Comparative studies of photoactivated H$_2$ evolution for nano-needle WO$_3$ films with crystalline 2H-WS$_2$ and amorphous a-MoS$_x$ co-catalysts

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Abstract. (Photo)electrocatalytic properties of nanostructured WO$_3$ films used for H$_2$ evolution reaction (HER) were modified by forming hybrid structures containing a crystalline 2H-WS$_2$ and an amorphous a-MoS$_x$ phases. For this, respectively, thermochemical treatment of metal oxide films in H$_2$S gas and reaction pulsed laser deposition of molybdenum in H$_2$S were applied. The functional characteristics of the hybrid structures were studied in a three-electrode electrochemical cell in an acid solution under intermittent illumination with a Xe lamp. a-MoS$_x$ film deposition caused a more significant improvement in the HER activity of MoS$_x$/WO$_3$ structure compared to that of WS$_2$/WO$_3$ structure. However, WS$_2$/WO$_3$ structures were superior to MoS$_x$/WO$_3$ structures in the efficiency of the photoactivated HER. The factors that could influence the (photo)electrocatalytic behaviour of the created structures were analysed.

1. Introduction
Obtaining and studying new nanomaterials for the formation of hybrid- and hetero-structures that provide effective photo-activated splitting of water to produce hydrogen and oxygen is a principal task of alternative energy [1]. Porous WO$_3$ is a transition metal oxide known for being an n-type semiconductor with a wide and stable tunable bandgap. Porous architectures tend to have larger specific surface areas and abundantly accessible channels, compared to their nonporous counterparts. They also allow a larger surface to volume ratio [2]. Preliminary studies have shown that porous tungsten oxide with various architectures can be obtained by pulsed laser deposition (PLD) [3-5]. The formed films showed quite good functional characteristics in several applications, including the detection of hydrogen and the production of oxygen by water splitting [6,7]. However, (photo)electrocatalytic properties of these films in the hydrogen evolution reaction (HER) were unsatisfactory.

One of the ways to use the high photoactivity of the porous WO$_3$ films in photo-HER is to create hybrid/heterostructures with a cocatalyst film, which should increase the catalytic activity of the surface and facilitate the separation of nonequilibrium charge carriers (electrons and holes) generated by light in the catalyst. Two methods can be proposed for modifying a porous WO$_3$ film to increase the photoelectrocatalytic activity of WO$_3$-based photocathode. One way is to form a thin WS$_2$ film of by thermochemical sulfurization. In this case, the functional properties of the photocathode will be determined by the characteristics of the heterostructure WS$_2$/WO$_3$ [8]. The second method consists in deposition of a thin film of catalytically active material, for example, molybdenum sulfide that will
cause the formation of heterostructure MoS$_2$/WO$_3$ [3,7]. The aim of the work was to carry out comparative studies of the photoelectrocatalytic properties of WS$_2$/WO$_3$ and MoS$_2$/WO$_3$ photocathodes in HER and to study the factors that can have important effects on their functional properties. For the MoS$_2$ film formation, the PLD method was used that makes it possible to flexibly control the thickness and chemical composition of the MoS$_2$ film with an amorphous structure [9,10].

2. Materials and Methods
The WS$_2$/WO$_3$ structure was obtained by combining reactive PLD and thermal sulfurization processes. The WO$_3$ films on FTO (SnO$_2$:F) substrates were prepared by reactive according to the standard technique. The radiation of the Solar LQ529 laser was directed at an angle of 45° to the surface of a W target installed in a vacuum chamber. The substrate was installed along the normal to the direction of expansion of the laser erosion plume and parallel to the target surface. The distance from the substrate to the target was 4 cm. To obtain nano-needle WO$_3$ films, the following reactive PLD modes were selected. The laser radiation wavelength was 1064 nm, the radiation pulse duration was 15 ns, the pulse repetition rate was 20 Hz, the radiation energy per pulse was ~40 mJ, and the laser fluence on the target was ~10 J/cm$^2$. After installing the target W and the substrate, the chamber was evacuated to a residual pressure of 40 Pa, and the substrate was heated to 450°C. After the WO$_3$ film deposition, the sample was cooled to 350°C and H$_2$S was introduced into the chamber to a pressure of 48 Pa. The sulfurization time for the WO$_3$ films was 7 min.

