Activation of electrocatalytic properties of a-C films by doping with MoSe$_x$ clusters

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Abstract. Nanocomposite a-C(Mo/MoSe$_x$) thin films containing amorphous carbon matrix a-C, nano-Mo and MoSe$_{x} \geq 2$ clusters were obtained by pulsed laser co-deposition of carbon and MoSe$_2$. The deposition was carried out at room temperature onto a graphite substrate. Atomic content of the MoSe$_{x} \geq 2$ phase did not exceed 25%. The use of a buffer gas at a pressure of 10 Pa allowed to obtain the maximum Se/Mo ratio in the films and to increase the concentration of sp$^2$-hybridized C atoms for high conductivity realization. The formation of MoSe$_{x} \geq 2$ cluster inclusions was the essential factor for activation of hydrogen evolution reaction (HER) in 0.5 M H$_2$SO$_4$ aqueous solution. These clusters also promoted cathodic deposition of Pt nanoparticles on the surface of a-C(Mo/MoSe$_x$) in a H$_2$SO$_4$/KCl solution when a Pt anode was used as a source of Pt. Hybrid Pt/a-C(Mo/MoSe$_x$) thin-film coatings with a low Pt loading (~6 µg/cm$^2$) exhibit excellent HER property, which noticeably exceeds that of relatively thick Pt coating prepared on a graphite substrate by pulsed laser deposition.

1. Introduction

Theoretical and experimental investigation results have indicated that the edge sites of the sandwich-type structure of transition metal dichalcogenides (TMDs), particularly molybdenum/tungsten disulphides/diselenides (Mo/W)(S/Se)$_2$, are catalytically active for hydrogen evolution reaction (HER) (e.g., Jaramillo et al. [1], Lu et al. [2]). The studies have shown that the exchange current density of TMDs nanocrystals is proportional to the length of the edge sites but not to the basal areas in truncated hexagons. However, Morales-Guio et al. [3] and Vrubel et al. [4] revealed that the increase in catalytic activity is possible for amorphous TMDs nanoparticles if they are used in a hybrid catalyst system with conductive carbon particles. Because TMD are semiconductors, the low conductivity of TMDs-based catalysts may limit their catalytic performance. Coupling TMD nanostructures with a highly conductive substrate should alleviate this problem.

The value of chalcogen/metal ratio ($x$) is another essential factor that can influence the HER activity of amorphous TMDs. Klein et al. [5] have shown that the excess of chalcogen atom concentration over the stoichiometric one ($x > 2$) decreases the electron transport resistance in these materials. Merki et al. [6] and Saadi et al. [7] prepared and studied TMDs films enriched with S or Se. The amorphous MoS$_3$ and MoSe$_3$ films was observed to become catalytically active due to cathodic
treatment in an acid solution. Merki et al. [6] suspect that prepared films may have specific unsaturated sites thanks to their amorphous nature.

To produce nanoparticles, thin films, and coatings based on TMDs, different methods of chemical synthesis are widely used. Various precursors with a wide spectrum of chemical composition and properties are required for TMDs preparation. As a rule, the used chemical procedures are not environmentally friendly methods. The production of hybrid TMDs-containing films with a specific structure by physical vapor deposition methods including pulsed laser deposition appears to be an intractable problem. This work aimed to investigate the adjustability of structure, chemical composition and catalytic properties of thin films based on molybdenum selenide and carbon, which were obtained using the method of pulsed laser co-deposition from MoSe₂ and graphite targets.

2. Experimental details
An electro-optically Q-switched Nd:yttrium-aluminium-garnet laser (wavelength 1.06 µm) was used with a pulse duration of 15 ns, a repetition rate of 25 Hz, and a pulse energy of 30 mJ. The fluence in the laser spot was ~8 J/cm². A laser beam was rapidly transferred from one target to another, so that the amount of deposited material in one cycle of irradiation of the target did not exceed one monolayer. For the graphite target, the total irradiation time was three times more than that for the MoSe₂ target. The chamber with targets and substrates was evacuated to a residual pressure below 10⁻⁴ Pa, and then argon (Ar) was introduced into the chamber to a pressure of 10 Pa. The laser-initiated plume was directed along the normal toward the substrate surface.

