



Ditungsten carbide nanoparticles embedded in electrospun carbon nanofiber membranes as flexible and high-performance supercapacitor electrodes



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ABSTRACT

Ditungsten carbide (W_2C) nanoparticles embedded in graphene nanoribbon/carbon nanotube-carbon nanofiber (GC-CNF) composite membrane has been prepared by one-pot electrospinning with subsequent carbonization. The homogeneous distribution of small-sized W_2C nanoparticles in-situ formed during carbonization within the carbon nanofibers, provides abundant electroactive sites for high electric double layer capacitance. The carbon nanotube bridged graphene nanoribbon hybrid could enhance the conductivity of carbon nanofibers, while the fibrous web structure favors rapid ion diffusion, thus offering fast electron/ion transport pathways during the electrochemical process. Moreover, the W_2C nanoparticles embedded in nanofiber structure could prevent their oxidation during the electrochemical process, contributing to enhanced cyclic stability. Consequently, the GC-CNF@ W_2C composite membrane exhibits high specific capacitance of 256 F g^{-1} at 1 A g^{-1} and good cycling stability of 95.6% retention after 2500 cycles. Therefore, the GC-CNF@ W_2C composite membrane shows great potential as electrode material for high-performance supercapacitors.

Supercapacitors owing to their high power density, long-cyclic lifetime and fast charge-discharge rate have attracted tremendous attention and been widely studied [1,2]. Typical supercapacitors can be divided into two categories, including electric double-layer capacitors (EDLCs) and pseudocapacitors [3–6]. Whatever the type is, the electrode material is the key factor affecting the performance of supercapacitor. In addition, with the rapid development of portable and flexible devices, searching for new and high-performance electrode materials with high flexibility and foldability attracts lots of attentions in recent years [7,8].

Transition metal carbides have emerged to be investigated as candidates for energy storage materials recently due to their good EDLC properties, excellent mechanical and chemical stability, and high electrical conductivity [9–12]. However, current reports on metal carbides as supercapacitor electrode is scarce. Ditungsten carbide (W_2C) is one of the most promising transition metal carbides with good physical and chemical properties such as excellent thermal stability and high electrical conductivity [13–16]. However, several problems exist when tungsten carbide is applied as electrode materials for supercapacitors. During the electrochemical process, the carbide could undergo oxidation that removes the carbon from the surface, resulting in modification of the chemical properties and affecting the electrochemical behaviors [17,18]. Furthermore, the nano-sized particles always tend to aggregate

severely, which would also lead to poor capacitive performance [19]. Therefore, proper substrate for preventing W_2C nanoparticles from oxidation and aggregation is urgently needed to improve the capacitive performance of ditungsten carbide.

Due to their unique three-dimensional (3D) fiber network, high electrical conductivity and good flexibility, carbon nanofiber membrane could perform as good template for electroactive nanoparticles [20–22]. Electrospinning is an effective and straightforward technique that produces free-standing carbon nanofiber membranes derived from carbonization of polymer precursors [23–25]. The as-obtained carbon nanofibers are outstanding substrates that could immobilize electroactive materials on the surface or incorporate them inside nanofibers, which would maximize the exposure of electroactive sites and improve the stability of metal carbides. In addition, the conductivity of the membrane greatly affects the performance as electrode for supercapacitors. Our previous reports show that incorporating graphene nanoribbon/carbon nanotube (GNR/CNT) hybrids into polyimide nanofibers by electrospinning can greatly improve their electrical conductivity along the fiber direction, which is due to the unique 3D interconnected structure of GNR/CNT hybrids [26].

In this communication, ditungsten carbide (W_2C) nanoparticles embedded in graphene nanoribbon/carbon nanotube-carbon nanofiber (GC-CNF) membrane was prepared by one-pot electrospinning with

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subsequent high temperature carbonization under H_2/Ar atmosphere. W_2C nanoparticles in-situ formed within the carbon nanofibers during carbonization show a homogeneous distribution within the nanofibers, providing high electric double layer capacitance. The CNT bridged GNR hybrid could enhance the conductivity of carbon nanofibers, which can facilitate electron transport of the electrode, resulting in improved rate performance. The carbon nanofiber enwrapping W_2C nanoparticles could prevent the oxidation of W_2C thus improving the cyclic stability, while the 3D fibrous web structure favors rapid ion diffusion. As a consequence, the GC-CNF@ W_2C composite membrane shows a specific capacitance of 256 F g^{-1} at a current density of 1 A g^{-1} , good rate capacitance retention of 71% at 10 A g^{-1} , and good cycling stability with 95.6% retention after 2500 cycles. Therefore, we have demonstrated a novel strategy to directly synthesize carbide nanoparticles within the carbon nanofibers, which opens a new way for fabricating high-performance electrode materials for supercapacitors.

