In Situ Growth of Oriented Polyaniline Nanorod Arrays on the Graphite Flake for High-Performance Supercapacitors

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ABSTRACT: Polyaniline with oriented nanorod arrays could provide high surface area and relaxed nanostructure to optimize ion diffusion paths, thus enhancing the performance of the device. In this paper, we designed an all-solid symmetrical supercapacitor with good performance based on polyaniline nanorod arrays in situ-grown on a graphite flake free-standing substrate. The specific capacitance, cycle stability, and energy density of the prepared supercapacitor device were 135 F/g, 75.4% retention after 1500 cycles, and the energy density is 18.75 W h/kg at a power density of 500 W/kg. The good performance of the supercapacitor device was obviously related to the oriented nanorod arrays of polyaniline/graphite flakes. In order to find the application of the prepared supercapacitor device, the tandem device consisting of three single supercapacitor devices connected in series had been used to drive small electronic equipment. The red light-emitting diode and chronograph could be easily driven by the 3-series supercapacitor devices. These results indicated that the prepared supercapacitor device based on the polyaniline/graphite flake electrode had potential applications in energy storage devices.

1. INTRODUCTION

The conductive polyaniline (i.e., PANI) is attracted by the field of chemical materials because of its low cost, high flexibility, good environmental stability, and ease of synthesis. 3−4 In particular, PANI with oriented nanorod arrays has been applied to energy conversion, 5,6 supercapacitors, 7−10 electromagnetic absorption 11,12 and chemical sensors. 13 The reason can be explained by the following aspects: (i) PANI nanorod arrays (PNA) can be easily grown in situ on appropriate substrates (such as filter paper, carbon nanotube (CNT) paper, conductive glass, graphene, and polymer film) to make a composite free-standing electrode. 14 (ii) PANI with oriented nanorod arrays can provide high surface area to obtain high adsorption performance. 15 (iii) Ordered PANI arrays can provide relaxed nanostructures to optimize the ion diffusion to enhance the energy conversion in solar cells or the specific capacitance in supercapacitors. 16 For example, He et al. reported that a highly ordered PANI was grown on a fluorine-doped tin oxide (FTO) substrate by electropolymerization, and the power conversion efficiency could reach 17.6% when PANI/FTO was used as the counter electrode of a dye-sensitized solar cell. 6 Kuila et al. showed that high-density PANI nanorods could be prepared on ITO glass using block copolymers as scaffold materials, with a specific capacitance value of 3407 F/g. 17 Yu et al. reported that the electromagnetic absorption properties of PANI/graphene nanocomposites were significantly enhanced when PANI nanorods grew on the surface of graphene. 18 Wei et al. had successfully introduced vertically aligned PNA onto graphene oxide nanosheets for high-performance NH3 gas sensors. 19

Recently, carbon materials combining with PANI nanorods arrays have received extensive attention in the application of supercapacitors because of their low cost, good chemical stability, thermal stability, electrical conductivity, and mechanical properties. 18,19 For instance, Yu et al. reported that the controllable PANI nanoarray could easily grow onto the surface of reduced graphene oxide nanosheets by chemical oxidation, and the prepared composite as an electrode material had a high specific capacitance (the specific capacitance is 752 F/g at 1 A/g) and good cycle stability (the specific capacitance could retain 90.8% after 10,000 charge/discharge cycles). 20 Wu et al. proposed a high-performance micro-supercapacitor based on a microfluid-oriented core-sheath PNA/graphene (PNA/G) composite fiber electrode. The micro-supercapacitor had excellent electrochemical performance, including large capacitance (230 mF/cm), high cycle stability (retention 86.9% after 8000 cycles), long-term bending durability, and high energy density (37.2 μW h/cm²). 21 Li et al. reported the growth of
PANI nanowire arrays on the inner surface of macroporous carbon derived from luffa sponge fibers. The specific capacitance was up to 1500 F/g at a current density of 1 A/g, and the maximum energy density was 19 W h/kg at a power density of 500 W/kg. It could be seen that the carbon material/PANI structure could improve the electrochemical performance of the composite electrode. It was attributed to the fact that the high-conductivity carbon material could provide a fast electron transmission channel for the composite electrode. On the one hand, it made full use of electric double layer capacitance of the carbon material and the high pseudocapacitance of the conductive polymer. On the other hand, it overcomes the shortcomings of low specific capacity of carbon materials and poor cycling charge/discharge stability of conductive polymers.

