



Molybdenum and tungsten disulfides surface-modified with a conducting polymer, polyaniline, for application in electrorheology



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ABSTRACT

Molybdenum and tungsten sulfides are semiconducting materials with flake-like morphology. Their applicability in electrorheological suspensions was enabled by the coating with a conducting polymer, polyaniline, after its conversion to non-conducting polyaniline base. For instance, the conductivity of tungsten sulfide, 0.056 S cm⁻¹, increased to 0.98 S cm⁻¹ after coating with polyaniline, and was conveniently reduced to 6.3 × 10⁻⁶ S cm⁻¹ after conversion to polyaniline base. Such approach reduces the potential current drifts in electrorheological suspensions and allows for the application of sulfides in electrorheology. The optical microscopy demonstrated the formation of particle chains in silicone-oil suspensions after application of electric field. The electrorheological performance was assessed by the measurement of viscosity on the shear rate in the absence and in the presence of electric field and it is discussed on the bases of dielectric spectra.

1. Introduction

Molybdenum sulfide is especially known as a heavy-duty solid lubricant operating at high temperatures and pressures, where its flaky morphology is exploited with benefit. Its layered structure, analogous to graphite or graphene [1,2], has stimulated the preparation of nanosized forms [3]. Semiconducting properties of molybdenum sulfide, however, have recently come to the forefront [4] and, for that reason, also the composites with organic conducting polymers have recently become investigated and applied especially in energy-conversion devices.

The composites of molybdenum sulfide with polyaniline have usually been prepared by the *in-situ* deposition of the conducting polymer on sulfide substrate during the oxidation of aniline. It has been established that any solid substrate immersed in the aqueous reaction mixture becomes coated with a thin overlayer of conducting polymer [5,6]. Molybdenum sulfide was coated with polyaniline in this way and applied as electrodes in supercapacitors [1,7–12] or solar cells [13], in electrocatalysis [14,15], photocatalysis [16], electromagnetic radiation shielding [17], electrorheology [17,18], sensors [19,20], lithium and sodium-ion storage medium [21], or for the adsorption of hexavalent chromium ions in environmental applications [16]. In reverse approach, polyaniline decorated with molybdenum disulfide was used in

the hydrogen evolution electrodes [22] or in supercapacitors [23,24].

Polyaniline has also served as the nitrogen source in the carbonization to nitrogen-containing carbons [25,26] followed by the deposition of molybdenum sulfide [27,28]. The resulting material was applied as an electrode in electrocatalytic hydrogen evolution reaction [27] or in lithium-ion batteries [28]. Molybdenum sulfide coated with polyaniline was used also after carbonization as electrode material in lithium-ion batteries [28–31].

The papers reporting the preparation of similar composites with tungsten sulfide are scarce [7,32]. The fabrication of micro-supercapacitor microrobots serves as an example of advanced application [33]. Some uses of composites have also been targeted to tumor treatment [34].

Despite the numerous papers reporting the electrochemical properties of composites, *viz.*, cyclic voltammetry, galvanostatic discharging and capacitance determination, there is limited information provided in the literature on their conductivity. It was reported that the conductivity of composites of polyaniline with molybdenum disulfide, up to 2.4 S cm⁻¹, was higher than the conductivities of corresponding components, 0.014 S cm⁻¹ for sulfide and 0.11 S cm⁻¹ for polyaniline [2]. Materials with moderate conductivity are suitable as a dispersed phase in electrorheological fluids, whose rheological parameters can be controlled by application of external electric field [35,36]. Such fluids

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thus undergo a transition from liquid to a viscoelastic-solid state due to internal chain-like structures produced by suspended particles in the presence of an electric field [37–40]. Polyaniline is one of the most common materials used in electrorheological fluids [41] due to its tunable conductivity and facile and inexpensive synthesis. Molybdenum sulfide possessing a plate-like morphology has also introduced as a novel dispersed phase in electrorheological fluids [18,42]. The combination of both materials, the flake-like molybdenum sulfide with polyaniline needles deposited on its surface, has recently been prepared and tested for electrorheological performance [17].

The flake-like morphology of molybdenum sulfide is better suited for electrorheology compared with spherical particles [43,44]. The molybdenum sulfide itself, however, is semiconducting and the current drifts in suspensions would reduce the electrorheological efficiency. In the present study, the coating with conducting polymer, polyaniline, in its non-conducting base form has conveniently been used to reduce the conductivity of particles. This novel approach has been extended to similar material, even more conducting tungsten sulfide, which has not been considered in electrorheology so far.

2. Experimental

2.1. Preparation

Conducting polymer composites were prepared by the standard procedure [45] using the oxidation of 0.2 M aniline hydrochloride with 0.5 M ammonium peroxydisulfate in the aqueous suspension of sulfides (Fig. 1). The content of polyaniline was selected to be 16 wt% of the mass of sulfides. In a typical preparation process, 1 g of molybdenum sulfide or tungsten sulfide (both from Sigma Aldrich) was dispersed in 5 mL distilled water and treated in ultrasonic water bath for 15 min. Then, 0.259 g of aniline hydrochloride (Penta, Czech Republic) was added into the sulfide suspension and further treated in ultrasonic water bath to dissolve the aniline hydrochloride. After that, 0.571 g of ammonium peroxydisulfate (Lach-Ner, Czech Republic) was dissolved in another portion of 5 mL distilled water and the solution was rapidly mixed with the sulfide suspension containing aniline hydrochloride. The mixture was left for 24 h at room temperature and then vacuum filtrated, rinsed with 10 mL of 0.1 M hydrochloric acid followed by 10 mL ethanol. Solids were left to dry in air. The deprotonation of the part of polyaniline in the composites to base form was carried out by immersion in 1 M ammonium hydroxide followed by separation and drying. The characterization of polyaniline has been reported elsewhere [46]; its weight-average molecular weight was ca 30,000 [46] when assuming that molecular weights of polyaniline in the coating and in the powder form were identical [47].

