Supporting Information

Low Temperature Solution Synthesis of Reduced Two Dimensional Ti_3C_2 MXene with Paramagnetic Behaviour

Yeoheung Yoon [‡], Thi Anh Le[‡], Anand P. Tiwari, Ikjoon Kim, Michel W. Barsoum[*], and Hyoyoung Lee[*]

Reaction mechanisms for solvate-electride salts ($[Li((NH_2)_2C_2H_4)_3]^+\cdot e^-$)

Reaction mechanisms for solvate-electride salts **($[Li((NH_2)_2C_2H_4)_3]^+\cdot e^-$)**

Since the Li-EDA reagent can generate solvated-electride salts in a phase under inert atmospheric condition, all reactions were carried out using fully dried-glassware under inert N_2 condition. This was done to prevent the oxidation of Li to Li_2O.

There are number of metals at a zero or low oxidation states that can readily donate one or more electrons to materials with accessible LUMO orbitals (Li°, Na°, K°, etc.). These metals can function as electron transfer reagents. For example, when Li metal is mixed with EDA the following reaction occurs[1]:

$$Li + (NH_2)_2C_2H_4 \rightarrow [Li((NH_2)_2C_2H_4)_3]^+\cdot e^- \qquad (1)$$

When Li metal was dissolved in our EDA solution, in the presence of bulk $Ti_3C_2T_x$ multilayers, the solution turned dark blue, indicating that free radicals or electride salts are formed during the reaction[1].

To indirectly test the importance of working in a reducing atmosphere we bubbled oxygen bubbling at 10 sccm through the reaction solution. In this case the reaction solution never turned blue; instead, the end result was a white powder, presumed to be Li_2O.

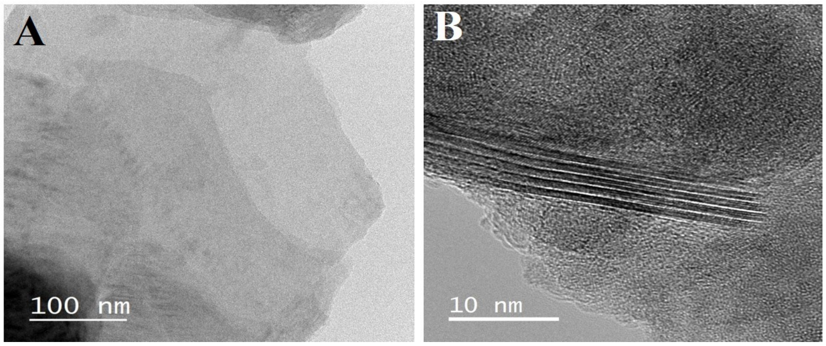

Fig. S1. (A) and (B) TEM images of r-$Ti_3C_2T_x$ nanosheets.

