Spontaneous exfoliation and tailoring of MoS₂ in mixed solvents†

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Spontaneous exfoliation of MoS₂ is achieved in H₂O₂–NMP mixed solvents with a yield of over 60 wt%, operated under mild conditions. H₂O₂–prompted sheet-tailoring effect induces a size evolution of MoS₂ nanosheets from micro-scale to nano-scale. Furthermore, the concurrent dissolution also affords an approach to introduce structural defects in the nanosheets.

Individual molybdenum disulfide (MoS₂) nanosheets are a type of semiconductor that reveals intriguing properties, including tunable electronic structure, high catalytic reactivity, excellent mechanical properties and lithium ion capacity.¹,² This makes them a powerful candidate material to be applicable in electronics,¹,³ optoelectronics,⁴,⁵ sensors,⁶ energy storage,⁷ and catalysis,⁸ and thus stimulates strong interest in developing low-cost, high-efficiency, scalable preparation methods for single- or few-layer of MoS₂.¹,²,¹⁰

The vapor phase growth of large-area MoS₂ films has achieved success,¹¹ similarly exfoliating the bulk material into MoS₂ nanosheets witnessed substantial progress in recent years.¹²–¹⁷ The latter is important, especially for applications in lithium ion batteries,⁷,¹⁸ supercapacitors,¹⁹ catalysts,²⁰ sensors,²¹ and composites.²² Liquid-phase exfoliation is promising in this regard.¹³,¹⁴ Direct sonication in solvents that have the surface energy comparable to that of MoS₂ can produce single- or few-layer nanosheets in large quantities, particularly when the interlayer interaction is mitigated by intercalation species.²³ In this regard, chemical exfoliation has emerged as an important approach because of their high exfoliation yields.⁵,¹²,¹⁶,²¹

Lithium intercalation, followed by hydrogen gas release by the reaction between lithium and water has been exploited to weaken the interactions between adjacent layers, which resulted in an exhaustive exfoliation of atomically thin MoS₂ nanosheets.²⁴ However, due to their large molecular sizes, aggregation propensity and limited diffusion rate of intercalation compounds such as n-butyl lithium, completing such intercalation processes is time-consuming even at high temperatures, e.g., at 100 °C for 2 days.⁵,¹² Electro-chemical intercalation¹⁷ and pre-expansion treatments²⁵ have been proposed to improve the intercalation efficiency while retaining good exfoliation yields. However, the spontaneous exfoliation of MoS₂ under mild conditions remains unknown, although similar phenomena have been observed in the exfoliation of graphene and layered double hydroxides.²²–²⁴

Spontaneous exfoliation implies that no external stimuli, such as sonication, shear or heating, are required.²²,²³ For layered materials, such exfoliation has two essential requirements to be fulfilled, i.e., sufficient driving force to enable the solvent molecules to diffuse into the interlayer space by overcoming interlayer interactions or exfoliation work, and good wetting capability of solvent for layer surfaces. In the course of such exfoliation processes, the contribution of entropy increase to the Gibb's free energy of the systems is generally negligible because of large lateral sizes and limited configuration numbers of two-dimensional nanosheets.²³ This makes the intercalation of exotic species to frequently require additional energies (higher than the critical value or (electro)chemical overpotentials) to overcome the interlayer interaction energy.²⁴ Oxidants can provide chemical overpotentials, which facilitate their diffusion into the interlayer space, as it occurs when preparing graphite intercalation compounds.²⁵ Unfortunately, MoS₂ is unstable in the presence of oxidants; for example, hydrogen peroxide (H₂O₂) is a leachant of molybdenite in hydrometallurgy, in which it is often used to extract the element molybdenum by oxidative dissolution.²⁶

Here, we demonstrate an oxidant-prompted spontaneous exfoliation process of MoS₂, nanosheets, and we achieve size evolution from large sheets to small sheets to nanodots (Fig. 1). Large scale production is also achieved through a simple process in mild reactions conditions (Fig. S1, ESI†). By suppressing the oxidative dissolution, ~60% of the pristine MoS₂ can be exfoliated into single- or few-layer nanosheets in mixed solvents containing H₂O₂ under ambient conditions. We also find that the presence of a small amount of H₂O₂ is beneficial for the sonication-assisted

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liquid exfoliation, with an exfoliation yield considerably higher compared to sonication exfoliation without oxidants. In addition, the dissolution, which occurred along with the exfoliation provides a way to introduce pore structures on MoS2 nanosheets, enabling the cycling and rate performance of the resulting lithium ion batteries to be remarkably improved.