Based on our previous studies, in this paper, we have successfully fabricated PANIs grown onto the surface of the graphite flake (i.e., GF, its thickness is 0.3 mm) by dilute-solution polymerization to assemble all-solid-state electrochemical energy storage. The GF as a free-standing substrate can be explained by the following reasons: (i) the PANIs can be directly grown on the surface of GF to fabricate a composite free-standing electrode. (ii) The conductive GF can be used as a high-quality free-standing electrode with excellent electrical contact with the substrate, which is in favor of the electrochemical test. (iii) The GF as one of the carbon materials combining with PANI can effectively increase the specific capacitance of the supercapacitor. Moreover, the GF is easily obtained and inexpensive compared with graphene and CNT. The all-solid-state electrochemical energy storage device of PANIs/GF showed a maximum capacitance of 135 F/g at a current density of 1 A/g, and the cycle stability was better than that of pure PANI devices. When the power density is 500 W/kg, the maximum energy density is 18.75 W h/kg. The prepared PANIs/GF supercapacitor device had good applications in small wearable electronic products. Therefore, it is considered to be an excellent candidate for energy storage devices.

2. RESULTS AND DISCUSSION
The formation process of PANIs in situ-grown on the surface of GF has been shown in Figure 1a, and the optical images of the GF and PANI/GF electrode can be found in Figure 1b. The morphology of the pure GF can be seen in Figure 2a. Under low magnification, the pure GF has a smooth surface, and it is stacked together to form an open structure by many thin graphite sheets (Figure 2b). PNAs are chemical polymerization on the GF electrode by the dilute-solution method (Figure 1a), and the dark green and uniform PANI film on the surface of GF electrode can be obtained (Figure 1b). The growth mechanism is detailed in our previous study. It is clearly observed that the aligned PANI nanorods are oriented perpendicular to the surface of the GF electrode, as
shown in Figure 2c−e. To get a cross-section of PANI nanorods arrays, the PANI/GF electrode is frozen and broken in liquid nitrogen, as shown in Figure 2f. It can be found that the PNAs are indeed grown vertically on the surface of GF, in consistent with our expected structure. In addition, the PNAs are evenly distributed on the whole surface of the GF electrode, which makes it very suitable to be an electrode material for the electrochemical measure.

Figure 3 shows the XPS survey spectra taken from the surface of the GF and PANI/GF. It reveals a predominant C 1s (284.80 eV), O 1s (531.46 eV), Sn 3d5 (487.36 eV), and Cl 2p peak (198.83 eV) which originates from the GF. In particular, the N 1s appearing at a binding energy of 399.93 eV may come from a small amount of carbon nitrides.29 The survey spectrum of PANI/GF contains the C 1s (284.79 eV), O 1s (531.46 eV), N 1s (399.43 eV), Sn 2p (168.38 eV), and Cl 2p peak (197.3 eV). The Sn and Cl elements exist in PANI/GF which come from the GF. For the PANI/GF, the Sn 3d5 peak cannot be found in the spectrum, and the Cl 2p peak shifts from 198.83 to 197.30 eV. Moreover, the N 1s spin−orbital splitting photoelectron for PANI/GF and GF appears in 399.43 and 399.93 eV, respectively,30,31 and the atomic percent of N 1s in PANI/GF is higher than that of N 1s in GF (the inset in Figure 3). The results suggest that as-prepared PNAs are successfully coated onto the surface of GF.

The Raman spectra of the GF and PANI/GF can be found in Figure 4a. For the GF, only one Raman peak occurring at 1580 cm$^{-1}$ is observed because the GF is composed by many single crystals.32 The band at 1580 cm$^{-1}$ is assigned to the G-band or Raman-active E$_{2g}$ mode which is the characteristic of the graphitic sheets.32,33 The PNAs on the GF are the doped PANI, which are shown in the Raman spectrum of PANI/GF. The C−C stretching vibration of benzenoid and quinoid rings is located at bands of 1584 and 1513 cm$^{-1}$, respectively. The C=N stretching band of quinoid ring can be found in the peak of 1485 cm$^{-1}$. The band at 1318 cm$^{-1}$ can be explained by the C−N$^+$ stretching vibration in the doped state of PANI nanorods arrays. The C−H bending of the quinoid benzene ring is centered at a band of 1168 cm$^{-1}$. The bands at 814, 587, and 516 cm$^{-1}$ are assigned to the C−H bending of quinonoid ring, in plane deformation of the benzenoid ring and C−N−C torsion in bipolaron, respectively. The results are in good agreement with the previous study.23,25,34,35 In addition, the Raman line of the GF is not observed in the spectrum of PANI/GF, suggesting the as-prepared PNAs are entirely coated onto the surface of the GF, as shown in Figure 4b,c. To further confirm the PNAs grown onto the GF, the Raman mapping of the selected area in the PANI/GF electrode (Figure 4c) is performed at an excitation wavelength of 532 nm; as shown in Figure 4d, the red area is almost PANI layer, and the dark purple area is the GF layer, in agreement with the result of optical image in Figure 4b,c. Figure 4e is the 2D overlay Raman mapping image which is transformed from (d) (the PANI/GF is prepared at 0.004 mol ANI).

