



# Synthesis of polyaniline nanoparticles deposited on two-dimensional titanium carbide for high-performance supercapacitors

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## ABSTRACT

A novel high-performance supercapacitor electrode material, polyaniline (PANI) modified two-dimensional Ti<sub>3</sub>C<sub>2</sub> composites (denoted as PANI-Ti<sub>3</sub>C<sub>2</sub>), has been synthesized via in situ polymerization. The experiment results showed that the introduction of PANI to Ti<sub>3</sub>C<sub>2</sub> can improve the electrochemical properties of Ti<sub>3</sub>C<sub>2</sub> because the amino groups in PANI not only increased the electric conductivity for faster ion transport but also improved the surface wettability of Ti<sub>3</sub>C<sub>2</sub> for more active sites and provided faradaic reactions for additional capacity. The specific capacitance of PANI-Ti<sub>3</sub>C<sub>2</sub> can achieve a maximum of 164 F g<sup>-1</sup> at 2 mV s<sup>-1</sup> and 1.26 times greater than that of Ti<sub>3</sub>C<sub>2</sub> (131 F g<sup>-1</sup>). Moreover, PANI-Ti<sub>3</sub>C<sub>2</sub> showed superior cycling stability, retaining ~96% of its initial capacitance after 3000 cycles.

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## 1. Introduction

Supercapacitors (SCs) own higher power density and longer cycle life than secondary batteries and higher energy density compared to conventional electrical double-layer capacitors [1]. Thus, considerable attention on SCs has been attracted over the past decades. The modification of supercapacitor electrode material is an excellent method for improving SCs performance [2].

Graphene is considered as a kind of great supercapacitor electrode materials because of its fast charge/discharge rate and good cycling stability. Meanwhile, the specific capacitance of graphene as the supercapacitor electrode material is to be improved. Due to the remarkable properties of graphene, increasing attention has been carried out on the other two-dimensional materials [3]. Recently, a new member in two-dimensional materials called MXene is produced successfully. Ti<sub>3</sub>C<sub>2</sub> is one of the most widely studied members of this family [4]. Particularly, Ti<sub>3</sub>C<sub>2</sub> is a kind of promising electrode materials for SCs because of its metallic conductivity, spontaneous ion intercalation upon immersion into solutions, capacitive behavior [4].

To further enhance electrochemical performance of Ti<sub>3</sub>C<sub>2</sub> electrode materials, one straightforward strategy is the introduction on Ti<sub>3</sub>C<sub>2</sub> [5]. Conducting polymers, such as polyaniline (PANI), is famous for its large specific surface area (SSA) and relatively high

specific capacitance [2]. Particularly, nitrogen-containing functional groups in PANI can enhance electrochemical performance of Ti<sub>3</sub>C<sub>2</sub> by increasing the electric conductivity for faster ion transport, improving surface wettability for more active sites and providing faradaic reactions for additional capacity [6,7].

In this work, multilayered PANI-Ti<sub>3</sub>C<sub>2</sub> was synthesized via in situ polymerization by low temperature, which could reduce the oxidation of Ti<sub>3</sub>C<sub>2</sub> during the polymerization. When used as supercapacitor electrode material, PANI-Ti<sub>3</sub>C<sub>2</sub> showed enhanced performance comparing with Ti<sub>3</sub>C<sub>2</sub>.

## 2. Experimental

### 2.1. Synthesis

Ti<sub>3</sub>C<sub>2</sub> was prepared by etching Al from Ti<sub>3</sub>AlC<sub>2</sub>. Aniline (ANI) was used after vacuum distillation. First, 0.2 g Ti<sub>3</sub>C<sub>2</sub> was dispersed to 30 ml 1 M HCl aqueous solution. Then, 100 μl ANI was added into the above solution and stirred for 30 min at 2 °C. The oxidation, 0.335 g ammonium persulfate (APS) were dissolved in 20 mL 1 M HCl aqueous solution. The mixture was stirring for 6 h at 2 °C. The precipitates of PANI-Ti<sub>3</sub>C<sub>2</sub> were washed by deionized water.

### 2.2. Material characterization

Field-emission scanning electron microscopy (FE-SEM) was performed using a Hitachi S-4800 & Hiroba. Transmission electron

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microscopy (TEM) used in this work is TecnaiG220 S-twin. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max 2200pc diffractometer using Cu K $\alpha$  radiation of wavelength  $\lambda = 0.15418$  nm at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Thermo ESCALAB 250 spectrometer.

