



Chromium–doped MoS₂ “inorganic fullerene” nanoparticles prepared by topotactic reaction from oxosalt precursor

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ABSTRACT

Hollow sulfides nanoparticles of MoS₂, Cr₂S₃ and Mo_{0.9}Cr_{0.1}S₂ (“inorganic fullerenes”) were prepared from SrMo(Cr)O₄ precursors by means of a topotactic solid-gas reaction with H₂S/CCl₄ mixture. The obtained hollow sulfide nanoparticles have narrow size distributions and high specific surface areas. In the Mo-Cr doped sulfide material, chromium is homogeneously distributed substituting molybdenum within the MoS₂ layers. While Cr₂S₃ hollow particles are inefficient as lubricant additive, introduction of chromium into MoS₂ improves the tribological properties of the “inorganic fullerene” material.

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1. Introduction

Layered sulfides MoS₂ and WS₂ are widely studied materials in modern nanotechnology, applied as catalysts [1,2], lubricants [3–5], supercapacitors [6], or electrodes in Li-ion batteries [7]. Transition metals dopants in layered sulfides affect electronic, mechanical, and catalytic properties. The role of impurities and dopants for versatile applications of layered sulfides is crucial as they provide a means for tuning the electronic structure and interface properties [8]. Controllable doping is desired for the tuning of such properties to improve performance [9]. Recent studies show that doping MoS₂ monolayers with chromium and vanadium produces interesting electronic effects [10–12]. In the CVD-synthesized MoS₂ monolayers, Cr and V substitute Mo atoms and are uniformly distributed throughout the MoS₂ layers [13]. Mechanical properties of Cr-doped MoS₂ are also strongly modified. Addition of chromium to the MoS₂ changed the failure mode from plastic deformation to brittle fracture [14].

Onion-like and hollow layered sulfides, “inorganic fullerenes” (IF) are widely studied for lithium batteries [15], lubricants [3] or shock absorbers [16]. Several techniques were proposed for IFs

synthesis, including oxides sulfidation [17,18], amorphous precursor decomposition [19], laser ablation [20], metal-organic CVD [21] or solution precipitation [22]. There are only few reports on the doped IF, because of the lack of appropriate preparation techniques. Previous works report on IF-MoS₂ doped with rhenium and tungsten [23]. Comparison of monometallic and W- or Re-doped IF-MoS₂ showed that rhenium improves electrocatalytic properties [24,25] and tribological performance [23,26].

In this work we report on the novel synthetic approach that allows obtaining doped hollow (IF) sulfides. Preparation of binary Cr and Mo sulfides and chromium doped IF-MoS₂ is described. The obtained materials are characterized with several techniques including XRD, nitrogen adsorption, Raman spectroscopy, TEM and STEM-EDS mapping. The tribological properties of the materials at stake are compared in PAO oil under boundary regime.

2. Experimental

2.1. Preparation of oxide precursors

Nanoparticles of SrCrO₄, SrMoO₄ and SrMo_{0.9}Cr_{0.1}O₄ were prepared by non-aqueous metathesis. All reactants and solvents were high purity grade from Aldrich. Sr(NO₃)₂, Na₂MoO₄·2H₂O and Na₂CrO₄ were applied as precursors. Formamide (FA), N-methylformamide (NMF) and dimethylsulfoxide (DMSO) were applied as

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reaction solvents. In a typical preparation, a mixture of salts (0.04 mol total) was loaded in a flask containing 50 ml of NMF and kept for 12 h under 500 min⁻¹ stirring. The precipitates were separated by centrifugation, washed with ethanol and then dried at room temperature.

2.2. Preparation of sulfides by solid-gas reaction

Solid-gas reaction was applied to transform mixed oxides to the mixtures of sulfides (Cr₂S₃, MoS₂ or Mo_{0.9}Cr_{0.1}S₂) and SrCl₂. A 10 mL/min flow of argon saturated with CCl₄ vapor at 0 °C was mixed with 30 mL/min flow of H₂S. The solids (1–2 g) were treated in a Pyrex reactor at 550 °C for 4 h. After the reaction, the solids were washed several times with distilled water and then dried under nitrogen. The solids were handled and kept under inert atmosphere to avoid interaction of sulfides with oxygen.

Bulk MoS₂ benchmark reference was prepared using ammonium thiomolybdate (ATM) decomposition, as described earlier [30]. The reference solid was prepared by heating ATM for 2 h under 10% H₂S/H₂ flow at 550 °C.

2.3. Characterizations

Transmission electron microscopy (TEM) was carried out on a JEOL 2010 device with an accelerating voltage 200 keV. The samples were dispersed in ethanol by ultrasound, and then put onto a holey carbon filament on a copper grid sample holder. The analysis of images was carried out using Digital Micrograph Gatan™ software. Particle size was estimated from the analysis of low-resolution images, using ca. 200 particles for each solid. Element distribution maps were obtained at a JEOL 2010 FEG device with a STEM HAADF detector and Oxford Instruments EDS analyzer.

