Hierarchical Nanocomposites of Polyaniline Nanowire Arrays on Reduced Graphene Oxide Sheets for Supercapacitors

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Here we reported a novel route to synthesize a hierarchical nanocomposite (PANI-frGO) of polyaniline (PANI) nanowire arrays covalently bonded on reduced graphene oxide (rGO). In this strategy, nitrophenyl groups were initially grafted on rGO via C-C bond, and then reduced to aminophenyl to act as anchor sites for the growth of PANI arrays on rGO. The functionalized process was confirmed by atomic force microscopy, scanning electron microscopy, Fourier transform infrared spectroscopy, Raman spectroscopy and thermogravimetric analysis. The electrochemical properties of the PANI-frGO as supercapacitor materials were investigated. The PANI-frGO nanocomposites showed high capacitance of 590 F g⁻¹ at 0.1 A g⁻¹, and had no loss of capacitance after 200 cycles at 2 A g⁻¹. The improved electrochemical performance suggests promising application of the PANI-frGO nanocomposites in high-performance supercapacitors.

Supercapacitors, also called electrochemical capacitors, have attracted considerable attentions due to their high-power density and long-cycle life. According to the charge storage mechanism, supercapacitors can be classified into two categories: electric double layer capacitors and pseudocapacitors¹. The former is usually made of carbon-based materials²–⁴, and the capacitance generates from charge separation at the electrode/electrolyte interface. The latter is mainly made of transitional metal oxide⁵–⁶ or conductive polymer⁷–⁸, and the capacitance generates from fast faradic reaction. To achieve high capacitance, composite materials of carbon and conductive polymers have been used in supercapacitors⁹–¹¹. Among them, graphene, graphene oxide (GO) or reduced graphene oxide (rGO)-polyaniline (PANI) composites have attracted significant attentions¹²–¹⁶.

Graphene, a single layer of sp²-hybridized carbon atoms, is a promising material for supercapacitors owing to its high conductivity, great mechanical strength and large specific surface. It can provide a long cycle life during the charge/discharge process. However, due to unavoidable aggregation of graphene nanosheets, the capacitance of graphene or graphene derivatives¹⁷–¹⁹ is generally 100–200 F g⁻¹. PANI is a famous conducting polymer for supercapacitor owing to its high conductivity, high flexibility, low cost and multi-redox state. It can offer especially high theoretical pseudocapacitances. But its poor stability during the charge/discharge process limits its real application in supercapacitors. The combination of graphene and PANI could overcome the drawbacks of graphene and PANI, and lead to good performance in supercapacitors¹⁸–²⁰. For example, Wu et al.¹⁷ reported on a graphene/PANI nanofiber exhibited capacitance of 210 F g⁻¹ at 0.3 A g⁻¹ and 194 at F g⁻¹ 3 A g⁻¹. Zhang et al.²⁰ reported on a GO/PANI composites exhibited capacitance of 320 F g⁻¹ at 0.1 A g⁻¹. It was also reported that, compared with randomly connected PANI nanowires, ordered PANI nanowires could reduce the ionic diffusion path, facilitate ionic motion to inner part, and improve unitization of electrode materials²¹–²². Therefore, many efforts have been paid to synthesize ordered PANI on graphene. For example, Xu et al.²² prepared PANI arrays on GO sheets based on van der Waals force at −10 °C with capacitance of 555 F g⁻¹ at 0.2 A g⁻¹ and 227 F g⁻¹ at 2 A g⁻¹.

Nevertheless, in previous works, most of the graphene-PANI composite materials were connected by non-covalent bond, such as van der Waals force, electrostatic interaction or π–π stacking. Compared to non-covalent connection, the covalent connection between PANI and graphene is expected to enhance the electrical conductivity and stability of the composites²³–²⁵. Only a few studies have dealt with the linkage of graphene and PANI by
using a covalent bond. Recently, PANI-graphene hybrid materials connected by covalent bonds have been reported by Kumar’s group. The strategy involves covalently functionalized acylated GO with amine-protected 4-aminophenol, which subsequently polymerized in the presence of aniline monomer to obtain PANI-graphene hybrid materials. Lai et al. has also synthesized PANI-graphene connected by covalent bond. In this method, the -NH₂ groups were introduced to rGO via reacted with ammonia water at 180 °C, then an in situ polymerization was used to prepare Amine-modified rGO/PANI. However, a facile method to prepare nanocomposites of vertical PANI array chemically bonded on rGO is still necessary.