The graphene oxide nanoribbon/carbon nanotube (GONR/CNT) hybrid was synthesized by partial longitudinal unzipping of pristine multi-walled CNTs according to our previous reports (Fig. S1) [27]. GC-CNF@ W_2C nanofiber membranes were prepared by a one-pot electrospinning of precursor solution containing polyacrylonitrile (PAN), GONR/CNT hybrid, and $(NH_4)_2WS_4$, followed by carbonization (see Supporting information for experimental details). During the high temperature carbonization under reducing atmosphere (H_2/Ar , 5%/95%, v/v), PAN nanofiber was turned into CNF, GONR/CNT was reduced to GNR/CNT, and $(NH_4)_2WS_4$ was converted to W_2C simultaneously, resulting in the final product of GC-CNF@ W_2C (Fig. 1). The morphology of GC-CNF@ W_2C is investigated by SEM observations as shown in Fig. 2a. It can be seen that GC-CNF@ W_2C composite membrane displays a web-like structure where the fibers interconnect with each other, which could offer a favorable pathway for electron transport and ion diffusion. Inset in Fig. 2a shows the digital photo of the nanofiber membrane, indicating its high flexibility and mechanically stability, which can be used as a binder-free electrode material for supercapacitors. Fig. 2b reveals that the electrospun GC-CNF@ W_2C nanofibers have an average diameter of 200–300 nm and smooth surface without beads or breakages, indicating that the metal carbides are formed within the nanofibers, instead of on the surface. The existence of GNR/CNT hybrid inside carbon nanofibers is also confirmed by the TEM image of GC-CNF in Fig. S2. EDX characterization shown in Fig. 2c indicates a homogeneous distribution of C and W elements in the nanofibers, indicating that W_2C nanoparticles have a uniform distribution within the carbon nanofibers. The morphology that W_2C nanoparticles embedded in the carbon nanofibers is further confirmed by TEM images as shown in Fig. 2d. W_2C nanoparticles are in-situ formed within the carbon nanofibers during the carbonization of PAN and $(NH_4)_2WS_4$,

resulting in the homogeneous distribution of nanoparticles within the nanofiber structure without any aggregation. A close observation of a single nanofiber indicates that W_2C nanoparticles are uniformly distributed and embedded in the nanofibers, with an average particle size of 4–6 nm (Fig. 2e–f). HRTEM image of GC-CNF@ W_2C demonstrates that W_2C has an interlayer spacing of approximately 0.228 nm, which is consistent with the d-spacing of (121) plane of W_2C (Fig. 2g).

The addition amount of $(NH_4)_2WS_4$ was varied to obtain GC-CNF@ W_2C nanofibers with different loading of W_2C nanoparticles. Correspondingly, the resulting membranes obtained from different amount of $(NH_4)_2WS_4$ (250, 500 and 750 mg) were denoted as GC-CNF@ W_2C -1, 2, 3, respectively. As the addition of $(NH_4)_2WS_4$ increases from 250 to 750 mg, all the three samples display fibrous structures with smooth surfaces as shown by SEM images (Fig. S3a, b). However, TEM images show a big difference as the loading of W_2C nanoparticles differs. In GC-CNF@ W_2C -1, the particles are sparsely distributed in the fiber as the initial addition of $(NH_4)_2WS_4$ is inadequate (Fig. S3c). However, it can be noticed that larger W_2C agglomerates (~20 nm) are gradually formed on the surface of the nanofibers for GC-CNF@ W_2C -3 by further increasing the initial $(NH_4)_2WS_4$ concentration (Fig. S3d). For comparison, W_2C nanoparticles cannot be observed for GC-CNF nanofibers without the addition of $(NH_4)_2WS_4$ (Fig. S2). TGA curves of GC-CNF@ W_2C -1, 2, 3 shown in Fig. S4 reveal that the loading of W_2C is 27, 41 and 45 wt%, respectively. The electrical conductivity of CNF, GC-CNF and GC-CNF@ W_2C -2 membrane is 7, 19 and 22 S m^{-1} , indicating that the incorporation of GNR/CNT hybrid and W_2C can enhance the conductivity of CNF backbone.

