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PAPER

Flexible solid state lithium batteries based on graphene inks

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Different formulations of solution-processable graphene have been characterised as electrode materials for use in electrochemical energy storage devices. Graphene was fabricated by chemical reduction of exfoliated graphene oxide (GO), and modified with either p-type (*e.g.* polyaniline) or n-type anionic groups (poly(styrenesulfonate) (PSS^-) and poly[2,5-bis(3-sulfonatopropoxy)-1,4-ethynylphenylene-alt-1,4-ethynylphenylene] sodium salt ($PPE\text{-}SO_3^-$) anion). Solutions of these graphene compounds were deposited on charge collecting electrodes and used as battery cathodes. Electrodes using the anionically-modified graphene inks containing anatase titanate (TiO_2) nanoparticles show improved performance over pristine graphene ink as well as the p-type conducting polymer modified ones. In addition, the open circuit voltage of batteries based on TiO_2 has been boosted over 3 V with good cyclability when mixed with the graphene ink. Combined with a polymer electrolyte, this work suggests a feasible route towards fully printable rechargeable lithium batteries based on graphene inks. This approach is both versatile and scalable and is adaptable to a wide variety of applications.

1 Introduction

High-performance lithium batteries attract much attention for use in high energy density storage for smart grid applications, electric vehicles and multi-functional mobile devices, and this trend is increasingly driven by the global adoption of low carbon emission regulations. The expanding capability and functionality of portable electronic devices places increasing demands on energy storage media and drives technological advancement in battery and supercapacitor technology. Next generation portable devices require solid-state batteries and supercapacitors with high power density and flexibility to meet the various power and design needs. Furthermore, in order to satisfy industry volume demands, energy storage media must be capable of mass production at a reasonable cost.

The use of carbon nanotubes as novel electrode materials to enhance the energy storage capacity of batteries and supercapacitors has been the focus of many studies.[1,2] Widespread adoption of these materials in commercial applications has been limited by the potential toxicity of carbon nanotubes,[3] and by the challenge of growing carbon nanotubes on substrates in sufficient volume to meet industry level requirements. Carbon nanotubes are also hard to dissolve in either organic or aqueous solutions for wet-processing methods such as printing and spin-coating. This limits their application in printable electronics, which is expected to be an enabling technology for low-cost future devices.

Graphene-based materials are intriguing from the perspective of fundamental science and technology because they are non-toxic, chemically and thermally tolerant, and mechanically robust. In the form of nanosheets with lateral sizes in the range of several hundred nanometres, graphene exhibits superior electrical conductivity, a high charge carrier mobility ($20\ m^2\ V^{-1}\ s^{-1}$),[4,5] fascinating transport phenomena such as the quantum Hall effect, high surface areas of over $2600\ m^2\ g^{-1}$ [4,5] and a broad electrochemical window that may be particularly advantageous for applications in energy technologies. In addition, graphene can be transferred to substrates for transparent electronic applications allowing the fabrication of transparent or semi-transparent energy storage devices. Graphene can be prepared in the form of a colloidal suspension with adjustable solubility and thus is suitable for printing applications. Graphene ink, containing polymeric binders and surfactant additives, has already been used as an electrode material for ultracapacitors.[6] The study of lithium storage and use of graphene in high-performance batteries has also been explored,[7,8] and as an additive, graphene exhibited superior performance to carbon nanotubes. Graphene nanosheets can be used as high capacity anode materials for rechargeable lithium secondary batteries due to the large reversible Li storage ability.

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Generally there are several ways to produce graphene: mechanical or liquid phase exfoliation,[9,10] chemical vapor deposition,[11,12] thermal decomposition of SiC,[13] and chemical reduction of graphene oxide (GO).[14] The chemical method is to reduce GO sheets to graphene and the subsequent concentration of colloid suspensions can be varied from 0.7 mg ml^{-1} to 7 mg ml^{-1} depending on the modifying functional group and solvent. We have used colloid suspensions to produce new materials composed of chemically modified graphene and titania (TiO_2) nanoparticles. This approach is both versatile and scalable and is adaptable to a wide variety of applications. In addition, a fully printed lithium battery may be realized by combining this type of fully printable cathode with a polymer electrolyte and sputtered lithium anode.

2 Results and discussion

Graphene sheets can be obtained from the chemical reduction of GO, and can then be subsequently chemically modified. Preparation of chemically converted graphene sheets modified by different chemical groups has been reported to produce polydisperse and very stable graphene sheets in different solvents.[15] Fig. 1 shows a transmission electron microscope (TEM) image of chemically converted graphene sheets fabricated by the reduction of GO.