![Figure 3. XPS survey spectra of the GF and PANI/GF. The inset (left) is the atomic percent in GF and PANI/GF. The inset (right) is N 1s spectra of GF and PANI/GF (the PANI/GF is prepared at 0.004 mol ANI).](image)

![Figure 4. (a) Raman spectra of the GF and PANI/GF. (b,c) Optical images of the GF and PANI/GF electrode. (d) Raman mapping of selected area in PANI/GF electrode. (e) 2D overlay Raman mapping is transformed from (d) (the PANI/GF is prepared at 0.004 mol ANI).](image)
from Figure 4d. It can be found that the GF layer displays only one characteristic peak centered at 1580 cm\(^{-1}\), while all of the characteristic peaks of the PANI can be revealed in the PANI layer. Obviously, the PNAs can be effectively directly grown onto the surface of the GF to fabricate a composite free-standing electrode, which is in favor of electrochemical testing.

To explore the practical applications of the PANI/GF electrode in the supercapacitor, the symmetric all-solid-state supercapacitor device has been assembled to form a sandwich structure using two pieces of PANI/GF electrodes, as shown in Figure 5a. The electrochemical performance of the as-prepared supercapacitor device in two-electrode configuration can be found in Figure 5. Figure 5b,c shows the cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) performance of the GF, PANI, and PANI/GF device, which are carried out from −0.3 to 0.7 V at a scan rate of 10 mV/s. The CV and GCD curves of PANI and PANI/GF device are nearly rectangular and symmetric triangle in shape, respectively, revealing that the as-
prepared device has the characteristics of pseudocapacitance.\textsuperscript{21} Moreover, the CV loop area and discharge time of PANI/GF device are larger than those of the pure GF and PANI device. It means that the PANI/GF supercapacitor device has a larger specific capacitance. The CV curves of PANI/GF supercapacitor device can maintain the stable rectangular shape at various scan rates with operating voltage ranging from $-0.3$ to $0.7$ V (Figure 5d), revealing a low internal resistance and good capacitance behavior for the as-prepared device. The maximum anode ($I_a$) and cathode ($I_c$) peak currents of the PANI/GF supercapacitor device have a linear relationship with the scan rate, as shown in Figure 5e, which means that the redox reaction occurring in the device conforms to first-order kinetics at scan rates of $10$–$200$ mV/s. Therefore, it can be regarded as the evidence that the PANI/GF supercapacitor device has a significant rate capability.

Figure 5f shows the GCD curves of PANI/GF supercapacitor devices under different current densities in the potential window from $-0.3$ to $0.7$ V. The specific capacitance ($C_s$) of as-prepared device is obtained from GCD curves using eq 1.\textsuperscript{36,37}

$$C_s = \frac{\Delta t \times I}{\Delta V \times m}$$ \hspace{1cm} (1)

where $\Delta t$ is the discharge time (s), $I/m$ is the current density (A/g), and $\Delta V$ is the potential window (V). It can be seen that the prepared device has a high $C_s$ of $135$ F/g, and the capacitance loss is about $55.6\%$ under a current density of $5$ A/g (Figure 5g), which further confirms the good capacitance and rate capability of the as-prepared symmetric device.

The specific energy ($E$) and power density ($P$) of the as-prepared device are calculated using eqs 2 and 3.\textsuperscript{37,38}

$$E = \frac{1}{2 \times (3.6)} C_s \times (\Delta V)^2 \text{ (W h kg$^{-1}$)}$$ \hspace{1cm} (2)

$$P = \frac{E \times 3600}{\Delta t} \text{ (W kg$^{-1}$)}$$ \hspace{1cm} (3)

The Ragone plot of the PANI/GF supercapacitor device is shown in Figure 6. The as-prepared device based on the PNA grown onto the surface of GF possesses an $E$ of $18.75$ W h/kg at a power density of $500$ W/kg. The $P$ reaches up to $2500$ W/kg at $E$ of $8.33$ W h/kg. The result is superior or close to recently reported PANI-based supercapacitor or other devices: PANI/CNT,\textsuperscript{39} PANI/PAN nanofibers,\textsuperscript{40} PANI/TiO$_2$,\textsuperscript{41} PANI/graphene,\textsuperscript{42} Wavy PANI/graphene,\textsuperscript{43} nanorods PANI/graphene,\textsuperscript{44} and MnO$_2$/graphene.\textsuperscript{45}