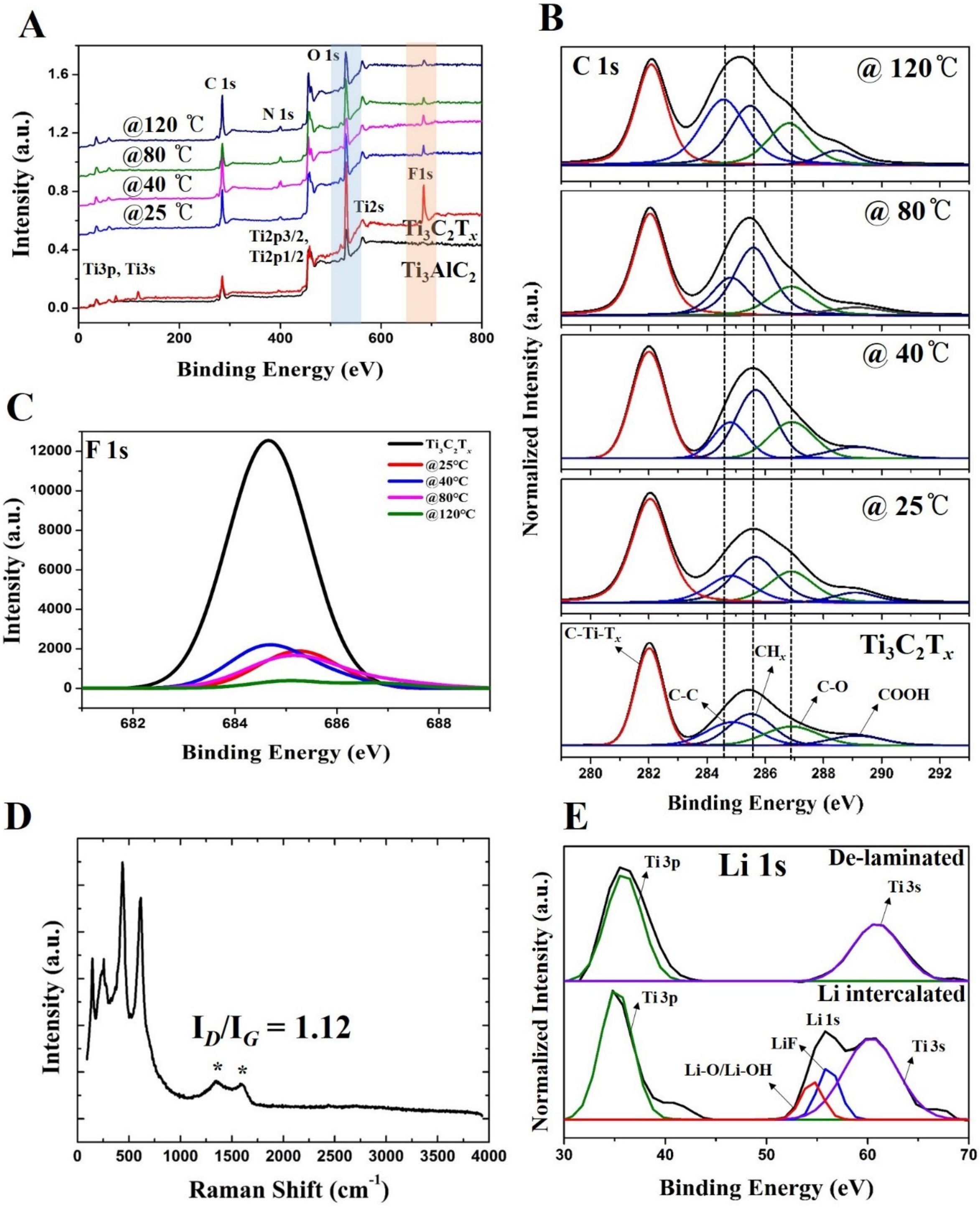

Fig. S2. XPS spectra obtained on $Ti_3C_2T_x$ and r-$Ti_3C_2T_x$ as a function of Li/EDA reduction temperature. (A) Overall spectra, (B) C 1s region, (C) F 1s region, (D) overall Raman spectra and (E) Li 1s region.

