Graphene-Based Nanowire Supercapacitors

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Supporting Information

ABSTRACT: We present a new type of electrochemical supercapacitors based on graphene nanowires. Graphene oxide (GO)/polypyrrole (PPy) nanowires are prepared via electrodeposition of GO/PPy composite into a microporous Al2O3 template, followed by the removal of template. PPy is electrochemically doped by oxygen-containing functional groups of the GO to enhance the charging/discharging rates of the supercapacitor. A high capacitance 960 F g−1 of the GO/PPy nanowires is obtained due to the large surface area of the vertically aligned nanowires and the intimate contact between the nanowires and the substrate electrode. The capacitive performance remains stable after charging and discharging for 300 cycles. To improve the thermal stability and long-term charge storage, GO is further electrochemically reduced into graphene and PPy is subsequently thermally carbonized, leading to a high capacitance of 200 F g−1 for the resultant pure reduced graphene oxide/carbon based nanowire supercapacitor. This value of capacitance (200 F g−1) is higher than that of conventional porous carbon materials while the reduced graphene oxide/carbon nanowires show a lower Faraday resistance and higher thermal stability than the GO/PPy nanowires.

Electrochemical supercapacitors have been considered as energy storage devices for a wide range of applications requiring a high power density, such as consumer devices, electric vehicles, electronic facilities, and energy back-up systems.1 In a typical supercapacitor, energy is stored in an electrical double layer at the interface between a high-surface-area electrode and electrolyte solution (electrical double layer capacitors, EDLCs). Pseudocapacitance involving electron transfers due to Faradic redox reactions could also occur. High-surface-area carbon electrodes, including activated carbon,2 mesoporous carbon,3 and carbon nanotubes,4−6 have been used for EDLCs. However, the capacitance of existing porous carbon materials (normally less than 100 F g−1) is still limited by the small effective surface area and low electrolyte accessibility of the electrodes.7 In order to achieve high capacitance values, numerous efforts have been tried to improve the electrochemical active surface area of the electrodes. In the case of carbon nanotube electrodes, reasonable capacitances have been reached (e.g., 102 F g−1 for multiwalled4 and 180 F g−1 for single-walled8). A new class of supercapacitors with a very high capacitance of 440 F g−1 based on plasma activated vertically aligned carbon nanotubes and ionic liquid electrolytes has been reported.9

On the other hand, various electroactive conducting polymers, such as polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh), and their derivatives, at different oxidation states have been considered as an important supplementary to improve the capacitive performance of microporous carbon electrodes.10 Of particular interest, PPy has been attractive as a promising EDLC electrode because of its unique properties, including high specific capacitance (normally higher than 100 F g−1) and good conductivity in the doped state.11−13 The reversibility and stability of PPy-based supercapacitors, however, were limited by volumetric shrinkage of the polymer during ejection of doped ions in discharge state, and high ohmic polarization arising from low conductance when polymer was at the dedoped state. The combination of conducting polymers and porous carbon materials (e.g., carbon nanotubes) has led to the rapid development of a new class of electrochemical supercapacitors with high capacitances up to 500 F g−1.14−16 More recently, the maximum capacitances of 763 F g−1 for the flexible graphene/PANI paper17 and 909 F g−1 for the graphene/PANi nanorods18 have been reported.
In this work, we developed novel supercapacitors based on graphene and PPy nanowires. As a new class of 2D carbon nanomaterials, graphene and its derivatives have been demonstrated to be attractive for a wide range of applications, including field effect transmitters\(^{19}\), biosensors\(^{20}\), and lithium-ion batteries\(^{14}\) due to its unique high surface area, electrical conductivity, and physical and mechanical properties. Of particular interest, graphene oxide (GO) nanosheets are soluble in water and many other common polar solvents suitable for the formation of large-scale uniform films on various substrates by solution processing. The presence of oxygen-containing functional groups limits the direct application of GO in electrically active devices\(^{22}\) but also provides effective ways for certain practical applications. In the present study, the negatively charged GO (with carboxyl and hydroxyl groups) was used for electrochemical doping of PPy, imparting the fast charging and discharging capability to the resultant composites. Furthermore, the formation of PPY/GO nanowires provides a large surface area for the electrode. Nanostructures also offer the possibility for the molecular-level control of the electrode, leading to a systematic variation of different parameters to optimize the charge storage.\(^{23}\) As a result, an excellent capacitance value of 960 F g\(^{-1}\) (compared to less than 500 F g\(^{-1}\) for the most carbon/polymer composites\(^{14–16}\) and maximum 909 F g\(^{-1}\) for the graphene/PANI nanorods\(^{18}\)) was obtained from the GO/PPy nanowires prepared in this work.

