Towards graphene-based new energy devices

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Abstract. The seeking for “killer application” of graphene has been the bottleneck for the industrialization of graphene. From its first application in sophisticated FET devices to many newly arising environment-friendly energy efficient devices, graphene seems to be an excellent candidate material when assembled with functional materials in new energy devices, such as current collector, lithium ion battery, photovoltaic cell or solar-thermal devices. Here, we reviewed the recent reports on these field, and prove that the existence of graphene could bring about a “win-win” outcome in above mentioned representative new energy devices, providing a new design paradigm to find out the “killer application” of graphene.

1. Introduction

Current applications of graphene has been extended to multifarious fields, from electronics to energy and environmental issues. However, the killer application of graphene is still an open question for many scientists. Once supposed to be an excellent candidate material in semiconductor industry during the past years, graphene is now suffering from doubts whether it could be suitable enough for the next ordained semiconductor to substitute silicon and overcome the Moore’s Law, because graphene’s dark current issue originating from its zero bandgap nature has become more as the Achilles’ heel than an advantage given its application to electronic devices. Besides, when used in field effect transistor (FET) devices, it always requires single crystalline high quality graphene samples, which are rare and expensive, and except for the mechanically exfoliated graphene from high quality graphite, only a few groups globally can synthesize inch-sized single crystalline graphene samples via the vastly adopted chemical vapor deposition (CVD) method.3. This reality makes it difficult for graphene to find its “killer application” in electronics. However, benefitting from the synthesis of various graphene products from CVD-derived graphene to solution-derived graphene, graphene could be applied to energy and environmental areas, where such light, highly thermo-/electro-conductive, flexible film has found its application in supercapacitors, or as seawater desalination films, or as component material for improving the performance of electrodes/carrier collector/collectors in new energy devices4-10.
Instead of searching the application of graphene in sophisticated FET devices at an expensive price, the assembly of traditional functional materials with graphene (we refer to it as “FunMat@Gr”) has proved to be a win-win strategy. WeiDong Fei and coworkers has reported a heterostructural graphene quantum dot/MnO$_2$ nanosheets toward high potential window electrodes for high-performance supercapacitors. Besides its application in supercapacitors, graphene could also be found in other “FunMat@Gr” assembly to bring in a win-win effect. Such as in a series of new energy devices shown in Figure 1: current collector, lithium battery, solar cell and solar thermal devices. In the following parts, we will focus our discussion on these four aspects to reveal the magic role of graphene.

**2. Graphene-based new energy devices**

**Current Collector** In rechargeable lithium-ion batteries (LIBs), Cu and Al are the most commonly used materials as current collectors, because of their cheap price and good electronic conductivity. However, the ubiquitous corrosion to current collectors severely hinders the lifetime of LIBs during long-term cycling, where anticorrosion techniques are highly in need. For example, the long-term performances of current 4 V LIBs are deteriorated by the corrosions of Al foil in LIB, which are believed to be a bottleneck for next-generation 5 V LIBs. Many protective methods have been adopted trying to solve this problem, for example, LiPF$_6$-based electrolyte is believed to be the benchmark electrolyte for LIBs and with its generation of about 1 nm thick insoluble protective layer of AlF$_3$, the corrosion of Al foil has been efficiently passivated. However, this ad-layer is tenuous and because of the inhomogeneities of local current density, pit corrosion to Al foil still exists, which will be further exacerbated by the use of high-voltage positive electrode materials, such as LiNi$_{0.5}$Mn$_{1.5}$O$_4$, LiCoPO$_4$, etc.

Comparatively, the direct growth of impermeable, high conductive graphene cover layer on Al foil via plasma-enhanced CVD method (PECVD) stands out. This sheath layer is impermeable to species except proton, thus minimizing the possibility of the coordination between Al and other species. As shown in Fig. 2a, the cells using graphene-armored Al foil as current collectors demonstrate enhanced...
electrochemical performance, including better long-term cycling performance at low rate, relieved self-discharge propensity, and enhanced rate/power performance.

