Supplementary Information (SI) for ChemComm.

Electronic Supplementary Information

Synergy of 2D/2D $Ti_3C_2T_x$ MXene-Graphene Oxide Heterostructure for Enhanced Hydrogen Storage

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Chemical and Materials

The natural graphite flakes (≤ 40µm) and Ti_3AlC_2 MAX phase (≤ 40µm) were procured from Sigma Aldrich. The sulfuric acid (H_2SO_4) was purchased from Central Drug House Pvt. Ltd. (CDH), India. Potassium permanganate ($KMnO_4$), Hydrogen peroxide (H_2O_2), Lithium fluoride (LiF), and Hydrochloric acid (HCl) were purchased from Sisco Research Laboratories Pvt. Ltd. (SRL), India. Commercially available hydrogen (purity ≥99.99%) gas was used as a hydrogenation source. The deionized (DI) water (18.00 Ωm) from Mili Q (USA) and the chemicals used as received were used for the whole experiment.

Characterization Techniques

Structural and morphological characterization of the synthesized $Ti_3C_2T_x$ MXene and $Ti_3C_2T_x$ -GO heterostructure was performed using various experimental physicochemical techniques. The crystalline structure of $Ti_3C_2T_x$ MXene and Ti3C2Tx-GO heterostructure was recorded using an X-ray diffractometer (Rigaku MiniFlex, Japan) with Cu K_α incident X-ray source (wavelength: 0.154 nm). A step size of 0.02° was used to collect the pattern from 5° to 80° of 2θ. The Raman spectra were recorded by the AIRIX Corporation STR 500 (Japan) to observe the different molecular interactions or chemical bondings, defects, and disorders in the prepared materials. The measurement was carried out for dry powdered samples using a green laser beam with a wavelength of 532 nm. To understand the morphology, TEM images were captured using a (JEOL JEM-F200, Japan) multipurpose electron microscope operated at 200 kV. The materials solution was diluted to a low concentration, then drop-cast on a copper lacey TEM grid and dried overnight in a vacuum oven. The Brunauer-Emmett-Teller surface area (S_{BET}), total pore volume (V_T), and pore size distribution were determined at 77.35 K using nitrogen as the probe gas (AUTOSORB IQ, Quantachrome Instruments, USA). The samples were degassed for 8 hrs. at 150 °C in an ultra-high vacuum. Twenty points were taken for the adsorption-desorption isotherm to calculate S_{BET} in the 0.05-0.35 relative pressure range (P/P_o). The pore volume was calculated using the density functional theory model. The surface chemistry of the samples was analyzed with X-ray Photoelectron Spectroscopy (XPS) and recorded by ESCA+ omicron nanotechnology, Germany. The Al K_α target is used for the X-ray source, and XPSPEAK41 is used for the peak deconvolution. Hydrogen adsorption was measured using an advanced and automated Sieverts-type volumetric setup (RuboSORP MPA, RUBOLAB, Germany) at various temperatures. A known quantity sample was loaded in the sample holder and sealed with a metallic gasket. Before recording the hydrogen isotherm, samples were subjected to pre-treatment under an ultra-high vacuum at a temperature of 150 °C with a heating rate of 10°C/min, for 1 hr, followed by helium pycnometry to measure the sample volume. Then, the hydrogen adsorption measurements were conducted at different temperatures and up to 30 bar hydrogen pressure.

Synthesis of GO, $Ti_3C_2T_x$ MXene, and $Ti_3C_2T_x$-GO heterostructure

GO was synthesized using a modified Hummers' method from natural graphite flakes. In this process, 2gm of graphite flakes were dispersed in 90 mL of H_2SO_4 while stirring for 20 min. Then, 7 g of $KMnO_4$ powder was slowly added to the above-mentioned mixture in an ice bath to avoid overheating (exothermic). The mixture was then continuously stirred for 24h at 35 °C. After completing the reaction, 1000 mL of deionized water (DI) and 35% H_2O_2 (25 mL) were added to the mixture with vigorous stirring. The obtained yellow mixture was filtered and then washed with 1 M HCl solution and deionized water. Then, the resulting product was redispersed in 2000 mL of DI water. Further, the mixture was sonicated for 30 minutes for single-layer or few-layer exfoliation. The obtained GO dispersion was centrifuged twice at 10000 rpm for 15 min to separate the unoxidized graphite flakes. After that, the single-layer exfoliated GO dispersion was purified using a dialysis membrane to remove ionic impurities.

