Supporting Information

Plasmon Resonances of Highly Doped Two-Dimensional MoS₂

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S1. Lateral size and thickness distributions of two dimensional (2D) MoS_2 nanoflakes

Table S1. Characterization of 2D MoS_2 nanoflakes: (a) Distribution of the lateral dimensionsand (b) The thickness distribution.

Lateral size distribution (nm)	Frequency (%)
0-10	1
10-20	13
20-30	34
30-40	29
40-50	14
50-60	6
60-70	2
>70	1

Number of layers	Frequency (%)
1	7
2	30
3	21
4	17
5	12
6	8
>7	5

S2. Mean crystallite dimension of lithium intercalated 2D MoS₂ nanoflakes at different applied voltages

The intercalated Li in the 2D MoS_2 nanoflakes strains the crystallite structure, which eventually produces cracking. In order to analyze the cracking process, X-ray diffraction (XRD) for the 2D MoS_2 intercalated at the applied voltages of -4, -6, -8 and -10 V as well as deintercalated at +10 V were obtained. The results are presented in Figure S1. Scherrer formula was used for calculating the mean values of crystallite dimensions. The results are summarized in Table S2 obtained based on the Scherrer equation:

$$\tau = \frac{K\lambda}{\beta \cos\theta} \tag{S1}$$

in which τ is the mean size of the crystalline domains; *K* is the dimensionless shape factor; λ is the X-ray wavelength of 0.15418 nm; β is the line broadening at half of the maximum intensity (in radians) and θ is the Bragg angle.

Samples	β (°)	θ (°)	τ (nm)
-4 V	0.21	14.45	43.27
-6 V	0.23	14.41	39.68
-8 V	0.28	14.29	32.58
-10 V	0.27	14.16	33.76
+10 V	0.28	14.31	32.58

Table S2. The crystallite domains mean dimensions as a function of the applied voltage.

From Figure S1, it can be observed that there is a dominant peak at 14.45° for 2D MoS₂ intercalated at -4 V, which reflect the (002) plane.¹ This peak location is close to the value reported for pristine 2H 2D MoS₂,¹ which indicates the crystal structure remains intact at such small applied electric field intensities. The estimated mean size of the crystallites is

43.27 nm (Table S2), which is in perfect agreement with the lateral size of the pristine 2D MoS₂ nanoflakes obtained using the AFM measurements (see Table S1). However, the mean crystallite size is reduced to 39.68 nm when the applied voltage decreases to -6 V, which indicates the crystallites begin cracking into smaller pieces. Further decrease of the applied voltages to -8 V and then to -10 V lead to the (002) peak shifting towards lower angles, which is the signature for the expansion of the crystal lattice along the *c*-axis and formation of stoichiometric compounds.² At the applied voltage of -8 V the mean value reaches the minimum value of 32.58 nm. However, no more broadening of the XRD peak is seen at lower voltages; a sign that no further cracking occurs. Interestingly, the peak shifts to a higher angle of 14.31° when the polarity of the applied voltage is reversed to +10 V and the deintercalation occurs. The β value shows no apparent change which indicates that the mean value of the crystallites lateral dimensions does not alter after the deintercalation process.



Figure S1. XRD patterns of 2D MoS₂ nanoflakes intercalated/deintercalated using Li⁺ ions at different applied voltages

S3. Active control of photoluminescence in 2D MoS₂ nanoflakes

We investigated the photoluminescence (PL) properties of 2D MoS₂ nanoflakes using the electrochemical intercalation process in our previous work.¹ From the tests, we noticed that there was only a small decrease in the PL intensity at the applied voltage of -4 V. Lower applied voltages resulted in a large decrease in the PL intensity. A complete PL quenching was observed at the electrochemical force of -10 V. Reversible intercalation effect of PL was also demonstrated by active control of PL in the 2D MoS₂ nanoflakes under different intercalating/deintercalating voltages of ± 4 , ± 6 , ± 8 and ± 10 V. A fairly short recovery time of less than 40 s and a large reversibility of over 0.9 were achieved.¹

S4. Justification for choosing 1 as the value for infinite frequency dielectric constant

The parameter ε_b in the Drude equation, which is the high frequency dielectric contestant (also called the polarization response from the core electrons), refers to the value of the dielectric constant of a material at infinitely large frequencies. The most common choice for ε_b is 1. This value is obtained from the Drude assumption that the material is conductive enough that electron gas in ideal metal condition exist and the electrons does not interact with each other. This assumption is correct for many metals and highly doped semiconductors that show metallic properties.³ We also used 1 in equation (5) for ε_b , which gave us a very good agreement between the plasmonic peaks appeared in the UV-vis measurements and the theoretical calculations. This means that the near metallic Drude assumption is valid in this case. This is in agreement with the implementation of Drude equation for reduced WO_{3-x} for which also the value of 1 was also suggested for ε_b .⁴

Considering $\text{Li}_x \text{MoS}_2$ and WO_{3-x} cases, which both have stratified structures, it seems that value of 1 for infinite frequency dielectric constant fits perfectly for highly doped or reduced layered materials with massive electron constants.

