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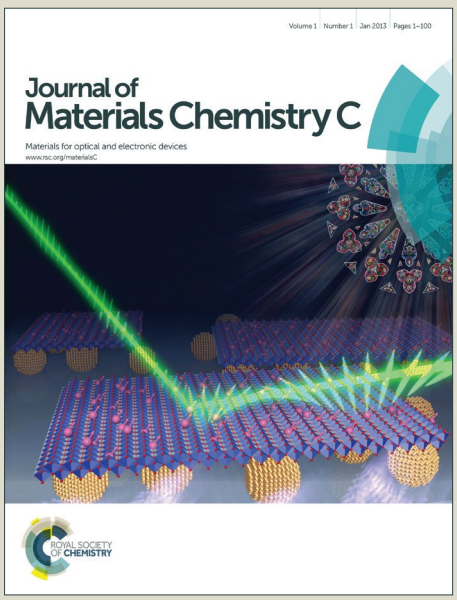

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Rapid, One-Pot Synthesis of Luminescent MoS_2 Nanoscrolls Using Supercritical Fluids Processing

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For the first time, we present a simple, rapid and one-pot exfoliation of layered bulk MoS_2 into luminescent MoS_2 nanoscrolls using supercritical fluids processing using dimethyl formamide as a solvent and with a short reaction time of 30 min. The exfoliated nanoscrolls were characterized using PXRD, UV-visible, Raman, FE-SEM and TEM. The MoS_2 nanoscrolls exhibit photoluminescence over the emission wavelength ranges from 420-600 nm is attributed to the size reduction and polydispersity nature.

Followed by the discovery of graphene, there has been a considerable interest in layered inorganic materials such as transition metal dichalcogenides (TMDCs), transition metal oxides (TMOs), hexagonal BN (h-BN), BCN and C_3N_4. Molybdenum disulphide (MoS_2) known as molybdenite has sandwich layer type structure. A single layer of MoS_2 consists of molybdenum atoms sandwiched between two layers of sulphur atoms in trigonal prismatic arrangement and the individual layers are held together by van der Waals forces. Recently, it has attracted much attention in material science due to its multifarious applications as catalyst, lubricant, hydrogen storage material, photovoltaic, double-layer capacitor and sensor.[1-6] Bulk MoS_2 is an indirect bandgap semiconductor with a bandgap of 1.2 eV and it transforms in to direct bandgap semiconductor when it is exfoliated into monolayer.[7] The band-gap of MoS_2 increases when the crystal thickness decreases below 100 nm, leading to an enhancement of the photoluminescence due to quantum confinement effect [8-10] and the theoretical calculations estimated that band gap may increase up to 1.9 eV for single layer MoS_2.[11] The relatively weak van der Waals interactions between the MoS_2 layers allow the foreign molecules to intercalate and that results the exfoliation of MoS_2. Until now, production of single layer or few layer MoS_2 has been achieved via mechanical exfoliation using scotch tape method,[12-15] liquid-based exfoliation,[16-22] chemical method by lithium intercalation[23-25] and chemical vapour deposition method.[26-35] Among them, lithium intercalation method is not preferred for exfoliation of MoS_2 since this method is air sensitive, introduce a large number of defects and results in the loss of semiconducting properties.[36,37] Thus, various attempts are under progress to synthesize 2D MoS_2 nanosheets with high quality. However, the 2D MoS_2 nanosheets are unstable against folding in order to minimize their surface energy leading to formation of nanotubes and fullerene-like structures.[38] Carbon nanoscrolls are known by rolling-up of graphene nanosheets into tube-like structure.[39] However, MoS_2 nanoscrolls are not the known in literature. Here, we report the formation of MoS_2 nanoscrolls by rapid and one-pot exfoliation of layered bulk MoS_2 using supercritical fluids processing. Supercritical fluids (SCFs) are unique reaction medium where the temperature and pressure of the solvent is above its critical temperature and pressure. The SCFs can diffuse through solids like a gas with liquid-like solvent properties. Attempts are in progress to exploit the unique nature of the SCFs in materials synthesis and functionalization.[40-42] In our present study, exfoliation of MoS_2 from layered bulk MoS_2 powder was achieved within a short time of 30 min in dimethyl formamide (DMF) as SCFs. As synthesized MoS_2 nanoscrolls exhibit a strong photoluminescence ranging from 420-600 nm which can be mainly attributed to the conversion of indirect to direct band gap semiconductor since the size reduction occurs during SCFs treatment.

