



# Synthesis and electrochemical performance of colloidal MoS<sub>2</sub> nanosheets as an anode material in sodium ion battery



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## ABSTRACT

MoS<sub>2</sub> nanosheets by utilizing MoO and Mo(CO)<sub>6</sub> as a precursor sources of molybdenum were prepared by a colloidal route at 270 °C in Schlenk flask under the inert atmosphere. The as obtained layered and wrinkled nanosheets were then applied as anode materials in a sodium ion batteries (NIBs) in order to elucidate the electrochemical performances, where an excellent first and second charge/discharge capacities of 150/310 mAhg<sup>-1</sup>, 125/148 mAhg<sup>-1</sup> with a good stability up to ~30 cycles were obtained with the precursor source of Mo(CO)<sub>6</sub>. However the MoO employed precursor based nanosheets shows a substantially low first and second charge discharge capacities of 12/37 mAhg<sup>-1</sup> and 10/14 mAhg<sup>-1</sup>. The FE-SEM and XRD shows the wrinkled layered structures in both the precursors with XRD pattern more prominent in the Mo(CO)<sub>6</sub> precursor with 2θ peaks at 34°, 36°, and 59°. The excellent performance of nanosheets in the Mo(CO)<sub>6</sub> precursor source could be ascribed to the efficient breakage of carbonyl ligands to form a well super saturated monomers followed by well crystallinity with defect free, stable morphology which could effectively withstand expansion/contraction occurring during the successive sodium ion insertion/extraction process.

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## 1. Introduction

It is abundantly clear that the large chunk (one-quarter) of the world's production of lithium metal are now consumed by the secondary battery technologies [1] pressing in a steep rise of Li<sub>2</sub>CO<sub>3</sub> prices worldwide [2]. Additionally, the pioneering success and widespread use of Li ion batteries in portable devices are expected to add more pressure on its consumption and the demand will further increase if it is utilized in the electric and hybrid electric vehicles (EV, HEVs) in near future. Furthermore, in a recent study, it has been predicted that the lithium supplies will run out in the foreseeable future [3] with the extension of battery technology towards the renewable energy such as wind and solar, which are expected to be more prevalent in near future owing to environmental stringent regulations and also the integration into the electrical grid will pressurized further in the sharp rise of costs for the lithium metal worldwide. Indeed, for the large scale application the constituent of element in earth crust must be in abundance, unfortunately lithium metal is found to be ~20 ppm only in earth crust in comparison to the sodium metal which is ~23600 ppm.

Since the supply of sodium resources are vast, abundant (4th most in the Earth crust), with a staggering reserves (23 billion tons) of soda ash in the United States alone [4] with a competitive cost of ~\$135–165/ton, compared to Li<sub>2</sub>CO<sub>3</sub> (~\$5000/ton) along with the environmental benign attributes giving ample of compelling rationales for the use of sodium in a large scale secondary battery applications because of the similar basic chemistry of both metals. However, the sodium is less reducing (–2.71 V vs. SHE) than lithium (–3.04 V vs. SHE) and its gravimetric capacity is much lower 1165 mAhg<sup>-1</sup> than lithium 3829 mAhg<sup>-1</sup>, though it is perceived that at a high gravimetric capacity is less critical for large scale storage [5]. Ong, et al. theoretically studied and compares the operation of Li-ion and Na-ion batteries [6] and deduced that its lower capacities are depends on its size (~3× larger mass of Na) and ionic radius of Na (0.3 Å larger than Li), so the emergent need lately is a development of new suitable host materials for reversible Na<sup>+</sup> insertion and extraction [7]. Furthermore, these Na-ion batteries are emerging technologies and the details of new materials and new redox couples are sought to be extensively studied for the identification of suitable negative electrode materials for the successful deployment of sodium-ion secondary batteries in near future. So far, the graphite known to be highly successful in the lithium ion cells as anodes, does not intercalate sodium ion to an appreciable extent [8], and other non-graphitic