The theoretical values for real and imaginary parts of relative permittivity of x = 0.5 lithium intercalated MoS₂ at the wavelength range of 200 to 2000 nm is shown in Figure S2 that were obtained using Drude equation using $\varepsilon_b = 1$.



Figure S2. Imaginary and real parts of the relative permittivity for Li_{0.5}MoS₂

S5: Table S3. The lattice parameters as calculated in this work using $2 \times 2 \times 1$ supercell of 2H MoS₂ for a set of Li_xMoS₂ intercalates with prismatic coordination of Mo atoms.⁵ Part of this table was reconstructed from a table in the supporting information of reference 5 with permission. Copyright 2012 Elsevier.

Li content, <i>x</i>	occupation sites	a, Á	b, Á	c, Á	α, °	β, °	γ, °	V, Á ³	$N \times 10^{27} \text{ m}^{-3}$
0.125	а	6.24	6.24	12.13	90.1	90.1	60.0	409.79	2.44
0.250	ab	6.24	6.25	12.47	90.0	90.1	60.0	421.49	4.745
0.250	ae	6.25	6.25	12.43	90.0	90.0	60.1	421.03	4.75
0.250	af	6.25	6.25	12.52	90.0	90.0	60.1	423.96	4.717
0.250	ah	6.25	6.25	12.47	90.0	90.0	60.1	422.08	4.738
0.375	abc	6.26	6.26	12.65	89.9	90.0	60.0	429.41	6.986
0.375	abe	6.29	6.26	12.81	90.0	89.7	60.3	438.24	6.846
0.375	bce	6.28	6.26	12.88	89.3	88.8	60.1	438.97	6.834
0.500	abcd	6.31	6.30	12.69	90.2	90.2	59.9	436.69	9.16
0.500	abce	6.29	6.29	13.03	90.3	90.3	59.9	445.93	8.97
0.500	abch	6.32	6.30	12.98	90.0	91.5	60.0	447.11	8.95
0.500	adeh	6.31	6.31	13.14	90.0	90.0	59.6	451.86	8.85
0.500	adfg	6.29	6.29	13.26	87.7	87.7	59.8	453.28	8.82
0.625	abcde								
0.625	abcef	6.33	6.33	13.24	90.7	90.7	60.0	459.94	10.87
0.625	abceh								
0.750	abcdef	6.38	6.35	13.24	90.0	89.0	60.0	464.00	12.93
0.750	abcefg	6.38	6.38	13.30	90.0	90.0	58.9	463.66	12.94
0.750	abdefg								
0.750	bcdefg	6.39	6.39	13.29	90.0	90.0	58.8	464.70	12.91
0.875	abcdefg	6.42	6.41	13.23	90.1	90.1	59.6	469.50	14.91
1.000	abcdefgh	6.37	6.47	13.27	90.0	90.0	60.3	475.12	16.84

S6: Table S4. The lattice parameters as calculated in this work using $2 \times 2 \times 2$ supercell of 1T MoS₂ for a set of Li_xMoS₂ intercalates with octahedral coordination of Mo atoms.⁵ Part of this table was reconstructed from a table in the supporting information of reference 5 with permission. Copyright 2012 Elsevier.