Herein, we proposed an effective route to prepare vertical PANI nanowire arrays modified rGO nanocomposites based on covalent connection. First, the rGO was functionalized by spontaneously grafting nitrophenyl groups on rGO based on C-C bond. Then the nitrophenyl groups were reduced to aminophenyl groups, and subsequently polymerization was carried out in the presence of aniline monomer to yield vertical PANI arrays on rGO. A large-scale π-π conjugated system is formed between PANI and rGO, which could improve charge transfer significantly. The electrochemical performance of PANI-frGO arrays in supercapacitor was explored in this work.

Results

Fig. 1A showed the atomic force microscopy (AFM) images of nitrophenyl-rGO nanocomposites. Section analysis revealed that the thickness of nitrophenyl-rGO nanocomposites sheets was about 1.2 nm. Since the length of the nitrophenyl was about 0.5 nm and the theoretical thickness of rGO was about 0.5 nm, it was reasonable to assume that the nitrophenyl-rGO nanocomposites were consisted of one layer of rGO and monolayer of nitrophenyl groups grafted on both sides of rGO. When nitrophenyl groups were grafted onto the rGO surface parallel to the surface normal axis, the thickness of the nanocomposites should be 1.5 nm. However, the height of nitrophenyl-rGO nanocomposites was only 1.2 nm. Thus it suggested that the nitrophenyl groups could not stand fully perpendicular to the substrate. After these nitrophenyl groups were reduced to aminophenyl groups, and subsequently polymerization was carried out in the presence of aniline monomer to yield vertical PANI arrays on rGO. A large-scale π-π conjugated system is formed between PANI and rGO, which could improve charge transfer significantly. The electrochemical performance of PANI-frGO arrays in supercapacitor was explored in this work.

Figure 1 | AFM images of nitrophenyl-rGO (A) and PANI-frGO (B).
due to the deintercalation of H2O. PANI-GO showed a rapid mass loss around 100°C, all these materials showed a little mass loss between 200 and 300°C. As shown in Fig. 2D, the mass loss of 60% between 130 and 750°C was investigated by thermogravimetric analysis (TGA). As shown in Fig. 2D, all these materials showed a little mass loss around 100°C. A band at 1040 cm⁻¹ was attributed to N–H bending in-plane of the benzenoid ring. The peaks at 1166 and 976 cm⁻¹ were attributed to C–H bending vibration of the benzenoid ring and C–H deformation out-of-plane of the benzenoid ring. The peaks at 890 cm⁻¹ was assigned to C-N-C wag out-of-plane of the benzenoid ring in EM salt state. All evidences supported that the PANI have been grafted onto the surface of rGO. The thermal stability of PANI-GO, PANI-rGO and PANI-frGO was investigated by thermogravimetric analysis (TGA). As shown in Fig. 2D, all these materials showed a little mass loss around 100°C due to the deintercalation of H2O. PANI-GO showed a rapid mass loss between 200 and 300°C due to the decomposition of oxygen-containing groups, such as –OH, –CO–, and –COOH groups. Another reason was ascribed to the partial decomposition of small PANI segments in the nanocomposites. As previous reported, PANI began to decompose at a relatively low temperature less than 150°C, and was completely oxidized at about 750°C. The residues of carbonized fragments were remained even at 800°C. Consequently, a mass loss of 60% between 130 and 750°C was observed for PANI-GO. Similar TGA features were observed for PANI-rGO, and the mass loss at 200 to 300°C was ascribed to the oxidative degradation of the nanocomposite itself and the decomposition of the PANI component in the nanocomposites. And the mass loss in this stage was much smaller than that of PANI-GO. The mass loss of PANI-rGO between 130 and 750°C was 47%. For PANI-frGO nanocomposites, the second stage of mass loss began at 290°C which was higher than that of PANI-GO and PANI-rGO (about 260°C). The result demonstrated that the covalent connection resulted in the best thermal stability among these samples. It was worth pointing out that there was hardly any mass loss at 150–250°C for PANI-frGO, which demonstrated that the oxygen-containing groups was very rare. It finally displayed a mass loss of 37% between 130 and 750°C, which was mainly ascribed to the decomposition of the PANI. The above results suggested that the interaction between PANI and rGO based on covalent connection was strongest, and finally played an important role in enhancing the thermal stability of the nanocomposites.

