In-situ Optical Measurement of the Rapid Li Intercalation and Deintercalation Dynamics in Colloidal 2D Layered TiS$_2$ nanodiscs

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- **Fabrication of TiS$_2$ film**

  The colloidal TiS$_2$ nanodiscs were deposited by partially submerging the ITO/glass substrate to colloidal TiS$_2$ nanodisc solutions dispersed in chloroform for 12 hours. Due to the absence of strong coordination of the surfactant to the polar basal planes of TiS$_2$ nanodiscs, they readily adsorb on the polar surface of ITO. ITO/glass substrate was rinsed with ethanol and dried with N$_2$ before use.

- **Optical measurement of Intercalation**

  Light source: Tungsten halogen light source
  Reference: ITO/glass substrate without TiS$_2$ immersed in the cuvette containing the same solvent (acetonitrile) and electrolyte (LiClO$_4$)

  (1) With CCD spectrometer: The reference data, $R(\lambda)$, was taken before making the measurement on sample $S(\lambda,t)$, and the absorbance $A(\lambda,t)$ was obtained by taking from -log $(S(\lambda,t)/R(\lambda))$.
  (2) With dispersive spectrometer at near-IR: The spectrometer was setup in dual-beam configuration and the signals from reference, $R(\lambda)$, and sample, $S(\lambda,t)$, were acquired simultaneously using two amplified InGaAs photodiodes as the detector.
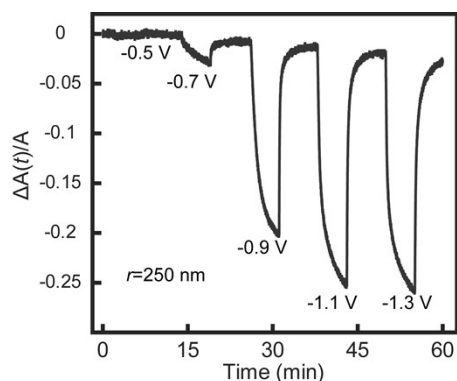
- **Electrode potential dependence of ΔA(*t*)/A**

Figure S1. Dependence of ΔA(*t*)/A on the reference electrode potential measured in TiS$_2$ nanodiscs with r=250 nm. The potential is with respect to Ag pseudo reference electrode. -1.1 V for intercalation was chosen since it shows the saturation of the modulation amplitude of ΔA(*t*)/A for intercalation.

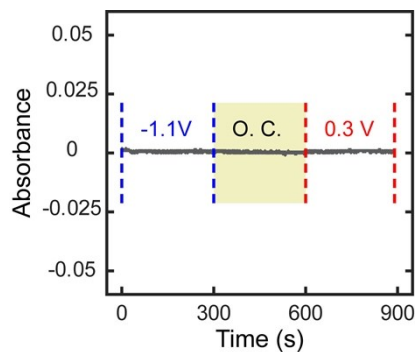- **Absence of contribution to ΔA(*t*)/A from the substrate**

Figure S2. Absorption value of ITO/glass at 600 nm at -1.1 V and 0.3V vs Ag pseudo reference electrode. ITO/glass substrate has no contribution the measured ΔA(*t*)/A.

- **Biexponential fitting of ΔA(*t*)/A**

The ΔA(t)/A data was fitting through biexponential model to extract time components.

$$\frac{\Delta A(t)}{A} = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + c$$
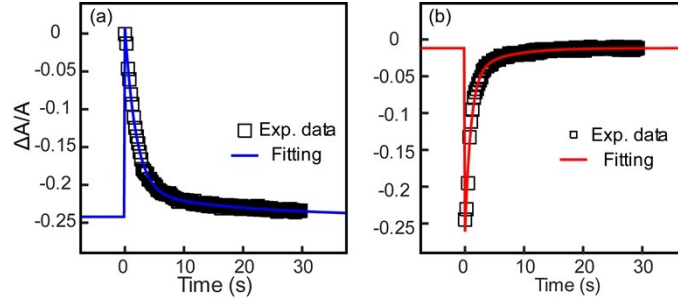

Figure S3. Fitting of ΔA(t)/A with bi-exponential model for r=80 nm sample at (a) -1.1V and (b) 0.3V.

