ChemComm

COMMUNICATION

Microwave assisted synthesis of Ti$_3$C$_2$-MXene for supercapacitor application

Prasad Eknath Lokhande,*[a] Udayabhaskar Rednam*[a], Vishal Kadam [b], Chaitali Jagtap[b], Deepak Kumar[c], Radhamanohar Aepuru

Experimentation

Materials

The required Ti_3AlC_2 MAX (Purity 99%, APS: 325 mesh) phase was obtained from Nanografi Nano Technology. Hydrofluoric Acid (48%), the etching agent, was sourced from Sigma Aldrich. All chemicals were used as received, without further purification.

Synthesis of $Ti_3C_2T_x$

The Ti_3C_2 MXene was synthesized from the Ti_3AlC_2 MAX phase by etching out the aluminum using a microwave-assisted method. The synthesis process is as follows: 1g of Ti_3AlC_2 MAX phase was placed in a Teflon-coated ceramic crucible, to which 10 mL of 48% HF was added. This was then subjected to microwave irradiation using commercial microwave oven (power 600 W, frequency 2.5 GHz) for 30 seconds inside the fume hood for filtration of the fumes. The resulting dry powder was washed with DI water until a pH of 5 was achieved. The washed sediments were then placed in an incubator at 70°C for 12 hours to obtain the dry MXene powder. Additionally, the synthesis time was altered and the change in morphology was checked. From that study optimized synthesis time achieved and in the current study presents the results for the material prepared at the optimized time of 30 seconds.

Characterization

Material characterization was conducted to analyse and understand the properties of synthesized materials. Crystallographic analysis utilized a slow scan X-ray Diffractometer, specifically the D-8 Advance Bruker AXS from Germany, with a Cu-Kα radiation source monochromator (λ = 1.54 Å). Fourier transform infrared spectroscopy (FTIR) identified functional groups within the material, performed between 400 to 4000 cm^{-1} wavelengths using PerkinElmer's FTIR Spectrum One. Raman spectroscopy, using a Reinshaw instrument, provided further confirmation by examining the vibrational modes of the elements. Morphological features were analysed using a Field Emission Scanning Electron Microscope (FESEM, JEOL JSM-7610 F+), and elemental composition was confirmed through energy dispersive X-ray spectra (EDX, Oxford Instruments, X-MaxN). X-ray photoelectron spectroscopy (XPS) measurements were done by using DESA150 electron analyzer (Staib Instruments, Germany). The surface area and porosity related details of the samples were estimated by BET (Brunauer–Emmet–Teller) technique using N2 adsorption/desorption in Nova 600 BET surface area analyzer (Anton Paar GmbH). Pore size distribution and pore volume were obtained by the BJH (Barrett–Joyner–Halenda) method.

The electrochemical performance was assessed using a Gamry electrochemical workstation. The synthesized powder was combined with PVDF (5%) and acetylene black (10%) to create a paste in an NMP solution. This paste

was then applied to Ni foam and dried at 70°C for 6 hours. The Ni foam was pre-cleaned with dilute HCl to eliminate impurities and oxides. A 2M KOH electrolyte was used in a three-electrode setup on the electrochemical workstation, with Ag/AgCl as the reference electrode and a platinum electrode as the counter. Electrochemical performance was determined using equations 1 and 2, derived from the cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) data.

$$C_s = \frac{i \int V dt}{m(V_f - V_i)}$$

(1)

$$C_s = \frac{I \Delta t}{m \Delta V}$$

(2)

Device Fabrication

The all-solid-state asymmetric supercapacitor device was constructed using a synthesized material for the positive electrode, activated carbon for the negative electrode, and PVA/KOH as the gel electrolyte. The PVA/KOH gel electrolyte was prepared through a straightforward mixing method, resulting in a transparent gel that was applied to both electrodes. The electrodes were then assembled to ensure the gel was sandwiched between them without any contact. The performance metrics derived from equations (3) and (4):

$$Energy\ Density\ (Wh\ kg^{-1}) = \frac{CV^2}{2} \times \frac{1000}{3600}$$

(3)

$$Power\ Density\ (W\ kg^{-1}) = \frac{E}{\Delta t} \times 3600$$

(4)