The morphology of the PANI nanowire array on rGO as function of concentration of aniline (cAn) was investigated. Fig. 3A showed the SEM image of aminophenyl-rGO, and it looks very smooth because the aminophenyl groups were grafted onto rGO to form an ordered monolayer. Fig. 3F showed the SEM image of pure PANI nanofibers, whose diameter was about 80 nm. The PANI nanofibers randomly lied on the substrate to form a network. SEM images of PANI-frGO obtained from different cAn were shown in Fig. 3B–E. At 0.01 M aniline, the sparse and short PANI was generated on rGO surface. As cAn increased, the PANI nanowire array became longer and longer (Fig. 3C). When the cAn was increased to 0.03 M, the ordered PANI nanowire array with several ten nanometers in length was formed on rGO (Fig. 3D). However, further increasing of cAn (0.04 M) led to a supersaturation state of aniline, which resulted in disordered PANI nanowires on rGO (Fig. 3E). According to the above results, a possible formation mechanism of PANI-frGO nanocomposites was proposed. Herein, there should be two competing nucleation mechanisms in PANI-frGO formation: heterogeneous nucleation and homogeneous nucleation. A large number of aminophenyl groups initially grafted on rGO could be used as nucleation sites to anchor PANI on rGO surface. The nucleation sites could minimize the interfacial energy barrier between the solid surface and bulk solution and benefit for polymerization of aniline on a solid surface. Thus, the initial polymerization of aniline tends to adopt heterogeneous nucleation. The ordered monolayer of aminophenyl groups as nucleation sites could play a main role in subsequent polymerization to form vertical PANI array on rGO surface. The vertical PANI array was not observed in previous works in such aniline concentration, suggesting the ordered monolayer of aminophenyl groups directed the oriented polymerization of aniline on the
In beginning of polymerization, the aniline monomer in bulk solution polymerized with aminophenyl groups on rGO and formed short PANI. As $c_{\text{an}}$ was increased, the polymerization further occurred to form PANI nanowire array. In case of high concentration of aniline, homogeneous polymerization also took place after the initial nucleation on the solid surface, which resulted in some disordered PANI nanowires on rGO.

To further explore the formation mechanism of the hierarchical nanocomposites, PANI-frGO samples were taken out from the reaction solution at different time intervals during the polymerization process ($c_{\text{an}}$ is 0.03 M). Fig. 4A–E showed the SEM images of PANI-frGO polymerized for 1 h, 1.5 h, 2 h, 3 h and 6 h, respectively. As shown in Fig. 4A, after reaction for 1.0 h, a few short PANI nanowires grew on the surface of rGO. While at 1.5 h, a large amount of PANI nanowires grew uniformly on rGO (Fig. 4B). The PANI nanowires gradually became longer as reaction time increased (Fig. 4C and D). At 3 h, well-ordered PANI nanowires array formed on rGO surface as shown by the high-magnification SEM in Fig. 4F. Further increasing reaction time might lead to the aggregation of individual PANI and form compacted PANI nanowire films on rGO surface (Fig. 4E). The morphology of the PANI-frGO obtained from further increasing reaction time was obviously different from that obtained from further increasing concentration of aniline. Supersaturation state of aniline led to homogeneous polymerization after the initial nucleation on the solid surface and formed disordered PANI nanowires. When suitable concentration of aniline was employed, homogeneous polymerization would not take place even if further increasing reaction time. The formation of compacted PANI nanowire films on rGO surface with further increasing reaction time might be ascribed to the high flexibility of PANI chains. It was very difficult for the longer PANI chains to stand vertically on rGO surface owing to its high flexibility and accordingly a bent structure was more favorable than a straight one as mentioned in previous works.41 With further increasing reaction time, the vertical PANI nanowires on rGO became longer and longer. The end of PANI chains stacked together to finally form compacted PANI nanowire films on rGO surface.

