Electronic Supplementary Information

Carbon dots promoted vanadium flow battery for all-climate energy storage

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Experimental Section

Materials

Polyacrylonitrile (PAN) based graphite felt (GF, 5 mm of thickness) was purchased from Ganshu Haosi Carbon Fiber Co., Ltd. Thermal activated GF (TGF) was obtained by thermally treated the GF in air at 420 °C for 10 h. O-, m-, and p-phenylenediamines were purchased from Aladdin. Ethanol was provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were of analytic grade and were used as received without further purification. Deionized (DI) water was used throughout this study.

Preparation of carbon dots (CDs) and carbon dots decorated graphite felt (CDs/GF)

The CDs/GF was synthesized by an optimized solvothermal process. The synthesis process is as follows: 0.6 g p-phenylenediamine was dispersed in 90 mL absolute ethanol under sonication. Then, a piece of GF (50 × 50 × 5 mm) was immersed into the solution, the solution and GF were transferred into an 200 mL poly(tetrafluoroethylene)-lined autoclaves, and the reaction was conducted at 180 °C for 9 h and cooled to room temperature naturally. After that, the modified GF was taken out and washed by DI water for several times. CDs/GF was obtained after drying at 60 °C for 12 h. The o-CDs/GF, m-CDs/GF were synthesized by same process with CDs/GF. The only difference was that the carbon sources were o-phenylenediamine and m-phenylenediamine, respectively. The three carbon dots were synthesized by the same process without the existence of GF. The solution after reaction (180 °C for 9 h) was freeze-dried to obtain carbon dot powder. The synthesize process and micromorphology were exhibited in Fig. S1.

Physical and electrochemical characterization

The microstructures of CDs/GF were characterized by scanning electron microscopy (SEM, ZEISS SUPRA® 55), transmission electron microscope (TEM, FEI Tecnai G2 F30), Raman spectrometer (HORIBA iHR320) and laser scanning confocal microscope (LSCM, OLYMPUS FV1000), respectively.

Cyclic voltammograms (CV) and electrochemical impedance spectroscopy (EIS) were recorded on a PARSTAT 2273 electrochemical workstation. A three-electrode system was applied with a 10 × 10 mm CDs/GF or GF as working electrode, a platinized platinum and a saturated calomel electrode (SCE) were utilized as counter electrode and reference electrode, respectively. CV was conducted in 0.1 M VO^{2+} + 2 M H_{2}SO_{4} solution with scan rates of 1, 3, 5, and 10 mVs^{-1} from 0.5 V to 1.2 V, and in 0.1 M V^{3+} + 2 M H_{2}SO_{4} solution...
H$_2$SO$_4$ solution with a scan rate of 1 mVs$^{-1}$ from -0.7 V to -0.3 V. EIS was carried out under 0.70 V in 0.1 M VO$^{2+}$ + 2 M H$_2$SO$_4$ solution and -0.2 V in 0.1 M V$^{3+}$ + 2 M H$_2$SO$_4$ solution respectively, with the frequency range of 100 kHz to 10 mHz.

**VFB single cell test**

The configuration of the VFB single cell was the same as in our previous work.$^{2-4}$ Wet treated (immersing in DI water for 24 h) Nafion 212 membrane (65 × 65 mm) was used as the separator, and CDs/GF or GF (50 × 50 × 5 mm) was used as electrode. Two 50 mL of electrolytes (1.5 M V$^{3.5+}$ in 2 M free H$_2$SO$_4$) were applied as positive and negative electrolyte, respectively. The electrolytes were cyclically pumped through the half-cells by peristaltic pumps with a flow rate of 60 mL min$^{-1}$. Both electrolyte tanks were purged with nitrogen gas for 10 min and then sealed prior to the single cell test. The charge-discharge of the cell was controlled by a battery testing system (BTS, CT-3008-5V10A, Neware) with voltage ranging from 0.8 V to 1.65 V. Rate performance test was carried out at current densities from 50 to 350 mA cm$^{-2}$, while long-term cycling performance test was conducted at a constant current density of 150 mA cm$^{-2}$.