Li content, <i>x</i>	occupation sites	a, Á	b, Á	c, Á	α, °	β, °	γ, °	V, Á ³	$N \times 10^{27} \text{ m}^{-3}$
0.125	а	6.50	6.50	11.52	90.2	90.2	58.2	413.66	2.42
0.250	ab	6.51	6.52	11.69	90.0	89.9	58.7	423.97	4.72
0.250	ae	6.48	6.48	12.13	90.6	90.6	58.5	434.53	4.60
0.250	af	6.47	6.47	12.17	85.4	85.5	58.7	433.46	4.61
0.250	ah	6.44	6.49	12.08	91.4	89.6	59.6	434.74	4.6
0.375	abc	6.53	6.53	11.68	87.6	87.6	59.6	429.27	6.99
0.375	abe	6.49	6.50	12.33	87.5	87.9	58.6	443.85	6.76
0.375	bce	6.48	6.48	12.40	84.2	84.2	59.5	445.21	6.74
0.500	abcd	6.58	6.58	11.72	90.3	90.3	59.0	434.69	9.2
0.500	abce	6.52	6.52	12.31	86.9	86.9	59.8	451.20	8.87
0.500	abch	6.54	6.53	12.18	89.9	89.6	59.7	449.09	8.91
0.500	adeh	6.52	6.52	12.41	87.5	87.5	59.7	454.60	8.8
0.500	adfg	6.49	6.49	12.72	83.7	83.8	60.0	460.83	8.68
0.625	abcde	6.59	6.59	12.13	90.0	90.0	58.8	450.98	11.09
0.625	abcef	6.56	6.57	12.36	90.0	90.0	59.2	457.97	10.92
0.625	abceh	6.58	6.58	12.32	92.0	92.1	58.9	456.28	10.96
0.750	abcdef	6.63	6.53	12.30	89.7	88.6	60.1	461.37	13
0.750	abcefg	6.61	6.63	12.36	90.0	90.1	58.8	463.27	12.95
0.750	abdefg	6.62	6.59	12.41	90.7	91.3	59.0	464.71	12.91
0.750	bcdefg	6.60	6.59	12.31	89.2	89.2	60.4	465.15	12.90
0.875	abcdefg	6.68	6.62	12.40	90.3	90.7	58.9	470.19	14.89
1.000	abcdefgh	6.73	6.68	12.38	90.0	90.2	58.6	474.65	16.85

S7: Optical absorption measurement of the lithium intercalated fluorine doped tin oxide (FTO) substrate



Figure S3. Absorption spectrum of FTO substrate intercalated using Li^+ ions at the applied voltage of -10 V.

As the 2D MoS_2 nanoflakes are drop-casted onto conductive FTO substrates for Li⁺ ion intercalation process and other tests, Li⁺ ion intercalation of FTO itself may interfere with the absorption properties of 2D flakes. Therefore, the UV-Vis spectrum of Li⁺ ion intercalated FTO at applied voltage of -10 V is obtained as a reference. From Figure S3, it is seen that there is a sharp optical absorption peak centred at 325 nm is found.

S8: Plasmon resonance quality (Q) factor for Li_xMoS₂



Figure S4. Gaussian peak-fitting for the UV-vis absorbance spectra of nanoflakes intercalated at -8 V.

The plasmon resonance quality (Q) factor for gold is theoretically between 5 to 20, ⁶ for silver is 20 to 60 ⁶ and the measured value for WO_{3-x} has been reported as $1.6.^4$ For MoS₂ intercalated at -8 V (-8 V was chosen as a clear baseline is available), it is estimated to be approximately 3.4, if we include the double adjacent peaks (Figure S4). If we estimate 4 Gaussian curves to fit to the data using the Fityk Software package (version 0.9.2), we obtain a value of 6.33 for the quality factor (380 nm peak). This shows that Li_xMoS₂ propagation loss is more in comparison with gold and silver nanoparticle systems, and less than that of the reduced WO_{3-x} system.

It is important to consider that the system is made of 2D Li_xMoS_2 flakes of different lateral dimensions. This polydispersity significantly reduces the Q factor and hence increases the

propagation loss. If the system is made with improved uniformity of Li_xMoS_2 , possibly this Q factor can be significantly increased.



S9: Electron Energy Loss Spectroscopy (EELS)

Figure S5. EELS spectra of (a) 2D MoS₂ and (b) 2D Li_xMoS₂

S10: X-ray photoelectron spectroscopy (XPS) of surface and bulk of the intercalated MoS₂ nanoflakes



Figure S6. XPS patterns of elemental Mo at surface for not etched and etched films made of drop casted intercalated nanoflakes.

After the MoS_2 nanoflakes were intercalated by Li^+ ions at -10 V, they were transferred to a cover glass substrate which was similar to that used in the SPMFM experiments (see main text). As can be seen in Figure S6, it was found that the nanoflakes in the surface (no etching) of the drop casted film remained predominately in the 2H phase while nanoflakes in the bulk (etched for 60s) were mainly in the 1T metallic phase. This suggests that the intercalated Li^+ ions diffuse out of the nanoflakes surface in time, resulting in the restoration of the 2H phase.

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