The crystal structures of GC-CNF and GC-CNF@ W_2C -2 were investigated by XRD. As revealed in Fig. 3a, the peaks centered at $2\theta = 38.0^\circ, 39.5^\circ, 61.8^\circ$ can be indexed to (200), (121), and (023) planes of W_2C , respectively (PDF 89–2371). And both samples have a significant peak at $2\theta = 26^\circ$ that can be assigned to the (002) plane of carbon. Therefore, XRD results confirm that W_2C nanoparticles have been successfully immobilized within the carbon nanofibers. Fig. 3b presents the Raman spectra of CNF, GC-CNF and GC-CNF@ W_2C -2. All the spectra show two typical peaks at $1300\text{--}1400\text{ cm}^{-1}$ and $1500\text{--}1600\text{ cm}^{-1}$ which are assigned as D band and G band of carbon, respectively. The intensity ratio of D band and G band (i.e., I_D/I_G) decreased from 1.09 for CNF to 0.99 for GC-CNF@ W_2C -2, implying the more ordered structure of carbon by the incorporation of GNR/CNT and W_2C .

The electrochemical performance of GC-CNF@ W_2C as electrode materials for supercapacitors were evaluated via a two-electrode system in 6 M KOH aqueous electrolyte. The GC-CNF@ W_2C nanofiber membranes were cut into slices with an area of $10\text{ mm} \times 10\text{ mm}$ and used directly as electrode material with the mass loading of about 1.2 mg for a single electrode. Fig. 4a illustrates the cyclic voltammetry (CV) curves

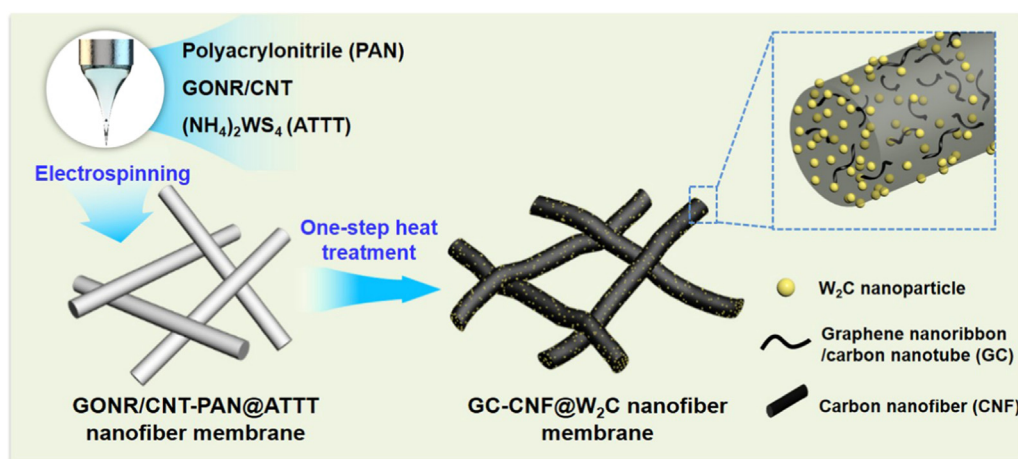


Fig. 1. Schematic illustration of the preparation of GC-CNF@ W_2C nanofiber membrane.