**Figure 2.** Synthesis and characterization of graphene-armored Al foil (GA) and comparison of performance over pristine Al foil (PA). (a) Digital camera image of GA. Inset is low and high-resolution TEM image of multilayer graphene. Scale bar: 500 nm and 5 nm, respectively. (b) Elemental mapping of GA. Platinum was thermally deposited to protect graphene from possible damage during sampling. (c) Typical Raman spectrum of GA. (d) XPS signal of C 1s of GA. (e, f) Enhanced anticorrosion performance of GA over PA: CV curves of GA (e) and PA (f) in LPF6 electrolyte. The number denotes the cycle index. (g) Enhanced electrochemical performance of GA over PA. Long-term low-rate (0.5 C, 1 C = 148 mA g\(^{-1}\)) cycling performance of LMO/PA and LMO/GA cells. Solid and circle represent the \(C_{\text{cha}}\) and \(C_{\text{dis}}\), respectively. Reprinted with permission from Ref. 17. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

**Lithium-ion battery** Benefiting from its high electronic conductivity, graphene has also been used as promising substrates in high energy and power density lithium-ion batteries\(^{18-20}\). As a key parameter to determine the reversible capacity of lithium-ion batteries, a faster and easier transfer velocity of Li ions is realized by incorporating large surface area graphene in the electrodes, and an improved final cycling performance of lithium ion battery was also achieved. For example, one work showed an enhanced Li ion and electron transfer rate in vertical graphene encapsulated SiO microparticles\(^{23}\), as shown in **Fig. 3a-b**. Another representative work done by Ouyang and coworkers\(^{21}\) reported an enhanced lithium-ion storage of 670 mAh g\(^{-1}\) with the capacity retention of 99% after 30 cycles at 100 mA g\(^{-1}\) based on a MoS\(_2\) anchored free-standing three dimensional vertical graphene foam (MoS\(_2\)@3DVG), much better than the 550 mAh g\(^{-1}\) at 100 mA g\(^{-1}\) based on MoS\(_2\) at planar graphene (MoS\(_2\)@3DG). **Fig. 3c** is the SEM image of the as-prepared MoS\(_2\)@3DVG, and from **Fig. 3d**, we can find both the charge and discharge capacity of MoS\(_2\)@3DVG are better than MoS\(_2\)@3DG after only 20 cycles. The MoS\(_2\)@3DVG sample was synthesized using the cost effective *M. alternifolia* as precursor via PECVD method. Afterwards, the binder-free MoS\(_2\)@3DVG anode to be used in the Li-ion battery was made by anchoring MoS\(_2\) nanosheets onto the free-standing 3DVG by a hydrothermal method. The merits of such hierarchical three-dimensional vertical graphene come from
its large surface area, inherent 3D network and excellent ion transport properties. The Raman spectrum indicated the existence of defects in 3DVG compared with 3DG (see Fig. 3b).

**Figure 3.** Typical graphene-based lithium ion batteries. (a) Schematic illustration of the coexisted pathways for Li ion diffusion and electron transfer in vertical graphene encapsulated SiO microparticles. (b) Specific capacity and cycling efficiency of d-SiO and d-SiO@vG electrodes, and the current density is 320 mA g⁻¹. (a, b) Reprinted with permission from Ref. 23. Copyright 2017 American Chemistry Society. (c) SEM image of the as-prepared MoS₂@3DVG. (d) The rate stability of MoS₂@3DVG and MoS₂@3DG electrodes at various current densities. (c, d) Reprinted with permission from Ref. 21. Copyright 2015 Elsevier.

To further improve the performance, nitrogen doped graphene is becoming more and more prevalent. Compared with traditional graphene, nitrogen doped graphene shows an enhanced electric conductivity and affinity to ions, providing more active site for the attachment of metal ions, as shown in Fig. 4d-e. Thus, compounds consisting of nitrogen doped graphene and another semiconductor have been fabricated as electrodes in Li-ion or Na-ion batteries. A typical device detection result is shown here, Fig. 4a shows nitrogen doped graphene could enhance the Na ion transfer because of the good conductivity of graphene and the negative electronic chemical
environment coming from the n-doping effect of nitrogen. And the SEM image revealed that graphene was vertically grown covering the SnSe nanobelts (Fig. 4b). The enhanced cycling performance and coulombic efficiency of SnSe/NC over pristine SnSe was obvious in Fig. 4c and after 150 cycles, the capacity of SnSe decreased hugely, while the capacity of SnSe/NC still maintained the same level as the beginning point, due to the enhanced conductivity of SnSe/NC (Fig. 4d-e).