For TiS$_2$ with r=80 nm

Cycle No.	Intercalation (-1.1V)					Deintercalation (0.3V)			
	A_1	τ_1 (s)	A_2	τ_2 (s)		A_1	τ_1 (s)	A_2	τ_2 (s)
1	0.87	1.9	0.13	20		0.85	1.0	0.15	5.6
2	0.94	2.0	0.06	132		0.92	1.4	0.08	8.9
3	0.96	1.8	0.04	39		0.93	1.2	0.07	11
4	0.96	2.0	0.04	59		0.92	1.2	0.08	11
5	0.94	2.0	0.06	42		0.91	1.3	0.09	10
6	0.92	2.1	0.08	26		0.91	1.3	0.09	16
7	0.91	2.5	0.09	30		0.92	1.7	0.08	22
8	0.89	2.5	0.11	26		0.89	1.7	0.11	28
9	0.87	2.8	0.13	29		0.89	2.1	0.11	28
10	0.85	2.8	0.15	33		0.89	2.4	0.11	32

For TiS$_2$ with r=250 nm

Cycle No.	Intercalation (-1.1V)					Deintercalation (0.3V)			
	A_1	τ_1 (s)	A_2	τ_2 (s)		A_1(%)	τ_1 (s)	A_2	τ_2 (s)
1	0.75	3.8	0.25	1.2×10^2		0.84	2.4	0.16	50

2	0.88	4.1	0.12	64		0.81	2.3	0.19	43
3	0.89	4.7	0.11	36		0.81	2.8	0.19	46
4	0.86	5.2	0.14	37		0.80	3.0	0.20	44
5	0.84	5.7	0.16	51		0.78	3.1	0.22	43
6	0.79	6.7	0.21	50		0.78	3.7	0.22	46
7	0.78	7.4	0.22	52		0.81	5.1	0.19	48
8	0.76	8.6	0.24	53		0.78	4.9	0.22	48
9	0.71	8.9	0.29	52		0.76	5.6	0.24	47
10	0.68	9.6	0.32	55		0.75	6.2	0.25	50

Table S1. Fitting parameter of $\Delta A(t)/A$ with biexponential function. The amplitudes (A_1 and A_2) are the fractional amplitudes.

- **Estimation of effective diffusion coefficient (*D*) of Li in TiS$_2$ nanodiscs.**

The normalized experimental data of $|\Delta A(t)/A|$ was fit with the following expression of $C(t,r)$, which represents average concentration of Li normalized to its terminal concentration in a cylinder of radius *r* under 2-dimensional radial diffusion condition. [1]

$$C(t,r) = 1 - \sum_{n}^{\infty} \frac{4}{a_n} \exp\left(-D\frac{a_n^2}{r^2}t\right)$$

For this fitting, the following 12 leading terms for a_n were used in the summation, which are the solutions of the Bessel function of the first kind $J_0(x)$.

2.405, 5.520, 8.654, 11.1975, 14.9309, 18.0711, 21.2116, 24.3525, 27.4935, 30.6346, 33.7758, 36.9171
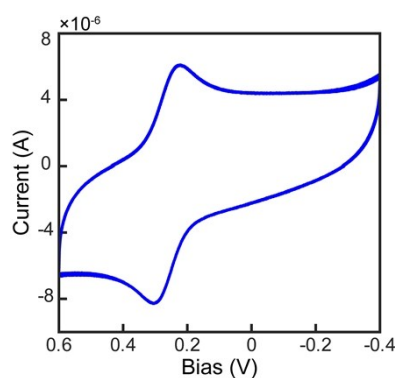
- **Calibration of Ag wire pseudo-reference**

Figure S4. Ag pseudo-reference electrode calibration. The working electrode was a glassy carbon electrode, with a Pt wire as the counter electrode. The electrolyte was $1\varnothing 10^{-4}$ M ferrocene in 0.1 M LiClO$_4$ acetonitrile solution. The average of the oxidation and reduction peak in 14 cycles as shown was around 0.25 V. Given that the potential of Fc$^+$/Fc in acetonitrile is 0.62 V versus standard hydrogen electrode (SHE),[2] the pseudo-reference of Ag electrode was around 0.37 V versus SHE.