The MoS$_2$/WO$_3$ structure was obtained by reactive PLD. After the WO$_3$ film preparation by reactive PLD, the sample was cooled to room temperature under vacuum conditions and then H$_2$S was introduced into the chamber to a pressure of 20 Pa. MoS$_2$ film was deposited by ablating Mo target for 3 min. The same laser was used for Mo target ablation. The results of a comprehensive study of MoS$_2$ films formed by the reactive PLD are presented in previously published works [7,10].

The surface morphologies of the prepared films and heterostructures were examined by scanning electron microscopy (SEM). The structure of the films was investigated by X-ray diffraction (XRD) and micro-Raman spectroscopy (MRS), using a 632.8-nm (He-Ne) laser. Band gaps (E$_g$) in the prepared films were measured optically by processing absorption spectra. The XPS measurements were used to determine the chemical state of the films and the mutual arrangement of valence bands in the heterostructures. To study the photoelectrocatalytical properties of the prepared photocathodes, the samples were irradiated with a Xe lamp in an 0.5 M H$_2$SO$_4$ aqueous solution in a three-electrodes electrochemical cell. The light intensity was 100 mW/cm$^2$. The polarization curves were measured using linear sweep voltammetry (LSV) with a change in the applied potential from -300 to 600 mV and a scan rate of 2 mV/s. When measuring LSV curves, the light source was turned on and off.

To reveal the influence of interfacial interaction in the obtained heterostructures on the HER activity of photocathodes we performed DFT (Density Functional Theory) simulation of several simplified atomic structures using the Quantum ESPRESSO package. The details of the simulation and the parameters used for the calculations of the change of Gibbs free energy (ΔG$_{\text{H}_2}$) for hydrogen adsorption on the active sites of MoS$_{2\text{c}}$ and WO$_3$-based HER catalysts can be found in [3,11].

3. Results and Discussions
SEM images of the WO$_3$ films prepared by reactive PLD and then subjected to sulfurization are shown in figure 1a and figure 1b, respectively. First, a film consisting of loosely packed crystals in the form of flattened needles (rods) was grown. The characteristic length of the crystals was 500 nm, their transverse size did not exceed 50 nm, and they were oriented in an arbitrary manner relative to the substrate surface. According to XRD studies (results not presented), the nanoneedles had a crystalline structure, and they could contain both monoclinic and triclinic WO$_3$ phases. Raman studies have confirmed the result of the formation of tungsten trioxide, which is quite perfect in terms of atomic packing (insert in figure 1a). In the Raman spectrum of crystalline WO$_3$, the most intense/narrow peaks were located at frequencies of 271.8, 722.3, and 806.7 cm$^{-1}$. 
Figure 1. SEM images and Raman spectra (in inserts) of WO₃ film a) before and b) after sulfurization in H₂S gas.

Figure 1b shows that sulfurization of WO₃ film caused a noticeable change in the size of structural elements in the film. The effect of shortening of nano-needles is most clearly revealed. As a result of thermochemical treatment, a film which consisted of more densely packed nanocrystals up to 100 nm in size was formed. Raman studies have shown that after sulfurization of the WO₃ film, along with the WO₃ phase, the 2H-WS₂ phase was formed (insert in figure 1b). This was indicated by the appearance of new lines in the Raman spectrum. The most intense new peaks in the spectra appeared at 350 cm⁻¹ (superposition of peaks from vibrational modes 2LA (M) and E₂') and at 416 cm⁻¹ (vibrational mode A₁'').

Raman and XPS studies of the MoSₓ film deposited on the WO₃ film by reactive PLD indicated the formation of amorphous a-MoSₓ film with S/Mo ratio x~4 (results not presented). This film consisted of Mo₃S₁₃ and/or Mo₃S₁₂ clusters. The deposition of a-MoSₓ film did not change the morphology of WO₃ film.