### 2.3. Electrochemical measurements

The electroactive materials, carbon black and poly(vinylidene fluoride) were mixed in a mass ratio of 20:2:1 and dispersed in N-methyl pyrrolidone. The resulting mixture was dropped onto the nickel foam substrate ( $1 \times 2$  cm) then dried in a vacuum oven. For comparison, PANI and Ti<sub>3</sub>C<sub>2</sub> were also used for the fabrication of electrode.

A conventional three-electrode system used in all electrochemical experiments, which consisted of a platinum sheet ( $1 \times 2 \times 0.1$  cm) as the counter electrode, an Ag/AgCl/3 M KCl as the reference electrode and the PANI, Ti<sub>3</sub>C<sub>2</sub>, PANI-Ti<sub>3</sub>C<sub>2</sub> as the working electrode.

Cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and galvanostatic cycling were performed. CV of the working electrode were measured at different scan rates of 2, 5, 10, 20, 50 and 100 mV s<sup>-1</sup>. GCD of the working electrode were performed at a current densities of 0.5 A g<sup>-1</sup>. Galvanostatic cycling was performed at a current densities of 3 A g<sup>-1</sup>. All electrochemical experiments were performed with a CHI660E electrochemical workstation (CH Instruments, Shanghai). Meanwhile, all experiments were conducted in 1 M Na<sub>2</sub>SO<sub>4</sub> as the electrolyte solution from  $-0.8$  V to  $-0.2$  V versus Ag/AgCl.

## 3. Results and discussion

The morphology and structure of Ti<sub>3</sub>C<sub>2</sub>, PANI and PANI-Ti<sub>3</sub>C<sub>2</sub> were investigated by SEM and TEM. As shown in Fig. 1(a), Ti<sub>3</sub>C<sub>2</sub> possessed layered morphology similar to graphene, which is consistent with the results of TEM (Fig. 1(d)). It is noticed that PANI

forms worm-like agglomerates as shown in Fig. 1(b) and (e). PANI-Ti<sub>3</sub>C<sub>2</sub> images were shown in Fig. 1(c) and (f), homogeneous PANI nanoparticles cover the surfaces of lamellar Ti<sub>3</sub>C<sub>2</sub>, which results in the increase in SSA of PANI-Ti<sub>3</sub>C<sub>2</sub> comparing with Ti<sub>3</sub>C<sub>2</sub> (Fig. S1).

Fig. 2(a) shows the XRD patterns of PANI, Ti<sub>3</sub>C<sub>2</sub>, PANI-Ti<sub>3</sub>C<sub>2</sub>. For PANI, the crystalline peak appears at  $2\theta = 20.7^\circ$ , corresponding to (0 2 0) crystal planes of PANI [8]. For Ti<sub>3</sub>C<sub>2</sub>, the peaks appear at  $2\theta = 7.1^\circ, 17^\circ, 28^\circ, 35^\circ, 41^\circ, 61^\circ$ , corresponding to (0 0 2), (0 0 6), (0 0 8), (0 0 10), (0 0 12), (1 1 0) crystal planes [9], while the peaks centered at  $2\theta = 18^\circ, 22^\circ$  that correspond to TiC. For XRD patterns of PANI-Ti<sub>3</sub>C<sub>2</sub>, a new peak around  $2\theta = 20.7^\circ$  compared with Ti<sub>3</sub>C<sub>2</sub>, corresponding to PANI. Another new peak appeared at  $2\theta = 26^\circ$  correspond to TiO<sub>2</sub>, which derives from the oxidation of Ti<sub>3</sub>C<sub>2</sub> by APS.

The XPS survey spectra of PANI-Ti<sub>3</sub>C<sub>2</sub> exhibit the presence of N in the nanocomposite (Fig. 2(b)), as compared to Ti<sub>3</sub>C<sub>2</sub>, which evidence the successful synthesis PANI-Ti<sub>3</sub>C<sub>2</sub>. The XPS N1s spectra of PANI-Ti<sub>3</sub>C<sub>2</sub> could be deconvoluted into four distinct peaks (397.1 eV, 398.2 eV, 400.1 eV, 400.5 eV) (Fig. 2(c)) [10], corresponding to neutral and imine-like (=NH-) structure, neutral and amine-like nitrogen (-NH-) atoms, the nitrogen atom with a delocalized positive charge N<sup>+</sup> on the polymer backbone compensated with the counterions (Cl<sup>-</sup>) and the protonated amine units [11,12].