Deposition of the films was carried out on the substrates at room temperature. Mechanically polished graphite and NaCl substrates were placed at 4 cm from the target. The film thickness was not greater than 70 nm. The obtained thin-film coatings were examined by the methods of scanning electron microscopy (SEM) using secondary electrons (SE) and back scattered electrons (BSE), energy dispersive X-ray spectroscopy (EDS), high resolution transmission electron microscopy and microdiffraction (HRTEM/MD), micro-Raman spectroscopy (MRS), and X-ray photoelectron spectroscopy (XPS).

The catalytic activity of thin-film coating was investigated by the electrochemical method at room temperature with the use of a traditional three-electrode electrochemical cell. Pure 0.5 M H₂SO₄ solution and mixture of this solution with low content of KCl were used as aqueous mediums for the electrochemical studies. The cathodic polarization curves were measured at a slow change in the voltage (1.5 mV/s). The potential was measured relative to the standard hydrogen electrode. Platinum foil was used as reference electrode. The catalytic activity of the prepared films was compared to the activity of a Pt coating produced on the graphite by pulsed laser deposition. The thickness of the Pt coating on the graphite electrode was about 80 nm.

3. Results and discussions
Figure 1 shows HRTEM and MD images that were obtained for the film prepared by co-deposition of MoSe₂ and carbon on NaCl substrate. This film was redeposited on metal grids in water and then placed in the column of the electron microscope.

Diffuse-broadened reflections on the MD and TEM contrast consisting of light and dark dots indicate an amorphous structure of the film matrix. A dark nanoparticle with a round shape corresponds to elemental molybdenum. Monocrystalline structure of this Mo nanoparticle results in a striped HRTEM image of (110) atomic planes. Romanov et al. [8] revealed that Mo nanoparticles could be formed during pulsed laser ablation of the MoSe₂ target. Grigoriev et al. [9] have shown that the Mo nanoparticles facilitate the HER activity of MoSe₂ films due to structure modification.

XPS spectra that were measured on the surface of the prepared film are shown in Figure 2. Model spectra for various chemical bonds in the film were constructed using characteristic XPS data that were obtained by Saadi et al. [7] for chemically synthesized MoSe₂ films.

Three sets of doublet peaks for Mo 3d are observed in Figure 2. The first doublet (binding energy for Mo3d₅/₂ is about 232.5 eV) is characteristic of MoO₃. The second doublet (signal for Mo 3d₇/₂ at
231.6 eV) was located in a region typically associated with Mo$^{6+}$. The third doublet (signal for Mo 3d$_{5/2}$ at 228.4 eV) could be due to Mo$^{4+}$ in MoSe$_{x}$ compound. The single peak at 230 eV is characteristic of Se 3s. The Se 3d region has two sets of 3d doublets: the higher-energy doublet that can be ascribed to Se$^{0}$ and the lower-energy doublet that can be ascribed to Se$^{2-}$. It should be noted that for amorphous MoS$_{x}$ films, S 3d doublet with high binding energy may be attributed to bridging and/or apical Sulphur atoms. Ting et al. [10] revealed that MoS$_{x}$ films with higher population of these active S sites will ultimately result in a more efficacious HER catalyst.

Deconvolution of C 1s spectrum allowed to reveal some different chemical states of carbon atoms. The main signal at 284.3 eV can be ascribed to C atoms in the film matrix that have predominantly sp$^{2}$ configuration of C-C bonds. Another intensive signal at 284.8 eV can be arise due to contamination of the film surface with very thin layer containing C-H compounds. The lines at 281.6 and 288.2 corresponded to different C-O bonds on the surface and in the bulk of the film. Any signal which could be attributed to C-Mo bonds (binding energy is about 282.2 eV) was not observed in the C 1s spectrum of the prepared film. Concentration of MoSe$_{x}$ phase in the film did not exceed 25 at.%. Thus TEM, MD and XPS studies have shown that pulsed laser co-deposition of MoSe$_{2}$ and carbon results in the formation of amorphous films that contain the inclusions of nano-Mo and clustered MoSe$_{x-2}$/MoSe$_{x-3}$ phases. MRS studies have shown that the MoSe$_{x}$ inclusions have not structural ordering and that the amorphous carbon matrix (a-C) is graphitic to a high extent (Figure 3).

