Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

Exfoliation of WS_2 in Semiconducting Phase using a Group of Lithium Halides: a New Method of Li Intercalation

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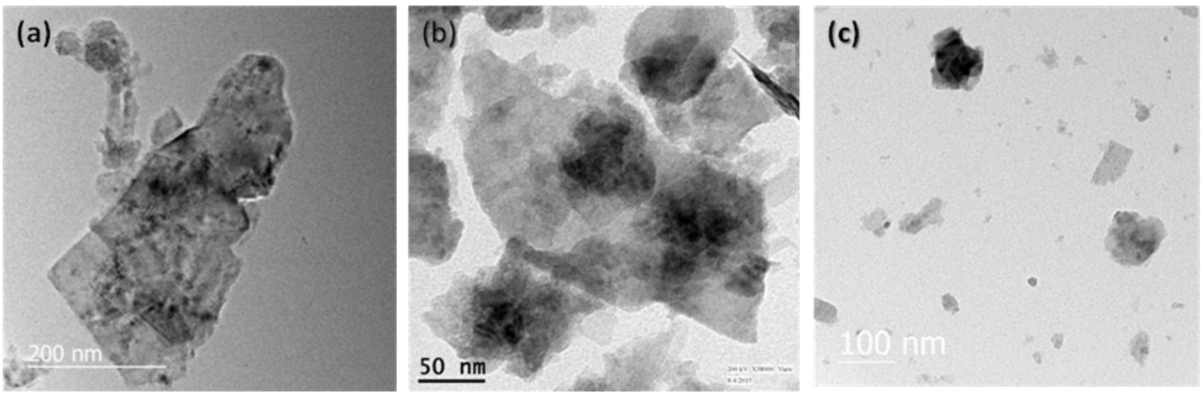


Figure S1: TEM images of few layer WS_2 flakes collected at (a) below 1000 rpm (WS_2 (1K), average size ≥ 500 nm); (b) below 2000 rpm (WS_2 (2K), average size ~ 300 nm); (c) collected above 3000 rpm (WS_2 (3K), average size ≤100 nm).

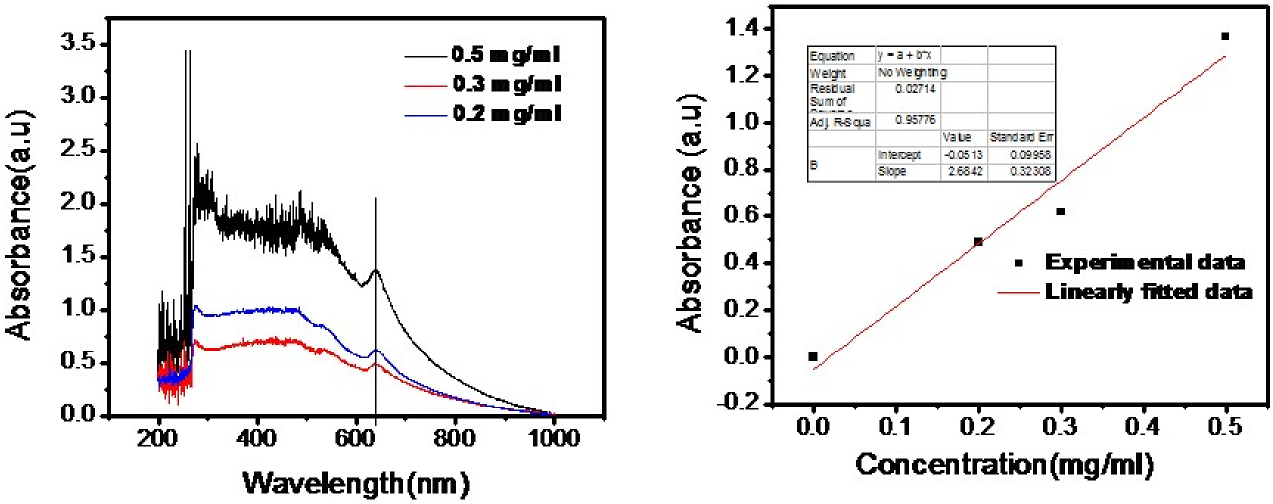


Figure S2: (a) Absorbance of WS_2 in DMF at 640 nm and (b) its corresponding absorbance with concentration. From the fitted curve slope, absorption coefficient is 2.68 ml mg^{-1} cm^{-1} at 640 nm.