The $Ti_3C_2T_x$ MXene is synthesized by aluminium (Al) etching from the Ti_3AlC_2 MAX phase by the chemical method. In this process, the etchant solution was prepared by using 1.6 g LiF in 20 ml of 9M HCl and stirred for 15 min to a uniform dispersion. Then, 1 g of Ti_3AlC_2 MAX phase is slowly added to the above-mentioned solution in an ice bath to avoid overheating. After the addition of Ti_3AlC_2 to the etchant, the reaction mixture was maintained at 35°C for 24 h with continuous stirring. After completion of the reaction, the suspension was washed with 1M HCl solution and DI water many times using centrifugation at 7000 rpm for 10 min, until the pH of the solution exceeded 6. After washing, the collected $Ti_3C_2T_x$ MXene sample is lyophilized.

To synthesize the $Ti_3C_2T_x$ MXene-GO heterostructure material, take a 100 ml aqueous solution of the $Ti_3C_2T_x$ MXene and GO with a concentration of 2mg/ml separately. Then, the GO suspension was added to the $Ti_3C_2T_x$ MXene suspension by simply pouring it entirely at once. Sonicated the mixture for 30 minutes at a lower temperature in the sonication bath for proper mixing. Then, the mixed suspension was stirred at 400 rpm for 10 hr. at a temperature of 15°-20°C in an ice bath to minimize the oxidation of the $Ti_3C_2T_x$ MXene sheets. After proper mixing and uniform crosslinking of both the layered structures, freeze the heterostructure in a deep freezer at -70°C to -78°C. Then, it is dried using a lyophilizer for 24 hr to make a fluffy powder.

XRD spectra of Ti_3AlC_2 MAX Phase and natural graphite flakes

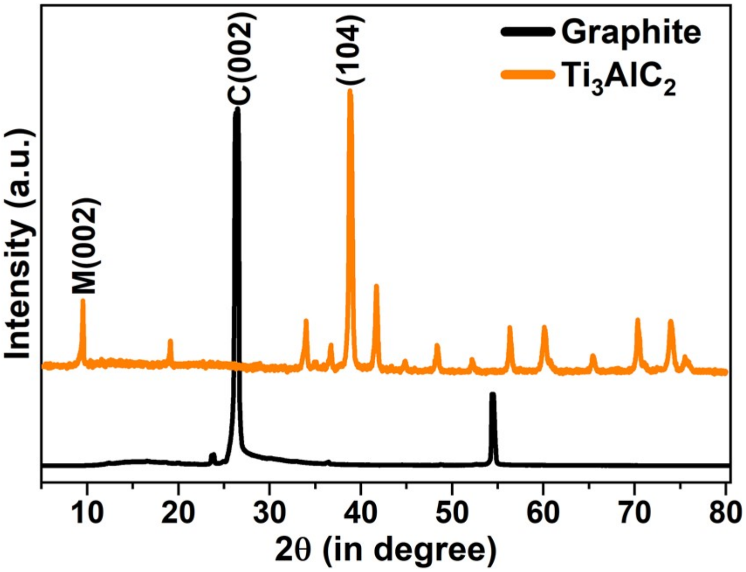

Fig. S1 XRD spectra of the natural graphite flakes and Ti_3AlC_2 MAX phase.