To improve the thermal stability and long-term charge storage, GO was further electrochemically reduced into graphene and PPy was subsequently thermally carbonized. The resultant reduced graphene oxide/carbon (rGO/carbon) nanowire supercapacitor exhibited a high capacitance of 200 F g\(^{-1}\), compared to less than 130 F g\(^{-1}\) for the graphene films\(^{24,25}\) and less than 180 F g\(^{-1}\) for the graphene/carbon nanotube hybrids\(^{26,27}\).

Figure 1a shows schematically the synthetic processes of the preparation of GO/PPy nanowires and rGO/carbon nanowires.

![Diagram of synthetic processes](image)

**Figure 1.** (a) Schematic synthesis of graphene-containing nanowires, (b) a typical AFM image of graphene oxide, (c) side view for SEM images of polypyrrole/graphene oxide nanowires after the removal of the Al\(_2\)O\(_3\) template, and (d) top view for SEM images of the polypyrrole/graphene oxide nanowires after the removal of the Al\(_2\)O\(_3\) template.

In a typical experiment, microporous Al\(_2\)O\(_3\) paper (with a hole diameter of 220 nm) was sputter-coated with a thin layer of gold on one side and used as the template for the electrodeposition of GO/PPy composite. GO/PPy was deposited from the GO/pyrrole mixture into the holes of the gold-supported Al\(_2\)O\(_3\) template using cyclic voltammetry with potential cycling between 0 and 1.2 V for 12 cycles at a scan rate of 0.1 V s\(^{-1}\) (see the Supporting Information for details). A much higher oxidation current was obtained during electro-deposition of PPY/GO compared to the deposition of pure PPY (Figure S1, Supporting Information), suggesting the successful incorporation of GO into PPy. The successful deposition of PPY/GO composite was further confirmed using Fourier transform infrared (FT-IR) spectra (Figure S2, Supporting Information). As shown in Figure S2 (Supporting Information), characteristic peaks of GO (C—O at 1100 cm\(^{-1}\), C—O—C at 1390 cm\(^{-1}\), C=C at 1640 cm\(^{-1}\), C=O at 1750 cm\(^{-1}\), and hydroxyl- at 3430 cm\(^{-1}\), blue line) were all observed in the spectrum of the as-synthesized PPY/GO composites (pink line). In the spectrum of the pristine PPy (green line), peaks at 1400 cm\(^{-1}\) and over 500–1000 cm\(^{-1}\) were associated with the alkane (C—H) deformation and bend vibration. The peak at 1605 cm\(^{-1}\) was attributed to vibration of the N—H deformation. The peak at 1320 cm\(^{-1}\) arose from stretch vibration of C—N. All of these peaks were found at the spectrum of the PPY/GO composite, confirming successful combination of GO and PPy. TGA results further confirmed that the thermal stability of both the pristine PPY and GO could be enhanced significantly with incorporation of GO with PPy (Figure S3, Supporting Information).

Figure 1b shows an AFM image for the smooth surface of GO nanosheets with an average thickness of 1.2 nm, indicating single- or few-layer graphene nanosheets. PPy mixed with GO was electrodoped into holes of the Al\(_2\)O\(_3\) (Figure 1a). A highly uniform and densely packed forest containing GO-doped PPy nanowires was observed after removal of the Al\(_2\)O\(_3\) template by soaking the composite in 1 M NaOH over 3 h (Figure 1c, d). The diameter of the GO/PPy nanowires was found to be around 220 nm from the TEM image, as shown in Figure S4a (Supporting Information). The GO-doped PPy composite was formed as a free-standing film which was readily used as the electrochemical electrode (Figure S5, Supporting Information). To obtain a more stable carbon-based graphene nanowire supercapacitor, we electrochemically reduced the GO/PPy/Al\(_2\)O\(_3\) in 0.1 M NaNO\(_3\) by cycling potentials between −1 and 0 V over 100 cycles, according to a published procedure.\(^{29}\) After the GO reduction, the sample was treated at 700 °C under the protection of N\(_2\) over 1 h to pyrolyze PPy, followed by soaking in 1 M NaOH to remove the template. The free-standing film structure remained well after thermal annealing (Figure S2, Supporting Information).