Different chemical groups such as polyaniline, poly(sodium 4-styrenesulfonate) (PSS^-) and poly[2,5-bis(3-sulfonatopropoxy)-1,4-ethynylphenylene-alt-1,4-ethynylphenylene] sodium salt ($PPE\text{-}SO_3^-$) can be inserted into the graphene sheets during the process of the chemical reduction of exfoliated GO (details below). These chemical groups not only help stabilize the dispersion but also tune the graphene inks for specific applications.

The significant structural changes that occur during the chemical processing from exfoliated GO to graphene is reflected in their respective Raman spectra (Fig. 2). Raman spectra were obtained with a Raman system (Renishaw model 1000) using an argon ion laser (514.5 nm) as the excitation source. The laser power at the sample position was typically 400 μW with an average spot size 1 μm in diameter. Raman spectroscopy is a sensitive tool to probe graphene samples, and can identify the number of graphene layers and provide information on the amount of disorder, doping and the orientation of edges.[16] The G and D peaks, which lie at around 1580 and 1360 cm^{-1}, respectively are common features for carbon-based materials. The G peak corresponds to the E2g phonon at the Brillouin zone center and reflects the first order scattering of the E2g mode.[17] The D peak is due to the breathing modes of sp^2 rings and requires a defect for its activation.[18,19] The 2D peak is the second order of the D peak and is activated by a resonance process thus does not require defect activation like the D peak. Width, shape, and intensity of the 2D peak are sensitive to the number of graphene layers.[20] The intensity ratio between the D and G peaks (I_D/I_G) has been used as a measure of disorder in graphene, which arises from ripples, edges, charged impurities and domain boundaries, amongst others.[21] In the Raman spectrum of GO (Fig. 2a), the I_D/I_G intensity ratio is about 0.85. When GO is chemically reduced to graphene (Fig. 2b), the I_D/I_G intensity ratio is increased to 1.23. This change suggests a decrease in the average size of the sp^2 domains upon reduction of the exfoliated GO.[22] In addition, the G peak (1587 cm^{-1}) is clearly present and a symmetrical 2D band could be seen in the 2500–2900 cm^{-1} region, as expected for well exfoliated graphene sheets. Comparing with the unmodified pure graphene solution, the I_D/I_G intensity ratio of PSS-modified graphene (Fig. 2c) decreases from 1.23 to 1.08, indicating that modification of graphene with PSS enhances the intensity of the G band of graphene sheets, due to its conjugated structure.

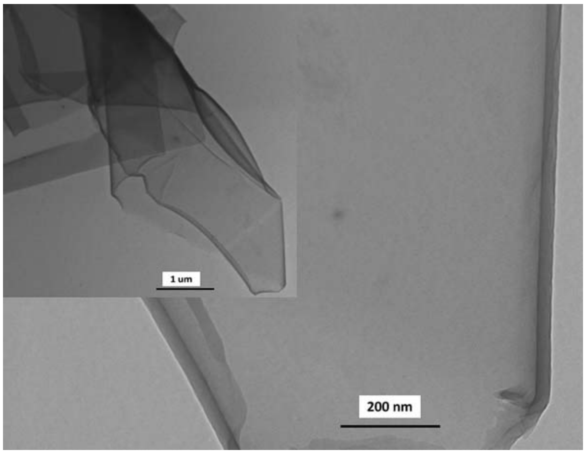

Fig. 1 TEM image of chemically converted, polydispersible and long-term stable graphene sheets.

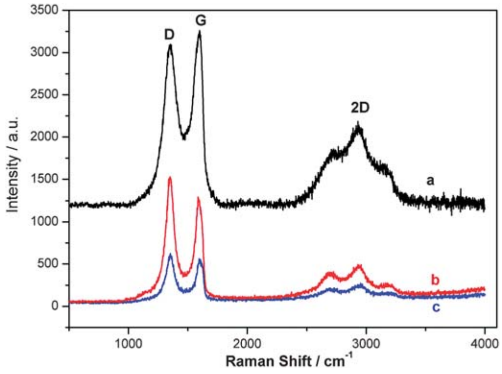

Fig. 2 Raman spectra of (a) GO in KOH solution (b) chemically converted polydisperse graphene in KOH solution and (c) PSS-modified graphene solution.