We first examined the effect of H2O2 concentration in mixed solvents on the exfoliation process of MoS2 with mechanical stirring at 35 °C. The size reduction and morphology evolution of MoS2 nanosheets shown in Fig. 2 demonstrated the occurrence of sheets tailoring along with spontaneous exfoliation, i.e., after MoS2 nanosheets were peeled off from the bulk counterpart, sheets tailoring causing morphology evolution subsequently got under way (Fig. 1). In detail, at low H2O2 concentrations (volume ratio of 30 wt% H2O2 aqueous solution to NMP, H2O2/NMP = 1 : 19), a dark homogeneous suspension was obtained after 10 h of stirring, except for the unexfoliated precipitates in the bottom (Fig. S2 in ESI†). After removing the precipitate, the exfoliated nanosheets afforded a yield of 25% relative to the starting material (Fig. S3 in ESI†). The AFM images show that the obtained nanosheets are 2.86 nm thick, 3–5 μm long and 2 μm wide (see Fig. 2a). While increasing H2O2 concentrations, the color of the dispersions became lighter and clearer, suggesting that more MoS2 particles could be dissolved or tailored into smaller nanosheets. Indeed, as shown in Fig. 2a and c, the lateral sizes of the nanosheets decreases from several microns to several hundreds of nanometers upon H2O2/NMP increasing from 1 : 19 to 5 : 15 (Fig. 2a and c), and finally completely turned into nanodots of ~5 nm in diameter (Fig. 2d and Fig. S4 in ESI†). Increasing the content of H2O2 did not enhance the yield of exfoliated nanosheets, but more MoS2 particles were dissolved. As shown in Fig. S3 (ESI†), when the amount of H2O2 increases, both exfoliated nanosheets and unexfoliated MoS2 particles display a decreasing tendency. This indicates that under such conditions, increasing the content of H2O2 is not a viable route for achieving high exfoliation efficiency.

The dissolution of MoS2 in H2O2 is a spontaneous, self-accelerated, exothermic process according to the reaction in eqn (1).26 This reaction is highly dependent on the experimental conditions, including feed ratio, liquid/solid ratio, reaction time and temperature.26 In our experiments, H2O2 is in large excess, as opposed to MoS2. To retard the dissolution of MoS2, we maintain the reaction temperature at 35 °C to suppress the self-accelerated reaction and introduce a large amount of NMP to decrease the probability of H2O2 contacting with MoS2 surfaces (NMP has better wetting capability compared to H2O2 for MoS2).15 Thus, H2O2 tends to preferentially react with highly reactive sites (defects and dislocation)27. This allows the outermost layer of MoS2 particles to first peel off, and subsequently exfoliate the other layers in sequence. However, it should be pointed out that we cannot rule out the possibility of H2O2-induced NMP or mixed solvent intercalating into the interlayer spacing of MoS2, although in our experiments no intercalation diffraction peak in XRD pattern was observed for the intermediate products. For those exfoliated single- or few-layer nanosheets, because more surfaces are exposed to H2O2 compared to unexfoliated particles, they prefer to be tailored into smaller nanosheets or introduce pits or pores on nanosheets. This would be the primary reason to produce porous nanosheets and nanodots in high H2O2 concentrations. The entire process is schematically represented in Fig. 1, suggesting that H2O2 can not only weaken the van der Waals (vdW) forces and lead to spontaneous exfoliation, but also break Mo–S bonds, which would give rise to sheet-tailoring.

To verify this mechanism, in situ tailoring experiment of pristine monolayer MoS2 was performed (see ESI† and Fig. S8). Note that the original MoS2 nanosheets were prepared by an ultrasonic treatment of raw MoS2 in NMP, and a complete profile was preserved for better observation (Fig. S9a, ESI†). As shown in Fig. S9b (ESI†), a porous pattern is visible after treatment with H2O2–NMP (5 : 15 v/v). Moreover, with increasing H2O2 content (20 : 0 v/v), MoS2 nanosheets were further cut to nanodots (Fig. S9c, ESI†) with ~0.94 nm in height and ~10 nm in diameter. This phenomenon clearly proves the H2O2-induced tailoring effect, opening a new approach for morphological control of MoS2 nanosheets. On the basis of the above observation, we reduced the reaction time to 5 h, separated the unexfoliated particles and subsequently exfoliated them again in fresh mixed solvent with the same H2O2/NMP (1 : 19). As expected, the reduced reaction time effectively suppressed the dissolution of the exfoliated...
sheets and enhanced the total exfoliation yield to 60.5% (relative to the starting material, Fig. S5 in ESI†). Such a spontaneous exfoliation process is in great contrast with many reported intercalation–exfoliation approaches6,12,16,17 and it apparently presents industrially potential, in view of its simplicity, low energy consumption (only mild stirring at low temperature) and low requirements of H2O2.