The potential application of the PANI-frGO nanocomposites as electrode materials for supercapacitors was tested by standard cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge. Fig. 5A showed the CVs of PANI, PANI-GO, PANI-rGO and PANI-frGO electrodes with same weight, respectively. Two pairs of redox waves related to reversible charge–discharge behaviour and pseudocapacitance characteristic of PANI were observed in four electrodes. The pair of peaks $O_2/R_1$ was attributed to the redox transition of PANI between leucoemeraldine and meraldine. Another pair of peaks $O_2/R_2$ was derived from the emeraldine–pernigraniline transformation. The peak current of PANI-GO electrode, PANI-rGO electrode and PANI-frGO electrode were higher than that of pure PANI electrode, indicating that the rGO and GO could effectively increase the capacitance of PANI. In comparison, the CV of PANI-frGO electrode exhibited a much larger rectangular area than that of PANI-GO electrode and PANI-rGO electrode, mainly due to its chemical bonding and ordered morphology. The large-scale π–π conjugation between PANI and rGO facilitated charge transfer and consequently improved electrochemical performance significantly.

The specific capacitance ($C_{\text{spec}}$) values were calculated from the charging and discharging curves (Fig. 5B and C) according to the following equation:

$$C_s = \frac{I\Delta t}{AV \times m} \quad (1)$$

where $I$ was the constant discharge current (A), $\Delta t$ was the discharge time (s), $AV$ was the potential change during discharge process, and $m$ was the mass of the active materials within the electrode (g).

The specific capacitances of PANI, PANI-GO, PANI-rGO and PANI-frGO electrodes were calculated from their charge/discharge curves were shown in Fig. 5D. At 0.1 A g$^{-1}$, the specific capacitance of PANI-frGO (590 F g$^{-1}$) was much higher than that of PANI-GO (262 F g$^{-1}$) and PANI-rGO (322 F g$^{-1}$). At the same time, the specific capacitance of pure PANI was 215 F g$^{-1}$. At 1 A g$^{-1}$, the specific capacitance of PANI-frGO (360 F g$^{-1}$) was still much higher than that of PANI-GO (220 F g$^{-1}$) and PANI-rGO (259 F g$^{-1}$). The results suggested that chemical bond and array morphology greatly promoted the capacitance of the PANI-frGO hybrid materials.

The cycle life of PANI, PANI-GO, PANI-rGO and PANI-frGO were conducted at 2 A g$^{-1}$. As displayed in Fig. 5E, PANI-frGO showed good cyclability without loss of capacitance over 200 cycles. After 1000 cycles, the specific capacitances of PANI-frGO retained 91%, which was much higher than that of pure PANI (69%), PANI-GO (84%) and PANI-rGO (81%).