In a typical synthesis, 200 mg of MoS_2 powder (SRL, India. 98%) dispersed in 25 mL DMF by sonication for 5 min and it was loaded into stainless steel tubular reactor (35 mL capacity) and sealed. Then, the sealed reactor was placed in a pre-heated (400 $^{\circ}$C) vertical tubular furnace for 30 min and removed from the furnace and rapidly quenched in an ice cold water bath (5 $^{\circ}$C). The supernatant solution was collected and centrifuged at 2000 rpm for 20 min for further studies.

The PXRD pattern of bulk MoS_2 used for SCFs treatment and as-synthesized MoS_2 nanoscrolls are shown in **Fig. 1**. The bulk MoS_2 diffraction lines were readily indexed based on hexagonal 2H-MoS_2 with lattice constants a = b = 3.1612 Å and c = 12.2985 Å and it is in good agreement with the ICDD pattern (No. 00-037-1492). The bulk MoS_2 shows highly intense reflections with maximum at 2θ = 14.64° (002) and 39.80° (103). Whereas, the SCFs treated MoS_2 exhibits only one broad line corresponding to (002) plane with slight shift towards higher 2θ (14.78°). The observed shift is the indication of the conversion of MoS_2 layer to nanoscrolls. The formation of nanoscrolls results in the compressive stresses that can be correlated to the reduction of interlayer d_{002} spacing. The absence of any other diffraction lines indicates the existence of few-layer MoS_2. It reveals that the few-layer MoS_2 are peeled off from bulk are rolled up in order to minimize their surface energy resulting in the formation of MoS_2 nanoscrolls. In addition, it is important to note here that the intensity of diffraction line corresponding to (002) plane decreases with respect to bulk. It ensures that decrease in lateral size after the SCFs treatment in DMF since the (002) peak mainly arises from interlayer Mo-Mo scattering.[43] Notably, the calculated interlayer spacing d_{002} for bulk and MoS_2 nanoscrolls was 6.04 and 5.99 Å, respectively. The observed shorter interlayer spacing is mainly due to strong coupling between the adjacent layers in few layer rolled nanoscrolls.

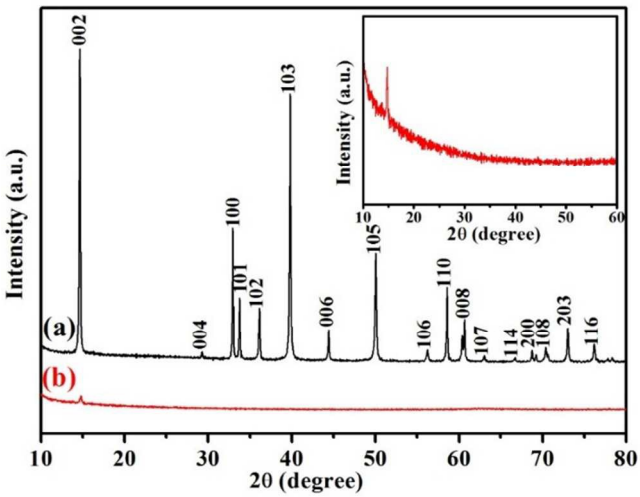

Fig. 1 PXRD patterns of (a) bulk MoS_2 powder and (b) exfoliated MoS_2 nanoscrolls. Expanded profile of MoS_2 nanoscrolls (inset)

The Raman spectra of bulk and exfoliated MoS_2 nanoscrolls are shown in **Fig. 2**. The bulk MoS_2 powder displays two prominent peaks at 383.4 and 409.1 cm^{-1} due to the in-plane ($^1E_{2g}$) and out-of-plane (A_{1g}) mode of vibration, respectively. The in-plane mode arising from the opposite vibration of sulphur and molybdenum atoms while the out-of- plane mode corresponds to the vibration of sulphur atoms only in the out-of-plane. After the layers are peeled from the bulk, the frequency of the $^1E_{2g}$ peak increases while that of the A_{1g} peak decreases with decreasing the number of layers.[14] Indeed, the number of layers can be unambiguously determined from these two modes by the decreases in peak spacing between these modes and the intensity of $^1E_{2g}$ and A_{1g} modes increases with increasing number of layers.[33] The SCFs assisted synthesis of MoS_2 nanoscrolls show a blue shift of $^1E_{2g}$ peak from 383.4 to 385.5 cm^{-1} and this is in consistent with previous report[33] while the position of A_{1g} peak does not change significantly. The unaltered A_{1g} mode due to the scrolling of MoS_2, where the interlayer Van der Walls forces suppress the atom vibration and also the strain built in the folded nanoscrolls may also alter significantly. [38,44].