Raman spectra of Ti_3AlC_2 MAX phase

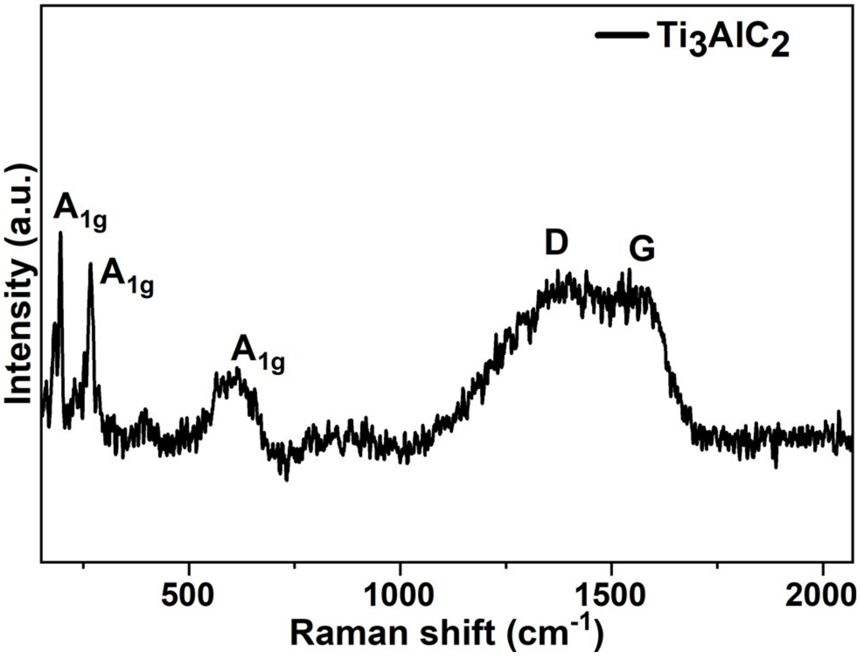

Fig. S2 Raman spectra of the Ti_3AlC_2 MAX phase.

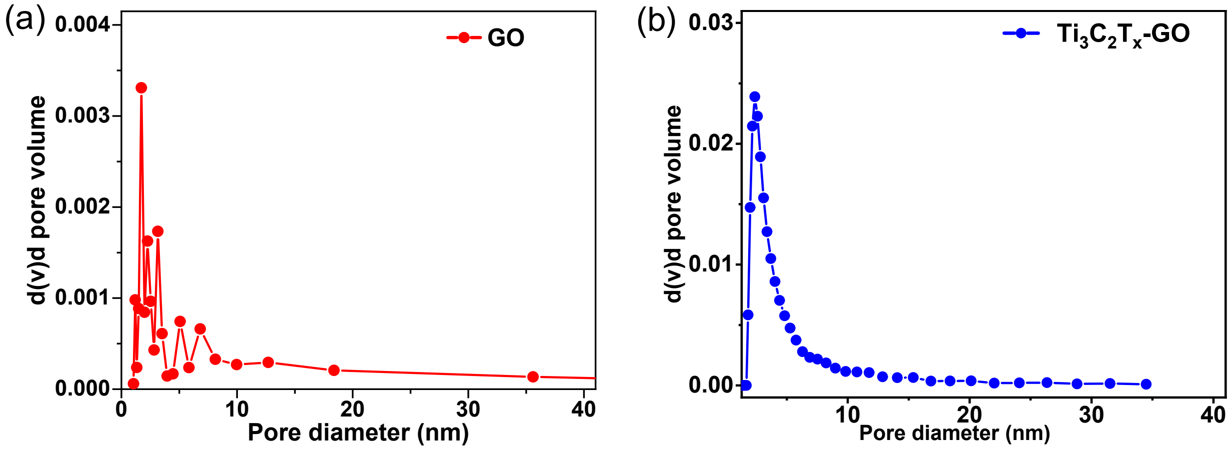

Fig. S3 Pore size distribution for the (a) GO and (b) $Ti_3C_2T_x$-GO heterostructure.