Subsequently, we characterized the resulting products to examine possible variations in the chemical component and structure of MoS2 nanosheets, given the oxidative dissolution occurred during the spontaneous exfoliation. Fig. 3a shows the field emission scanning electron microscopy (FE-SEM) image of the MoS2 nanosheets exfoliated in the mixed solvent of νH2O2/NMP = 1 : 19. Fig. 3b and c presents the corresponding mapping results of energy disperse spectroscopy (EDS), from which the element proportion of Mo : S is 1 : 1.96 indicates that the chemical component of exfoliated MoS2 nanosheets remains essentially unaffected. These nanosheets exhibit a wide lateral size distribution, and agrees with the mechanism presented in Fig. 1; i.e., the exfoliation of the bulk particles accompanying the concurrent tailoring of the nanosheets. Fig. 3d shows UV-vis absorption spectroscopy of the supernatant (νH2O2/NMP = 1 : 19, reaction time 10 h) obtained after centrifuging it for 30 min at 5000 rpm. Four characteristic absorption bands appear at 399, 473, 627, 681 nm, which coincide with the results reported28 and reflect the strong characteristic absorption bands appear at 399, 473, 627, 681 nm, compared to the raw MoS2, which would arise from the partial dissolution of MoS2 during the exfoliation. As mentioned previously, the oxidation reaction preferably occurs at relatively high reactive boundary regions between two phases. In addition, compared to the stable 2H phase, the 1T phase has a distorted lattice structure,30 and thus, higher reactivity upon exposure to oxidants such as H2O2. As a result, the fact that dissolution and exfoliation occur simultaneously also provides a facile approach to diminish the metallic 1T phase and introduce in-plane pore defects in exfoliated MoS2 nanosheets. The latter is true, especially for a high H2O2 concentration of mixed solvents (see Fig. 2b and c).

Interestingly, H2O2 is also able to substantially improve the efficiency of sonication exfoliation of MoS2. In a 100 mL mixed solvent (νH2O2/NMP = 1 : 19) containing 100 mg raw MoS2, 1 h of sonication treatment (500 W) resulted in 63% of MoS2 being exfoliated with 26.6 wt% of unexfoliated particles (10.4% of MoS2 was dissolved). Such exfoliation efficiency is apparently attractive compared to reported exfoliation methods, as summarized in ref. 1 and 2. Nevertheless, we also note that this H2O2-prompted sonication exfoliation is sensitive to the experimental conditions, including H2O2 concentration and sonication time, the latter governs the dissolution process of MoS2 in H2O2 to a large extent. These factors should be carefully considered upon optimizing the exfoliation efficiency and the morphology of nanosheets (see Fig. S10 in ESI†). Compared to the spontaneous exfoliation in the mixed solvent with the same νH2O2/NMP (1 : 19), the sonication exfoliation can yield irregular micron-scale nanosheets with porous structures (Fig. S11 in ESI†). This structure feature is expected to prompt the charge transfer efficiency and improve lithium ion batteries (LIB) performances.

To evaluate the properties and application potential of the resulting MoS2 nanosheets, we further studied the electrochemical performance of a MoS2–graphene (MoS2–G, weight ratio 4 : 1) two-electrode cell by comparing with a MoS2 cell (no graphene), and some details are presented in the ESI.† It was determined that the MoS2 nanosheets revealed a lithium storage capacity comparable to the MoS2 obtained by the traditional lithium intercalation exfoliation (Li–MoS2).18 Fig. 4a presents the cycling performance of the MoS2 and MoS2–G electrodes over the voltage range 0.01–3.0 V. The initial discharge capacities at current density 200 mA g−1 are 866 mA h g−1 and 865 mA h g−1, and after 50 cycles, the coulombic efficiencies are
98.2% and 98.6% for MoS$_2$ and MoS$_2$–G electrodes, respectively. Interestingly, after 50 cycles, the MoS$_2$ electrode still reveals a charge capacity of 227 mA h g$^{-1}$, which is superior to that of the Li–MoS$_2$.\(^{19}\) It is believed that the specific porous structure of H$_2$O$_2$–MoS$_2$ plays an important role in improving the charge transfer efficiency, although Li–MoS$_2$ has also been suggested to have certain pore structures. In addition, distinct from those reported MoS$_2$-based approaches to prepare few-layer MoS$_2$ nanosheets under mild conditions, this new protocol will be helpful for practical applications of MoS$_2$ nanosheets and MoS$_2$–G.

In summary, herein, we report a novel spontaneous exfoliation approach to prepare few-layer MoS$_2$ nanosheets under mild conditions. It is determined that H$_2$O$_2$ can induce the spontaneous sonication exfoliation of MoS$_2$ in NMP, although accompanying a concurrent dissolution of MoS$_2$. The dissolution of MoS$_2$ is suppressed by controlling the amount of H$_2$O$_2$ in NMP and an exfoliation yield of 60% is achieved in a mixed solvent of H$_2$O$_2$/NMP volume ratio = 1 : 19. Moreover, the concurrent dissolution also provides a facile method to introduce porous structures and diminish the metallic phase in nanosheets. Such porous MoS$_2$ nanosheets exhibit the potential to improve the cycling and rate performance of lithium ion batteries. Given the simplicity, low energy consumption of this H$_2$O$_2$-prompted exfoliation method and the specific structures of MoS$_2$ nanosheets, we believe that this new protocol will be helpful for practical applications of MoS$_2$ in energy storage, catalysis and composites.

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Notes and references