. In another case, hydrogen sulfide (H_2S) was used as the background gas at a pressure of 36 Pa. The structure, composition, and chemical state of Mo-S-P films were studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive x-ray spectroscopy (EDS), and x-ray photoelectron spectroscopy (XPS). Electrocatalytic properties were measured in a three-electrode electrochemical cell in 0.5 M H_2SO_4 solution. Linear voltammograms (LV) were measured at a potential change rate of 2 mV/s, and cyclic voltammograms (CV) were measured at a sweep rate of 50 mV/s.

To reveal the influence of P atoms on the HER activity of Mo-S-P electrocatalyst, the density function theory (DFT) calculation was applied. All DFT calculations were performed using a Quantum ESPRESSO package. The Perdew-Burke-Ernzerhof (PBE) of the projector augmented-wave method (PAW) was used as the exchange-correlation function. Geometry optimization was carried out using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm. Kinetic energy cutoff was 60 Ry while charge density cutoff was 500 Ry. First irreducible Brillouin zone has been sampled by $4 \times 4 \times 1$ set of k-points generated through the general Monkhorst-Pack scheme. Bottom two layers were fixed, while all other layers and adsorbate were allowed to relax until the total energies are converged up to 1.0×10^{-5} and force convergence criterions were set as 0.07 eV/Å.

3. Results and discussion

Figure 1 shows the SEM image of a Mo-S-P film deposited on glass carbon in a vacuum. It can be seen that the morphology of the film is structured at the micro-and nanoscale levels. TEM studies have shown that the structural state can be described as a composite containing a nanocrystalline phase of pure Mo (nc-Mo) and an amorphous MoS_xP_y . According to EDS measurements, the composition of the films was described as $\text{MoS}_{1.2}\text{P}_{0.6}$. Comparison of this result with the XPS ($\text{MoS}_3\text{P}_{1.5}$) method indicated a relatively large contribution of the nc-Mo to the composition of the films.

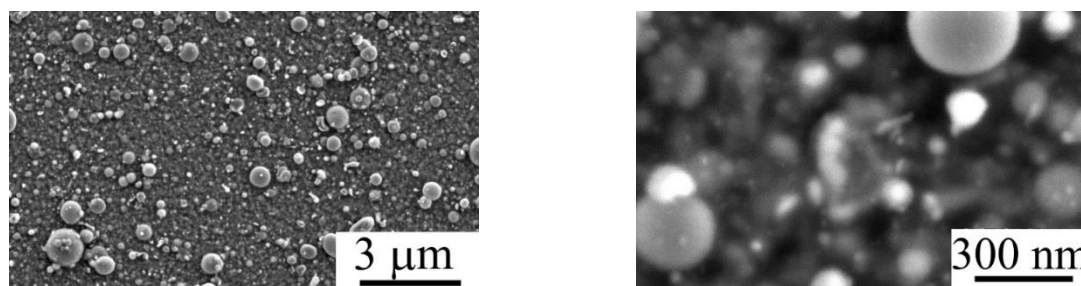


Figure 1. SEM image (at two magnifications) of a $\text{MoS}_x\text{P}_y/\text{nc-Mo}$ film obtained by PLD in vacuum.

XPS studies of $\text{MoS}_x\text{P}_y/\text{nc-Mo}$ film surfaces showed (Figure 2) that when deposited in vacuum, in Ar and in H_2S , they were described by the formulas $\text{MoS}_3\text{P}_{1.5}$, $\text{MoS}_2\text{P}_{1.5}$ and MoS_6P , respectively. It was assumed that MoS_xP_y films completely shielded the signal from nc-Mo. The oxygen concentration reached 10 at.%. The Mo atoms were mostly in the Mo^{4+} state, which is typical for bonds with S. The

S atoms occupies several local states characteristic of amorphous sulfides consisting of $\text{Mo}_3\text{-S}$ clusters. When the S concentration increased, the relative contribution of the doublet with higher binding energy grows. This doublet is typical for bridging and apical S ligands. For the chemical state of P, it was possible to identify two states corresponding to bonding with S and O [7,8]. Probably, on the surface of the films, phosphorus interacted most effectively with air. For the surface, the Mo^{6+} state appeared due to Mo-S-O compounds formation. In the P 2p XPS spectrum at least three phosphorus P 2p_{3/2} components were observed at 134.9, 132.8 and 131.7 eV. The P 2p_{3/2} peak at the high binding energy of 134.9 eV attributable to the phosphorus compounds oxidized by oxygen impurities.