**Solar energy** Graphene shows its application in photovoltaic solar cells in mainly three different aspects. First, graphene may be used as electrode\textsuperscript{27}, such as counter electrode or transparent conductive electrode\textsuperscript{28-30}. Second, graphene can be diffused in solution and then spin coated on the electrode to improve the power conversion efficiency (PCE)\textsuperscript{31}. Third, graphene could be used in heterostructures with another semiconductor, like GaAs\textsuperscript{32,33}, Si\textsuperscript{34,35} and so on\textsuperscript{36}. Benefiting from its high transparency and conductivity, graphene can act as the transparent electrode. Notte\textsuperscript{27} and coworkers tried to substitute indium tin oxide (ITO) with graphene in polymer solar cells. The graphene was fabricated via CVD method, and the multilayer graphene was synthesized by transferring complementary graphene layers onto other graphene substrate. Then the graphene was treated with oxygen plasma and SOCl\textsubscript{2} chemical doping, respectively. Afterwards, the wettability and sheet resistance of the oxygen plasma-treated graphene, SOCl\textsubscript{2} chemically doped graphene and the pristine graphene was measured for comparison. From Fig. 5a-b, we found that the wettability change of graphene (contact angle decrease from 90° to 58°) and the sheet resistance decreased with the increasing of graphene layer number. The five-layer SOCl\textsubscript{2} chemically doped graphene showed the lowest sheet resistance, because of the covalent attachment of Cl atoms, which served as electron acceptors in graphene, while the oxygen-plasma treatment graphene presented the highest $R_s$ compared to the other two graphene samples, for the top layer has been etched during the plasma treatment. At last, the photovoltaic device measurement results also showed the performance of photovoltaic devices based on graphene treated by oxygen plasma is able to provide a higher photo conversion efficiency (PCE) than the graphene treated by SOCl\textsubscript{2} chemical doping. This result revealed the fact that the wettability is more crucial than the Ohmic contact in solar cell devices. Subsequently, the device based on ITO gets a highest PCE among the three devices, because the water contact angle of ITO is even lower than the oxygen plasma treated graphene.

In addition, graphene/semiconductor heterostructure are fabricated by some groups to make use of the wonderful properties of graphene. For example, Li and coworkers\textsuperscript{28} made a photovoltaic device based on the peculiar nature of graphene that the Fermi level of graphene can be tuned by gate structure relatively independent of semiconductor substrate, the structure is shown in Fig. 5c. PCE of previously reported solar devices based on gated graphene/GaAs heterostructure was generally less than 10%. Herein, the author developed an improved graphene-dielectric-graphene gated structure for graphene/GaAs heterostructure. In this structure, PCE and open circuit voltage of device is able to achieve 18.5% and 0.96 V, respectively. This structure could merge the merit of anti-reflection property of the dielectric layer with high transparency and highly tunable Fermi level of graphene together. In this report, heterostructure with trilayer graphene indicates the best performance. This is
mainly for the reason that sunlight absorbed by graphene cannot transfer into electricity, due to the zero band gap of graphene. Therefore, monolayer graphene would absorb 2.3% of sunlight which leads to a 2.3% decrease in the short circuit current density ($J_{sc}$). On the contrary, multilayer graphene with more layers in the device means lower series resistance. Finally, comprehensively considering these features affected the nature of graphene, a conclusion was drawn that photovoltaic device based on trilayer graphene could get the best performance and the highest PCE obtained by solar cells fabricated as mentioned above is 9.20%. The relation between the Graphene layer number and PCE is demonstrated in Fig. 5d.

Figure 5. The structure scheme and characterization of different categories of graphene and solar cells. (a) The comparison of contact angles of pristine graphene, oxygen plasma treated graphene and SOCl$_2$ chemical doping graphene, respectively. (b) The relation between resistant and number layers of pristine graphene, oxygen plasma treated graphene and SOCl$_2$ chemical doping graphene. (a, b) Reprinted with permission from Ref. 27. Copyright 2013 Royal Society of Chemistry. (c) The scheme of the structure of the graphene/semiconductor heterostructure solar cell. (d) The relation between the graphene layer number and PCE of five sets of solar cells. (c, d) Reprinted with permission from Ref. 32. Copyright 2015 Elsevier. (e) The Raman scheme of graphene coated with Au NPs. (f) The impact of size of Au NPs on PCE of the solar cell. (e, f) Reprinted with permission from Ref. 33. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weiheim.