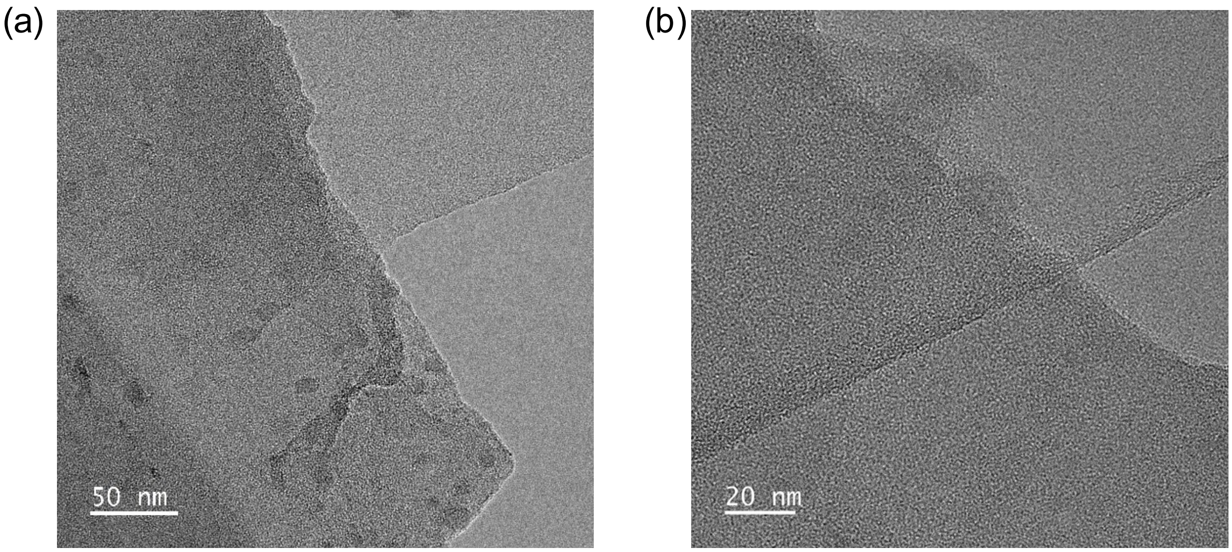

Fig.S4 (a,b) High-resolution TEM image of $Ti_3C_2T_x$-GO heterostructure.

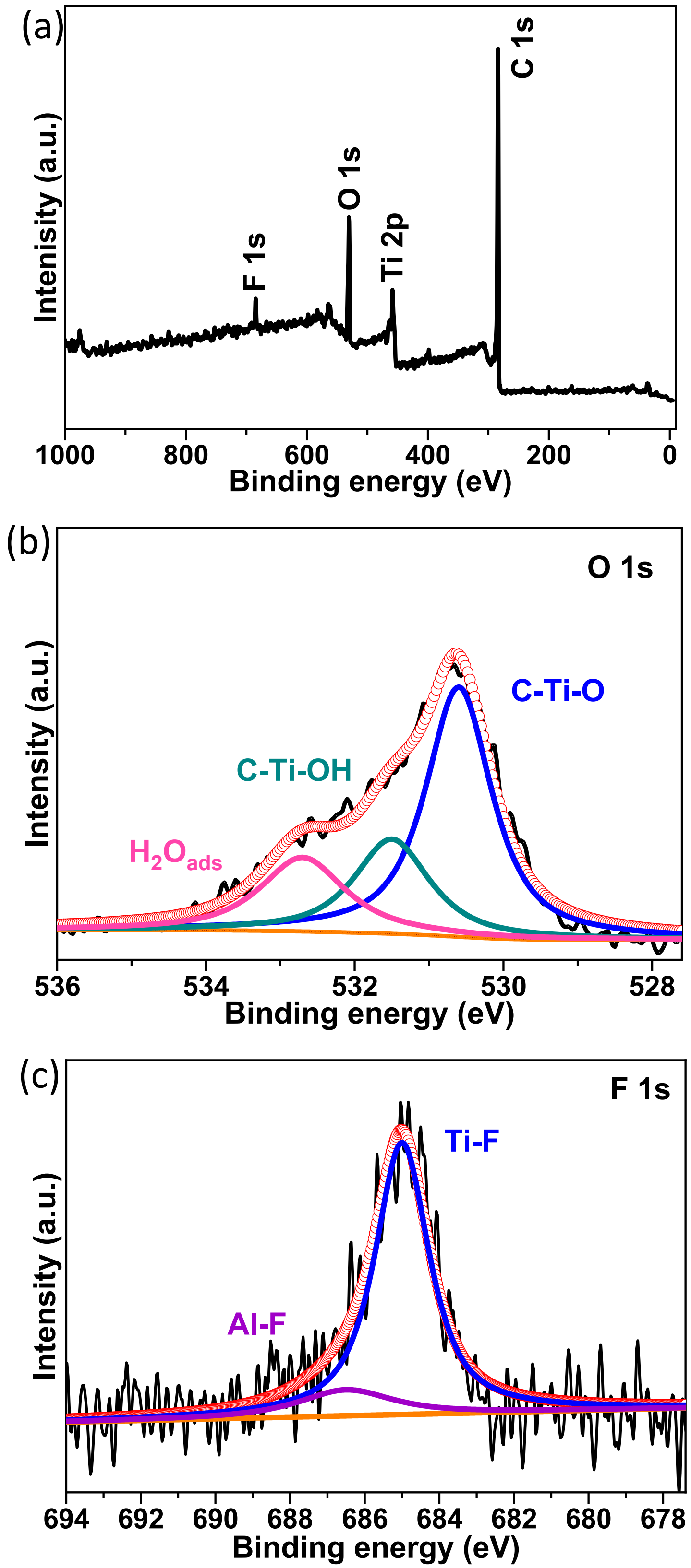

Fig. S5 (a) XPS survey, high-resolution core-level spectra of **(b)** O 1s, and **(c)** F 1s.