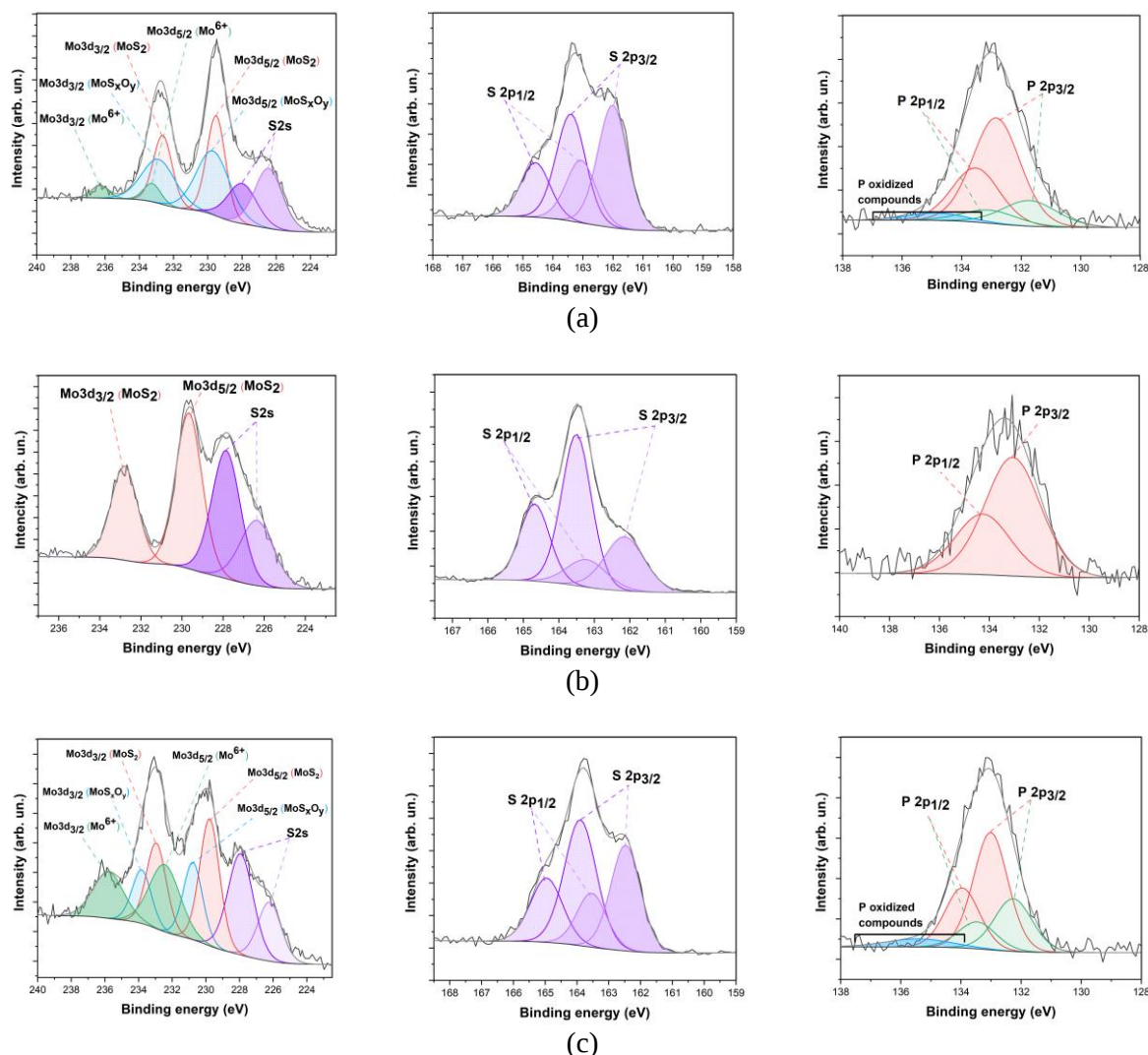


Figure 2. XPS spectra of Mo, S, and P in MoS_xP_y films which were obtained at room temperature by PLD method in (a) vacuum; (b) Ar and (c) H_2S .