To further study the applications of the as-prepared PANI/GF device based on the PANI/GF electrode, the tandem device in series construction has been used to drive small electronic equipment. Figure 7a,b are the CV and GCD curves of both single device and 3-series device. It is found that the available potential window is from $1.0$ V extending to $3.0$ V when three single devices are connected in series to form a tandem device. In addition, shapes of GCD curves of a single and a series device are highly similar, and the charge–discharge time has a small deviation, which shows that the electrochemical performance of each device in the 3-series configuration is well maintained. Therefore, the red light-emitting diode (LED) and chronograph (CG) can be easily driven by the 3-series supercapacitor device, as shown in Figure 7c (see the Videos S1 and S2 in Supporting Information). These results demonstrate that the PANI/GF supercapacitor device has a potential application in energy storage device.

As shown in Figure 7d, the long-term cycles of a single supercapacitor device based on GF, PANI, and PANI/GF electrodes are measured for 1500 cycles under a current density of $10$ A/g. The capacitance loss of a single PANI device is $32.4\%$ of its initial value, and after 1500 cycles, the capacitance loss of a single PANI/GF device is $24.6\%$. In addition, the GCD curve of the PANI/GF single device in the initial and last 25 cycles has the same triangle, and the charging and discharging time also has a very small deviation (the inset of Figure 7d). Obviously, the PANI/GF composite material used as the electrode in the supercapacitor device has better stability than pure PANI.

3. CONCLUSIONS

In this article, we have successfully prepared PNAs grown on the surface of GFs by dilute solution polymerization to assemble all-solid-state electrochemical energy storage devices. The all-solid-state electrochemical energy storage based on PANI/GF exhibited a maximum capacitance of $135$ F/g at a current density of $1$ A/g, and after 1500 cycles, the long-term cycle performance can maintain $75.4\%$. Moreover, the maximum energy density was $18.75$ W h/kg at a power density of $500$ W/kg, while small wearable electronic devices (such as LEDs and chronographs) can be driven by 3-series supercapacitor devices. Therefore, it is considered as an excellent candidate material for supercapacitors.

4. EXPERIMENTAL SECTION

4.1. Synthesis of PANI Nanorod Arrays Grown onto the GF (i.e., PANI/GF). The GF was obtained from North China Science and Technology Metal Material Co. Ltd. (China). The ammonium sulfate [(NH$_4$)$_2$S$_2$O$_8$, APS] and aniline (i.e., ANI) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

The purchased GF was first cut at about $1 \times 5$ cm$^2$ to form a rectangular free-standing substrate, and then, it was first washed ultrasonically in ethanol and deionized water. The washed GF was used as a free-standing substrate for the assembly of PNAs by dilute solution polymerization. The experimental details were as follows: add ANI monomer (0.001 mol) and APS (0.001 mol) in a 2.0 mol/L H$_2$SO$_4$ solution (25 mL) to form A and B solutions, respectively. Put the GF substrate into the A solution.
vertically, and then, add the B solution dropwise to the A solution to react 12 h in an ice water bath. The as-prepared PANI/GF electrode was washed with ethanol and deionized water successively and then dried in vacuum at 30 °C for 2 h. Adjusting the molar mass of the ANI monomer, the scanning electron microscopy (SEM) image of the prepared product can be found in Figure S2 in the Supporting Information under the same conditions. The compared pure PANI was prepared with the same method for PANI grown onto the surface of GF. The pure PANI electrode was prepared as follows: the pure PANI (90 wt %), carbon black (5 wt %), and polytetrafluoroethylene (5 wt %) are mixed, and then, the above mixture was pressed onto the GF to form the PANI electrode.

4.2. Designing of the Symmetric All-Solid-State Supercapacitor. PVA powder (1.0 g) and H₂SO₄ (1.0 g) were added into 10 mL distilled water to prepare the PVA/H₂SO₄ hydrogel electrolyte. The PANI/GF electrodes and normal filter paper (it acts as a separator) were immersed in the PVA/H₂SO₄ solution overnight, and then, the prepared electrodes were dried at room temperature. The symmetric supercapacitor was stacked by two pieces of the PANI/GF electrode and filter paper together to form the sandwich structure.

4.3. Characterization. The CV and GCD were carried out in three-electrode and two-electrode configurations by electrochemical workstation (CHI 660E, Shanghai Chenhua Inc., China). The morphology, molecular structure, and elemental analysis of sample were observed by field-emission SEM (SEM, SU8000, Hitachi), Raman spectroscopy (532 nm inVia Laser, Renishaw), and X-ray photoelectron spectroscopy (Thermo Fisher Scientific, K-ALPHA™), respectively.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04212.

Video of red LED driven by 3-series tandem device (MP4)
Video of chronograph driven by 3-series tandem device (MP4)

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Notes
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