The surface morphology of bulk and exfoliated MoS_2 was investigated using FE-SEM analysis (**Fig. 3 & Fig S1).** The bulk MoS_2 powder shows the layered-like morphology with lateral size of 10 to 20 µm and several micrometres in thickness. After the SCFs treatment in DMF for 30 min, it transforms in to scrolled rod-like morphology with diameter of 50 nm to 150 nm. Also, it can be seen that the length of the nanoscrolls are varying from 0.2-3 µm. It is apparent from the FE-SEM images that in addition to the exfoliation process, a significant size reduction is also taking place during the SCFs processing.

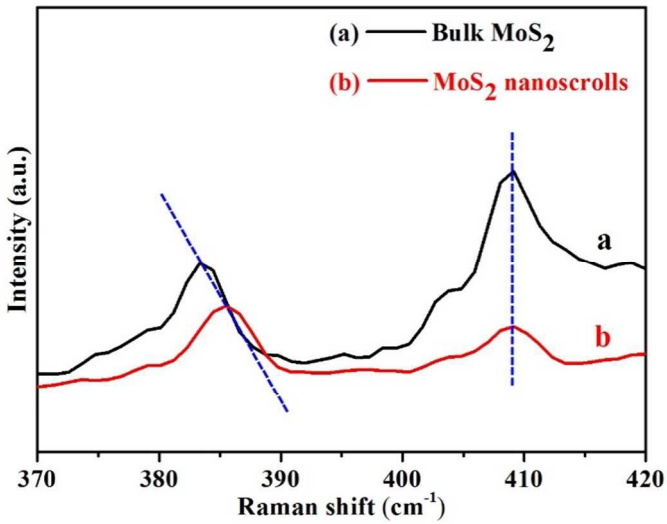

Fig. 2 Raman spectrum of (a) bulk MoS_2 powder and (b) exfoliated MoS_2 nanoscrolls.

Fig 4 and Fig S2 shows the representative TEM images of bulk MoS_2 powder and exfoliated MoS_2 nanoscrolls. The sheet-like image with many layers could be clearly seen for the bulk MoS_2 powder. The nano-tubes like images (Fig 4b&c) with transparent nature confirms the formation of MoS_2 nanoscrolls from the exfoliated MoS_2 nanosheets. The formation of MoS_2 nanoscrolls due to the rolling of nanosheets can be further confirmed from the partially rolled nanosheets as shown in Fig 4d. The size reduction by the SCFs treatment can be confirmed by comparing the TEM images of bulk and exfoliated a MoS_2 nanoscroll which is in good agreement with FE-SEM observations. The selected area electron diffraction (SAED) pattern of nanoscrolls shown in **Fig. 4f** demonstrates that the MoS_2 nanoscrolls are crystalline in nature. To confirm the how many layers are present in the MoS_2 scrolls, HR-TEM analysis was conducted and presented in **Fig. 4(g&h).** **Fig. 4h** clearly demonstrates that the rolled sheet comprises of two to three atomic layers and it is in good correspondence with AFM thickness analysis. The thickness of MoS_2 nanoscrolls was analysed using AFM. The AFM image of smallest nanoscrolls and its corresponding height profile are shown in **Fig. 5**. Additional AFM images for

slightly higher size nanoscrolls are shown in **Fig S3**. The formation of rod-like nanoscrolls can be clearly seen from the AFM images. The height profile analysis indicates that the thickness of MoS_2 nanoscrolls is around 2.0-3.0 nm with a length of ~ 3µm.