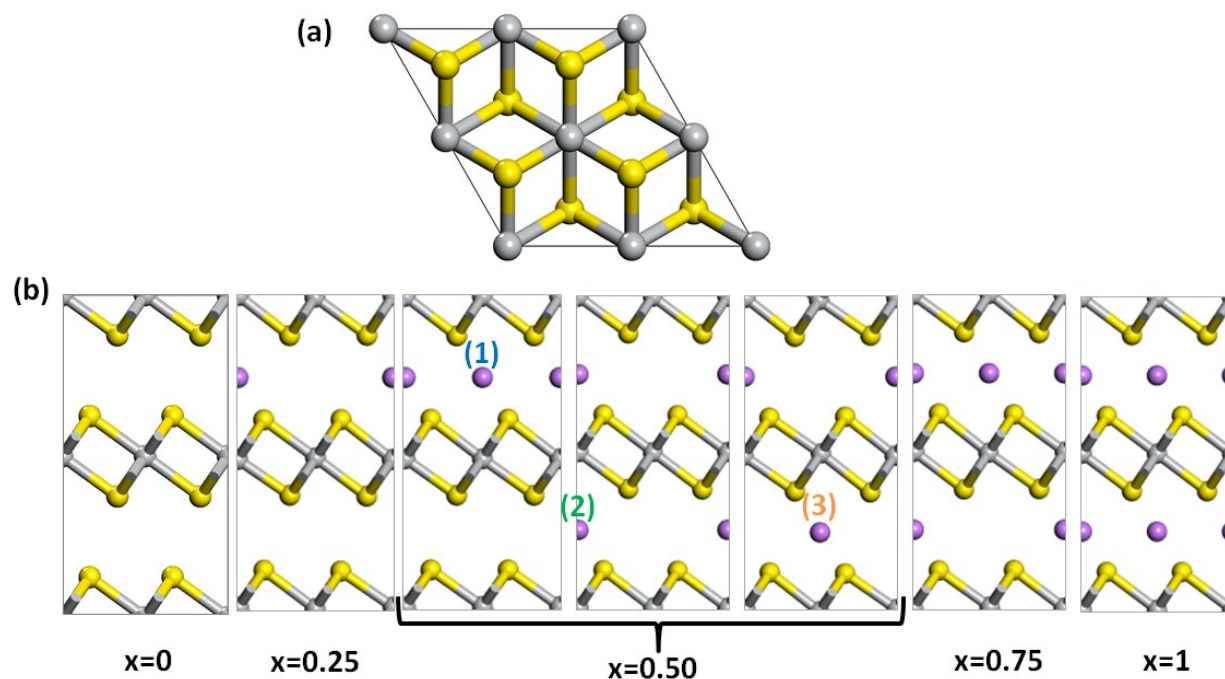- **Li$_x$TiS$_2$ model and respective cell parameters**

Figure S5. Li_xTiS_2 model. (a) top view of 2×2×2 supercell Li_xTiS_2 bulk; Li cannot be seen because they are in the same plane as Ti atoms. b) All different configurations for Li_xTiS_2. Gray, yellow, and pink spheres represent Ti, S, and Li atoms, respectively.

x	Supercell			Ave. per unit cell*	
	a (Å)	b (Å)	c (Å)	a_u (Å)	c_u (Å)
0.00	6.792	6.792	11.411	3.396	5.705
0.25	6.777	6.784	11.783	3.390	5.892
0.50-(1)	6.792	6.792	11.827	3.396	5.914
0.50-(2)	6.766	6.786	12.183	3.388	6.092
0.50-(3)	6.779	6.787	12.135	3.392	6.068
0.75	6.791	6.798	12.188	3.397	6.094
1.00	6.806	6.806	12.221	3.403	6.110

$$* a_u = (a + b)/4; a_u = c/2$$

Table S2. Optimized lattice parameters (a, b, and c) for different ratios and configurations of Li-intercalated in TiS_2 (Li_xTiS_2) in the supercell 2×2×2. a_u and c_u stand for the equivalent lattice parameters per unit cell.