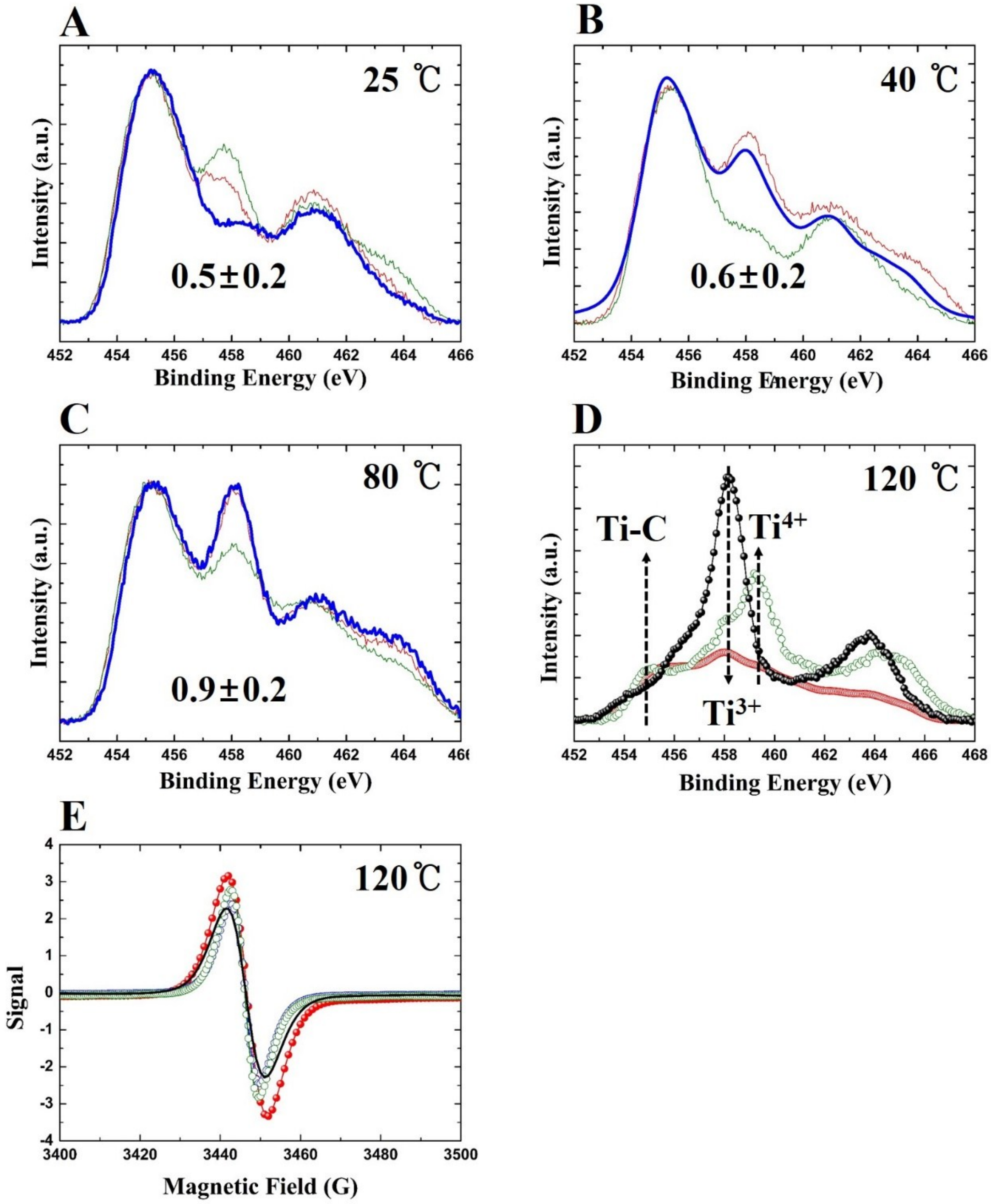

Fig. S3 (A) XPS spectra of Ti 2p region obtained on 3 different samples reduced at 25 °C; (B) Same as a, but reduced at 40 °C; (C) Same as a but reduced at 80 °C; (D) Same as a, but reduced at 120°C; (E) ESR signals of three samples reduced at 120 °C.

