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# Flexible titanium carbide–carbon nanofibers with high modulus and high conductivity by electrospinning

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ABSTRACT

Titanium carbides are well-known for their outstanding mechanical and thermal stabilities. However, the studies on the mechanical properties and the conductivity of titanium carbide–carbon nanofibers (TiC/CNF) are missing. This work prepared TiC/CNF by electrospinning and highlighted the high modulus of single TiC/CNF, the flexibility and the excellent electrical conductivity of TiC/CNF felt even under 100 bending cycles. This flexible TiC/CNF felt with distinguished mechanical and electrical properties are promising to apply in titanium matrix composites (TMC), efficient catalyst scaffolds and electronic devices.



## 1. Introduction

As one of the refractory transition metal carbides, titanium carbide (TiC) has been extensively investigated due to its high Young's modulus (300–480 GPa), low mass density (4.91 g/cm$^3$), superior hardness (28–35 GPa), thermal stabilities and chemical resistance [1–5]. In particular, hybrid TiC nanofibers produced by electrospinning have drawn more and more attentions because of their advantages like free-standing, low electrical resistance, binder-free, excellent electrochemical stability, etc., in supercapacitor application [6,7]. However, to the best of our knowledge, there are no reports regarding the mechanical properties and the conductivity of continuous titanium carbide–carbon nanofibers (TiC/CNF).

In this work, we fabricated continuous TiC/CNF nanofibers by electrospinning and carbothermal reduction, and studied the mechanical properties and electrical conductivity of TiC/CNF under bending conditions. It was found that the TiC/CNF possessed excellent mechanical properties, high electrical conductivity and conductivity retention after many bending cycles.

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## 2. Experimental

Polyacrylonitrile (PAN, $M_w$=86000), *N,N*-dimethylformamide (DMF, 99.9%), titanium tetrachloride ($TiCl_4$), polyvinylpyrrolidone (PVP, $M_w$=1,300,000) and $Ni(NO_3)_2 \cdot 6H_2O$ were obtained from Sigma Aldrich.

$TiCl_4$ (0.81 g), $Ni(NO_3)_2 \cdot 6H_2O$ (0.07 g) and PVP (0.40 g) were dissolved in DMF (5.8 g) under Argon atmosphere and magnetically stirred for 30 min at room temperature. Then, PAN/DMF (7.0 g, 15 wt%) was added to the PVP/$TiCl_4$ solution with continuous stirring. The as-prepared PAN/PVP/$TiCl_4$ solution was electrospun into nanofibers by applying electrical potential, collecting distance, flow rate and humidity of 27 kV, 20 cm, 0.9 ml/h and 34%, respectively. The nanofiber felt was collected by a rotating drum (diameter: 0.3 m; rotation speed: 30 rpm) for 10 h. The as-spun PAN/PVP/$TiCl_4$ felt was pre-oxidized at 220 °C (air, 1 °C/min, 3 h) and carbonized at 1000 °C (vacuum, 15 °C/min, 0.5 h). To remove the impurities, the obtained TiC/CNF felt was soaked in 6 mol/L hydrochloric acid for 30 min, washed with distilled water and absolute ethanol and dried at 80 °C for 6 h. As comparison, carbon nanofiber (CNF) felt from PAN/PVP solution was also prepared with the same treatments as TiC/CNF.

The surface morphology and microstructure of TiC/CNFs were examined by field-emission scanning electron microscope (SEM, FEI Quanta 200, USA) equipped with an energy dispersive X-ray spectroscopy (EDS) detector, transmission electron microscopy (TEM, JEM-3010, Japan), X-ray diffraction (XRD, Bruker D8