EIS was used to further study the internal resistance, charge transfer kinetics, and ion diffusion process of PANI, PANI-GO, PANI-rGO and PANI-frGO electrodes. The EIS was measured in a frequency range of 10 kHz to 10 mHz. As shown in Fig. 5F, the intercept between the impedance spectrum and real impedance axis
was very small (about 0.6 Ohm) for all the four electrodes. The small intercept indicated that the series resistance, which included the electrolyte solution resistance and contact resistance at the interface of active material/current collector, was very low for all four electrodes. All of the Nyquist plots of the four nanocomposite electrodes showed an incomplete semicircle in the high-frequency region and a straight line in the low-frequency region. The semicircle impedance plots were associated with charge transfer resistance at the electrode/solution interface, while the straight line was determined by ion diffusion. Among the four nanocomposite electrodes, the slope of the straight line for PANI-frGO electrode was largest, closest to the imaginary impedance axis ($Z''$). The diameter of semicircle for PANI-frGO electrode was smallest. The results implied that PANI-frGO exhibited the highest conductivity or lowest internal resistance, including polarization impedance.

The Nyquist plots of all the four electrodes could be well-modeled using a complex equivalent circuit, as shown by the inset in Fig. 5F. $R_s$ was the series solution resistance, which included the electrolyte resistance and the active material/current collector contact resistance. $C_1$ represented double-layer capacitance and $C_2$ represented Faradic capacitance. $R_{ct}$ in parallel to $C$ was the charge transfer resistance at the electrode/solution interface. These components formed a mixed-controlled Randles circuit, which was usually used to model capacitance in a process with a combination of kinetic and diffusion processes determining the rate. At high frequencies, the capacitor impedance became much smaller and the system resistance was dominated by the resistors and polarization impedances. At low frequencies, an ideal polarizable capacitance would give a straight line with large angles with respect to $Z'$ or almost parallel to $Z''$. It was noted that in Fig. 5F the semicircles partially (in the mid-frequency region) disappeared. The absence of the semicircle in the complex impedance plane had been reported and was explained by high ionic conductivity at the electrode/electrolyte interface. In the PANI-frGO case, the $R_s$ and $R_{ct}$ was the lowest among the four composites. And the phase angle increased continuously as further decreased in frequency. This meant that the contribution of polarization impedance reduced (the kinetic and charge transfer were no longer rate-determining steps), while mass capacitance remained the dominant component of the system impedance. The largest slope of vertical curve for PANI-frGO indicated that PANI-frGO could provide the best capacitance. As discussed above, we might conclude that PANI-frGO was the best electrode material for supercapacitor appli-
| Materials                      | morphologies | Connecting mode  | Specific capacitance (F g\(^{-1}\)) | Cycle life                          | Ref       |
|-------------------------------|--------------|------------------|--------------------------------------|-------------------------------------|-----------|
| rGO-PANI\(^a\)               | nanoparticles | Non-covalently   | 361 at 0.3 A g\(^{-1}\)              | 82% after 1000 cycles at 0.3 A g\(^{-1}\) | [44]      |
| GO-PANI\(^b\)                | nanoparticles | Non-covalently   | 425 at 0.2 A g\(^{-1}\)              | 83% after 500 cycles at 1 A g\(^{-1}\) | [45]      |
| Graphene/Polyaniline\(^c\)   | nanoparticles | Non-covalently   | 257 at 0.1 A g\(^{-1}\)              | 98% after 1000 cycles at 2 A g\(^{-1}\) | [46]      |
| Porous Graphene/Polyaniline\(^d\) | nanowires    | Non-covalently   | 385 at 0.5 A g\(^{-1}\)              | —                                   | [47]      |
| rGNs/cMWCNT/PANI\(^e\)       | nanotubes    | Non-covalently   | 107 at 1 A g\(^{-1}\)                | 91% after 5000 cycles               | [48]      |
| PANI-GO–CNT\(^f\)            | nanosheets   | Non-covalently   | 589 at 0.2 A g\(^{-1}\)              | 81% after 1000 cycles               | [49]      |
| Graphene oxide doped PANI\(^g\) | nanofibers   | Non-covalently   | 531 at 0.2 A g\(^{-1}\)              | —                                   | [13]      |
| PANI/rGO\(^i\)               | nanorod      | Non-covalently   | 970 at 2.5 A g\(^{-1}\)              | 90% after 1700 cycles at 1 A g\(^{-1}\) | [16]      |
| PANI arrays on GO\(^j\)      | nanowires    | Non-covalently   | 555 at 0.2 A g\(^{-1}\)              | 92% after 2000 cycles at 1 A g\(^{-1}\) | [22]      |
| Amide group-connected graphene—PANI | nanofibers   | Covalently       | 579.8 at 0.3 A g\(^{-1}\)             | 96% after 200 cycles at 3 A g\(^{-1}\) | [25]      |
| PANI grafted rGO\(^k\)       | rod-like     | Covalently       | 250 at 100 mV s\(^{-1}\)             | —                                   | [26]      |
| Amine-modified rGO/PANI\(^l\) | nanofibers   | Covalently       | 388 at 1 A g\(^{-1}\)                | no lose over 680 cycles at 2 mV s\(^{-1}\) | [27]      |
| PANI-grafted graphene with amide groups\(^m\) | nanowires | Covalently       | 623.1 at 0.1 A g\(^{-1}\)             | no lose over 500 cycles at 50 A g\(^{-1}\) | [31]      |
| PANI-rGO                     | nanowires    | Covalently       | 590 at 0.1 A g\(^{-1}\)              | 91% after 1000 cycles at 2 A g\(^{-1}\) | This work |

