The adsorption behavior of lithium on spinel titanium oxide nanosheet exposed by (1-14) high-index facet

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1. Recyclability of adsorbents

The reuse of $H_4Ti_5O_{12}$ nanorods was performed based on desorption and regeneration processes. Firstly, 0.8 g $H_4Ti_5O_{12}$ was added into 400 mL LiCl solution (pH 13) with initial concentration of 24 mM, and equilibrated for 4 h. Afterwards, the $H_4Ti_5O_{12}$ after Li^+ adsorption was immerged into 0.2 M HCl solution and stirred for 24 h to carry out the regeneration process. Then, the sample was collected by centrifugal and white precipitates were washed by ethanol and deionized water for three times, respectively. Then the precipitates were dried in an oven at 60℃ for 12 h. In the next reutilization experiments, the volume of LiCl solution was obtained according to adsorbent dosage (In this study, $H_4Ti_5O_{12}$ dosage was 2 g/L), and reuse process was repeated the above steps.

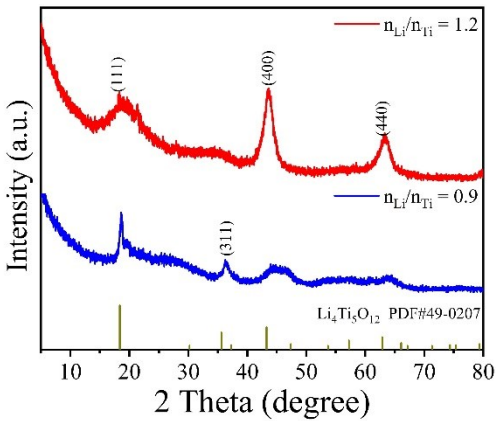

Fig. S1 XRD patterns of titanium oxides with different molar ratios of Li/Ti obtained by acid

treatment.

Fig. S2 shows the TEM images of $Li_4Ti_5O_{12}$. Fig. S2a-d shows sheet-like shape with large surface area, which matches well with the SEM results. The lattice spacing of nanosheet are 2.96 nm and 2.52 nm in Fig. S2e, which can be concluded to (220) and (-311) or other equivalent crystal planes, respectively. Fig. S2f also concludes similar (220) and (3-11) facets of $Li_4Ti_5O_{12}$ and this nanosheets can be concluded that the exposed facet of $Li_4Ti_5O_{12}$ nanosheets is (1-14) (inset in Fig. S2d). From the above results, the morphology of $Li_4Ti_5O_{12}$ is nanosheets with the high-index (1-14) facet exposed.

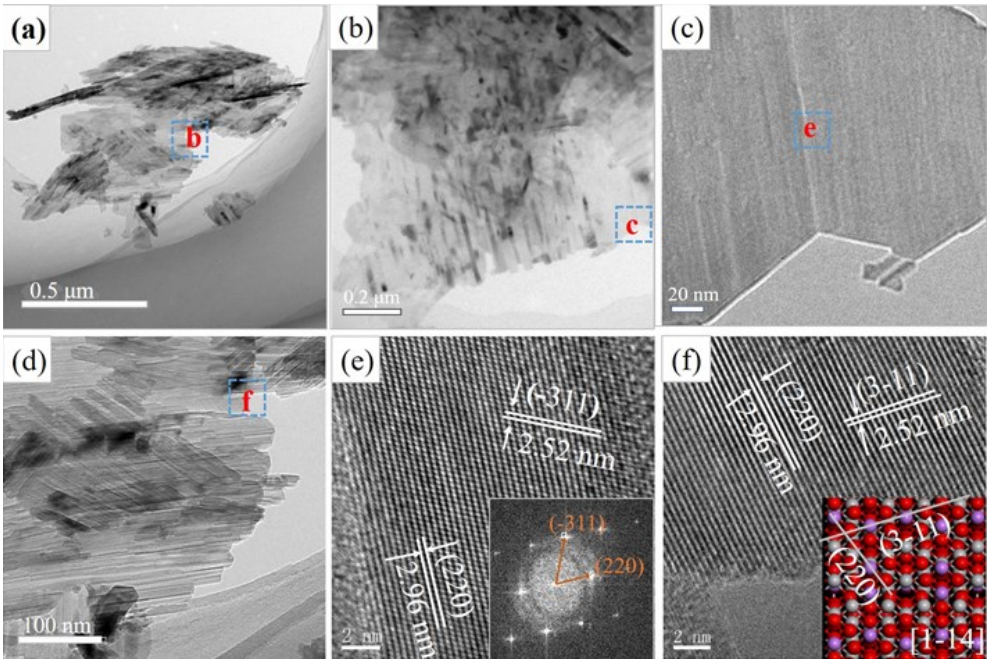

Fig. S2 (a)(b)(c)(d) TEM images of $Li_4Ti_5O_{12}$ (e) and (f) high-resolution TEM imagines of $Li_4Ti_5O_{12}$. The inset images of (e) is FFT and the inset of (f) is $Li_4Ti_5O_{12}$ (1-14) facet.