Furthermore, Lin and coworkers recently fabricated a graphene/GaAs heterostructure solar cell and Au nanoparticles were deposited near the photoactive layer to enhance the PCE of the solar device by increasing the light absorption in the photoactive layer$^{33}$. As is shown in Fig. 5e, the Raman spectrum of graphene coated with Au NPs and that of pristine graphene are resemble. The same position of G and 2D peaks illustrates the coating of Au NPs have no bearing on the graphene. After antireflection coating and chemical doping, the PCE is improved from 8.83% to 16.2%. In their report, Au NP with diameters of 30, 50, 80, 120, and 150 nm are spun on graphene to compare with each other’s size and find out whose PCE is the highest. Fig. 5f shows the PCE value of solar cells with different diameters Au NP and different particle densities. Obviously, solar device with 80 nm NP could get the highest PCE which is 11.8%. Measurement of PCE of solar cells among different particle densities was also
taken, and Au NPs density with $1 \times 10^8$ cm$^{-2}$ could best ameliorate the device performance. Eventually, after TFSA doping of graphene and ARC coating on the front surface, device performance was further improved to 16.2%.

**Solar-thermal** Except being used in supercapacitor, lithium-ion battery and solar cell, an aspect normally with scant attention will be introduced here. The solar-thermal property of graphene, given to the low thermal conductivity and large surface area, graphene is a promising material in this field. Normally, the solar-thermal application serves as a “light trap”, by reducing the reflection and transmittance, to convert sunlight to heat and then generate vapor to make seawater desalination. In recent reports, there are three kinds of ways to fabricate light trap, the corrugated surface of graphene glass, multi-walled carbon nanotubes of graphene oxide (GO)-based aerogels and the graphene nanoplates (GNPs) secondary structure of the hierarchical graphene foam (h-G foam). Among them, the h-G foam has the best performance that the solar thermal conversion rate of the h-G foam is 93.4%. Moreover, when the length of the GNPs grow longer, the quality of the h-G foam is better. Besides, when the corrugated surface of graphene glass grow, the length and width of it increases. Then the performance got improved. In these reports, the porous structure and the excellent wettability of the carbon material endow the application to possess a good solar-thermal property. Fig. 6a illustrated the porosity of h-G foam, graphene glass and GO aerogels. Furthermore, the defects of the graphene contribute to the low thermal conductivity of the application, which in turn to preserve heat. In Ren and coworkers’ work, the color difference of three foams made by different kinds of material demonstrated in Fig. 6a shows the difference in the absorption among these three foams. In addition, h-G foam is the darkest one, which means the absorption of h-G foam is the highest among these foams. Fig. 6b illustrates the measurement of three samples’ solar-thermal conversion, which was taken with various incident angles. Although the solar-thermal conversion performance kept stable until the incident angle was increased to 55°, the solar-thermal performance would only drop a little when the incident angle was increased to 70°, which is caused by the dramatically decreased projected area. Furthermore, the surface temperature of these three samples show rising trend when the radiation power of the solar illumination improved from 1 to 5 kW/m$^2$. Among these three samples the h-G foam’s surface temperature increases drastically (Fig. 6c). Graphene based solar-thermal devices are very promising in seawater desalination applications to help tackle the environmental problems.
3. Comparison and Conclusion

Raman spectra are widely adopted to characterize the quality of graphene. Here, as shown in Fig. 7, the Raman spectra of graphene used in four new energy devices are compared. They share a same feature, that is, all of the Raman spectra show the appearance of a high intensity D band, corresponding to the lattice defect of graphene. This indicates that when used in new energy devices, the domain size of crystallized graphene don’t have to be very large size, μm-sized domain of graphene flakes or sheets in combination with functional materials are suitable enough to guarantee both the high electronic and thermal conductivity of graphene to improve the performance than pure functional materials.

Figure 7. The Raman scheme of graphene which are applied in different kinds of devices: (a) Current collector. Reprinted with permission from ref. 17. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weiheim. (b) Lithium ion battery. Reprinted with permission from Ref. 21. Copyright 2015 Elsevier. (c) Solar cell. Reprinted with permission from ref. 36. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weiheim. (d) Solar thermal devices. Reprinted with permission from Ref. 39. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weiheim.

Thus, to seek for the killer application of graphene, given with the strict synthesis and fabrication requirements on graphene used in FET device, we believe this cheaper and simpler strategy by the assembly of functional materials with less perfect graphene flakes or graphene oxides in new energy devices is providing a new design paradigm for the exploitation of graphene’s “killer application”.
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