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anodes such as petroleum cokes, [9] carbon black, [10] pitch-based carbon fibers, [11] and polymers (poly(*para*-phenylene)) [12], hard-carbons, [13] that have been tried in addition to early transition metal oxides such as sodium titanate  $\text{Na}_2\text{Ti}_3\text{O}_7$  [14],  $\text{TiO}_2$  [15], a SnSb/C nanocomposite as anodes [16] are not very successful. Inspired by the pioneering success of graphene research [17,18], the layered materials such as hexagonal Boron Nitride (h-BN), the transition-metal dichalcogenides have received considerable attention recently [19,20] and a large number of chalcogenide have been used to probe dimension-dependent optical, [21,22] electrical [23], magnetic [24], and superconducting [25] properties. These transition metal dichalcogenides  $[\text{MX}_2$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{X} = \text{S}, \text{Se}$ )] are layered materials, whose crystal structures are covalently bonded with S–M–S single-layers that interacts by van der Waals forces like the graphitic materials [26]. Particularly, the  $\text{MoS}_2$  is interesting and is a nonvolatile and insoluble compound where several methodologies in literature have been employed to obtain  $\text{MoS}_2$  layer such as scotch-tape based micromechanical cleavage technique [5], liquid exfoliation to produce 2D exfoliated  $\text{MoS}_2$  nanosheets [27] exhibiting distinct properties. However, chemical synthesis of dichalcogenide are limited owing to the scalability and particle controlled mediated process. Although, this approach of synthesis can be successful in the CdSe [28], and FeSe [29], solar cells by controlling the characteristic features of colloidal nanosheets; their edge dimensions, lateral uniformity, and thicknesses that holds critically important for the diverse range photovoltaic applications. Here in, we studied a precursor influenced colloidal synthesis of layered  $\text{MoS}_2$  chalcogenide and applied it as an anode materials for electrochemical performance (NIBs) study, since the hot-injection method (colloidal) can produce nanosheets directly in solution that adopted layered crystal structures by utilizing a suitable precursors at a particular reaction condition. The rationale behind using different precursor source might modulate the superior optoelectronic and performance characteristics even for the same material, since the breakage of precursor ligands at the reaction medium are crucial for the nucleation and growth of the ensuing products which directly influences the performance.

## 2. Experimental

### 2.1. Synthesis of chalcogenide $\text{MoS}_2$ layers

The  $\text{MoS}_2$  sheets are synthesized as follows: 2 mmol of  $\text{Mo}(\text{CO})_6$  (Aldrich), 10 mL of octylamine (Aldrich) were loaded in the Schlenk flask. Then purge out three times in argon gas and heated at  $110^\circ\text{C}$  under argon atmosphere. Then this mixture was heated continuously to  $270^\circ\text{C}$  under an argon atmosphere. The sulfur in octylamine was mixed in another Schlenk flask and heated under vacuum at  $80^\circ\text{C}$  for 24 h as stock solution (S powder, 4 mmol dissolved in octylamine, 10 mL), it was rapidly injected into the first three neck flask. After injection temperature was dropped down to  $250^\circ\text{C}$ . After the injection, then crystals were grown at  $270^\circ\text{C}$  for 1 h. Then cooled the solution up to  $60^\circ\text{C}$ , and then 15 mL of methanol was added to precipitate the nanoparticles, which were recovered by centrifugation at 5000 rpm for 15 min. The precipitate was washed three times with methanol to remove the excess ligand and then vacuum dried to obtain the  $\text{MoS}_2$  nanosheets.