- **Complex dielectric function ($\varepsilon_\parallel, \varepsilon_\perp$) and refractive index ($k_\parallel$) as a function of x in Li$_x$TiS$_2$**
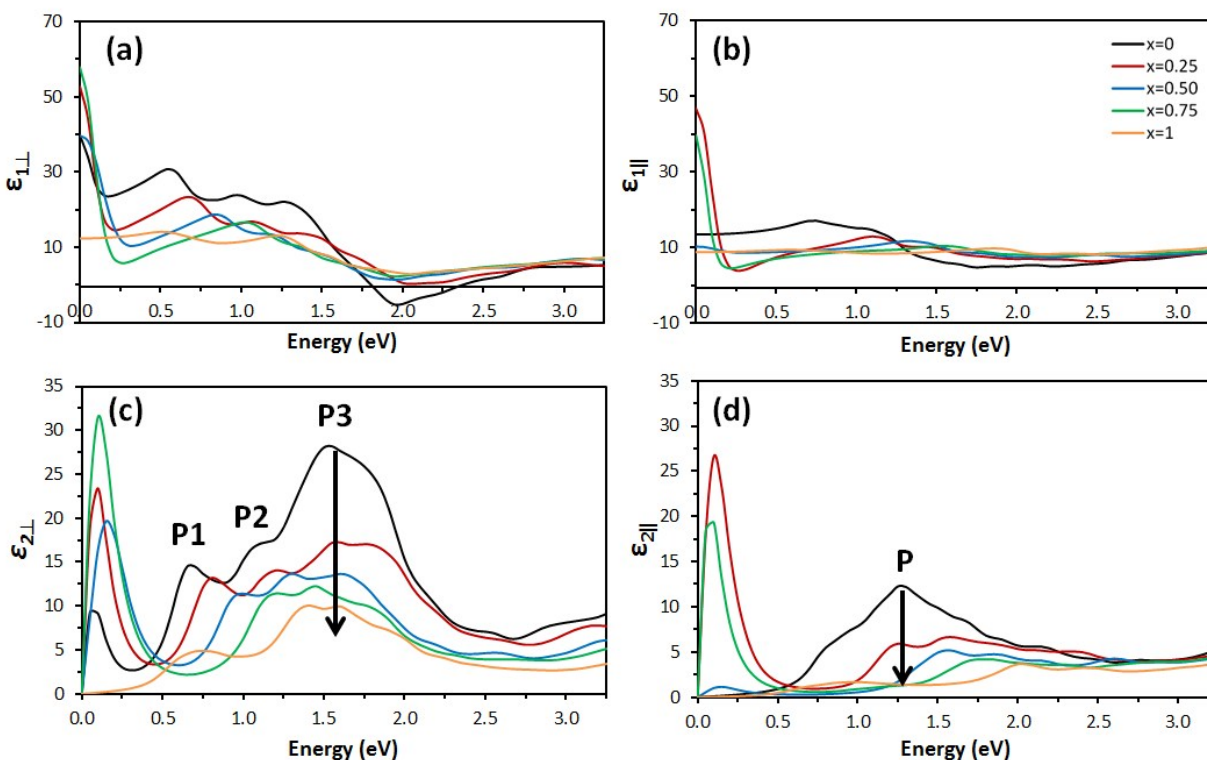

Figure S6. Complex dielectric function parallel ($\varepsilon_\parallel$) and perpendicular ($\varepsilon_\perp$) to the *c*-axis of TiS$_2$. Real and imaginary part of the dielectric function, (a, b) ε_1 and (c, d) ε_2 respectively, as a function of *x* in Li$_x$TiS$_2$. Arrows indicate the change of intensity at the main peaks as the concentration of lithium increases.
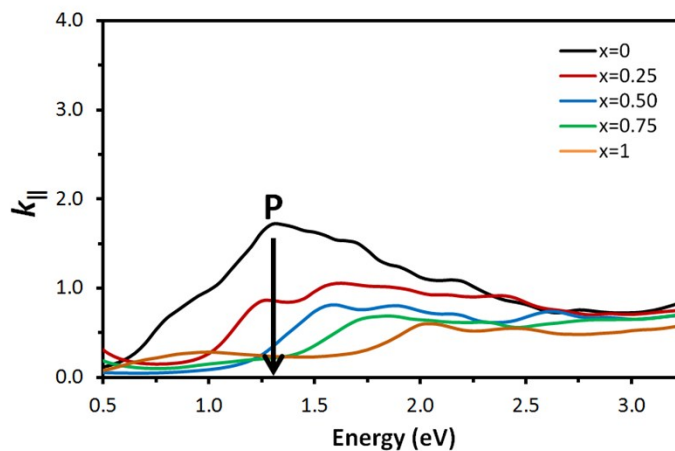

Figure S7. Parallel (out-of-plane) component of the imaginary part of refractive index ($k_\parallel$) as a function of *x* in Li$_x$TiS$_2$. Arrow indicates change of intensity at the main peak as the concentration of lithium increases.

(1) Crank, J. Diffusion in a cylinder. In *The Mathematics of Diffusion*; Oxford University Press: Bristol, England, **1975**; pp 73-74.

(2) Pavlishchuk, V. V.; Addison, A. W. Conversion constants for redox potentials measured versus different reference electrodes in acetonitrile solutions at 25°C. *Inorg. Chim. Acta* **2000,** *298,* 97-102.