Table S1

WS_2:Alkali halide (mole ratio)	**LiCl, (4h sonication at the first step)**
(1:1)	**~5.5 mg / mL**
(2:1)	**~2 mg/ml**
(1:2)	**~1 mg/ml**
1:0	**0**

$$\sigma_{sl} = \sigma_{solid} + \sigma_{liquid} - 2\left(\sqrt{\sigma_{solid}^{d} . \sigma_{liquid}^{d}} + \sqrt{\sigma_{solid}^{p} . \sigma_{liquid}^{p}} \right)$$

$$= \sigma_{solid}^{d} + \sigma_{solid}^{p} + \sigma_{liquid}^{d} + \sigma_{liquid}^{p} - 2\left(\sqrt{\sigma_{solid}^{d} \cdot \sigma_{liquid}^{d}} + \sqrt{\sigma_{solid}^{p} \cdot \sigma_{liquid}^{p}} \right)$$

Where σ_{solid} and σ_{liquid} are the surface tension of the solid and solvent, respectively and *p* indicates the polar component and *d* represents the dispersive component of surface tension. σ_{sl} is the interfacial surface tension between liquid solvent and solid. For efficient exfoliation σ_{sl} should be minimised.[1] Thus the polar and dispersive part of the surface tension played an important role in liquid phase exfoliation. Generally the solvents having surface tension value around 40 mN/m (DMF-37.1 and for Hexane-18.43 mN/m) are good exfoliating agent for exfoliation,[2] because those solvents have lower interfacial surface tension. The ratio of σ_{solid}^{p} to σ_{solid}^{d} of WS_2 is around 0.563 and surface tension is around 40 mN/m.[2] The interfacial surface tension is calculated for WS_2 in DMF as 0.86 mN/m and that of WS_2 in hexane as 15.5 mN/m.

The solvents which have minimum interfacial surface energy are a good solvent for liquid exfoliation.

As we know that total surface tension σ_{solid} is equal to the sum of polar and dispersive components of the surface tension. So we can write

$$\sigma_{solid} = \sigma_{solid}^{d} + \sigma_{solid}^{p} \text{ .... (2)}$$

Now total surface tension of WS_2 is 40 mN/m, so we can write,

$$\sigma_{solid}^{WS2} = \sigma_{solid}^{d(WS2)} + \sigma_{solid}^{p(WS2)} = 40 \text{ ....(3)}$$

Again we know that the ratio of σ_s^p and σ_s^d of WS_2 is around 0.563, so

$$\sigma_{solid}^{p(WS2)} / \sigma_{solid}^{d(WS2)} = 0.563 \text{ ....(4)}$$

From equation (2) we can calculate,

$\sigma_{solid}^{d(WS2)} - \sigma_{solid}^{p(WS2)}$ =11.18 ....(5)

By solving equation (1) and (3) we get, $\sigma_{solid}^{p(WS2)} = 14.91$ and $\sigma_{solid}^{d(WS2)} = 25.09$

So using this value we calculate the interfacial surface tension of different solvents which is shown in following table S2. The exfoliation yield is also tabulated for comparison.