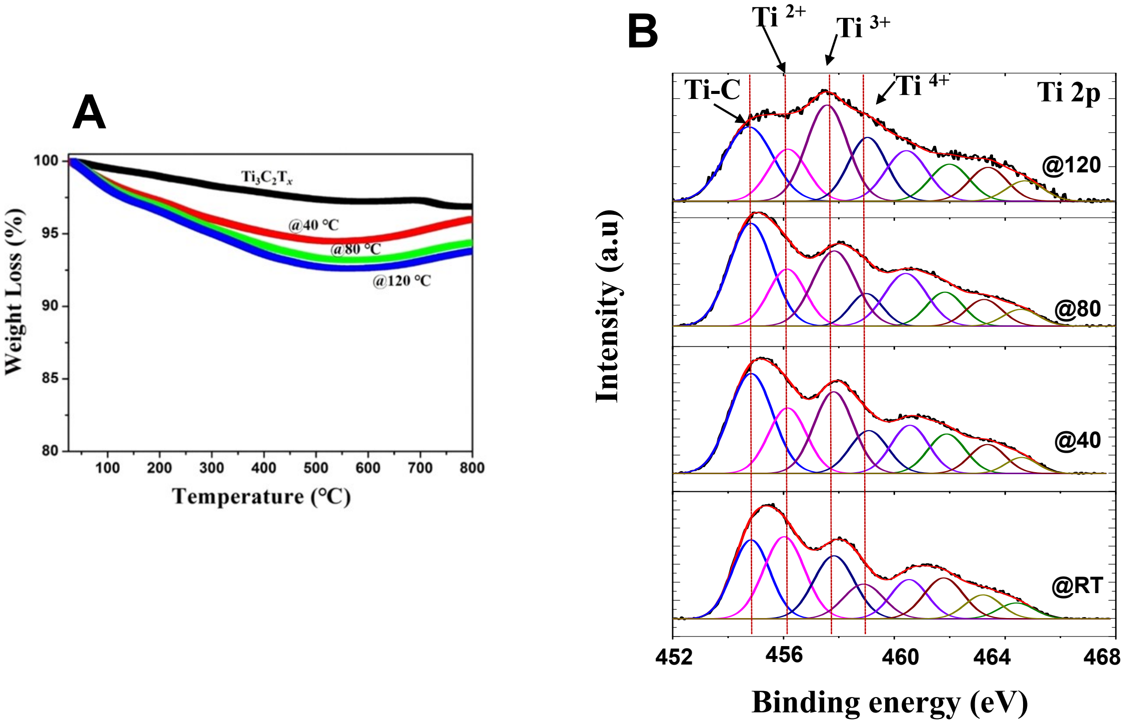

Fig. S4 (A) TGA results of $Ti_3C_2T_x$ and r-$Ti_3C_2T_x$ films reduced at various temperatures indicated.

(B) Deconvolution of XPS Ti 2p core level r-$Ti_3C_2T_x$ films reduced at various temperatures indicated.

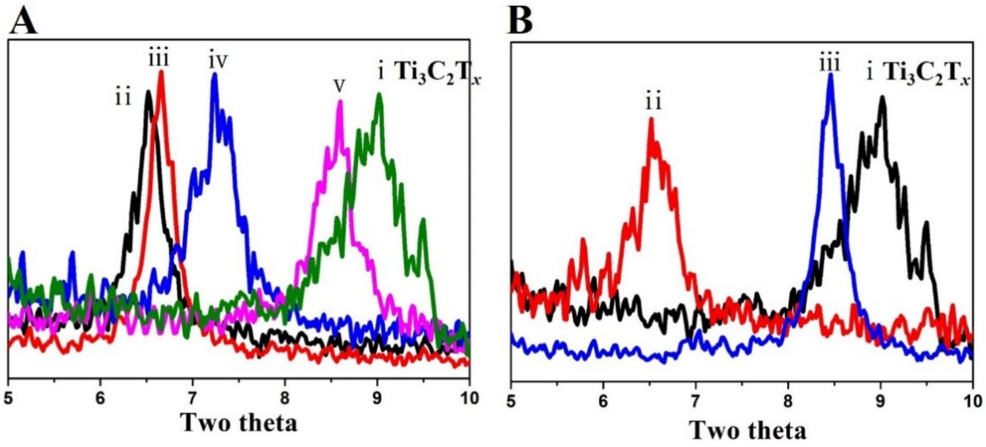

Fig. S5 Changes in (0002) XRD diffraction peaks of r-$Ti_3C_2T_x$ flakes as a result of intercalation and de-intercalation processes. (A) EDA intercalated r-$Ti_3C_2T_x$ dried under various conditions: 1: EDA intercalated, 2: dried at 25 ℃ for 24 h, 3: dried at 80 °C for 48 h, 4: dried at 150 °C for 72 h. (B) Li intercalated r-$Ti_3C_2T_x$ washed with EtOH and 5 wt.% HCl solution to remove Li ions from the r-Ti_3C_2 layers: 1: Li intercalated prior to washing; 2: same as 1 but washed with EtOH and 5 wt.% HCl solution.