### 2.2. Electrochemical analysis

The electrode was prepared by mixing a mixture of 75 wt% of  $\text{MoS}_2$  nanosheet as active material, 17 wt% acetylene black carbon, and 8 wt% as polyvinylidene fluoride (Kynar HSV 900) in *N*-methyl-2-pyrrolidone (NMP) solvent. Then the obtained slurry was coated by doctor blade method on copper foil and dried under vacuum at

$110^\circ\text{C}/6$  h. The working electrode was assembled in Ar filled glove box into a coin cells (CR2032) for anodic performance evaluation. The metallic sodium foil was made from ingots as counter electrode, a porous polypropylene films as separator; electrolyte was 1 M  $\text{NaPF}_6$  dissolved in ethylene carbonate, dimethyl carbonate and diethyl carbonate at a volumetric ratio of 1:1:1. Similarly other nanosheet sample was also used as active material for the performance evaluation. X-ray diffraction (XRD) was analyzed by Bruker D8 Advance X-ray diffractometer. Thin nanosheets microstructure were investigated by field emission scanning electron microscopy (FESEM, S-4800, Japan) and TEM were collected by JEOL (JEM- 2010) transmission electron microscope operating at acceleration voltage of 200 kV. The discharge-charge tests were conducted from 1 V to 3.5 V (vs.  $\text{Na}/\text{Na}^+$ ) by TOSCAT 3000U (TOYO SYSTEM Co., Ltd).

## 3. Results and discussion

Fig. 1 a–d shows the field emission scanning electron microscopy (FE-SEM) images of the synthesized samples by colloidal method by using molybdenum precursor ( $\text{MoO}$  and  $\text{Mo}(\text{CO})_6$ ) sources to visualize the differences in the morphological outcome of the product chalcogenide nanosheets, since it has been well known that the precursors sources influences remarkably the morphology and optoelectronic properties in the colloidal synthetic method in order to designed the desired materials suitable for application. In the low resolution images (a) where  $\text{MoO}$  precursor was employed, the morphology of thin sheets were not fully established and uniformity was not so clear rather sheets and particles were observed, whereas  $\text{Mo}(\text{CO})_6$  precursor (b) uniform sheets were observed homogeneously and smoothly without any particles. In the high resolution FESEM images (c, d), it was clearly observed that the wrinkles of sheets were formed by employing both the precursors under the same reaction condition, however the wrinkles of sheets are more prominent, clear, smoother and with well-defined edges in case of molybdenum carbonate (d) precursors ( $\text{Mo}(\text{CO})_6$ ). However, in case of  $\text{MoO}$  as precursor source the wrinkles are shallow, rugged with some nanoparticles are seen in the FE-SEM image (c), where it can be speculated that the some particles are not fully formed into the sheets owing to strong bonding interactions in molybdenum oxide precursor. Fig. 2 shows the TEM analysis of nanosheets synthesized in the precursor source of ( $\text{Mo}(\text{CO})_6$ ), where thin individual sheets with partial folding can be clearly observed. The inset shows the typical FFT pattern of the thin sheets showing a well crystallization.

Fig. 3 shows the XRD pattern of the as synthesized samples by colloidal method using precursors molybdenum oxide ( $\text{MoO}$ ) (a) and molybdenum carbonate ( $\text{Mo}(\text{CO})_6$ ), (b) at the  $270^\circ\text{C}$  for 1 h reaction time in the Schlenk flask. Although both the samples shows well crystallized  $\text{MoS}_2$  by utilizing different precursor sources but the molybdenum carbonate precursor shows a more clearer  $2\theta$  positions of  $34^\circ$ ,  $36^\circ$ , and  $59^\circ$  are corresponding to the crystal phases of (101), (103) and (110) respectively, matching well with the characteristic peaks of JCPDS No. 37-1492. However, discrepancy in (002) peak is arises which is not visible in the usual  $2\theta = 15^\circ$ , but an visible prominent peak at  $2\theta = 19^\circ$  was observed in both the samples with high intensity in  $\text{Mo}(\text{CO})_6$  precursor source, this peak could be result of either octylamine or  $\text{MoS}_2$  complex where (002) might be buried in the complex or the shift of (002) characteristic peaks. The peak corresponding to the (002) becomes broadened indicating that the interlayer spacing of the film was partially expanded and the crystal structure was not destroyed. The peak broadening might be due to defects and nanometer scale of their stacked  $\text{MoS}_2$  sheets.

Fig. 4a and b shows the discharge and charge capacities of the first two cycles as an anode material in sodium ion battery (NIBs)

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