To fully evaluate the performance of CDs/GF electrode in all-climate condition, the VFB was also tested at different temperatures including -20, -10, 0, 10, 20, 30, 40, 50, and 60 °C using a thermostat (Guangdong Hongzhan, PU-80) at a current density of 100 mA cm$^{-2}$. The temperature deviation of the thermostat was ± 0.5 °C.
Fig. S1. (a) Schematic illustration for the preparation of CDs. (b) Tyndall phenomenon of CDs solution. (c) Photographs of CDs solution in nature light (left) and 365 nm UV light (right). (d) HRTEM image of CDs.

Fig. S1a shows the synthesis process of CDs, which is described detailedly in experimental section mentioned above. Tyndall phenomenon can be observed when the CDs solution irradiated by laser, it can be inferred that the size of CDs are nanometer grade. Furthermore, the solution of CDs is brown in nature light and turned to be red under the irradiation of 365 nm UV light. This is consistent with literature.¹ The microstructure of CDs is revealed by TEM. As can be seen from Fig. S1d, the diameter of CDs is around 3-6 nm with 0.21 nm of lattice spacing.
Fig. S2. STEM element mapping of CDs: (a) C and O element mapping images, (b) EDS spectra.

Fig. S2 shows the STEM element mapping and EDS spectra of CDs. As we can see from Fig. S2, elements C and O are uniformly distributed on the selected area, while N element does not appear. Element ratios of C and O in Fig. S2 are 91.8% and 8.2%, respectively, also confirms N element is not doped into CDs. Thus, there is no N-doped CDs formed in this work.
**Fig. S3.** CV curves of various carbon dots decorated GF electrodes at a scan rate of 1 mV s\(^{-1}\) in 0.1 M VOSO\(_4\) + 2 M H\(_2\)SO\(_4\) electrolyte.

GF modified by three types of carbon dots are prepared by the same method in experimental section mentioned above. Electrochemical performances of three modified electrodes are evaluated by CV test in positive electrolyte. As shown in Fig. S3, the CDs/GF (i.e. p-CDs/GF) exhibits the highest electrochemical activity towards the redox reaction of VO\(^{2+}/VO_2^+\) couple. Therefore, CDs/GF electrode is chosen for further investigation.
Fig. S4. CV curves of CDs/GF electrodes with different dosage of p-phenylenediamine at a scan rate of 1 mV s$^{-1}$ in 0.1 M VOSO$_4$ + 2 M H$_2$SO$_4$ electrolyte (a) and 0.1 M V$^{3+}$ + 2 M H$_2$SO$_4$ electrolyte (b).

The dosage of p-phenylenediamine also has great impact on the electrocatalytic activity of CDs/GF. To characterize the effect of the dosage of p-phenylenediamine, various samples were prepared with 0.3, 0.6, 0.9, 1.2, and 1.5 g of p-phenylenediamine, respectively. As shown in Fig. S4, the CDs/GF electrode with 0.6 g p-phenylenediamine shows the highest peak current density and smallest peak potential separation in both positive and negative electrolytes, indicating the best electrochemical activity towards vanadium redox reaction. Therefor, 0.6 g is the best dosage in this synthesis process.
The electrocatalytic activity of CDs/GF is affected by not only dosage of p-phenylenediamine but also the solvothermal temperature. Various samples were prepared with 0.6 g p-phenylenediamine at temperature of 140, 160 and 180 °C, respectively. As shown in Fig. S5, the CDs/GF fabricated at 180 °C shows the best performance among other two samples no matter in positive or negative electrolyte. Thus, according to the discussion above (Fig. S3-S5), 0.6 g of p-phenylenediamine and 180 °C of solvothermal temperature are the best synthesis conditions.
Fig. S6. CV curves at different scan rates in 0.1 M VOSO$_4$ + 2 M $\text{H}_2\text{SO}_4$ electrolyte: (a) GF, (b) TGF, and (c) CDs/GF. (d) Plots of the redox peak current density versus the square root of scan rate for GF, TGF and CDs/GF.
Fig. S7. Charge-discharge curves of VFBs assembled with GF, TGF and CDs/GF electrodes at various current densities: (a) 100 mA cm$^{-2}$, (b) 150 mA cm$^{-2}$, and (c) 200 mA cm$^{-2}$. 
Fig. S8. Electrolyte utilization and power density of VFBs assembled with GF, TGF and CDs/GF electrodes.
Fig. S9. Photograph of the all-climate test platform

References