Initial studies of graphene employed in rechargeable lithium ion batteries found an open circuit voltage lower than 3 V.[8] Enhanced cycling performance and a modest increase in lithium storage capacity was obtained by the addition of rutile tin dioxide (SnO_2) nanoparticles, but in this case the open circuit voltage was reduced to ~2 V.[7] Enhanced conductivity of lithium ions has been observed when adding titanium dioxide nanoparticles to solid electrolytes.[23] This effect has been linked to local structural modification of the titanium dioxide which promotes localized amorphous regions, thereby enhancing the transport of lithium ions. Batteries have also been made with lithium titanate spinel nanocrystals on their electrode surfaces. TiO_2 has a higher volumetric capacity for lithium ions (1307 mA h cm^{-3}) than that of graphite (837 mA h cm^{-3})[24,25] and this enables lithium titanate batteries to charge and discharge faster than standard lithium ion batteries. Lithium titanate spinel is a zero-strain insertion material meaning that, unlike other materials with high volumetric lithium capacity such as Si nanowires, insertion of lithium ions does not cause significant deformation of and damage to the crystal lattice. It is also intrinsically safe since it avoids electrochemical deposition of lithium. In addition, titanium dioxide is abundant, low cost and environmentally friendly. Since the conductivity of lithium titanate is limited, it is important that the electrode structure is such that the lithium titanate nanocrystals contact a conductive material to facilitate charge transfer. Self-assembled TiO_2–graphene hybrid nanostructures have been tried in lithium ion batteries. The hybrid material showed significantly enhanced lithium ion insertion/extraction in TiO_2. The specific capacity was more than doubled (87 mA h g^{-1}) at high charge rates, as compared to pure TiO_2 phase (35 mA h g^{-1}).[26] The highest specific capacity for batteries made of such hybrid material is about 375 mA h g^{-1} when they are discharged at C/5.

In this work, rechargeable Li batteries are fabricated using different formulations of graphene inks and their performance compared at room temperature. The batteries are constructed from a solid polymer electrolyte sandwiched between a lithium foil anode and a cathode deposited from graphene ink deposited onto carbon fiber Al foil charge collector, whose total thickness is about 30 μm. The polymer electrolyte used is a high molecular weight poly(ethylene glycol) borate ester, the details of which are described in the literature.[27,28] The Lewis acid centers of the borate esters interact with the anion resulting in enhanced lithium ion transport and the resulting performance of such polymer electrolytes is comparable with conventional liquid organic electrolytes at room temperatures. The polymer solid electrolyte additionally provides mechanical flexibility and improves the integrity of the battery structure. The batteries were initially discharged at a constant rate of 100 mA g^{-1} and Fig. 3 compares the first discharge behaviour of batteries with differing formulations of graphene cathode. It can be seen that the open circuit voltage drops very quickly for the battery with a cathode deposited using KOH treated graphene ink with 0.1 M TiO_2 nanoparticles (Fig. 3, curve a). The battery with a cathode made from graphene modified with a p-type conducting polymer, polyaniline (PANI) together with 0.1 M TiO_2 nanoparticles improves open circuit voltage fall off, but such improvement for the polyaniline-modified graphene cathode with addition of TiO_2 nanoparticles is not substantial (Fig. 3, curve b). This discharging performance is inferior to those obtained from batteries with cathodes formed from the anionically (PPE-SO_3^- and PSS^-) modified graphene with added TiO_2 nanoparticles (Fig. 3, curves c and d). Only batteries with an anionically-modified graphene cathode show such enhanced plateau at the end of the discharging period. This may be due to the anionic structure stabilized graphene that can attract and keep the positively-charged lithium ions by Coulombic forces. In other words, the large polymer anions may ensure the effective solubilisation of graphene and simultaneously attract positively-charged lithium ions into the graphene electrode matrix.