Figure 4 shows the results of polarization curves measurements for graphite substrate before and after deposition of a-C(Mo/MoSe$_{x}$), Pt/a-C(MoSe$_{x}$) and Pt thin-film coatings. The pulsed laser deposition of pure a-C film on the graphite has not changed the electrochemical properties of the graphite cathode. Covering of the graphite substrate with the a-C(Mo/MoSe$_{x}$) film caused the decrease of HER overpotential from ~330 to ~250 mV (to produce a current density of -10 mA/cm$^{2}$). The Tafel slope of a-C(Mo/MoSe$_{x}$) film was determined to be about 86 mV/dec with an exchange current density of ~10$^{-5}$ A/cm$^{2}$. The a-C(Mo/MoSe$_{x}$) catalyst exhibits rather good HER property, which is comparable to that of the MoSe$_{3}$ catalyst which was chemically synthesized by Saadi et al. [7].
Figure 2. XPS spectra of Mo3d, Se3d, and C1s on the surface of the film prepared by pulsed laser co-deposition from the MoSe₂ and graphite targets in the buffer Ar gas at a pressure of 10 Pa. Doublets for different chemical states of Se 3d are presented as single colored peaks.

Figure 3. MRS spectra of graphite substrate measured before and after deposition of a-C(Mo/MoSeₓ) film. Only a broad line was observed in a region of 200 – 300 cm⁻¹ typically associated with Mo-Se and Se-Se compounds. The spectrum of a-C matrix in a region of 1000 – 1600 cm⁻¹ was typical of the amorphous carbon film possessing a high concentration of sp²-hybridized C atoms.
To form Pt/a-C(Mo/MoSe$_x$) film, the graphite substrate with a-C(Mo/MoSe$_x$) film was undergone the cathodic treatment in Cl-containing sulfuric acid solution at a potential of -350 mV. Ions of Cl interacted with Pt anode and the formed Pt-containing molecules could migrate to cathode for deposition on its surface. The MoSe$_x$ clusters have activated the processes of Pt nanoparticle growth on the surface of a-C(Mo/MoSe$_x$) film (Figure 5). The used time of cathodic treatment allowed to prepare catalytically effective Pt/a-C(Mo/MoSe$_x$) thin-film coating with lower Pt loading.

Figure 5 shows the results of SEM study of the surface of the bare graphite electrode and graphite electrode with deposited thin-film coatings of Pt/a-C(Mo/MoSe$_x$). The graphite consisted of plate microcrystals which formed relatively loose packing of the matrix and provided the large effective surface of the electrode. Pulsed laser ablation of the MoSe$_2$ and carbon in the Ar buffer gas provided conformal deposition of a-C(Mo/MoSe$_x$) film on graphite microcrystals with round-shaped nanoparticles formation. The size of nanoparticles was 50 – 100 nm.

**Figure 4.** Polarization curves for the bare graphite substrate and the graphite substrate covered with a-C(Mo/MoSe$_x$), Pt/a-C(Mo/MoSe$_x$) and Pt thin-film coatings.

**Figure 5.** SE (a,b) and BSE (c) SEM images of the graphite substrate before (a) and after the Pt/a-C(Mo/MoSe$_x$) deposition (b, c).

BSE SEM (Figure 5c) and EDS (Figure 6) studies revealed that Pt nanoparticles have grown on the enriched with Se/Mo areas of a-C(Mo/MoSe$_x$) film. The Pt nanoparticle were quite evenly distributed on the surface without the formation of large conglomerates and the size of Pt nanoparticles was ~5 nm. The HER property of the hybrid Pt/a-C(Mo/MoSe$_x$) catalyst with a Pt loading of ~6 µg/cm$^2$ noticeably superior that of Pt/graphite catalyst with a Pt loading of 170 µg/cm$^2$ (Figure 4).
4. Conclusions
Pulsed laser co-deposition of carbon and MoSe$_2$ at room temperature resulted in the formation of nanostuctured thin-film coating which includes the amorphous a-C matrix with a high sp$^2$ content, the nanocrystalline Mo and the disordered MoSe$_{<2}$ clusters. The Mo nanoparticle deposition caused an increase of the surface roughness. The MoSe$_{<2}$ clusters formation is very important for providing a large amount of active sites. The formation of the active sites results in both a significant H$_2$ evolution and an effective cathodic deposition of nano-Pt onto the a-C(Mo/MoSe$_x$) film. Even with a low Pt loading, the hybrid Pt/a-C(Mo/MoSe$_x$)/graphite catalyst exhibits excellent HER properties superior to those of the pure Pt coatings deposited by pulsed laser ablation onto the GC substrate.

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