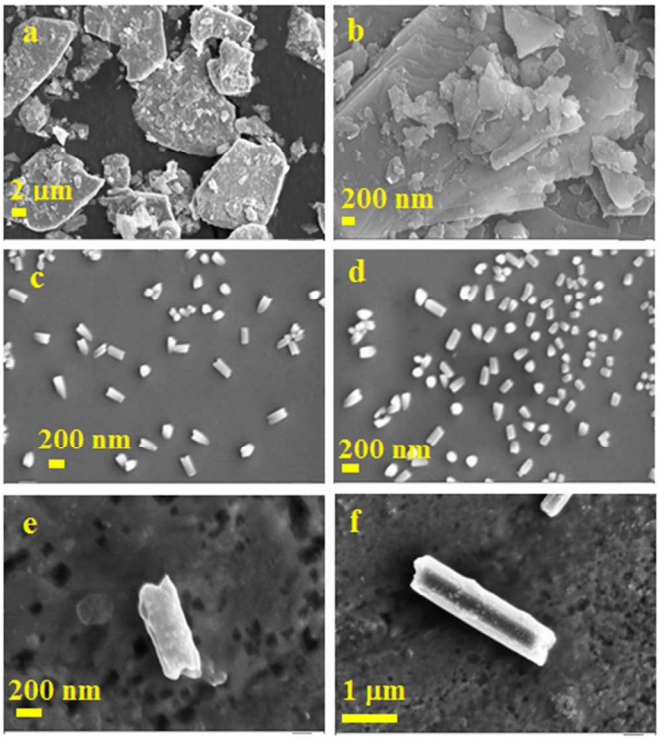

Fig. 3 FE-SEM images of (a-b) bulk MoS_2 powder and (c-f) exfoliated MoS_2 nanoscrolls.

Thus, the SCFs treatment is very efficient for exfoliation as well as size reduction. In addition, it is worthy to mention here that this is a short, surfactant free and one-step direct exfoliation route for MoS_2 nanoscrolls from bulk MoS_2 powder. It is important to note that the dispersion of exfoliated MoS_2 nanoscrolls in DMF solution is stable for more than few months without any significant aggregation or precipitation. Optical absorption spectrum of MoS_2 nanoscrolls dispersion in DMF is recorded and shown in **Fig 6**. It can be seen that an intense broad absorption with maximum at 328 nm and there is no other discrete absorption peaks are identified in the entire visible region. Earlier reports suggest that the single layer MoS_2 nanosheets exhibits two prominent absorption peaks around at 670 and 627 nm, attributed to the A1 and B1 direct excitonic transitions of MoS_2 with the energy split from valence band spin-orbital coupling.[45,46] The absence of such peaks in the MoS_2 nanoscrolls clearly indicates that these excitations are susceptible to MoS_2 nanosheets. This may be further explained by the exfoliated MoS_2 sheets that curled themselves into nanoscrolls to minimize the surface energy. For comparison, the optical absorbance spectrum of blank solution (DMF) and bulk MoS_2 in DMF are shown in **Fig S4**. **Fig. 7** shows the photoluminescence excitation and emission spectra of as synthesized MoS_2 nanoscrolls. A strong emission band was observed with its maximum at 420 nm when the excitation wavelength was 360 nm.