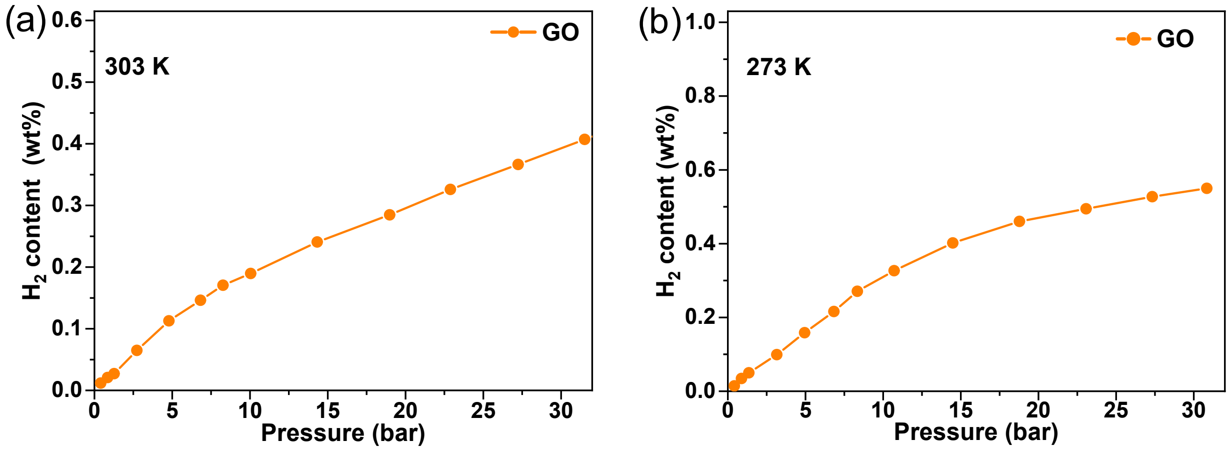

Fig. S6 (a) hydrogen storage profile for GO at (a) 303 K and (b) 273 K.

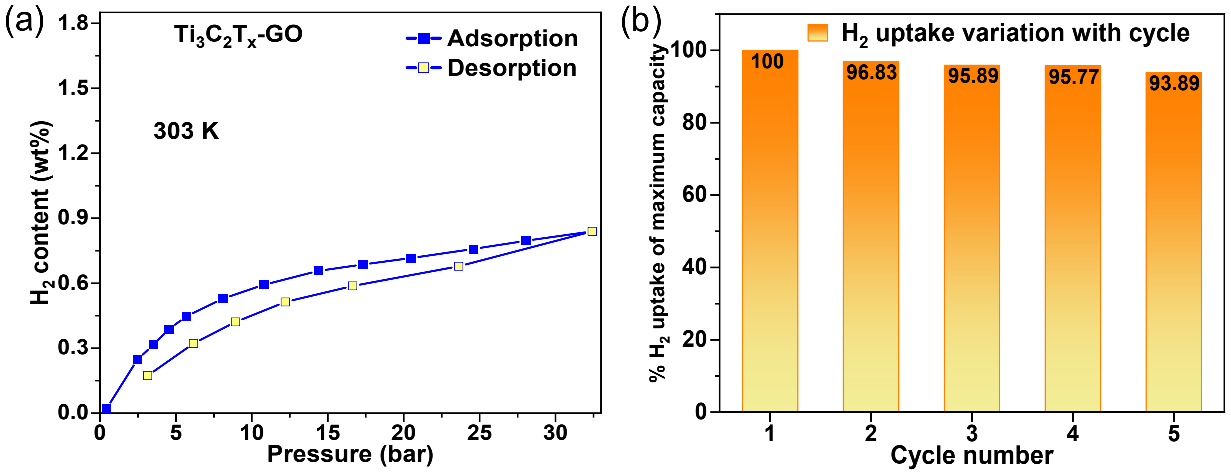

Fig. S7 (a) Reversibility study and (b) cyclic stability of the developed $Ti_3C_2T_x$-GO heterostructure at 303 K.