2.2. Characterization

Morphology was characterized with a scanning electron microscope JEOL 6400. Thermogravimetric analysis exploited a Pyris 1

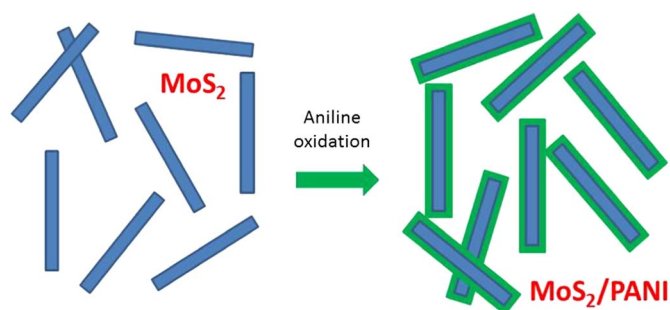


Fig. 1. Flakes of molybdenum sulfide become coated with a conducting polyaniline overlayer during the oxidation of aniline in acidic aqueous medium.

Thermogravimetric Analyzer (Perkin Elmer) in an air flow. For the determination of conductivity, the sulfides or their composites with polyaniline were compressed into pellets of 13 mm diameter and ≈ 1 mm thick with a manual hydraulic press Trystom H-62. The conductivity measurement using van der Pauw configuration was carried out with a Keithley 230 Programmable Voltage Source, a Keithley 196 System DMM and a Keithley 181 Nanovoltmeter at 24 ± 1 °C and relative humidity $35 \pm 5\%$. A Thermo Nicolet NEXUS 870 FTIR Spectrometer was used to record Fourier-transform infrared (FTIR) spectra of the samples dispersed in potassium bromide. A Renishaw InVia Reflex Raman microspectrometer was used to collect the spectra excited with a laser operating with 587 nm wavelength. The beam was focused with a research-grade Leica DM LM microscope on the sample. A Peltier-cooled CCD detector (576×384 pixels) registered the dispersed light.

2.3. Dielectric properties

Dielectric properties were measured with an impedance dielectric spectroscopy analyzer, Novocontrol Concept 50 (Novocontrol, Germany) connected to the cylindrical sample cell BDS 1307 for liquid materials. Dielectric properties, such as relative permittivity, ϵ' , and dielectric loss factor, ϵ'' , were investigated in a frequency range from 0.5 Hz to 2 MHz. The dielectric spectra are usually analyzed using the Havriliak-Negami (HN) model [48](1) in the papers concerning electrorheology [49,50],

$$\epsilon_{HN}^*(\omega) = \epsilon'_{\infty} + \frac{\Delta\epsilon'}{(1 + (i\omega \cdot t_{rel})^a)^b} \quad (1)$$

where $\Delta\epsilon' = \epsilon'_s - \epsilon'_{\infty}$ is dielectric relaxation strength, ϵ'_s and ϵ'_{∞} are relative permittivities at zero and infinite frequencies, f , respectively, ω , is angular frequency ($= 2\pi f$), t_{rel} is the relaxation time, and a and b are the shape parameters describing the asymmetry of the dielectric function.

In some systems, however, the materials exhibit electrode polarization and thus typical interfacial polarization cannot be recognized easily by fitting HN model. Therefore, the model in the form of electric modulus (2) can be plotted, similarly as reported by Mrlik et al. for aniline oligomers [51],

$$M_{HN}^*(\omega) = M_{\infty} + \frac{\Delta M}{(1 + (i\omega \cdot t_{rel})^{\alpha})^{\beta}} \quad (2)$$

where t_{rel} is the relaxation time, ΔM is dielectric relaxation strength, M_{∞} is unrelaxed value of electric modulus, the parameters α and β represent the width and the skewness of the relaxation, respectively.

2.4. Optical microscopy

Optical microscopy using an optical microscope (Leica DVM2500; Leica Microsystems, UK) was used to study the behavior of the particles within the prepared silicone-oil suspensions in the presence of an electric field. The suspensions consisting of 2 wt% of the prepared particles were placed on the glass between two copper electrodes, and a DC high-voltage source (Keithley 2400, USA) was used as a source of electric field of a strength 0.5 kV mm^{-1} .

2.5. Electrorheology

Dry composite particles were mixed with silicone oil (Lukosiol M200, Chemical Works Kolín, Czech Republic, viscosity $\eta_c = 194 \text{ mPa s}$, conductivity $\sigma_c \approx 10^{-11} \text{ S cm}^{-1}$) in a 1:9 w/w ratio. Before each measurement, the suspensions were stirred with a glass rod and sonicated for 1 min to ensure to homogeneous distribution of the particles within silicone oil.

Rheological measurements were performed using a rotational rheometer Bohlin Gemini (Malvern Instruments, UK) with a plate–plate

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