LV curves (Figure 3) indicated that the HER efficiency was the highest for the films obtained in H_2S , and it was lowest for vacuum-deposited films. CV measurements indicated a correlation between the efficiency of HER and the surface density of the catalytically active sites for these films. A comparison of U_{10} potential measurements (this potential provides the current density $j=10 \text{ mA/cm}^2$) for $\text{MoS}_x\text{P}_y/\text{nc-Mo}$ films and $\text{MoS}_x/\text{nc-Mo}$ films showed that the P doping reduced the U_{10} by more than 30 mV.

To investigate the influence of P on the HER activity of MoS_xP_y films, several model structures consisting of MoS_x and $\text{MoS}_x(\text{P})$ clusters were analyzed with DFT (Figure 4). In $\text{MoS}_x(\text{P})$ clusters, some S atoms were replaced by P atoms. The MoS_x clusters (Mo_3S_{13}) with the highest content of S atoms were selected. The change of Gibbs free energy for hydrogen adsorption was calculated using standard relation $\Delta G = \Delta E_H + \Delta E_{\text{ZPE}} - T\Delta S_H$ where ΔE_{ZPE} is the zero-point energy difference between the adsorbed state of the system and the gas phase state, and ΔS_H is the entropy difference between the adsorbed state of the system and the gas phase standard state. A cubic cell with parameters $12.28 \text{ \AA} \times 9.2 \text{ \AA} \times 17 \text{ \AA}$ was used. In the process of geometry optimization, the atomic position of the lower layers was fixed. The calculated free-energy changes during HER which proceeded by the Volmer–Heyrovsky reaction are shown in the energy diagram in Figure 5.

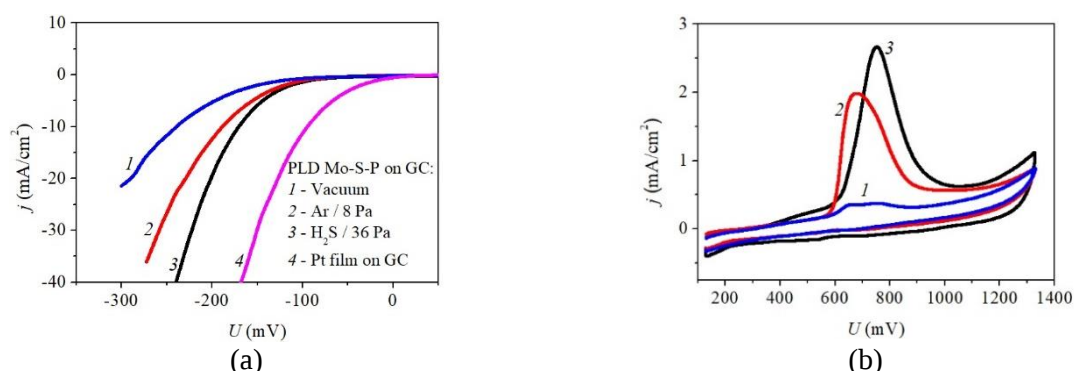


Figure 3. (a) LV and (b) CV curves for different MoS_xP_y films. LV curve for Pt film obtained by PLD on GC substrate is shown for comparison. The potential is measured relative RHE.