Results and Discussion

XPS

X-ray photoelectron spectroscopy (XPS) analysis of $Ti_3C_2T_x$ MXene provides vital insights into its surface chemistry, elemental composition, and functional groups. The core spectra for C 1s, shown in **Fig. S1(a),** reveal the degree of functionalization. The C 1s spectrum is deconvoluted into five peaks at 281.7, 284.2, 284.6, and 285.1 eV, corresponding to C–Ti, C–C, C–O, and C–F bonds, respectively. The high-resolution Ti 2p spectrum, presented **in Fig. S1(b),** fits three doublets (Ti 2p3/2–Ti 2p1/2). The Ti 2p3/2 peaks at 454.7, 455.5, and 457.4 eV are associated with Ti-C, Ti(II), and Ti(III) bonds, respectively, while the peak at 460.9 eV indicates $TiO2$[1–3]. The O 1s spectra of $Ti_3C_2T_x$ MXene, depicted in **Fig. S1(c)**, suggest an abundance of adsorbed oxygen and various functional groups, with peaks at 529.3, 531.6, and 533.4 eV representing O_{ads}, Ti–O, and –OH, respectively. The core spectra for the -F functional group, shown in **Fig. S1(d)**, display peaks at 685.2 and 686.2 eV, attributed to Ti-F and F-Ti-F bonds, respectively.
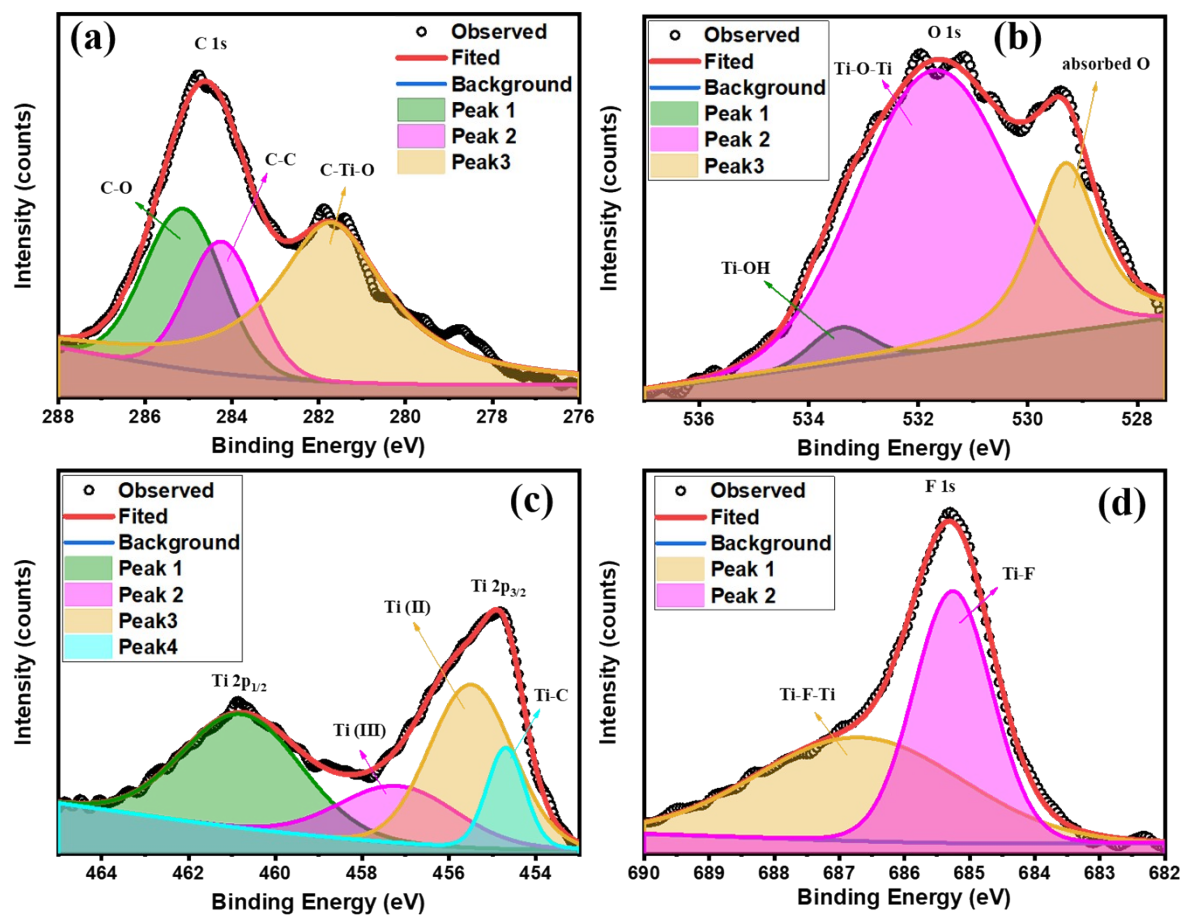
Fig. S1 High-resolution XPS spectra of (a) C 1s (b) Ti 2p, (c) O 1s (d) F 1s of $Ti_3C_2T_x$.