Electronic Supplementary information

# Titanium carbide sheets based high performance wire type solid state supercapacitors

Karthikeyan Krishnamoorthy[a], Parthiban Pazhamalai[a], Surjit Sahoo[a], and Sang Jae Kim[a,b*]

[a]Nanomaterials and System Lab, Department of Mechatronics Engineering, Jeju National University, Jeju 690-756, South Korea.

[b]Department of Advanced Convergence Technology & Science, Jeju National University, Jeju 690-756, South Korea.

*Corresponding Author

Email: kimsangj@jejunu.ac.kr

**Methods:**

**Instrumentation.**

A Rigaku X-ray diffractometer system (operated at 40 KeV and 40 mA with Cu Kα radiation) was employed to examine the phase purity and crystallinity of the materials. A LabRam HR Evolution Raman spectrometer (Horiba Jobin-Yvon, France) was used to measure the Raman spectroscopy of the samples. A field emission-scanning electron microscopy (FE-SEM, JSM-6700F, JEOL Instruments) was used to analyze the surface morphology of the prepared materials. The morphology of prepared materials was investigated by high resolution transmission electron microscopy (HRTEM; JEM 2011, JEOL cop.) with CCD 4k x 4k camera (Ultra Scan 400SP, gatan cop.). The Raman system used an $Ar^+$ ion laser operating at a power of 10 mW with an excitation wavelength of 514 nm; a 10 s data-point acquisition time was used to acquire the data. The FT-IR spectrum was measured using a Thermo scientific FT-IR spectrometer with pure KBr as the background. The samples were mixed with KBr and the mixture was dried and compressed into a transparent tablet for measurement. The $N_2$ adsorption-desorption isotherms of the prepared materials was measured at 77 K using a NOVA 2000 system (Quantachrome, USA) and the pore size distribution was calculated using Horvath-Kawazoe (HK) method.

**Preparation of PVA/KOH polymer gel electrolyte.**

The PVA/KOH polymer gel electrolyte was prepared using the method reported in literature [1]. Breifly, 1 g of PVA is dissolved in deionized water using mechanical stirring at a temperature of 80 °C. After complete dissolution of PVA, a transpired solution was obtained to which solution containing 1 g of KOH was added and allowed to vigorous stirring under heat until a clear and transparent gel was obtained. Finally, the prepared gel is allowed to cool at room temperature and used for device fabrication.

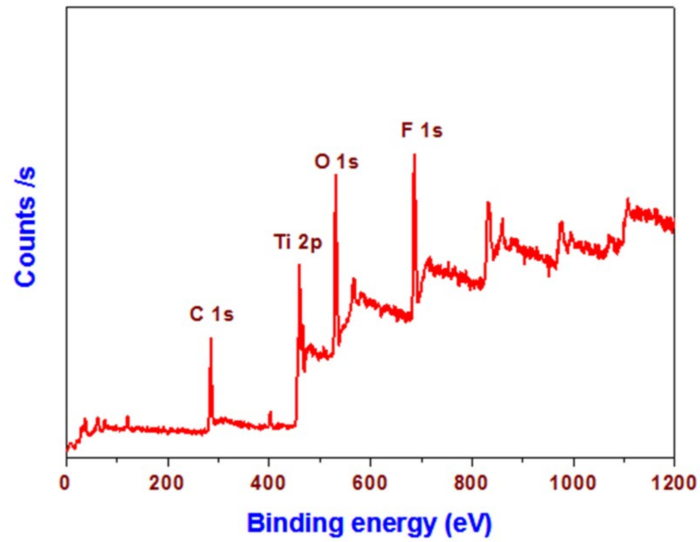


**Fig. S1. X-ray photoelectron spectroscopy of titanium carbide sheets (survey scan) after HF etching showing the presence of carbon, titanium, oxygen and fluorine groups.**

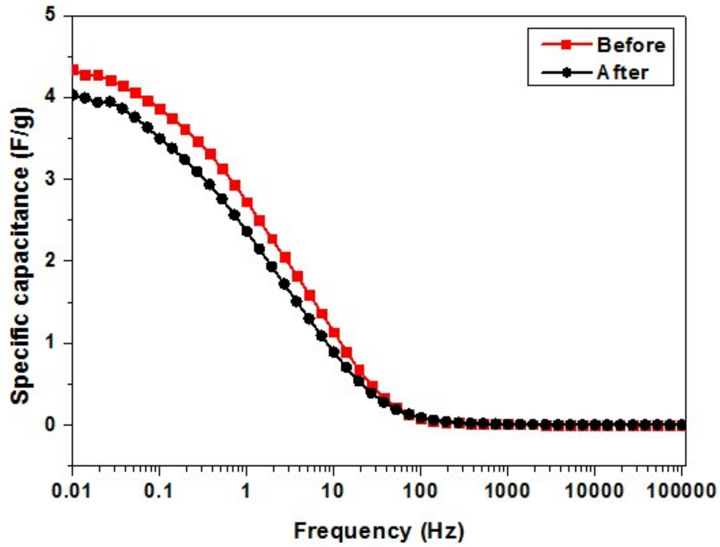


**Fig. S2. Plot of specific capacitance of titanium carbide WSCs before and after cyclic tests as function of applied frequency.**