Table: S2

Solvent	**Surface Tension (mN/m)** (σ)	**Polar Component of Surface Tension (mN/m)** (σ_{liquid}^{p})	**Dispersive Component of Surface Tension (mN/m)** (σ_{liquid}^{d})	**Interfacial Surface Tension between WS_2 and solvents (mN/m)** (σ_{sl})	**Experimental Yield (mg/ml) LiI , 30 min sonication 1st step**
DMF	36.50	11.30	25.20	0.26	4.81
EtOH	23.70	4.40	19.30	3.52	0.18
IPA:Water (1:1)	25.13	8.17	16.96	1.81	1.1
Water	72.75	50.65	22.10	10.71	0
Hexane	18.43	0	18.43	15.499	0
Acetone	23.30	16.50	6.80	5.82	0
NMP	40.79	11.58	29.21	0.59	2.5

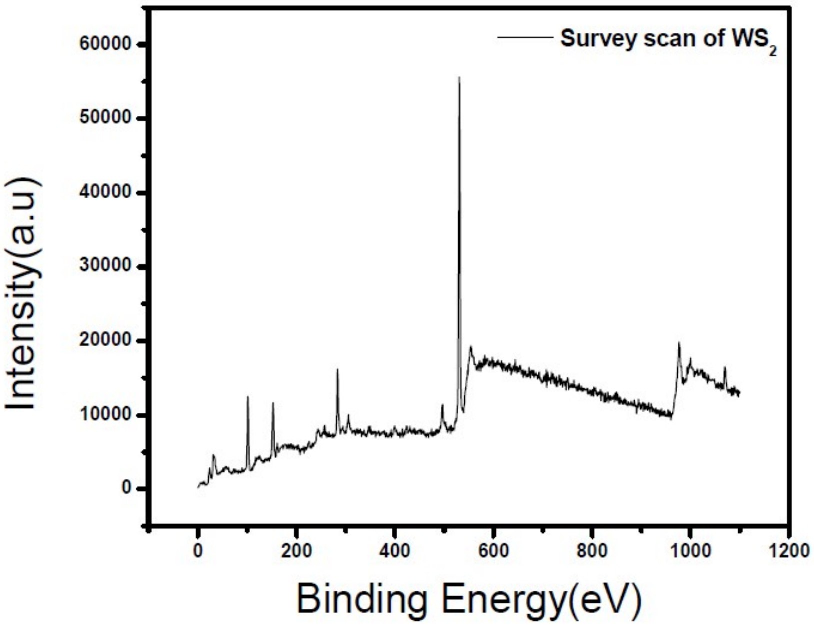
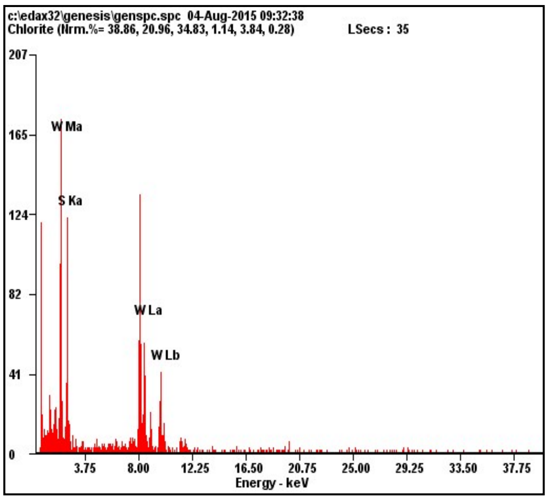


Figure S3: XPS Survey scan of WS_2 nanosheet



Element	*Wt %*	*At %*
W M	69.53	31.04
S K	26.20	67.05
W L	04.28	01.91

Figure S4: EDAX spectra of WS_2 nanosheet

[1] Shen, J.; He, Y.; Wu, J.; Gao, C.; Keyshar, K.; Zhang,X.; Yang, Y.; Ye, M.; Vajtai, R.; Lou, J.; Ajayan.; P. M. Liquid Phase Exfoliation of Two-Dimensional Materials by Directly Probing and Matching Surface Tension Components. *Nano Lett.* **2015,** *15*, 5449−5454.

[2] Cunningham, G.; Lotya, M.; Cucinotta, C. S.; Sanvito, S.; Bergin, S. D.; Menzel, R.; Shaffer, M. S. P.; Coleman, J. N. Solvent Exfoliation of Transition Metal Dichalcogenides: Dispersibility of Exfoliated Nanosheets Varies Only Weakly between Compounds. *ACS Nano* **2012**, *6*, 3468−3480.