Fig. 3(a) shows the CV curves of Ti<sub>3</sub>C<sub>2</sub>, PANI, PANI-Ti<sub>3</sub>C<sub>2</sub> at the scan rates of 10 mV s<sup>-1</sup>. CV curve of Ti<sub>3</sub>C<sub>2</sub> presents a rectangular shape, revealing that the electrode is charged and discharged at a pseudoconstant rate during the voltammetric cycle [4,13]. CV curve of PANI-Ti<sub>3</sub>C<sub>2</sub> presents a rectangular shape with peaks, which can be attributed to the redox reactions of nitrogen active atoms of the electrode. The intercalation/de-intercalation processes of the cations (Na<sup>+</sup>) that result in the reversible and successive redox reactions on/near PANI-Ti<sub>3</sub>C<sub>2</sub> are based on the following reactions [14,15]:

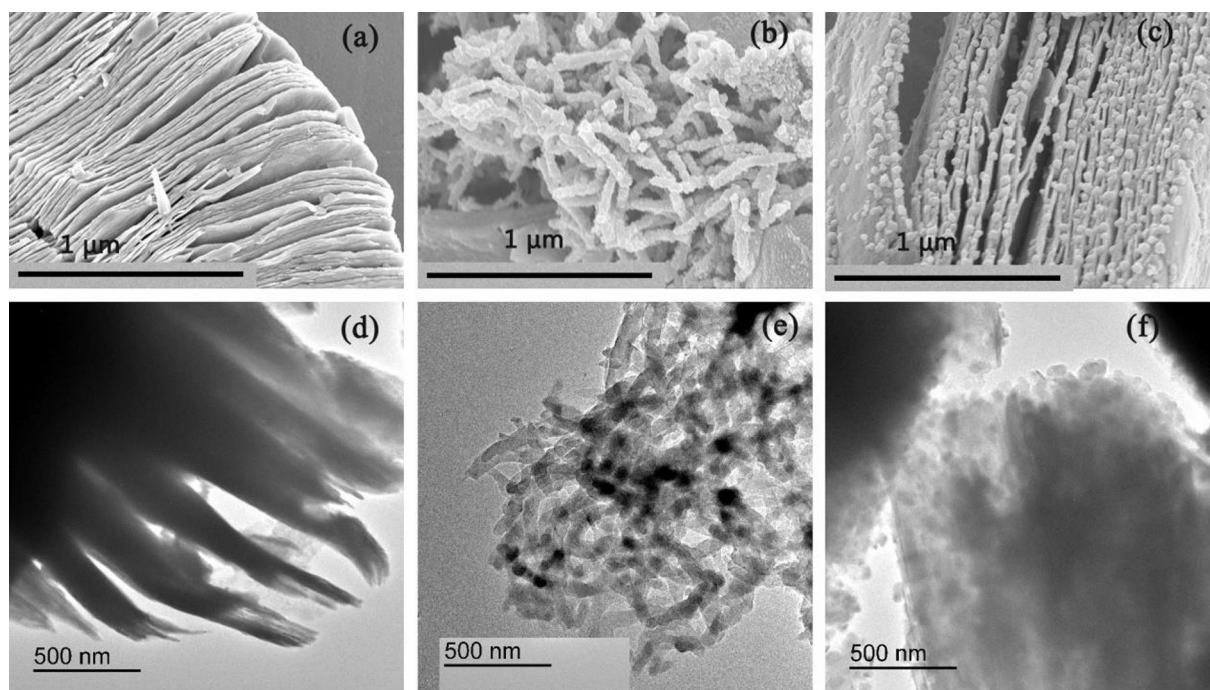
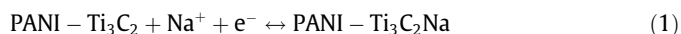


Fig. 1. SEM and TEM images of Ti<sub>3</sub>C<sub>2</sub> (a),(d); PANI (b), (e); PANI-Ti<sub>3</sub>C<sub>2</sub> (c), (f).

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