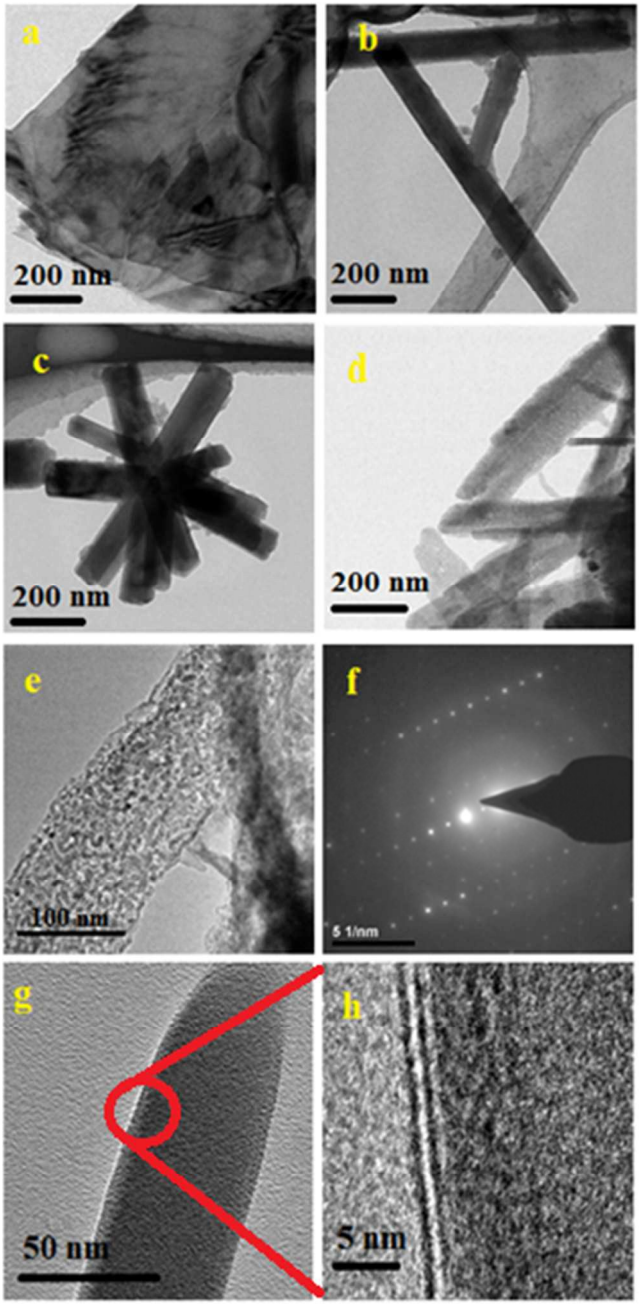

Fig. 4 TEM images of (a) bulk MoS_2 powder and (b-e) exfoliated MoS_2 nanoscrolls, (f) SAED pattern of exfoliated MoS_2 nanoscrolls, (g-h) HR-TEM images of exfoliated MoS_2 nanoscrolls.

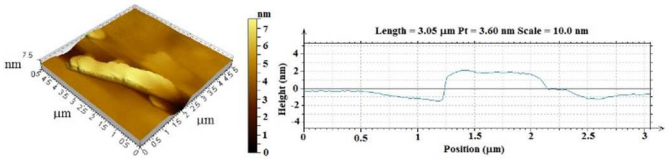

Fig. 5 AFM image and corresponding height profile of exfoliated MoS_2 nanoscrolls on silica substrate.

The obtained results are in good agreement with luminescent properties of MoS_2 quantum dots reported by Štengl et al.[47] There the MoS_2 quantum dots were prepared by exfoliation in ethylene

glycol using a high intensity cavitation field in a pressurized (6 bar) ultrasound reactor for 30 min and followed by refluxing the solution for 24 hours. In our study, the MoS_2 nanoscrolls were prepared by rapid, one-pot exfoliation using SCFs processing in 30 min. Photographs of photoluminescent MoS_2 nanoscrolls dispersion in DMF before and after UV light illumination is shown in **Fig 7 (inset)**. As DMF itself has a PL behaviour under UV illumination, the PL spectrum of exfoliated MoS_2 nanoscrolls was recorded in water (**Fig S5 & Fig S6**). It was found that the MoS_2 nanoscrolls show PL properties in water also.

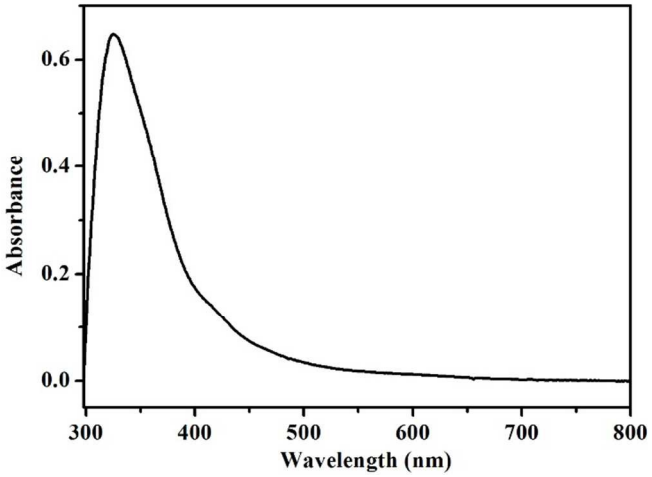

Fig. 6 UV-Visible spectrum of exfoliated MoS_2 nanoscrolls in DMF.

