Electronic Supplementary Information

Graphene/Silk Fibroin Based Carbon Nanocomposites for High Performance Supercapacitors

Yaxian Wang, Yanfang Song, Yu Wang, Xin Chen, Yongyao Xia, Zhengzhong Shao*

The detailed experimental procedure

Preparation of well-dispersed RGO with SF nanofibrils suspension

GO was prepared according to the previous reports.¹ $NH_3 \cdot H_2O$ was added to GO/RSF solution (respectively) to adjust the pH to 10. GO was dripped into RSF solution with slowly stirring in a beaker. Then the mixture were transfered into a three-necked round-bottom flask at 80°C with slowly stirring. After adding hydrazine (hydrazine : GO = 7:10 by weight), the suspension was incubated for 3 h. The ratio can be changed in a wide range. Here we used 2% RSF solution and 0.04% GO solution, the final mass ratio of GO to RSF is 1 to 50.

Preparation of RGO - porous carbon nanocomposite

After adding KOH solution to well-dispersed RGO with SF nanofibrils suspension (weight $_{\text{KOH}}$ / weight $_{\text{complex solution}} = 0.5$ or 0.2), the whole solution was liquid N₂ quenched and freezedried. Herein, we use freeze-drying rather than solution casting to get the aerogel because the freeze-drying method is more conducive to maintain the composite structure, and can ensure the full and homogeneous carbonization of the material. The aerogel is obtained with the density about 10mg/cm³. Then the aerogel was carbonized from room temperature to 700 °C for 3 hours under N₂ atmosphere with heating rate of 5 °C/min. The products were washed using distilled water and ethanol repeatedly and were then dried in a vacuum oven at 30 °C. The final products were named GCN-S-0.5/0.2/0 according to the weight ratio of KOH to complex suspension. We also used RSF solution of same concentration to carbonization for comparison, the preparation process was the same as that mentioned above and the final products were named C-SF.



Figure S1. Photograph of (a) the mixture of GO and SF after 3 days; (b) the mixture of GO and SF within 1 hour; (c) RGO with SF nanofibrils suspension (d) RGO with SF nanofibrils suspension after 3 month at room temperature, the composite suspension become hydrogel, still remains homogeneous (The concentration of SF for all the samples are 1 wt% and the weight ratio of GO/SF or RGO/SF are all 1/50); (e)RGO without SF after reduction (The concentration of RGO is 0.02%)



Figure S2. Raman spectra of GO and RGO/SF nanofibrils composite aerogel. The increase of

D/G intensity ratios proves the graphene oxide is well reduced.



Figure S3. Transmission electron microscopy (TEM) images of the suspension of RGO with SF nanofibrils.



Figure S4. AFM images of GO (a), RGO/SF nanofibrils composite (b) and their height profiles.



Figure S5. Scanning electron microscopy (SEM) image of the mixture of GO and SF after liquid N_2 quenched and freeze-dried and its magnifications (inset)



Figure S6. SEM image of C-SF.



Figure S7. SEM images of the GCNs-0.2 (a) and the enlarged image of GCNs-0.2 (b,c); TEM images of GCNs-0.2 at different viewing angles and magnifications (d and e)



Figure S8. TGA curves of silk, RGO and RGO/SF nanofibrils composite aerogel. The TGA samples of SF and RGO was prepared by adding same amount of NH_3 · H_2O and hydrazine with sample RGO/SF nanofibrils composite aerogel, the reaction also lasted for 3 hours at the same temperature of 80°C with slowly stirring. The final solid samples were obtained by liquid N_2 quenched and freeze-dried.



Figure S9. XPS spectra for N1s and O1s of GCNs



Figure S10. AFM images of RGO and BSA



Figure S11. Photograph of (a) RGO with gelatine suspension after 1 day (b) RGO with casein suspension after 1 week (c) RGO with BSA suspension after 1 week (The concentration of protein(gelatin/casein/BSA) are all 1 wt% and the weight ratio of RGO/protein are all 1/50.)



Figure S12. AFM images of RGO and gelatin at different magnifications(a-b); (c) Galvanostatic charge–discharge curves of GCN-G-0.2 at current densities from 5 to 50 A g^{-1} ; (d) Rate performance of GCN-G-0.2 and GCN-S-0.5 at different current densities varying from 0.2 to 50 A g^{-1}

BSA, casein, gelatin were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received. Gelatin solution (2%) was prepared at 40 °C, NH₃•H₂O was added to GO, gelatin, BSA and casein solution respectively to adjust the pH to 10. The preparations of RGO/gelatin, RGO/BSA and RGO/casein suspension are the same with that of RGO with SF nanofibrils suspension. The preparation process of GCN-G-0.2(graphene/gelation based carbon nanocomposites) is the same with that of GCN-S-0.2.



Figure S13. The CV curves of CMs-FD-SF (a), CMs-D-Silk (b) at different scan rates varying from 5 mV s⁻¹ to 200 mV s⁻¹.



Figure S14. Rate performance of CMs-FD-SF and CMs-D-Silk different current densities varying from 0.5 to 100 A g^{-1}

References:

1 Z. Xu and C. Gao, *ACS Nano*, 2011, **5**, 2908.