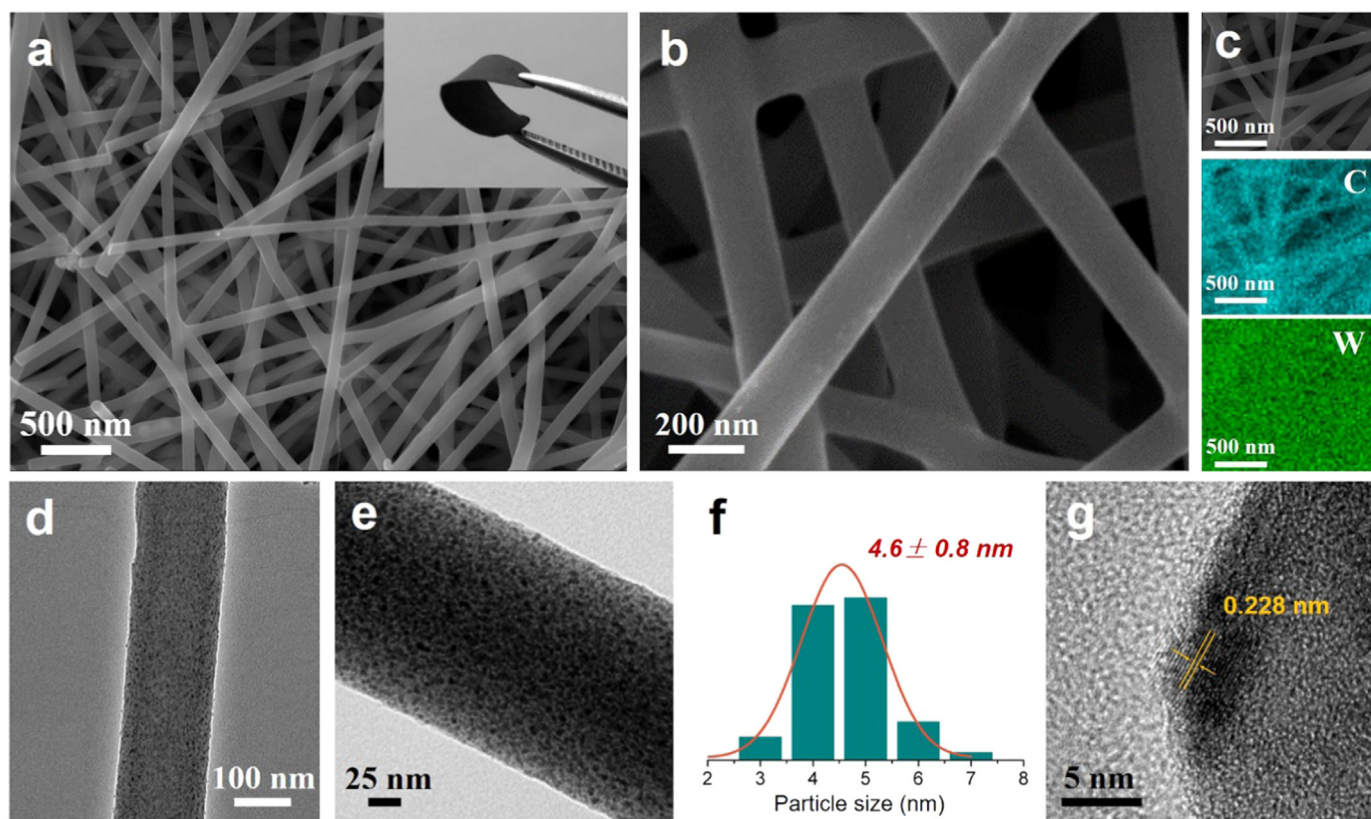


Fig. 2. Morphology characterization of GC-CNF@W₂C. SEM images of GC-CNF@W₂C-2 at (a) low and (b) high magnifications. Inset shows a photograph of GC-CNF@W₂C-2. (c) EDX mapping of GC-CNF@W₂C-2. TEM image of GC-CNF@W₂C-2 at (d) low and (e) high magnifications, (f) size distribution of W₂C nanoparticles, and (g) HRTEM image of GC-CNF@W₂C-2.

of GC-CNF, CNF@W₂C, GC-CNF@W₂C-1, 2, 3 at a scan rate of 2 mV s⁻¹. All CV curves show a moderately distorted rectangular shape, indicating their EDLC characteristics. In particular, the GC-CNF@W₂C-2 has the highest specific current intensity, revealing that GC-CNF@W₂C-2 has the best electrochemical performance among these samples. Fig. 4b illustrates the galvanostatic charge-discharge curves of GC-CNF, CNF@W₂C, GC-CNF@W₂C-1, 2, 3 at a current density of 1 A g⁻¹. Notably, GC-CNF@W₂C-2 displays a specific capacitance of 256 F g⁻¹ at a current density of 1 A g⁻¹, which is higher than or comparable to those reported electrospun carbon nanofiber-based electrodes (Table S1). Among these GC-CNF@W₂C composites, GC-CNF@W₂C-2 exhibits better performance than GC-CNF@W₂C-1 and GC-CNF@W₂C-3, which can be due to its proper loading and uniform distribution of W₂C nanoparticles. In addition, GC-CNF@W₂C-2 displays a higher capacitance than CNF@W₂C without incorporation of GNR/CNT hybrids, which could be attributed to the enhanced conductivity of the carbon

nanofiber membrane. Therefore, GC-CNF@W₂C-2 with proper amount of both W₂C and GNR/CNT hybrids could obtain optimized specific capacitance.