This clearly confirms that the PL arises mainly from the MoS_2 nanoscrolls. However, the PL intensity of exfoliated MoS_2 nanoscrolls in DMF is higher than water due to more number of electrons excited to excited state in DMF **(Fig S7).**

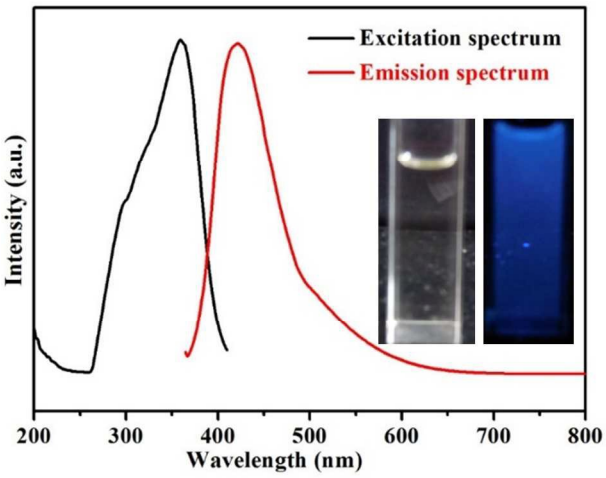

Fig. 7 The excitation and emission spectrum of exfoliated MoS_2 nanoscrolls and photographs of photoluminescent MoS_2 nanoscrolls dispersion in DMF before and after UV light illumination (inset).

The luminescent behavior of MoS_2 nanoscrolls was further investigated in detail by using different excitation wavelengths ranging from 330 nm to 530 nm are shown in **Fig S8**. It can be clearly seen that the increase in excitation wavelength leads to a red shift in the luminescence spectra over the emission wavelength ranging from 420-600 nm. It clearly indicates that the MoS_2 nanoscrolls luminescence properties are strongly dependent on the particle size.

For the first time, we demonstrated a rapid, one-pot synthesis of MoS_2 nanoscrolls from layered bulk MoS_2 using SCFs processing. SCFs processing significantly reduces both the size and thickness of MoS_2. PXRD and Raman spectroscopic analyses confirmed the exfoliation of MoS_2 nanoscrolls from bulk MoS_2 powder. FE-SEM, TEM and AFM analyses revealed the nanoscrolls formation with the lateral size of ~ 50 to 150 nm and a length of 0.2 µm to 3.0 µm. The MoS_2 nanoscrolls exhibit photoluminescence over the emission wavelength ranges from 420-600 nm. The unique characteristics of the SCFs, such as gas-like diffusivity, liquid-like solubility, low interfacial tension, excellent wetting of surfaces and high diffusion coefficients leads this method as a simple, scalable, and convenient one for direct exfoliation of MoS_2.

Notes and references

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Structural characterization, additional FE-SEM and TEM images of bulk MoS_2 and additional images for MoS_2 nanoscrolls are available in the Electronic Supplementary Information (ESI): [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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Graphical abstract

Rapid, One-Pot Synthesis of Luminescent MoS_2 Nanoscrolls Using Supercritical Fluids Processing

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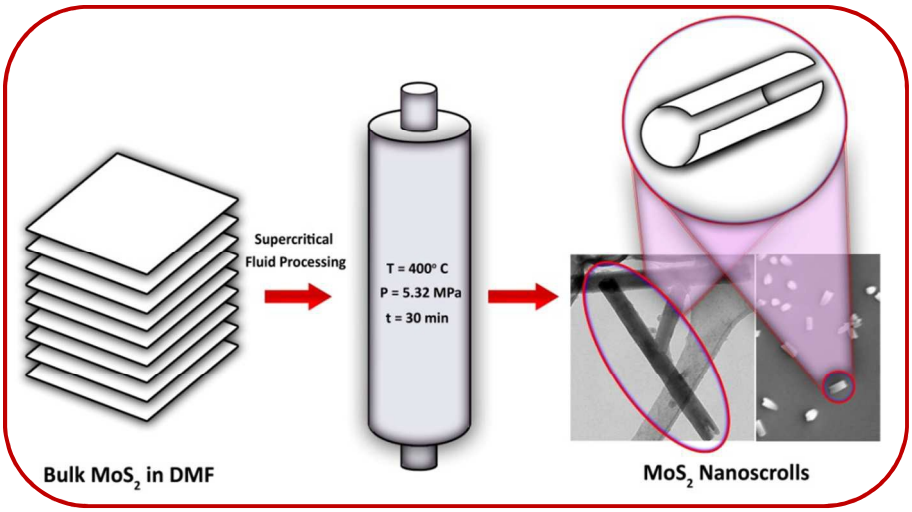

A rapid, one-pot synthesis of surfactant-free MoS_2 nanoscrolls by supercritical fluid processing is demonstrated. The MoS_2 nanoscrolls showed size depended luminescent behaviour. This method is promising for direct exfoliation of other 2D layered materials.