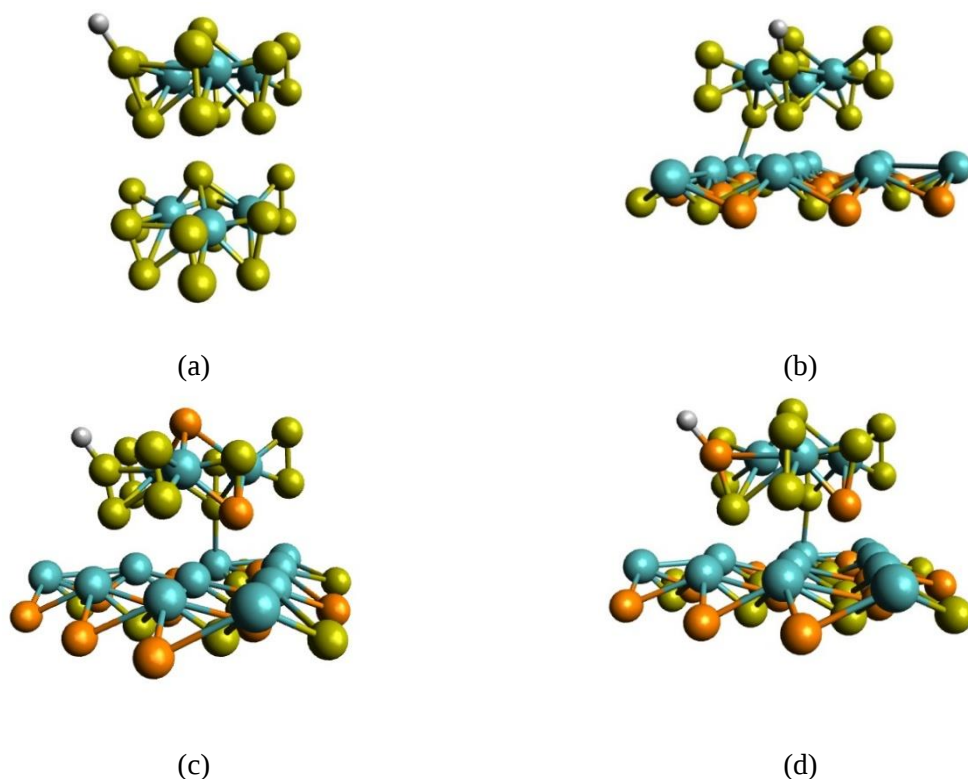


Figure 4. Local structures of simulated clusters: (a) $\text{Mo}_3\text{S}_{13}/\text{Mo}_3\text{S}_{13}$; (b) $\text{Mo}_3\text{S}_{13}/\text{MoS}(\text{P})$; (c) $\text{Mo}_3\text{S}(\text{P})_{13}/\text{MoS}(\text{P})$ with hydrogen on S; (d) $\text{Mo}_3\text{S}(\text{P})_{13}/\text{MoS}(\text{P})$ with hydrogen on P. Color scheme: Mo: light blue; S: yellow; P: orange; hydrogen: gray. One period of crystal structure is shown.

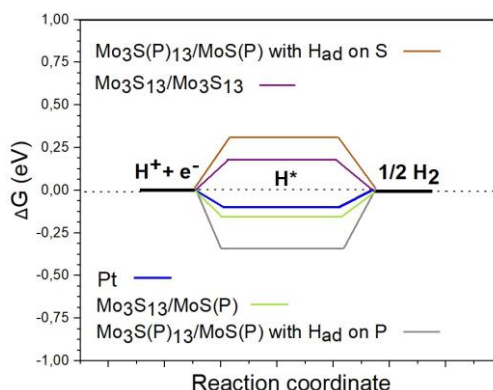


Figure 5. Calculated energy diagram of HER process for different nano-catalysts: $\text{Mo}_3\text{S}_{13}/\text{Mo}_3\text{S}_{13}$; $\text{Mo}_3\text{S}_{13}/\text{MoS(P)}$ with hydrogen on P; $\text{Mo}_3\text{S(P)}_{13}/\text{MoS(P)}$ with hydrogen on S; $\text{Mo}_3\text{S(P)}_{13}/\text{MoS(P)}$.

DFT calculations showed the following. The incorporation of P atoms into Mo_3S_{13} clusters could not cause a noticeable improvement in the catalytic properties of the MoS_xP_y films. When comparing the P-containing Mo_3S_{13} -based structures (see Figures 4 (c) and (d)), the location of the adsorbed hydrogen atom (S or P atoms) did not significantly influence on the value of ΔG . An improvement of catalytic properties of the MoS_xP_y films (due to a decrease of the ΔG value) could arise as a result of the synergistic interaction of Mo_3S_{13} and $\text{Mo}_3\text{S(P)}_{13}$ clusters (Figures 4 (a) and (b)). In this case, the HER reaction proceeds on the active site (sulfur atom) localized on the Mo_3S_{13} cluster. But its effectiveness increases due to the interaction of this cluster with the $\text{Mo}_3\text{S(P)}_{13}$ cluster.

4. Conclusion

Using of pulsed laser ablation allowed the formation of a nanostructured $\text{MoS}_x\text{P}_y/\text{nc-Mo}$ films, which significantly increased the currents caused by the evolution of H_2 compared to that for the $\text{MoS}_x/\text{nc-Mo}$ films. Adding phosphorus to the target affected the S/Mo ratio in the film, significantly reducing it. To increase this ratio, the reactive PLD in H_2S was used. The composition of the films possessing the best electrocatalytic performance in HER was described by the formula MoS_6P . The improvement of catalytic properties of these films could be caused by the synergistic interaction of Mo_3S_{13} and $\text{Mo}_3\text{S(P)}_{13}$ clusters.

Acknowledgments

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