The CV curves of GC-CNF@W₂C-2 at different scan rates are also presented in Fig. 4c. It is notable that the synthesized materials exhibit excellent electrochemical behavior in a wide range of scan rates. The specific capacitance of GC-CNF@W₂C-2 and CNF@W₂C electrode at different current densities are shown in Fig. 4d. The specific capacitance of GC-CNF@W₂C-2 remained 71% of its initial value (in contrast to 56% for CNF@W₂C) as the current density increased from 1 to 10 A g⁻¹, indicating good rate ability of the electrode by incorporating GNR/CNT hybrids. The improved rate capability can be attributed to the enhanced conductivity of the GC-CNF membrane, which can be evidenced from the Nyquist plots. As shown in Fig. 4e, GC-CNF shows the most vertical line indicating its good capacitive behavior due to the good conductivity of carbon. Compared with CNF@W₂C, GC-CNF@

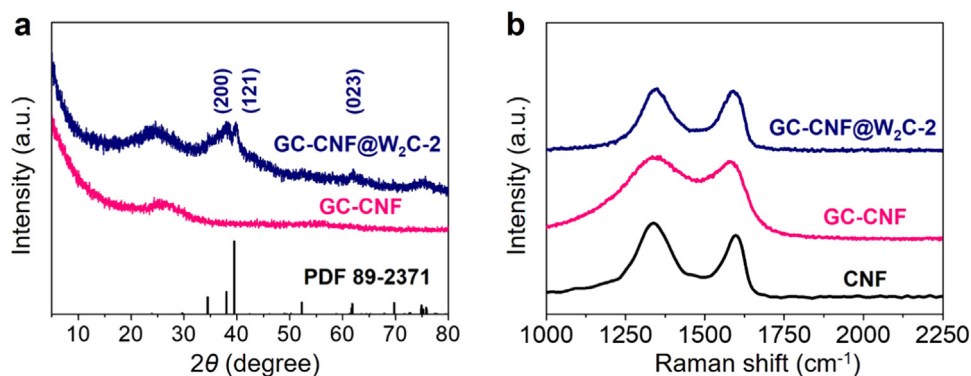


Fig. 3. (a) XRD patterns of GC-CNF and GC-CNF@W₂C-2. (b) Raman spectra of CNF, GC-CNF and GC-CNF@W₂C-2.