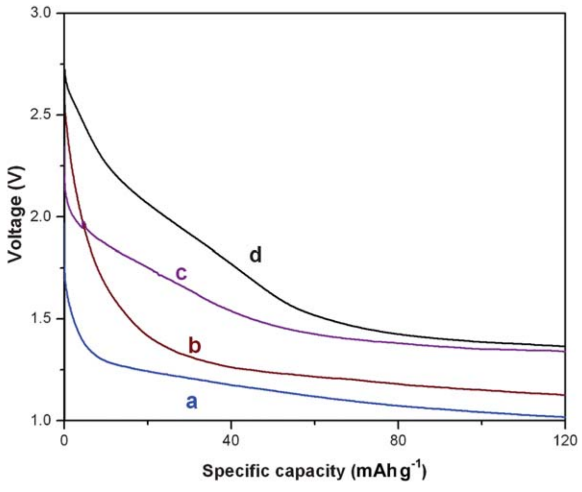

Fig. 3 Comparison of the first discharging performance of batteries made with cathodes deposited from (a) KOH treated graphene ink with 0.1 M TiO_2, (b) PANI-modified graphene ink with 0.1 M TiO_2 (c) PPE-SO_3^--modified graphene ink with 0.1 M TiO_2 and (d) PSS^--modified graphene ink with 0.1 M TiO_2.

Whilst the addition of TiO_2 can increase the lithium ion storage of a lithium-ion battery, too high a concentration of TiO_2 can reduce the conductivity of the electrodes and limit the solubility of the electrode formulation. Addition of a lithium salt (*e.g.* $LiClO_4$) to the graphene ink emulsion with TiO_2 nanoparticles will improve the dispersion of lithium ions into the TiO_2 lattice and improve the battery performance. When the concentration of titanium dioxide nanoparticles (anatase) and lithium salt in the ink is optimised (0.2 M of TiO_2 and 1 M of $LiClO_4$ in the current case), battery electrodes can be made by drop casting the PSS-modified graphene ink onto a charge collecting substrate. Unlike all the other methods reported,[26] which used conventional ways to fabricate electrodes by mixing the hybrid materials with additives and PVDF binders, in our case, the ink can be either drop-cast or printed on the carbon fiber sheet, which is heated on top of Al foil to evaporate the solvent. Carbon fibres function as scaffolds to hold the ink and after solvent evaporation they are closely attached to the Al foil charge collector automatically by strong van der Waals forces, which give a stable performance when used as battery cathodes. Fig. 4 shows the picture of the ink (Fig. 4a) and the structure of the battery (Fig. 4b and c). Polymer

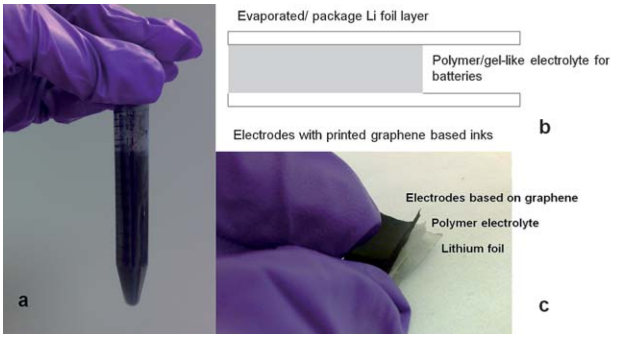

Fig. 4 (a) PSS^--modified graphene ink containing 0.2 M TiO_2 nanoparticles and 1 M $LiClO_4$. (b) and (c) Structure and image of the rechargeable lithium battery based on graphene-ink cathode and polymer electrolyte.

electrolyte (in our case, polymer electrolyte containing borate ester groups) allows the packaging of battery without separators.

The assembled battery cathode comprises a suspension of graphene platelets modified by large PSS$^-$ counter anions together with TiO_2 nanoparticles and lithium salt. The graphene has a large surface area and is a good electrical conductor, whilst the TiO_2 nanoparticles accommodate high concentrations of lithium ions but themselves are not conducting. By binding the two together using the bulky PSS$^-$ anion, a material is created which has the lithium storage capability of TiO_2 and the electrical conductivity of graphene. By adding lithium salt to the material, lithium ions are incorporated into the electrode structure which further enhances the battery performance. The battery is then characterized by galvanostatic charging and discharging measurements at room temperature. The discharging and charging curves are shown in Fig. 5, and they show that this battery is fully rechargeable. Batteries incorporating such graphene cathodes have an open circuit voltage over 3 V, which is comparable to that of commercial lithium ion batteries.

