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Microscale control of edge defect and oxidation on molybdenum disulfide through thermal treatment in air and nitrogen atmospheres

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ABSTRACT

The formation rule and mechanism of edge defect and oxidation on MoS_2 through thermal treatment in air and nitrogen atmospheres were explored in this work. Atomic force microscope (AFM), X-ray photoelectron spectroscope (XPS), and scanning electron microscope-energy dispersive spectrum (SEM-EDS) demonstrated that both edge defects and surface oxidation occurred on MoS_2 when being thermally treated in air atmosphere, while pure defective MoS_2 structure formed in N_2 atmosphere. The degrees of defect and oxidation increased with the increase of temperature and time under thermal treatment. Auger electron spectrometer (AES) revealed that the oxidation of MoS_2 was limited on the top surface and the mechanism for the oxidation was the substitution of O for the top S layer. AES and SEM-EDS results suggested that the origin of defects on MoS_2 in air atmosphere was a combination of MoS_2 oxidation and thermal effect, while that in N_2 atmosphere was simply because of the thermal effect. This work indicated that defects and oxidation on MoS_2 could be well controlled through the modification of thermal temperature, atmosphere and time, which might give a significant guidance for the better application of MoS_2.

1. Introduction

Molybdenum disulfide (MoS_2), as one of layered transition metal dichalcogenides (TMDCs), has attracted widespread attention in various domains due to its promising chemical characteristics [1]. As a semiconducting material, the 1.8 eV direct energy gap of monolayer MoS_2 makes it widely studied as photoelectric materials [2,3]. The abundant catalytic sites on the surface lead MoS_2 having excellent catalytic characteristics and make it a potential catalyst [4–6]. The large surface area and the S atoms exposed on the surface enable molybdenum disulfide as a highly effective adsorbent for the removal of heavy metals from aqueous solutions [7,8]. Previous researches revealed that the surface property of MoS_2 would largely affect its behaviors when being applied as catalysts, adsorbents, etc. [9,10]. For example, the oxidation and edge defects enabled the surface of molybdenum disulfide highly reactive as Hg^{2+} adsorbent because the oxidation could provide O active sites to strongly adsorb Hg through the formation of Hg-O complex, while the presence of defects improved the affinity of Hg to molybdenum disulfide [10]. When molybdenum disulfide was applied as electrode candidate for capacitive deionization process, the abundant defects on MoS_2 made it more negatively charged, higher specific capacitance and lower inner resistance, which promoted the desalination capacity. These researches demonstrated that oxidation and defect etching should be recommended when defect and oxidation improve their performances. Therefore, introduction of oxidation and defect on the surface of MoS_2 and further control of the oxidation and defect degree are of great importance.

Many techniques have been reported in introducing defects or oxidation on MoS_2. Chemical dry-etching method could be used for the induction of defects on MoS_2, during which XeF_2 was added as a reactant [11]. Electron beam lithography and plasma were also reported to etch defects on the surface of MoS_2 [12]. Due to the easy oxidation, MoS_2 could be etched by acids and oxidizing agents [13]. However, the above methods involved the production of dangerous gas or complicated process.

Thermal treatment was a simple and secure pathway to introduce defects or oxidation on MoS_2 [14]. Under thermal treatment with O_2, MoS_2 could transform into MoO_3 and result in etch pits on its surface at

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a given temperature. According to non-isothermal studies, the oxidation of bulk MoS_2 started at about 350 °C [15]. Another report showed similar results that no MoO_3 films were formed on the thin MoS_2 crystals below 340 °C in O_2 flow [16]. When heating MoS_2 samples above 400 °C, well-formed microscopic crystals of MoO_3 have been found [17]. The oxidation of MoS_2 started from the physisorption of oxygen on the surface of MoS_2 and then converted to chemical formation of Mo oxides. MoS_2 oxidation increased with the increase of heating temperature [18]. In addition to oxidation during thermal treatment, triangular etch pits defect with uniform orientation could be induced on the surfaces of MoS_2 at 300 °C for 4 h [16]. The first-principle calculations and Raman spectroscopy results revealed that temperature and the number of MoS_2 layers might influence the etch pits [14]. The etchings initiated at intrinsic sulfur defects on MoS_2 basal plane and enlarged under thermal treatment [14]. These researches were carried out in air atmosphere and failed at building a quantitative relation between the defect or oxidation degree and the thermal treatment condition.

An attempt was made to modify the degrees of defects and oxidation on MoS_2 in microscale through the control of atmosphere and temperature during thermal treatment in this work. The formation of defect, introduction of oxidation and their degrees were investigated detailly through the measurements of atomic force microscope (AFM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and X-ray diffraction spectrum (XRD). The origin of defect and oxidation in thermal treatment at different atmospheres was studied with the help of auger electron spectroscopy (AES), scanning electron microscope-energy dispersive spectra (SEM-EDS), and thermogravimetric analysis (TGA). The object was to build a quantitative correlation between the defect or oxidation degree and the thermal treatment condition, further to give a better guidance for the surface modification of MoS_2.

