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# Photoactive TiO<sub>2</sub>/MoS<sub>2</sub> electrode with prolonged stability

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## ABSTRACT

TiO<sub>2</sub>/MoS<sub>2</sub> composites are synthesized by means of a novel and environmentally friendly electrodeposition technique. MoS<sub>2</sub> is prepared via the hydrothermal process from Na<sub>2</sub>MoO<sub>4</sub> and CH<sub>4</sub>N<sub>2</sub>S with the use of different surfactants such as Pluronic, SDBS, CTAB, and PEG-1000. TiO<sub>2</sub> in the form of nanotubes grows on Ti foil via anodization. The physico-chemical properties of the obtained materials are studied by means of XRD, Raman spectroscopy, and SEM. MoS<sub>2</sub> forms a layered structure, while TiO<sub>2</sub> features well-defined and highly crystallized nanotubes. The deposition of MoS<sub>2</sub> on the surface of TiO<sub>2</sub> via the electrochemical method is conducted in a three-electrode cell with the use of a water-based suspension of MoS<sub>2</sub> at a pH close to neutral. The morphology and photoelectrochemical properties of the MoS<sub>2</sub>-modified TiO<sub>2</sub> photoanodes are studied. The stability of TiO<sub>2</sub>/MoS<sub>2</sub> composites is successfully investigated by repeating photocurrent-time characteristics in the period of 8 months. A shift in flat-band potential accompanied by increased photocurrent and hydrogen production indicate a type II heterostructure.

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## Introduction

The photoelectrolysis of water into hydrogen and oxygen upon the absorption of light is considered an important and non-conventional future energy source [1]. This process proceeds in photoelectrochemical cells (PECs), composed of an aqueous electrolyte and two electrodes. At least one electrode (most often the anode) should consist of a semiconductor material. In order for this process to find practical application, it is necessary to find an electrode material that provides highly efficient energy conversion. The solar energy conversion efficiency of PECs is strongly dependent on specific processes in the photoactive anode, including light absorption, charge separation and migration, and competition between charge recombination on the surface and in the bulk of

photoanodes [2,3]. Titanium dioxide (TiO<sub>2</sub>) was the first material applied as a photoanode in photoelectrochemical solar cells, and it still serves as a reference wide-band-gap semiconductor [4]. Several ways of improving the photo-response of TiO<sub>2</sub> have been proposed, including doping, precipitating with metal particles, crystal growth design, and heterostructuring; however, these attempts have met with limited success as far as efficiency is concerned [2]. The functionalization of TiO<sub>2</sub> by means of graphene-like materials for hydrogen generation is a very promising strategy of enhancing the efficiency of the photodecomposition of water. Bulk and mono- or few-layer MoS<sub>2</sub> forms have found application in electronics and optoelectronics, sensing, energy storage, and catalysis. Its unique properties become apparent when bulk MoS<sub>2</sub> is thinned down to a single layer. A transition from an indirect band gap (1.3 eV) in bulk MoS<sub>2</sub> to a direct band

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gap (1.8 eV) in MoS<sub>2</sub> monolayers can be observed; this phenomenon makes this compound promising for photoelectrochemical and photocatalytic applications [5]. Photoelectrodes in the form of composites can provide new functionality [2,3]: 1) extend the light absorption spectral range, 2) enhance charge separation and suppress charge recombination, 3) protect the narrow-band-gap semiconductor from photocorrosion. Based on the band positions and band gaps of the components of TiO<sub>2</sub>/MoS<sub>2</sub>, it has been suggested that they constitute type I heterojunctions [2]. In type I band alignment, the valence band (VB) of TiO<sub>2</sub> is lower than that of MoS<sub>2</sub> and the conduction band (CB) of titanium dioxide is higher than that of MoS<sub>2</sub>. For this type of heterostructure, both photogenerated charge carriers (electrons – e<sup>-</sup>, holes – h<sup>+</sup>) are transferred to the narrow-band-gap semiconductor (MoS<sub>2</sub>). In this case, neither an improvement in charge carrier separation nor the enhancement of photocatalytic activity are expected. However, several research groups claim that they had observed improved photoactivity for a composite with a type I band alignment [2,6–8]. The photogenerated electron in the conduction band of TiO<sub>2</sub> can be transferred to the MoS<sub>2</sub> sheet, which can effectively reduce hydrogen ions to H<sub>2</sub>. The layered MoS<sub>2</sub> not only acts as a “highway” for the transport of electrons, but is also used as an effective co-catalyst for the photosplitting of water. Additionally, King et al. postulated that electrons that had entered the upper *d*-orbitals of MoS<sub>2</sub> can be injected into the TiO<sub>2</sub> conduction band. On the other hand, a type II heterojunction has been reported in the literature. The conduction and valence bands of MoS<sub>2</sub> have a higher energy position than those of TiO<sub>2</sub>. The electrons originating from molybdenum sulfide can be injected into titanium dioxide as a result of visible light irradiation, whereas holes move from the valence band of TiO<sub>2</sub> to the VB of MoS<sub>2</sub> [9–11]. These processes promote the separation of electron-hole pairs. Ren et al. [10] pointed to the possibility of using layered MoS<sub>2</sub> as a conductive pathway for electron transport with the formation of a type II heterostructure, in the case of which a synergetic effect between TiO<sub>2</sub> and MoS<sub>2</sub> had been observed. Electronic band structure is also correlated to the corrosion of a semiconductor electrode in the dark and under illumination. There is a general rule that the stability of an electrode in an aqueous electrolyte grows worse for lower band gaps of a semiconductor [12]. Contact of typical semiconductors, like silicon, arsenide, sulfide, selenide, telluride and phosphor-based materials, with aqueous electrolyte results in a rapid change in the surface composition by formation of the oxide layer. However, most often the corrosion has an electrochemical nature. Based on the thermodynamic criteria for corrosion of semiconductors, formulated by Gerischer [13], was shown that majority of narrow-band-gap semiconductors are unstable as photoelectrodes. In fact, the photodecomposition of a semiconductor depends on the kinetics of the process. If activation energy is high, a semiconductor electrode can be stable even under thermodynamic conditions that promote its instability. Photoelectrodes based on pure and doped TiO<sub>2</sub> are well-known for their long-term stability. MoS<sub>2</sub> should be very easily decomposed via oxidation, but photocorrosion does not affect MoS<sub>2</sub>. Experimental evidence [14] shows that surface states at layer semiconductor play an important role in the