**Table S1: Comparative performances of titanium carbide WSC device with recent works**

| No | Electrode material | Capacitance in length | Ref |
|---|---|---|---|
| **1** | CNT fiber springs | 510 μF/cm | 2 |
| **2** | Graphene/CNT composite fiber | 27.1 μF/cm | 3 |
| **3** | rGO on Au wire | 107.9 μF/cm | 4 |
| **4** | CNT fiber | 13.3 μF/cm | 5 |
| **5** | PEDOT CNT | 0.47 mF/cm | 6 |
| **6** | Pen ink fibers | 0.504 mF/cm | 7 |
| **7** | CNT arrays WSCs | 0.73 mF/cm | 8 |
| **8** | MWCNT/OMC composite fibers | 1.91 mF/cm | 9 |
| **9** | $MoS_2$ WSCs | 119 μF/cm | 10 |
| **10** | Titanium carbide WSCs | 3.09 mF/cm | This work |

**Calculation of specific capacitance (length and gravimetric) from CD profiles:**

The specific capacitance in terms of both length and gravimetric values has been calculated from the CD profiles using the equation given below [11]:

$$C_G = (I \times T_d) / (M \times \Delta V) \ldots. (1)$$

$$C_L = (I \times T_d) / (L \times \Delta V) \ldots\ldots\ldots\ldots\ldots.. (2)$$

Here *"$C_G$"* is the specific gravimetric capacitance (F/g), *"$C_L$"* is the specific length capacitance (F/cm), *"$I$"* is the discharge current density, *"$T_d$"* is the discharge time, *"$M$"* is the mass of the electroactive material, *"$L$"* is the length of the electroactive material and *"$\Delta V$"* is the potential window.

**Energy and power density calculations:**

The energy and power density of the titanium carbide WSC device are calculated in terms of both length and gravimetric scale using the relations given below [11]:

$$E_G = [C_G \times \Delta V^2]/2 \text{ and } E_L = [C_L \times \Delta V^2]/2 \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

$$P_G = E_G / T_d \text{ and } P_L = E_L / T_d \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Here *"$E_G$"* and *"$P_G$"* are the gravimetric energy and power density of the device, *"$E_L$"* and *"$P_L$"* are the energy and power density (in length) of the device, *"$C_G$ and $C_L$"* is the specific gravimetric and length capacitance, *"$\Delta V$"* is the potential window and *"$T_d$"* is the discharge time.

**References:**


1. Ma, G.; Li, J.; Sun, K.; Peng, H.; Mu, J.; Lei, Z. High Performance Solid-State Supercapacitor with PVA–KOH–K3[Fe(CN)6] Gel Polymer as Electrolyte and Separator. *J. Power Sources* **2014**, *256*, 281–287.
2. Zhang, Y.; Bai, W.; Cheng, X.; Ren, J.; Weng, W.; Chen, P.; Fang, X.; Zhang, Z.; Peng, H. Flexible and Stretchable Lithium-Ion Batteries and Supercapacitors Based on Electrically Conducting Carbon Nanotube Fiber Springs. *Angew. Chem. Int. Ed. Engl.* **2014**, *53*, 14564–14568.
3. Sun, H.; You, X.; Deng, J.; Chen, X.; Yang, Z.; Ren, J.; Peng, H. Novel Graphene/carbon Nanotube Composite Fibers for Efficient Wire-Shaped Miniature Energy Devices. *Adv. Mater.* **2014**, *26*, 2868–2873.
4. Li, Y.; Sheng, K.; Yuan, W.; Shi, G. A High-Performance Flexible Fibre-Shaped Electrochemical Capacitor Based on Electrochemically Reduced Graphene Oxide. *Chem. Commun. (Camb).* **2013**, *49*, 291–293.
5. Xu, P.; Gu, T.; Cao, Z.; Wei, B.; Yu, J.; Li, F.; Byun, J.-H.; Lu, W.; Li, Q.; Chou, T.-W. Carbon Nanotube Fiber Based Stretchable Wire-Shaped Supercapacitors. *Adv. Energy Mater.* **2014**, *4*, n/a – n/a.
6. Lee, J. A.; Shin, M. K.; Kim, S. H.; Cho, H. U.; Spinks, G. M.; Wallace, G. G.; Lima, M. D.; Lepró, X.; Kozlov, M. E.; Baughman, R. H.; *et al.* Ultrafast Charge and Discharge Biscrolled Yarn Supercapacitors for Textiles and Microdevices. *Nat. Commun.* **2013**, *4*, 1970.
7. Fu, Y.; Cai, X.; Wu, H.; Lv, Z.; Hou, S.; Peng, M.; Yu, X.; Zou, D. Fiber Supercapacitors Utilizing Pen Ink for Flexible/wearable Energy Storage. *Adv. Mater.* **2012**, *24*, 5713–

5718.

8. Zhang, K.; Zhao, H.; Zhang, Z.; Chen, J.; Mu, X.; Pan, X.; Zhang, Z.; Zhou, J.; Li, J.; Xie, E. Cooperative Effect of Hierarchical Carbon Nanotube Arrays as Facilitated Transport Channels for High-Performance Wire-Based Supercapacitors. *Carbon N. Y.* **2015**, *95*, 746–755.
9. Ren, J.; Bai, W.; Guan, G.; Zhang, Y.; Peng, H. Flexible and Weaveable Capacitor Wire Based on a Carbon Nanocomposite Fiber. *Adv. Mater.* **2013**, *25*, 5965–5970.
10. K. Krishnamoorthy, P. Pazhamalai, G.K. Veerasubramani, S.J. Kim, Mechanically delaminated few layered $MoS_2$ nanosheets based high performance wire type solid-state symmetric supercapacitors, J. Power Sources. 321 (2016) 112–119. doi:10.1016/j.jpowsour.2016.04.116.
11. Senthilkumar, S. T.; Selvan, R. K. Flexible Fiber Supercapacitor Using Biowaste-Derived Porous Carbon. *ChemElectroChem* **2015**, *2*, 1111–1116.