This battery delivered a specific capacity of 582 mA h g^{-1} in the initial discharging, which is approximately 78% of the theoretical capacity (744 mA h g^{-1}) of graphene sheets through the formation of Li_2C_6.[29] The specific capacity value is almost twice that of the battery made of the self-assembled TiO_2 graphene hybrid nanostructures.[26] The voltage capacity profile of Fig. 5 shows a plateau at 1.7 V during the first discharging and then the voltage of the plateau dropped to about 1.3 V in the following galvanostatic dischargings. The plateaus may be related to the phase transition between the tetragonal and orthorhombic phases with lithium ion insertion into anatase TiO_2. The cyclability of the electrode made from the graphene ink was examined under longer term cycling for about 100 cycles, which demonstrated a good cyclic performance and reversibility. After 4 cycles, the graphene electrode still maintained a specific capacity of approximately 250 mA h g^{-1} as shown in Fig. 6. It kept the value of about 240 mA h g^{-1} after 100 cycles at C/5 discharge/charge rate, which shows good capacity retention of lithium ion insertion/extraction. The storage capacity of prototype batteries using pure TiO_2 electrodes is 160 mA h g^{-1}.[30] When using the TiO_2 nanoparticles and nanowires, the capacity can be improved to about 200 mA h g^{-1} for the initial discharging.[31] The improved capacity and the voltage of the battery made of graphene ink with TiO_2 nanoparticles over pure TiO_2 may be due to the increased conductivity of the hybrid ink with addition of graphene. There also may be some synergistic effect on electron and lithium ion transport.

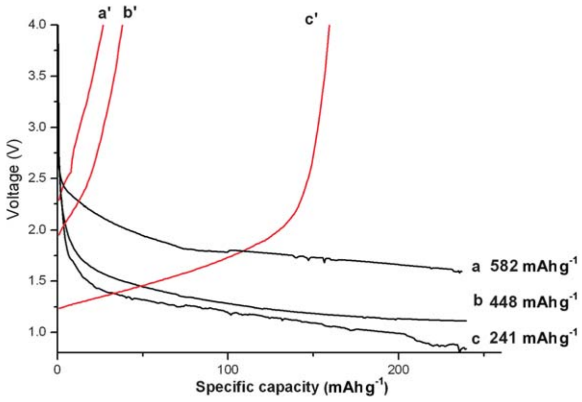

Fig. 5 Charge discharge figures of batteries made from optimized ink composing PSS-modified graphene with 0.2 M TiO2 nano-particles and 1 M $LiClO_4$. (a) and (a′) is for the 1st discharge and charge cycle, (b) and (b′) for the 2nd and (c) and (c′) for the 10th. Charge–discharge current density is 100 mA g^{-1}.

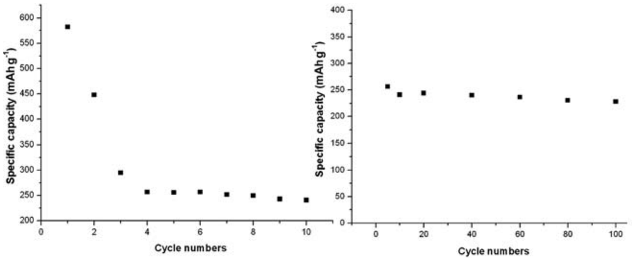

Fig. 6 Discharge capacity of the battery based on graphene ink *versus* cycle numbers.

TiO_2 electrodes offer superior safety (overcharge protection) compared with graphite and high rate performance because they can operate safely as nanomaterials. However, using pure TiO_2 nanoparticles in electrodes limits the low open circuit voltage (about 2 V) of the cell. By combining TiO_2 nanoparticles with graphene ink, an overall cell potential over 3 V with good cyclability can be obtained.

3 Conclusions

Flexible, potentially printable, lithium battery electrodes were made by depositing suspensions of graphene nanoplatelets modified with large counteranions with TiO_2 nanoparticles and lithium salt ($LiClO_4$). This cost-effective material can be used as an ink and printed on to charge collecting substrates. The open circuit voltage of such printed batteries can exceed 3 V. Suitable counteranions include, but are not limited to PSS derivatives. Colloid suspensions have been used to produce new materials composed of such chemically modified graphene and TiO_2 nanoparticles in either aqueous or organic solutions. By controlling the concentration and composition of these suspensions, electrodes of desired properties can be produced. Addition of suitable concentrations of lithium salts to such solutions paves the way for inexpensive titanium dioxide nanoparticles to replace the expensive, rare-earth metals or fire-prone carbon-based materials used in today's lithium-ion batteries. The polymer electrolyte used here allows the battery to function without separators. Solution processing of graphene sheets by chemical reduction may enable the mass-production of graphene solutions for printing processes. This approach is scalable (allowing the possibility of high-volume production) and versatile (in terms of being well-suited to chemical functionalisation). These advantages mean that the colloidal suspension method for producing graphene could be used for a wide range of applications, in particular, for the fabrication of battery/supercapacitor electrodes. In the form of a colloidal suspension, graphene is also a non-toxic nanomaterial with adjustable solubility suitable for printing applications.