SEM images for the resulting rGO/carbon nanowires after electrochemical reduction and annealing treatment of GO/PPy nanowires at 700 °C under N\(_2\) are given in parts a and b of Figure 2, respectively, which shows that the resulting nanowire structure remains aligned well after the reduction and pyrolysis treatment. The TEM image further confirmed that the diameter of the rGO/carbon nanowires was reduced to about 160 nm (Figure S4b, Supporting Information) which could be attributed to the decomposition of PPy during the annealing process. As can be seen, the nanowires exhibit a uniform diameter and length. The presence of PPy and GO in the resulting GO/PPy nanowires before annealing is confirmed by Raman spectra given in Figure 2c. Two peaks at 1337 and 1573 cm\(^{-1}\) (pink line, Figure 2c) can be attributed to the D band (associated with induced disorder) and G band (from the symmetric graphic structure) of graphene, respectively. The peak intensity ratio of the D band to the G band (I\(_D\)/I\(_G\)) is around 0.5, higher than that of a high crystalline quality graphene sheet (normally 0.06–0.25).\(^{29}\) The relatively high D
The absence of PPy-related bands over 1000 cm\(^{-1}\) and 1320 cm\(^{-1}\) in the spectrum of the rGO/carbon after annealing at 700 °C, as observed elsewhere.\(^{30}\) The presence of PPy is evidenced by the bands around 1000 cm\(^{-1}\), as observed elsewhere.\(^{30}\) The absence of PPy-related bands over 1000 cm\(^{-1}\) and 1320 cm\(^{-1}\) suggests that PPy was successfully reduced to graphene and the pyrolysis of GO from 0.5 for the GO/PPy nanowires to 0.89, suggests that the GO/PPy composite is less than 30% (w/w), suggesting an ideal capacitive behavior for the nanowire electrode. More specifically, the capacitive current is found to increase by 1.5 times with introduction of 10% (w/w) GO (black line, Figure 3a) into the PPy nanostructure compared to the pristine PPy nanowires (pink line, Figure 3a). The capacitive current of the PPy/GO composite can be further increased up to 10 times (blue line, Figure 3a) that of the pure PPy nanoelectrode when composite nanowires consist of 30% (w/w) GO. The increased capacitance with the addition of GO is attributable to the following: (1) The large surface area of GO, combined with the microporous nanowire structure, provides a sufficient large electrochemical active surface area for charging and discharging, and (2) the presence of negative charge functional groups (e.g., carboxyl) in GO enables the electrochemical doping of PPy, enhancing the conductivity for charge transport in the supercapacitor. Furthermore, the combination of the doped conductive GO/PPy nanowires and their vertical alignment with a large surface area allows a fast interfacial electron transfer between the electrode and the electrolyte solution. However, the CV curve for the GO/PPy nanowires with a GO mass percentage higher than 30% (e.g., 50%, orange line, Figure 3a) is no longer a rectangle shape, which indicates a resistance-like electrochemical behavior. Therefore, the addition of an excessive amount of GO might have led to the formation of aggregates with a high electrical resistance, and hence the decrease in capacitance. The 30% GO/PPy composite was further measured by cycling potentials between −0.1 and 0.5 V for 100 cycles to identify the long-term cycling stability. As shown in Figure S6a (Supporting Information), the difference between the first cycle and the 100th cycle was ignorable, suggesting good long-term cycling stability of the nanowire electrode. The specific capacitances of both the GO/PPy nanowire and the pristine PPy nanowire were calculated from their respective CV curves (Figure S7, see the Supporting Information for calculation details). Our results indicate that the highest specific capacitance of the GO/PPy nanowires is around 960 F g\(^{-1}\), 6 times that of the pure PPy nanowires (∼160 F g\(^{-1}\)). These values of capacitance are stable over a wide range of potential scan rates from 0.01 to 0.1 V s\(^{-1}\) (Figure 3b), indicating a fast charging/discharging process in the capacitor.\(^{31}\)

We further carried out constant current charging and discharging measurements on GO/PPy nanowires (Figure 3c). During the charge and discharge steps, a slight, but noticeable, slope variation of the potential vs time is evident, indicating somewhat pseudocapacitance behavior originated from electrochemical redox reaction at the electrode/electrolyte interface.\(^{32}\) The apparent asymmetry of the charge and discharge curves suggests the more or less ideal capacitive nature and superb reversible redox reaction of the GO/PPy nanowires. The specific capacitance can be calculated from the discharging curve: \(C = \frac{I_p \times \Delta t}{\Delta V}\), where \(I_p\) is the constant discharging current density, \(I_p = 1 \text{ mAm}^{-2}\) (around 14 A g\(^{-1}\)). \(\Delta t\) is the discharge time, and \(\Delta V\) represents the potential drop during discharge. Thus, the specific capacitance is 933 F g\(^{-1}\) at a
constant current of 1 mA cm$^{-2}$ in the potential range of $-0.1$ to 0.5 V. This value is similar to the capacitance obtained from CV. The excellent electrochemical stability of the GO/PPy nanowire can also be seen from Figure 3c. The charging and discharging curves remain unchanged after 300 cycles, suggesting a good long-term stability of the GO/PPy nanowire supercapacitor.