2. Experimental

2.1. Materials

The molybdenum disulfide used in this study was purchased from Wuzhou Mine, Guangxi Province, China. The purity of nitrogen used in the experiments was higher than 99.999%, and the oxygen content was less than 3 ppm. The molybdenite sample was cleaved to expose a fresh surface before experiments to avoid the interference of existing surface oxidation on the experimental results. The samples used for AFM and XPS studies were of cuboid form with dimensions of 0.5 × 0.5 × 0.1 cm. The sample used for Raman and XRD analysis was powder which had size between 37 μm and 74 μm.

2.2. Thermal treatment

The thermal treatment of molybdenum disulfide was going through a simple process. Several grams of molybdenum disulfide particle or a cleaved molybdenum disulfide bulks were placed in a porcelain boat, then transferring the porcelain boat to a muffle furnace (Vulcan 3–550) or a tube furnace (MXG1200-S40). The samples were thermally treated from room temperature to a given value (300 °C, 400 °C and 500 °C in muffle furnace and 500 °C in tube furnace) with a heating rate of 10 °C/min and the set temperature was kept constant for a specified time. During the thermal treatment, the samples in muffle furnace and tube furnace were exposed to air and nitrogen atmosphere, respectively. After cooling down to room temperature, the samples were taken out without further processing. Molybdenum disulfide samples before and after the thermal treatments were named as M (untreated), M-300-2H-A (300 °C in muffle furnace under air atmosphere for 2 h), M-400-2H-A (400 °C in muffle furnace under air atmosphere for 2 h), M-500-2H-A (500 °C in muffle furnace under air atmosphere for 2 h), and M-500-3H-N (500 °C in tube furnace under nitrogen atmosphere for 3 h), respectively.

2.3. Measurements

The defective observation of MoS_2 crystals was performed by a MultiMode 8 atomic force microscope (AFM) instrument (Bruker, USA) in PeakForce tapping mode with a ScanAsyst-Air silicon nitride probe on a V-shaped cantilever. The silicon nitride probes had a nominal tip radius of 2 nm. A fresh surface was cleaved to roast and then experiments. Each image of the MoS_2 surface were obtained at a scan rate of 0.977 Hz and a scan area of 5 × 5 μm. In each processing condition, a total range of 750 μm^2 were selected randomly for statistic processing. The original image used NI Vision Assistant 2014 to count about the area and the perimeter of MoS_2 defect. In this software, the processing of the image went through five steps including image calibration, color plane extraction, filters, threshold and particle analysis.

A D8 Advance X-ray diffractometer and a Prodigy 7 inductively coupled plasma-optical emission spectr was performed to obtain the XRD pattern and element content to characterize the composition of the sample. A Zeiss Ultra Plus field emission scanning electron microscope (FESEM, Zeiss, Germany) was used to analyze the morphology of the molybdenite, and the elemental distribution of a sample was determined by the energy dispersive spectra (EDS). Raman spectra were collected with an INVIA Raman microscope with a 633 nm Ar laser (Renishaw, UK). XPS spectra were collected with an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher Scientific, USA). The C 1 s peak (BE = 284.6 eV) was used as an internal reference line to accurately determine the positions of other spectral lines. A STA449F3 simultaneous thermal analyzer was used to analyze the thermostability of MoS_2 in air and in N_2 atmospheres with the heating rate of 10 °C/min from room temperature to 1000 °C. A PHI-700 auger electron spectrometer (AES) was used to analyze the distribution of O and S elements on molybdenite surface before and after thermal treatment.

3. Results and discussion

3.1. Characterization of molybdenum disulfide sample

Fig. 1a showed a typical scanning electron microscopy (SEM) of the sample. A smooth surface was observed and no obvious defect was detected on MoS_2. The energy dispersive spectroscopy (EDS) pattern indicated that the sample was of high purity (Fig. 1b). Fig. 1c and d were EDS elemental mapping images of Mo and S, respectively. The two elements distributed evenly and covered all the sample surface. Inductively coupled plasma (ICP) showed that the sample assayed 58.47% Mo, 35.72% S, 2.25% Al, 2.20% Bi, 0.76% Si, 0.21% Li, and 0.39% others (as shown in Fig. 2), indicating that the purity of molybdenum disulfide was 89.3% in natural molybdenite.

3.2. Effect of temperature on MoS_2 defects under thermal treatment

Representative AFM images (two-dimensional and three-dimensional views) of MoS_2 before and after thermal treatment at different conditions were shown in Fig. 3a–e. A smooth surface of MoS_2 was observed before being thermally treated (Fig. 3a). No obvious change had occurred after 300 °C thermal treatment for 2 h in air atmosphere (Fig. 3b), indicating that defects were difficult to be etched under low temperature thermal treatment in air. When the temperature was raised to 400 °C, well-oriented equilateral triangular pits with length of 0.428 μm appeared on MoS_2 surface (Fig. 3c). The inserted figure showed the corresponding height cross-section profile of the marked white line. It showed that the etched thickness was around 0.75 nm, which corresponded to a single MoS_2 layer [16]. The results demonstrated that equilateral triangular defects were produced on the top surface layer of MoS_2. With raising the thermal temperature to 500 °C, these triangular etchings extended laterally and their shape became irregular (Fig. 3d). As a consequence, more than half surface on the top layer was etched. The insert figure showed that the defects along the

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