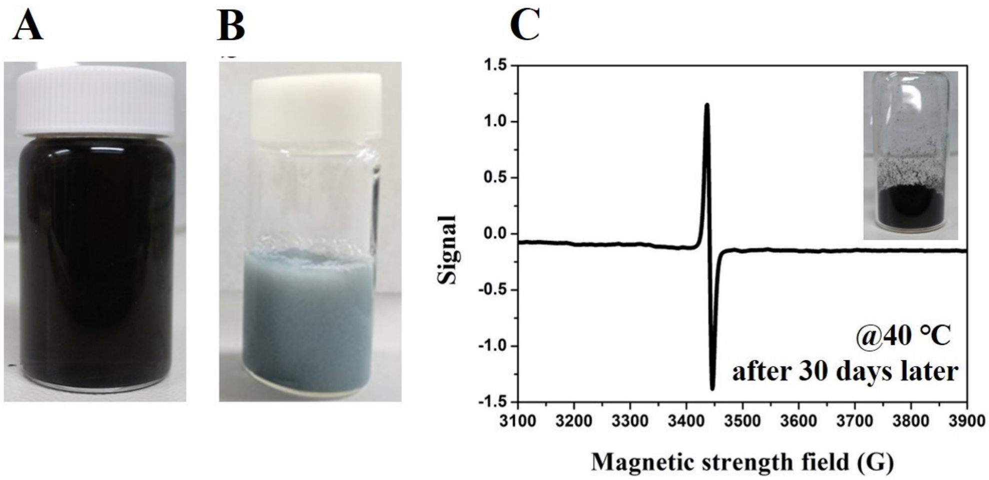

Fig. S6 Chemical stability of r-$Ti_3C_2T_x$ dispersed in water and its dried powder. (A) When r-$Ti_3C_2T_x$ is dispersed in water (0.1 wt.%), the solution is black; (B) 2-3 days later the color changes to sky-blue. This implies that the r-$Ti_3C_2T_x$ was not stable under oxygen-rich solution conditions. (C) However, when the powder type of r-$Ti_3C_2T_x$ was stored in air, their paramagnetic property was still maintained even after 30 days later.

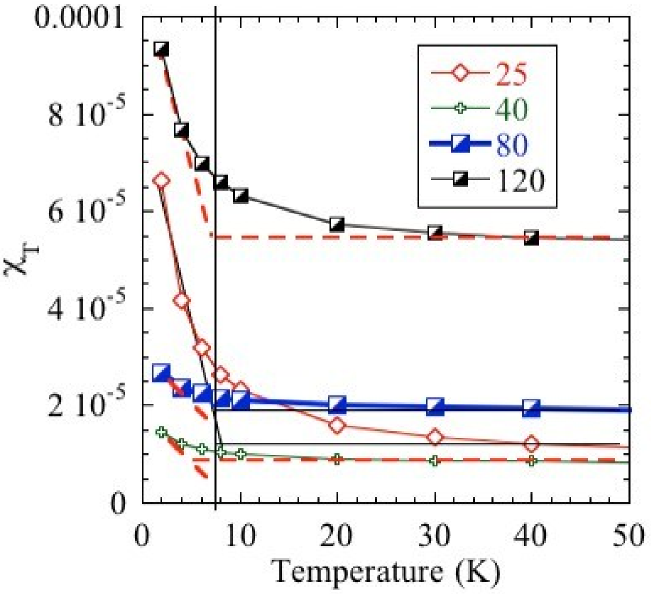

Fig. S7. Temperature dependence of of r-$Ti_3C_2T_x$ after reduction at low temperature (~ 50 K) illustrates intersecting tangent method of Curie temperature (T_c) estimation

Peak	Energy (eV)	Assignment (Color in Fig. S2B)	Intensity as function of reduction temperature	Ref.
C 1s, Fig. S2B	282.0±0.2	C-Ti-T_x (red)	≈ constant	(*31*)
	284.8±0.2	C-C (blue)	Increases substantially	(*18, 32*)
	285.5±0.2	CH_x (navy)	Decreases	(*18, 32*)
	286.8±0.2	C-O (green)	Increases slightly	(*18, 32*)
	289.0±0.2	-COOH (grey)	Decreases	(*18, 32*)

Table S1. Summary of XPS peak positions of C 1s. Column four qualitatively describes how the intensity of these peaks change with increasing reduction Temperature.

Reference

1. L. Reggel, R. Friedel, and I. Wender, *J. Org. Chem,* 1957, 22, 891.