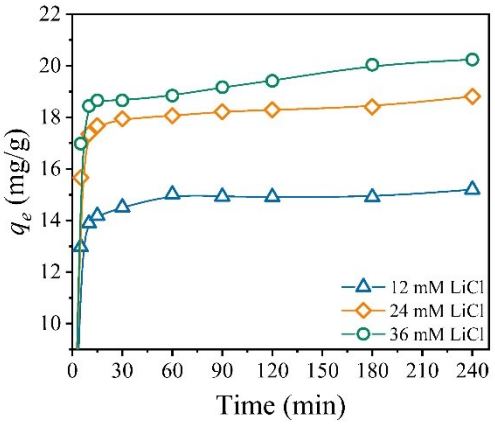

Fig. S3 Li^+ adsorption capacities of $H_4Ti_5O_{12}$ nanosheets at various Li^+ concentrations.

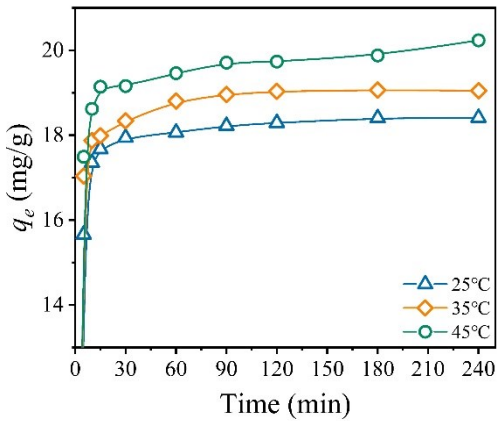

Fig S4 Li^+ adsorption capacities of $H_4Ti_5O_{12}$ nanosheets at various temperatures.

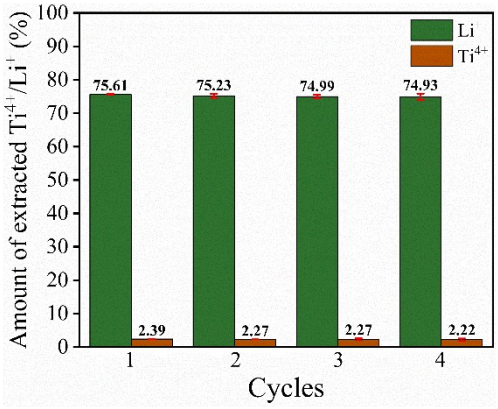

Fig. S5 The amount of extracted lithium and the dissolution of titanium in recycle process.

Table S1 The parameters of Dubinin-Radushkevich and Temkin isotherm models

Material	Dubinin-Radushkevich				Temkin		
	T (K)	q_m (mg/g)	E (kJ/mol)	R^2	k_T (L/g)	b (kJ/mol)	R^2
$H_4Ti_5O_{12}$ Nanosheets	298.15	20.42	0.066	0.95	1.94	5.11	0.99
	308.15	20.78	0.066	0.94	1.42	4.91	0.99
	318.15	21.21	0.065	0.95	1.71	5.18	0.99

Computer methods and details

Density functional theory (DFT) [1, 2] calculations were implemented by the Vienna Ab-initio Simulation Package (VASP) with the projector-augmented wave (PAW) [3] method, and the Perdew-Burke-Ernzerh (PBE) exchange-correlation functional [4] of the

Generalized Gradient Approximation (GGA) [5-7]. Owing to the strong-correlation d-electrons of Ti metals, the Hubbard-type U correction was adopted. In order to gain accurate computation, the U values of 2.5 eV were used [8, 9]. The cutoff energy of 500 eV was adopted in all calculations. The thickness of the vacuum is set to the 15 Å. An appropriate k-point mesh of 3×3×1 for the $Li_4Ti_5O_{12}$ (1-14) surface was adopted, respectively. In order to improve the quality of charge density, the k-point mesh of 4×4×1 was adopted. The electronic total energies convergence criterion was set at 10^{-4} eV. The atomic positions were stable until Hellmann-Feynman forces on each atom were less than a threshold value of 0.01 eV. The adsorption energy (E_{ad}) for Li adsorbed on optimized (1-14) surface slab of $H_4Ti_5O_{12}$ is calculated as Eq. (1):

$$E_{ads} = E_{(Adsorbate/substrate)} - [E_{(Adsorbate)} + E_{(substrate)}] \quad (1)$$

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