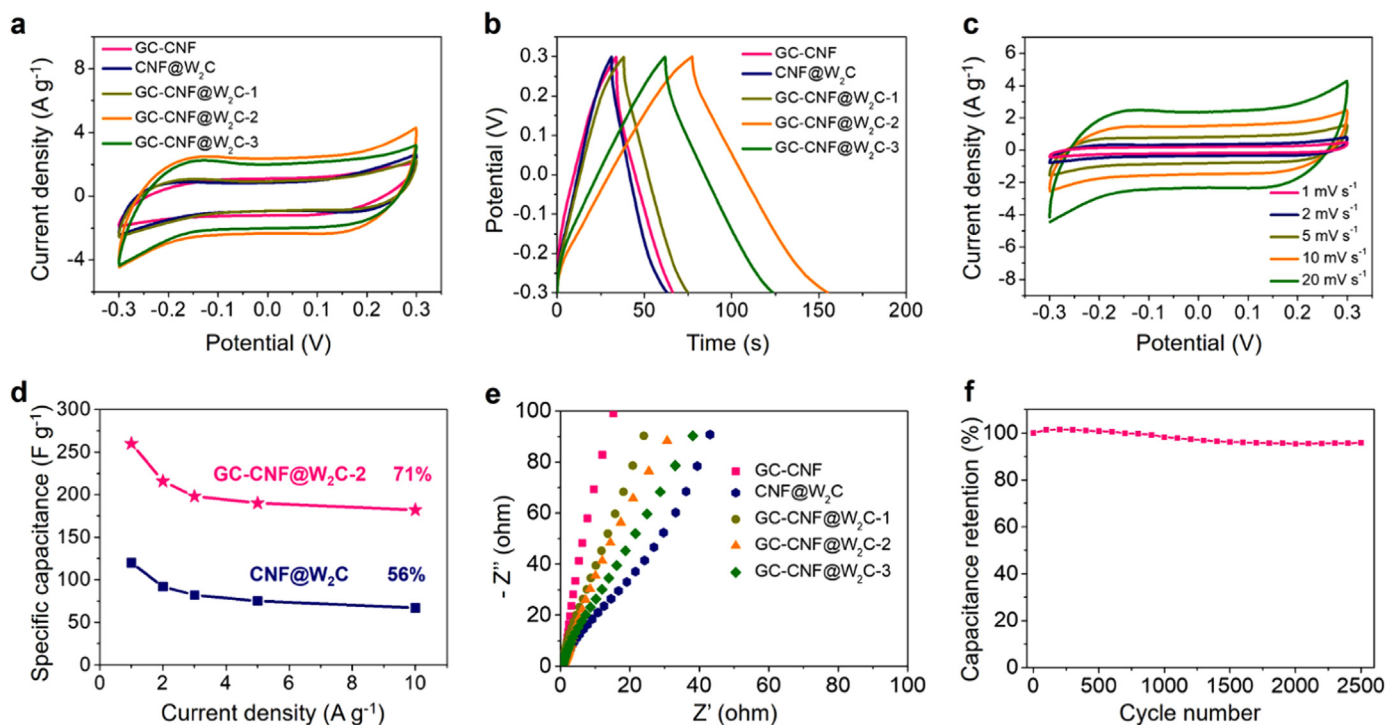


Fig. 4. Electrochemical performance of GC-CNF@W₂C as electrode materials for supercapacitors. (a) CV curves at a scan rate of 2 mV s⁻¹, (b) galvanostatic charge-discharge curves at a current density of 2 A g⁻¹, (c) CV curves of GC-CNF@W₂C-2 at different scan rates from 2 mV s⁻¹ to 20 mV s⁻¹, (d) specific capacitance of CNF@W₂C and GC-CNF@W₂C-2 at different current densities, (e) Nyquist plots for GC-CNF, CNF@W₂C and GC-CNF@W₂C-1,2,3, and (f) cycling performance of GC-CNF@W₂C-2 measured at a scan rate of 50 mV s⁻¹ for 2500 cycles.

W₂C-2 shows a more vertical line in the low-frequency region, indicating the incorporated GNR/CNT hybrid can significantly enhance the conductivity of CNF backbone. Among the three GC-CNF@W₂C samples, GC-CNF@W₂C-1 shows a more vertical line than the other two samples, which is derived from the fast electron transport rate of carbon backbone. Cycling test for GC-CNF@W₂C-2 was performed by sweeping CV curves at a scan rate of 50 mV s⁻¹ for 2500 cycles, as shown in Fig. 4f. The specific capacitance of the electrode decreases less than 5% after 2500 charge/discharge cycles, demonstrating good cyclic stability of the hybrid material as electrode materials. Furthermore, XRD pattern of GC-CNF@W₂C-2 shows almost no changes and the impedance only exhibit a slight increase after cycling test (Fig. S5), demonstrating good structural stability of the hybrid material during cycling, which can be attributed to the W₂C nanoparticles embedded in carbon nanofiber structure.

In summary, we have fabricated W₂C embedded GNR/CNT incorporated carbon nanofibers by one-pot electrospinning and subsequent carbonization. The W₂C nanoparticles in-situ formed during carbonization are dispersed uniformly in the nanofibers with several nanometers in size, affording high capacitance, while the GNR/CNT hybrid can improve the conductivity of the fibrous web. The GC-CNF@W₂C displays an enhanced specific capacitance of 256 F g⁻¹ at a current density of 1 A g⁻¹, and excellent cycling stability with 95.6% retention after 2500 cycles. The good performance and free-standing character make GC-CNF@W₂C a novel metal carbide-based electrode material for flexible supercapacitor.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.coco.2018.12.003.

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