Nitrogen adsorption isotherms were measured on a Micromeritics ASAP 2010 instrument. Specific surface areas and pore size distributions were determined using BET and BJH equations, respectively. Prior to measurements, the samples were heated in a secondary vacuum at 350 °C for 4 h. The X-ray diffraction (XRD) patterns were obtained on a Bruker diffractometer with Cu-K α emission and crystalline phases were identified using standard JCPDS files. Mean size of coherent scattering domains was determined using the Scherrer equation. The metal content in the synthesized solids was determined after dissolution in a HNO₃–H₂SO₄ mixture by plasma-coupled atomic emission spectroscopy (AES-ICP). The sulfur and carbon contents were measured with a Strohlein Instruments CS-MAT 5500 analyzer. Raman spectra were recorded with a Lab Ram HR Raman spectrometer (Horiba-Jobin Yvon). The exciting Ar laser at 514 nm and 1 mW power was focused using a $\times 50$ long working distance objective. The spectral resolution was < 4 cm⁻¹.

2.4. Tribological experiments

Suspensions of sulfides 1% wt. in PAO4 were prepared by ultrasound dispersion for 1 h. at room temperature. A linear reciprocating friction tribometer with a ball-on-flat configuration was used to generate tribofilms in mild/severe tribological conditions. The selected contact configuration was composed of AISI 52100 steel ball/AISI 52100 steel flat. The friction experiments were performed at 383 K with a maximum sliding speed of about 0.1 m s⁻¹ (center of the track) for one-hour duration, no run-in period prior to the sliding experiment is performed. The maximum initial contact pressure was 500 MPa. In these sliding conditions, the thickness of the lubricant film, at the maximum speed, is equal to about 15 nm corresponding to a λ ratio of about 1. Prior to the experiment, both ball and flat specimens were cleaned in ultra-sonic heptane

bath in order to remove surface contaminants. An average friction coefficient for each sliding cycle was calculated from one thousand measurements of instantaneous friction coefficients recorded during the cycle.

3. Results and discussion

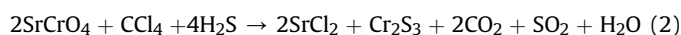
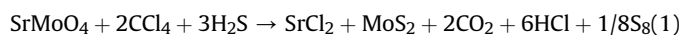
3.1. Preparation of solid materials and their characterizations

The synthetic approach combines two original techniques described in our earlier papers [27,28]. First, nanoparticles (NP) of SrMoO₄, SrCrO₄ and SrMo_{0.9}Cr_{0.1}O₄ precursors were obtained by non-aqueous reaction of strontium nitrate with sodium chromate and/or sodium molybdate [27]. Preparation of SrMoO₄ Scheelite has been described in details previously [27], but no reports existed on the non-aqueous synthesis of SrCrO₄ or mixed Cr-Mo oxosalt.

Depending on the non-aqueous solvent applied, SrCrO₄ was obtained as anisotropic agglomerates (DMSO), highly acicular nanorods (FA) or isotropic particles (NMF), Fig. 1. For the purposes of this study we chose isotropic SrCrO₄ particles prepared in NMF, which have particle size between 20 and 50 nm and after washing contain pure SrCrO₄ phase with no noticeable impurities from the precursors (Fig. S1 of Supplementary Information). The NPs of SrCrO₄, SrMoO₄ and SrMo_{0.9}Cr_{0.1}O₄ have narrow size distributions and respective particle size of 38, 29 and 31 nm (Figs. 1c and 2; Fig. S3).

Powder XRD shows that both SrMoO₄ and SrMo_{0.9}Cr_{0.1}O₄ materials are single phases with Scheelite structure. No additional reflections and no significant shift of XRD peaks were observed due to doping of SrMoO₄ with chromate. The average XRD size of NPs calculated from lines broadening according to Scherrer equation was 33, 21 and 18 nm for SrCrO₄, SrMoO₄ and SrMo_{0.9}Cr_{0.1}O₄ respectively, which is smaller than the corresponding TEM sizes, indicating that the particles observed by TEM are not perfect single crystallites. The EDS analysis in several zones showed homogeneous distribution of chromium and molybdenum over the SrMo_{0.9}Cr_{0.1}O₄ material grains. Therefore, non-aqueous precipitation allows obtaining single phase homogeneous strontium molybdate-chromate solid solution with Scheelite structure.

On the second step of the synthesis, oxide precursors NPs were transformed to hollow sulfides NPs by means of solid-gas reaction using as a reactive gas a mixture of CCl₄ vapor and H₂S [28]. Carbon tetrachloride reacts as oxophilic species and increases the reactivity of oxides towards H₂S. The overall reaction pathway is complex, as several parallel processes may occur with their relative importance depending on the temperature [28]. The solid-gas reactions leading to the main observed products can be expressed by equations (1) and (2). The mechanism of such reactions has been studied previously [28,32,33] and here we focus our attention on the solid products.



As compared with known process of oxides sulfidation using sole hydrogen sulfide, introduction of CCl₄ into the gas mixture leads to a drastic decrease of the solid-gas reaction free energy due to formation of CO₂ and SrCl₂. After washing with distilled water to remove soluble SrCl₂, hollow sulfide NPs were obtained, with particle size close to that of the oxide precursors (Fig. 2d and e; Fig. S2a). The sulfide materials prepared at 550 °C contain small amounts of broken particles, most NPs being closed shells. According to XRD, the reaction products are pure Cr₂S₃ for SrCrO₄ and MoS₂ phase for both SrMoO₄ and SrMo_{0.9}Cr_{0.1}O₄ (Fig. 2f, Fig. S2b).

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