Figure 3d shows the Nyquist plots produced by electrochemical impedance spectroscopy (EIS) using a sine-wave amplitude of 5 mV, a frequency range of 500 000 to 0.01 Hz, and a bias voltage of 0.4 V. Both plots can be divided into a high-frequency component with well-defined semicircles and a low frequency range with straight sloped lines. The interfacial charge-transfer resistance ($R_{ct}$), also called the Faraday resistance, can be determined by the diameter of the semicircle. The value of $R_{ct}$ would determine the power density of a pseudocapacitor. $R_{ct}$ of the GO/PPy nanowire is around 20 $\Omega$, decreased from 200 $\Omega$ for the PPy nanowire electrode. The lower $R_{ct}$ could significantly improve the power density of the capacitor.

In addition to the above electrochemical characterization for the GO/PPy and PPy electrodes, we have also investigated the rGO/carbon nanowires after pyrolysis of PPy in the GO/PPy nanowires using CV, EIS, and chronopotentiometry. As shown in Figure 4a, the GO/carbon nanowire electrode in 1 M NaCl also exhibited a rectangularly shaped CV, suggesting a good capacitive behavior for the graphene based nanowires. Compared to the GO/PPy nanowires, the rGO/carbon nanowires showed a 5 times decrease in the charging currents, suggesting the decreased capacitance without the redox reactions of PPy. The rGO/carbon nanowire electrode exhibited a well long-term cycling stability when the potential was cycled between $-0.1$ and 0.5 V for 100 cycles (Figure S6b, Supporting Information). The scan rate dependent specific capacitance given in Figure 4b shows a steady value of 200 F g$^{-1}$ over scan rates from 0.01 to 0.4 V s$^{-1}$ (Figure S8, see the Supporting Information for calculation details). The capacitance of the rGO/carbon nanowires is about 5 times lower than that of the GO/PPy nanowires (960 F g$^{-1}$), while the capacitance of the rGO/carbon nanowire electrode remains unchanged even at a scan rate up to 0.4 V s$^{-1}$, indicating a very fast electron transfer and low resistance of the electrode. This is also evidenced by the EIS (Nyquist) plots given in Figure 4d, which shows a lower resistance (5 $\Omega$) for the rGO/carbon nanowire than that of the GO/PPy nanowire (20 $\Omega$). Figure 4c shows the charging and discharging curves for the rGO/carbon nanowire supercapacitor over 300 cycles, indicating an excellent electrochemical stability. Since the rGO/carbon nanowires were obtained after annealing GO/PPy nanowires at 700 °C over 60 min, the excellent thermal stability of the rGO/carbon supercapacitor is self-evident. The specific capacitance of the rGO/carbon nanowire capacitor was calculated to be 190 F g$^{-1}$ from the discharging curve, which is also consistent with the corresponding value obtained from CVs. The specific capacitance of the rGO/carbon nanowire is also higher than those of conventional porous carbon materials and even graphene/carbon hybrids (normally, less than 180 F g$^{-1}$) due to the aligned structure of the as-synthesized nanowires.

We have developed a new type of electrochemical supercapacitor based on vertically aligned GO/PPy hybrid nanowires with the PPy electrochemically doped by GO. A rather high specific capacitance (960 F g$^{-1}$) was obtained from the GO/PPy nanowires, which is about 6 times higher than that of the pristine PPy nanowires, due to the large surface area of the vertically aligned nanowires and the intimate contact between the nanowires and the substrate electrode. The GO/PPy nanowire supercapacitor also shows a good long-term stability with a high power density, suggesting potential applications in energy storage devices. To improve the thermal stability and long-term charge storage, GO was further electrochemically reduced into graphene and PPy was subsequently thermally carbonized, leading to a high capacitance of 200 F g$^{-1}$ for the resultant pure rGO/carbon based nanowire supercapacitor. This value of capacitance (200 F g$^{-1}$) is higher than that of conventional porous carbon materials. The rGO/carbon supercapacitor also shows a superb electrochemical and thermal stability.

![Figure 4.](image-url)
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REFERENCES