Figure 2 shows the results of electrochemical studies for the WS₂/WO₃ and MoSₓ/WO₃ heterojunction systems under light chopping. The MoSₓ/WO₃ sample provided the highest efficiency in activating the HER at negative potentials without illumination. The overvoltage of HER for this sample (at current density of 1 mA/cm²) was 100 mV less than that for the WS₂/WO₃ sample. However, the photoactivated process of hydrogen evolution proceeded more efficiently for the WS₂/WO₃ sample. At positive voltages from 0 to 600 mV, the photocurrent density for the WS₂/WO₃ sample was 2 – 3 times higher than that for the MoSₓ/WO₃ sample.

Figure 2. LSV curves for WS₂/WO₃ and MoSₓ/WO₃ heterojunction systems measured under light chopping.
DFT calculations of free energy change upon hydrogen adsorption were carried out for Mo$_3$S$_{13}$/WO$_3$ and WS$_2$/WO$_3$ combinations of clusters (figure 3). For the Mo$_3$S$_{13}$ cluster, the H atom was attached to bridging or terminal S ligands. A basic plane of the WS$_2$ cluster was oriented parallel to the WO$_3$ cluster surface. The WO$_3$ phases with monoclinic and triclinic crystalline lattice were analyzed. The DFT results correlated well with the results of electrochemical studies. The lowest value of $\Delta G$ was found for terminal S ligands in Mo$_3$S$_{13}$ cluster located on the surface of WO$_3$ cluster.

![Figure 3](image)

**Figure 3.** Results of DFT calculation of free energy change due to adsorption of H atoms to different S ligands (bridging/terminal) in Mo$_3$S$_{13}$ and WS$_2$ clusters attached to WO$_3$ (monoclinic/triclinic).

Figure 4 shows the energy band diagrams for the WS$_2$/WO$_3$ and MoS$_x$/WO$_3$ heterojunction systems which were constructed using the results of optical properties studies of the created films and their XPS analysis. The XPS studies allowed to determine the VBO (valence band offset) and CBO (conductive band offset) characteristics of the heterojunction systems.

![Figure 4](image)

**Figure 4.** Energy band alignment in MoS$_x$/WO$_3$ (left) and WS$_2$/WO$_3$ (right) heterostructures.

The diagrams of the energy bands for the two heterosystems are in many respects similar. They indicate that in both heterojunction systems the photoactivated HER should proceed according to Z-scheme. It should be assumed that difference in photoactivated HER efficiency for these samples which was experimentally found could be due to features of the generation and transport of nonequilibrium...
charge carriers in the bulk of the sample. One of the reasons is the relatively reduced efficiency of light-initiated generation of nonequilibrium carriers in the MoS$_x$ film. It is also possible the influence of MoS$_x$/WO$_3$ interface on the photoactivated HER process. The interface could hinder the processes of recombination of electrons from the WO$_3$ film and holes from the MoS$_x$ film that resulted in the recombination of electrons and holes in the bulk of MoS$_x$ and WO$_3$ films. During reactive PLD of MoS$_x$ film, the surface of WO$_3$ film is exposed to ultraviolet irradiation and ion bombardment. UV irradiation in a reactive gas environment could change the chemical composition of the surface [12]. Ion bombardment could both change the chemical composition and cause the formation of defects in the surface layer of the crystalline WO$_3$ film [13]. During thermochemical treatment of WO$_3$ film in hydrogen sulfide, the interface structure is formed under specific conditions and, therefore, will differ from that in the MoS$_x$/WO$_3$ sample. To elucidate all the possible reasons of the different behavior in photoelectrochemical HER for the WS$_2$/WO$_3$ and MoS$_x$/WO$_3$ heterojunction systems, additional studies are required.

4. Conclusion
The intrinsic catalytic activity of thin amorphous a-MoS$_x$ and crystalline 2H-WS$_2$ co-catalytic films has a significant effect on the electrochemical process of HER in the hybrid WO$_3$-based cathodes. However, a decrease in the resistance to current transport in the electrocatalytic process does not always provide a high efficiency of the photoactivated HER reaction. It is necessary to ensure the high efficiency of photogeneration of nonequilibrium carriers (electrons and holes) in the co-catalytic film, the separation of electrons and holes in this film, and adequate transport of these charged particle through the interface in heterostructure.

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