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\(^{a}\)PANI were directly coated on rGO via in situ polymerization process.

\(^{b}\)The nanocomposite were prepared by in situ polymerization with the assistance of supercritical carbon dioxide (SC CO\(_2\)).

\(^{c}\)Graphene/polyaniline (PANI) nanocomposites were prepared by reducing graphene oxide with hydrazine in the presence of different amounts of polyaniline nanoparticles.

\(^{d}\)CaCO\(_3\) particles formed in situ in GO dispersion to obtain porous Graphene. Then Porous Graphene/Polyaniline was synthesized via in situ polymerization.

\(^{e}\)rGNs/cMWCNT/PANI synthesized via in situ polymerization.

\(^{f}\)PANI–GO–CNT was synthesized by a one-step process using a simplified template-free polymerization method.

\(^{g}\)PANI-doped with GO sheets was synthesized via in situ polymerization of monomer in the presence of GO (mass ratio of aniline/GO is 100:1).

\(^{h}\)PANI-grafted GO was synthesized via in situ polymerization at -10°C.

\(^{i}\)The microelectrodes of the supercapacitor are prepared by in situ electrodeposition of polyaniline (PANI) nanorods on the surface of rGO patterns that are fabricated by micromolding in capillaries.

\(^{j}\)PANI arrays on GO was synthesized via in situ polymerization at \(-10^\circ\)C.

\(^{k}\)Graphene is activated using SOCl\(_2\) and reacts with PANI to form an amide group that intimately connects graphene and PANI.

\(^{l}\)GO was acylated in the presence of excess SOCl\(_2\) and then reacted with amine-protected 4-aminophenol, following the deprotection of amine groups, an in situ polymerization was carried out to obtained PANI-GO.

\(^{m}\)The NH\(_2\) groups were introduced to rGO via reacted with ammonia water at 180°C, then an in situ polymerization was used to prepare Amine-modified rGO/PANI.

\(^{n}\)The GO is activated using SOCl\(_2\) and reacts with PANI to form PANI-GO, then reduced to PANI-graphene.
and Co-porphyrin multilayers/rGO have been investigated and the properties of the capacitances strongly depended on morphology of PANI on graphene surface, connecting mode between PANI and graphene-PANI nanocomposites were listed in Table 1. Obviously, our strategy, the covalent connecting between PANI and frGO and graphene-PANI was affected by various parameters together. In addition, the mass ratio of PANI and graphene also affected the capacitances of the graphene-PANI greatly, since the ionic diffusion path was different in various morphologies. Moreover, the connecting mode (non-covalent connecting and covalent connecting) might be critical to the capacitance of the graphene-PANI. Compared to covalent connecting, non-covalent connecting was weaker and lacked π–π conjugated system between PANI and rGO. It might have negative impact on the capacitance and cycle life of material. In addition, the mass ratio of PANI and graphene also affected the capacitances of the graphene-PANI greatly, since the capacitance of the nanocomposites might mainly derive from pseudocapacitive of PANI. Generally speaking, the capacitance of the graphene-PANI was affected by various parameters together. In our strategy, the covalent connecting between PANI and frGO and vertical PANI nanowires array improved the capacitance and cycle life than other graphene-PANI nanocomposites in together. It suggested that our product has certain advantages among the materials from various synthesis routes.