4 Experimental details

In general, all the modified graphene inks reported in this paper are based on the chemical reduction of the exfoliated graphene oxide (GO).

(1) Preparation of graphene oxide (GO)

Graphene oxide (GO) was prepared by oxidizing natural graphite powder (SP, 320 mesh) based on a modified Hummers method[32] as originally presented by Kovtyukhova and colleagues.[33]As-prepared graphene oxide was suspended in ultra-pure water to give a brown dispersion, which was subjected to dialysis to completely remove residual salts and acids for 4 days. The resulting purified graphene oxide powder was collected by centrifugation and then air-dried. Graphene oxide powder was dispersed in water to create a 0.05 wt% dispersion. Then the dispersion was exfoliated through ultrasonication for 1 h, during which process, the bulk graphene oxide powder was transformed into GO nanoplatelets.

(2) Synthesis of polyelectrolyte and poly(sodium 4-styrenesulfonate) modified graphene

First, 20 mg of as-prepared GO was distributed in 40 ml of ultra-pure water and mixed in an ultrasonic bath (KQ218, 60 W) for 15 min to obtain a homogeneous and stable dispersion. Following this, 60 mg of an ionic polymeric binder (such as poly(sodium 4-styrenesulfonate), or poly[2,5-bis(3-sulfonatopropoxy)-1,4-ethynylphenylene-alt-1,4-ethynylphenylene] sodium salt) was added to the graphene oxide dispersion, and mixed in an ultrasonic bath (KQ218, 60 W) for another 15 min. The resulting mixture was then reduced by hydrazine monohydrate (1.950 ml, 50%) at 80 °C for 24 h to obtain a homogeneous black-coloured dispersion. This dispersion was then filtered through a polycarbonate membrane (0.22 μm pore size) and repeatedly washed with water to remove any excess binder/free ionic fluid (polymer). The resulting powder (comprising graphene platelets modified by these polymers) was then redistributed into water by ultrasonication in a water bath (KQ218, 60 W) for 15 min and centrifuged at 5000 rpm for 20 min. A dark, homogeneous supernatant solution was obtained after removing the sediment. Finally, after synthesis of the functionalised graphene suspension, titanium dioxide nanoparticles and lithium salt (*e.g.* $LiClO_4$) were mixed into the solution by ultrasonication (KQ218, 60 W) for 15 min. The titanium dioxide nanoparticles (anatase) used here were less than 25 nm in size. The resulting colloidal suspension can then be used as a printable ink to form the battery/supercapacitor electrodes.

(3) KOH treated graphene

As-prepared GO was purified *via* dialysis for 4 days. In a typical procedure for chemical re-graphitization by KOH, 10 ml of the aqueous GO dispersion (0.5 mg ml^{-1}) was mixed with 10 mg KOH (82%, Tianjin Chemicals, China) in a 50 ml flask, and the homogenous and yellow suspension was obtained. After ultrasonication for a few minutes, the yellow suspension changed to be a homogenous, yellow-black dispersion. Then, the flask was put in a oil bath (~80 °C) for 24 h. During refluxing, the yellow-black suspension became black when adding reducing agent of hydrazine solution in water (50%). A homogeneous long-term stable black graphene nanosheet dispersion was obtained after 24 h.

(4) PANI modified graphene

In a typical hierarchical structured polyaniline synthesis, 5 ml brown GO dispersion was added to 10 ml of 0.05 M aniline and 0.1 M H_2SO_4 aqueous solution, under ambient conditions with vigorous stirring. 1 ml of aqueous ammonium peroxydisulfate (APS) (0.2 M) as the oxidant was added dropwise into the mixture over the course of one minute. The resulting green material was rinsed with distilled water and methanol several times and collected *via* centrifugation at 5000 rpm after 24 h stirring. The washed residue was dispersed into 30 ml of water. An adopted method to reduce GO to graphene was used here. 5 μl of hydrazine solution was added to 25 ml of the resulting dispersion. After being vigorously stirred for a few minutes, the flask was put in an oil bath (95 °C) for 1 h. A blue dispersion was obtained instead of the black graphene solution. The obtained, as-prepared hierarchical structured polyaniline (HSPAN) can be re-dispersed readily in cold water with aid of ultrasonication.

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