kinetics of decomposition reactions and can be protected against destruction. Moreover, heterojunctions can also be used to improve the stability of one of the components [2].

In our previous work [15], we proposed a novel, environmentally friendly method – the electrodeposition of MoS<sub>2</sub> onto TiO<sub>2</sub>. For comparison, the hydrothermal approach was also applied. The influence of the deposition technique on the electro- and photoelectrochemical properties of MoS<sub>2</sub>/TiO<sub>2</sub> was studied. In that work, we found that the dense and thick form of MoS<sub>2</sub> leads to the instability of photoanodes based on TiO<sub>2</sub> with a layer of sensitizer. The layers subsequently degrade due to a chemical reaction as a result of which MoS<sub>2</sub> is transferred into the electrolyte during photoelectrochemical tests. The cited study provided a new strategy for MoS<sub>2</sub>/TiO<sub>2</sub> formation, which determines the quality of contact between the layered MoS<sub>2</sub> and TiO<sub>2</sub>.

The aim of the current work was to study the influence of the parameters of MoS<sub>2</sub> synthesis (time of reaction and type of surfactant), the parameters of the electrodeposition of MoS<sub>2</sub> onto TiO<sub>2</sub>, and the properties of the composite on the performance of a photoelectrochemical cell. Consequently, a detailed study of the crystal structure, morphology, and photoelectrochemical properties of photoanodes based on TiO<sub>2</sub>/MoS<sub>2</sub> is presented. The important advantage of TiO<sub>2</sub> over narrow-band-gap semiconductors is its long-term stability. Last but not least, the mechanism of charge transfer between TiO<sub>2</sub> and MoS<sub>2</sub> is proposed.

## Materials and methods

### Materials

Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (ACS reagent), CH<sub>4</sub>N<sub>2</sub>S (pure), PEG-1000 (analytically pure, ACS reagent), C<sub>2</sub>H<sub>5</sub>OH (99.8%, analytically pure), C<sub>3</sub>H<sub>6</sub>O (analytically pure), C<sub>3</sub>H<sub>8</sub>O (analytically pure), C<sub>3</sub>H<sub>8</sub>O<sub>3</sub> (analytically pure), Na<sub>2</sub>SO<sub>4</sub> (analytically pure), and KNO<sub>3</sub> (analytically pure) were purchased from Avantor Performance Materials (Gliwice, Poland). NH<sub>4</sub>F (≥98.0%, ACS reagent), Pluronic F-127 (BioReagent, suitable for cell culture), SDBS (technical grade), CTAB (BioXtra, ≥ 99%) and Ti foil (0.127 mm, 99.7%) were bought from Sigma-Aldrich. Argon (pure) was purchased from Air Liquide.

### Synthesis of MoS<sub>2</sub>

MoS<sub>2</sub> powders were synthesized with the use of the hydrothermal method, with the following reactants: Na<sub>2</sub>MoO<sub>4</sub> (0.03 mol) as a molybdenum precursor, CH<sub>4</sub>N<sub>2</sub>S as a sulfur precursor, and PEG-1000 as a surfactant. The molar ratio between the reactants was fixed at 1: 4.56: 0.03, respectively. Two hundred ml of the reaction mixture was magnetically stirred for 15 min at a speed of 500 rpm. Chemical reactions were conducted in a Teflon-lined hydrothermal reactor at 200 °C for 6, 12, 18, or 24 h. The powders obtained in this way were marked 6, 12, 18 and 24. Additionally, three other surfactants were used in 24-h synthesis; the designations of the obtained powders were the same as the names of the applied surfactants: Pluronic, CTAB, SDBS. The final products were washed with a mixture of distilled water and absolute ethanol

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