Except for application in supercapacitors, the PANI-frGO obtained from our strategy might also have many potential applications due to the enhanced properties of rGO and PANI. Recently many graphene-based hybrid materials with superior properties such as Au cluster/graphene, metal oxide nanoparticle/graphene and Co-porphyrin multilayers/rGO have been investigated and used in oxygen reduction reaction and capacitive deionization. Therefore, the PANI-frGO containing unique properties of rGO and PANI could also act as specific supports to form hybrid nanocomposites. The PANI-frGO-based materials were also expected for using in sensors, solar cells, lithium ion batteries, fuel cells.

In summary, we have developed a novel method to obtain PANI-frGO hybrid materials based on chemical bond. AFM and SEM revealed that the vertical PANI nanowire array was grafted on rGO sheets. TGA result showed that the PANI-frGO nanocomposites were more thermal stable than the two nanocomposites connected by van der Waals force. The results of the galvanostatic charge/discharge tests illustrated the higher specific capacitances and longer cycle life of the PANI-frGO hybrid materials than the two nanocomposites connected by van der Waals force. With enhancing performance, this hierarchical nanocomposite might have great potential applications.

### Methods

#### Materials

Graphite powder (spectrum pure) was purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Nitrophenyl diazonium tetrafluoroborate and tetrabutylammonium were obtained from Sigma–Aldrich (St. Louis, USA). Aniline, ammonium peroxydisulfate, Zn powder (>99%), H2SO4 (98%), CH3COOH (>99.5%) and CH3CH2OH (>99.7%) were purchased from Shanghai Chemical Reagent Company (Shanghai, China). Aniline was distilled under reduced pressure and other reagents were used as received without further treatment. All aqueous solutions were prepared with ultra-pure water, purified by a Millipore-Q system (18.2 MΩ cm−1).

#### Instrumentation

Atomic force microscopy (AFM) measurements were carried out with an AJ–III (Shanghai Aijian Nanotechnology, China) using a tapping mode. Standard silicon cantilevers (spring constant 0.6–6 N m−1) were used under their resonance frequency (typically, 60–150 kHz). All AFM images were acquired under ambient conditions, and images were raw data except for flattening. The scanning electron microscopy (SEM) analysis was taken using a XL30 ESEM–FEG SEM at an accelerating voltage of 20 kV equipped with a Phoenix energy dispersive x–ray analyzer (EDXA). FTIR spectroscopy was recorded on a Perkin–Elmer Spectrometer 100 spectrometer (Perkin–Elmer Company, USA) using KBr pellets. Raman spectra were performed at room temperature with a MicroRaman System RM3000 spectrometer and an argon ion laser operating at a wavelength of 514 nm as the excitation. The decomposition patterns were determined thermogravimetrically using a TGA analyzer (Q200, TA Instruments, USA) at a ramp rate of 10 °C min−1 in nitrogen. All electrochemical tests were carried out on a CHI 660 C electrochemical workstation (Shanghai, China) in 2 M H2SO4 aqueous with three-electrode cells where Pt wire serves as the counter electrode and Ag/AgCl as the reference electrode. The working electrodes were prepared by mixing products with acetylene black and polytetrafluoroethylene (PTFE) (mass ratio of 85 : 10 : 3). The mixture was kneaded to obtain a paste, and then the paste was pressed onto the SS sheet (1 cm2) at 10 MPa for 1 min in order to assure a good electrical contact. The mass of active ranges from 2 mg to 6 mg. EIS was characterized at open circuit potential in the frequency range from 10 Hz to 0.01 Hz.

