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

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Ditungsten carbide (W₂C) nanoparticles embedded in graphene nanoribbon/carbon nanotube-carbon nanofiber (GC-CNFW₂C) composite membrane has been prepared by one-pot electrospinning with subsequent carbonization. The homogeneous distribution of small-sized W₂C 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 W₂C nanoparticles embedded in nanofiber structure could prevent their oxidation during the electrochemical process, contributing to enhanced cyclic stability. Consequently, the GC-CNFW₂C 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-CNFW₂C 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 are scarce. Ditungsten carbide (W₂C) 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 W₂C 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 (W₂C) nanoparticles embedded in graphene nanoribbon/carbon nanotube-carbon nanofiber (GC-CNFW₂C) composite membrane was prepared by one-pot electrospinning with...
subsequent high temperature carbonization under H2/Ar atmosphere. W2C 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 enveloping W2C nanoparticles could prevent the oxidation of W2C thus improving the cyclic stability, capacitance retention of 71% at 10 A g⁻¹, and good cycling stability with.

The addition amount of (NH4)2WS4 was varied to obtain GC-CNF@W2C nanofibers with different loading of W2C nanoparticles. Correspondingly, the resulting membranes obtained from different amount of (NH4)2WS4 (250, 500 and 750 mg) were denoted as GC-CNF@W2C-1, 2, 3, respectively. As the addition of (NH4)2WS4 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 W2C nanoparticles differs. In GC-CNF@W2C-1, the particles are sparsely distributed in the fiber as the initial addition of (NH4)2WS4 is inadequate (Fig. S3c). However, it can be noticed that larger W2C agglomerates (~20 nm) are gradually formed on the surface of the nanofibers for GC-CNF@W2C-3 by further increasing the initial (NH4)2WS4 concentration (Fig. S3d).

The crystal structures of GC-CNF and GC-CNF@W2C-2 were investigated by XRD. As revealed in Fig. S2, the peaks centered at 2θ = 38.0°, 39.5°, 61.8° can be indexed to the (200), (121), and (023) planes of W2C, respectively (PDF 89-7031). The intensity ratio of D band and G band (i.e., ID/IG) decreased from 1.09 for CNF to 0.99 for GC-CNF@W2C-2, implying the more ordered structure of carbon by the incorporation of GNR/CNT and W2C. The electrochemical performance of GC-CNF@W2C as electrode materials for supercapacitors were evaluated via a two-electrode system in 6 M KOH aqueous electrolyte. The GC-CNF@W2C nanofiber membranes were cut into slices with an area of 10 mm × 10 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 resulting in the homogeneous distribution of nanoparticles within the nanofiber structure without any aggregation. A close observation of a single nanofiber indicates that W2C 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@W2C demonstrates that W2C has an interlayer spacing of approximately 0.228 nm, which is consistent with the d-spacing of (121) plane of W2C.
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@


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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.

**References**