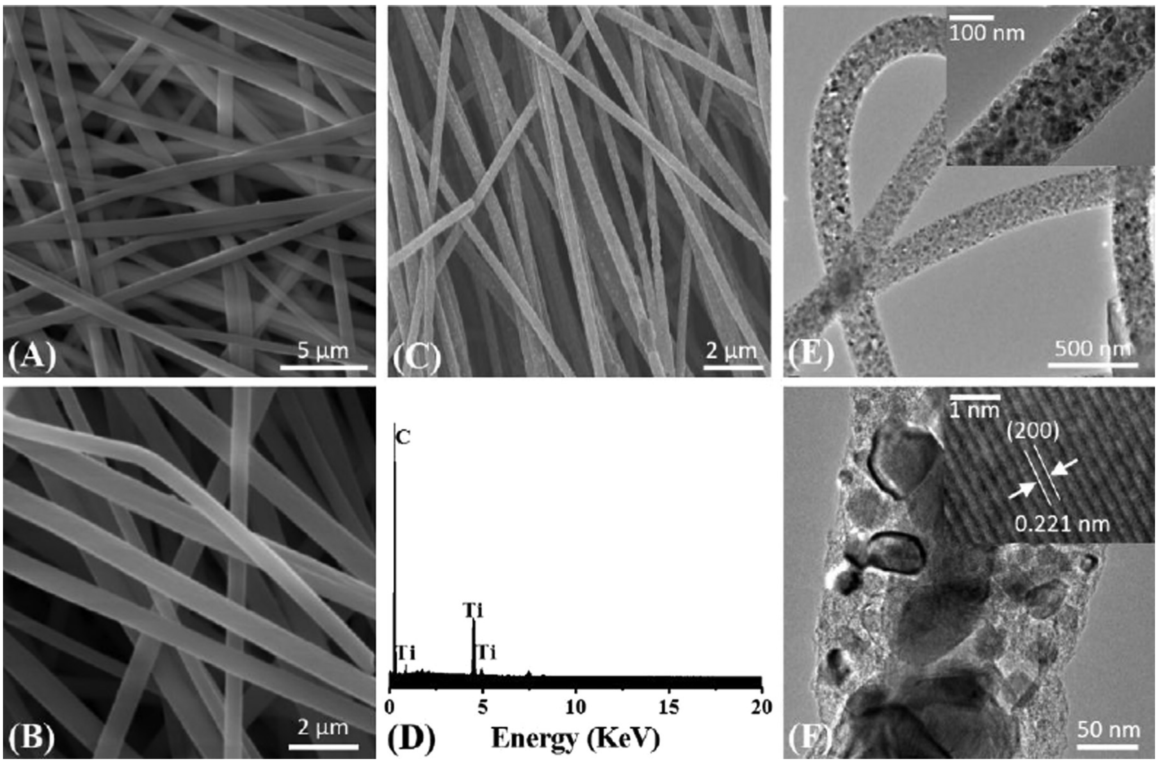


**Fig. 1.** SEM images of as-spun (A), pre-oxidized (B) and carbonized PAN/PVP/$TiCl_4$ nanofibers (C); EDS spectrum of TiC/CNF (D); TEM images of TiC/CNF (E and F). Insets in (E) and (F) are high magnification image and the nanocrystal structure of an individual TiC nanoparticle.

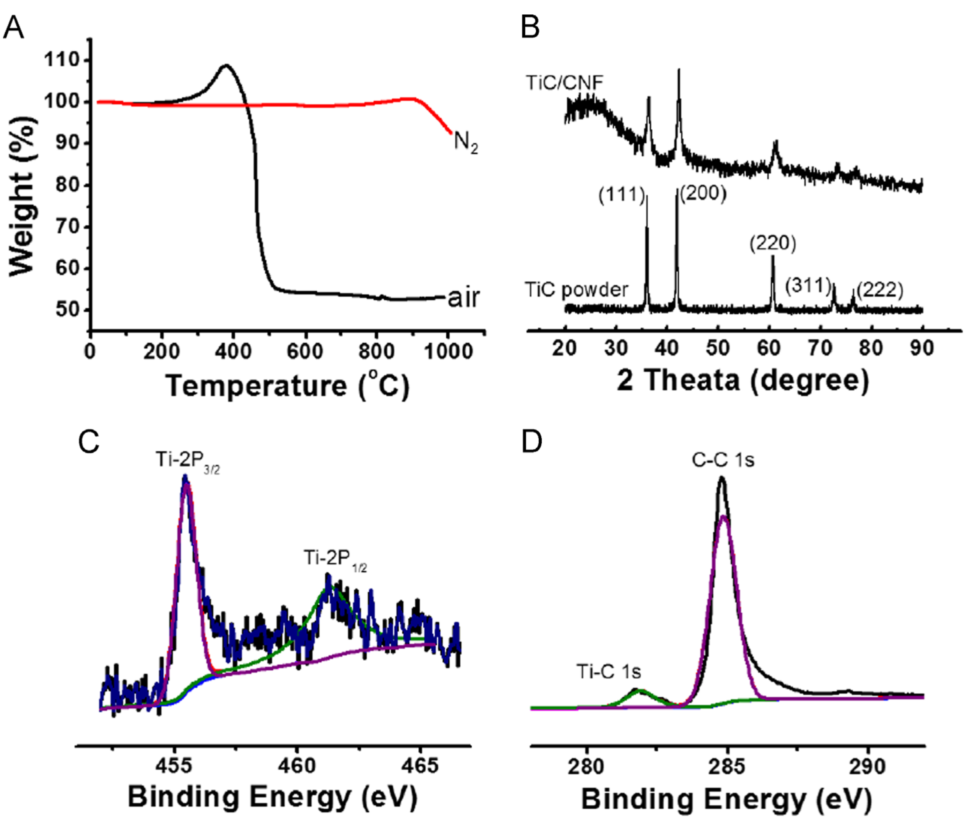


**Fig. 2.** TGA curves of TiC/CNF felt in air and $N_2$ atmosphere (A), XRD patterns of TiC/CNF felt and TiC powder (B), and XPS spectra of Ti-2p (C) and C-1s (D).

Advance diffractometer) and X-Ray photoelectron spectroscopy (XPS, Thermo ESCaLAB 250, USA). The electrical conductivity of TiC/CNF felt was measured by a four-point probes resistivity measurement system (RST-8 model, Guangzhou four-point probe technology Co., LTD, China). The mechanical property of TiC/CNF felt was measured by a universal testing machine (SANS, Shenzhen, China) at a tensile speed of 5 mm/min. The oxidation behavior and thermal stability of TiC/CNF felt were examined by the