#### Synthesis of GO and rGO

GO was synthesized according to previous methods. Briefly, graphite powder (1.0 g) was dispersed into 23 mL concentrated H2SO4 (18.0 M) in ice bath. Then, KMnO4 (3.0 g) was gradually added into above solution under continuous vigorous stirring at the temperature below 20 °C. After that, the ice bath was replaced by an oil bath and the mixture was heated to 35 °C for 30 min under continuous stirring. Then, ultra-pure water was slowly added into above solution, which produced a rapid increase in solution temperature up to a maximum of 100 °C. The reaction was maintained at 98 °C for a further 15 min, and terminated by sequential addition of more ultra-pure water (140 mL in total) and H2O2 (30%, 10 mL). The solid product was separated by centrifugation at 5000 rpm and washed.
with 5% HCl until SO₄²⁻ ions were no longer detectable with BaCl₂. Finally, the solid product was washed three times with acetone and dried overnight at 65°C. The rGO was prepared by reduction of GO with hydrazine. Typically, hydrazine (0.12 mL) was added into the dispersion of GO (100 mg GO in 100 mL water) and sonicated for 1 h. Then the mixture was reacted at 90°C under constant stirring for 1 h. rGO was obtained by filtering the product and drying in vacuum. The procedure was shown in Fig. 6.

**Synthesis of nitrophenyl-rGO nanocomposites.** The nitrophenyl-rGO nanocomposites were prepared by spontaneous grafting nitrophenyl groups to the basal carbon atoms according to previous procedure. Briefly, rGO (12 mg) was dispersed in 10 mL degassed acetoneitrile by ultrasonication for about 1 h. Then nitrophenyl diazonium tetrafluoroborate (24 mg) and tetrabutylammonium (0.329 mg) were added into the above solution. The mixtures were placed in a glove box in the absence of light for 5 h. The nitrophenyl-rGO was obtained by filtering the product and washing with acetone and acetonitrile and drying at 80°C for 4 h. The procedure was shown in Fig. 6.

**Synthesis of aminophenyl-rGO nanocomposites.** The aminophenyl-rGO was prepared by reduction of nitrophenyl-rGO with Zn in CH₃COOH solution. Briefly, The nitrophenyl-rGO (6 mg) was dispersed in 20 mL CH₃COOH-H₂O (3:2) by ultrasonication, then Zn (104 mg), NH₄Cl (1 mg) and CH₃COOH (2.3 mL) were added. The mixture solution was refluxed at 60°C for 3 h. The product was centrifuged and washed with 0.1 M HCl and ultra-pure water three times each and dried at 60°C for 4 h in an oven. The procedure was shown in Fig. 6.

**Synthesis of PANI-frGO.** PANI-frGO composite were produced by in situ polymerization of aniline. The aminophenyl-rGO (3.4 mg) were dispersed in 5 mL aqueous solution containing aniline and H₂SO₄ (1 M). Then another 5 mL aqueous solution containing ammonium persulfate (APS) was added in, and stirred for a while. The molar ratio of aniline/APS was 4/1. The polymerization was carried out under nitrogen in an ice-water bath with the temperature 0–5°C. After polymerization for about 3 h, the composite cloths were collected, washed with water and ethanol and dried at 60°C for 6 h. A series of PANI-frGO were prepared in a solution with different aniline concentrations (The cₕ₂,₉ was 0.01 M, 0.02 M, 0.03 M and 0.04 M, respectively). The similar method was used to obtain PANI-GO and PANI-rGO. The procedure was shown in Fig. 6.

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**Author contributions**

L.W. and H.H. wrote the main manuscript text. Y.S. and Y.Y. performed the experiments and prepared figures 2–4 and figure 6. Z.L. prepared figure 1. X.L. synthesized the rGO. Z.W. and Y.Y. prepared figure 5 and table 1 and synthesized the PANI-frGO. All authors reviewed the manuscript.

**Additional information**

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