

# THREE-DIMENSIONAL GRAPHENE-BASED HYDROGEL/AEROGEL MATERIALS

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**Abstract.** Graphene-based hydrogels/aerogels (GHA) have attracted widespread attention due to its excellent mechanical strength, electrical conductivity, thermal stability and adsorption capability. In this article, some research achievements are reviewed on preparation strategies, formation mechanisms and potential applications of GHA. Except for the normal method of self-assembly, some new technologies for fabricating GHA framework were summarized including chemical reduction self-assembly, polymerization, adding cross-linking agents and so on. Meanwhile, we concluded the applications in various fields, such as environmental protection, biomedicine and energy sources. Finally, a perspective in the future challenge about fabricating GHA is also given.

## 1. INTRODUCTION

Graphene, a two-dimensional (2D) one-atom thick carbon sheets with a similar benzene-ring structure, has attracted tremendous interest among researchers from different fields, due to its outstanding physiochemical properties, such as a large specific surface area ( $2630 \text{ m}^2 \text{ g}^{-1}$ ) [1], high-speed electron mobility ( $20000 \text{ cm}^2 \text{ Vs}^{-1}$ ) [2], excellent thermal conductivities ( $5000 \text{ W m}^{-1} \text{ K}^{-1}$ ) [3], and well electrocatalytic activity [4]. In recent years, graphene and its derivatives were used to assemble into kinds of carbon-based materials, for instance, one-dimensional (1D) tube-in-tube nanostructures [5], two-dimensional (2D) layer-stacked films [6-8] and three-dimensional (3D) graphene hydrogels [9-12] and aerogels [13-17]. On the other hand, graphene oxide (GO) has plenty of hydrophobic basal plane and hydrophilic oxygen-containing groups, including epoxy, hydroxyl, carboxyl and carbonyl groups, which promote GO to be functionalized through co-

valent and non-covalent approaches [18-21]. Thus, GO and its derivatives have become new candidate materials for various technological fields including optoelectronics, energy storage, catalysis, nano-electronic devices, gas sensors, super capacitors, and drug delivery systems [22-24]. Meanwhile, plenty of hydrophobic basal plane and hydrophilic oxygen-containing groups also provide great possibility to achieve self-assembly of graphene nanosheets (GNS). It is generally recognized that various non-covalent forces (including hydrogen bonding, ionic, amphiphilic and  $\pi$ - $\pi$  interactions) are exist in graphene-based hydrogels. As we know, traditional hydrogels, due to its excellent properties, such as biocompatibility, rubber elasticity, equilibrium swelling, network structure characteristics and environmental sensitive, has been widely used in agriculture, biomedicine and industry [25]. However, traditional hydrogels and aerogels have the drawbacks, such as poor mechanical properties and

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limited functional properties [26]. In order to achieve nanostructural materials integrating into macroscopic devices, a large amount of efforts has been endow to make GNS self-assemble and to improve traditional hydrogels. Since a pH-sensitive GO composite hydrogel was reported by Bai et al. [27], some graphene-based hydrogels were starting to emerge, such as GO/conducting polymer composite hydrogels [11], macroscopic multifunctional graphene-based hydrogels and aerogels (GHA)[13], temperature-sensitive GO nanocomposite hydrogels [28], supramolecular hybrid hydrogels from graphene with block copolymers [29]. As for a graphene-based aerogel, it was usually obtained from a graphene hydrogel, which needed a drying process, such as freeze-drying process [9,10,13,14], or supercritical-CO<sub>2</sub>-dried [14,16]. Graphene-based aerogel, with interconnected 3D macroporous graphene network structures [9,10,13,14], high electrical conductivity [14,16], ultra-flyweight and highly compressible properties [30], has also aroused tremendously interesting in researchers. GHA have many potential applications in catalysis, oil and water separation, super capacitors, and drug delivery systems, etc. Thus, the macrostructures by self-assembly of GNS can sufficiently expand potential applications of graphene. In this article, we focus on recent progresses on preparations, formation mechanisms and special applications of 3D GHA framework.

## 2. PREPARATION OF GHA MATERIALS

3D GHA materials, which possess abundant interconnected micropores or mesopores, have drawn great interest for their unique properties, including low density, high storage moduli, large specific surface, fine elasticity and good electrical conductivity [28-31]. Recently, great efforts have been devoted to produce GO-containing macrostructures [9-17]. However, these methods are limited to prepare graphene-based macroscopic framework on a large scale because of the need for special equipment and extra chemical reagents. So it is critically important to develop gentler, simpler and environmental-friendly approaches to achieve GNS macro-assembly. Here some techniques for fabricating 3D graphene framework are simply divided by three methods: chemical reduction [9,10,13,14,32-34], polymerization [11,12,15,16,26,27], and cross-linking agents [28-29,35-37].

GO, as a precursor for constructing carbon-based materials, is usually synthesized by chemical oxi-

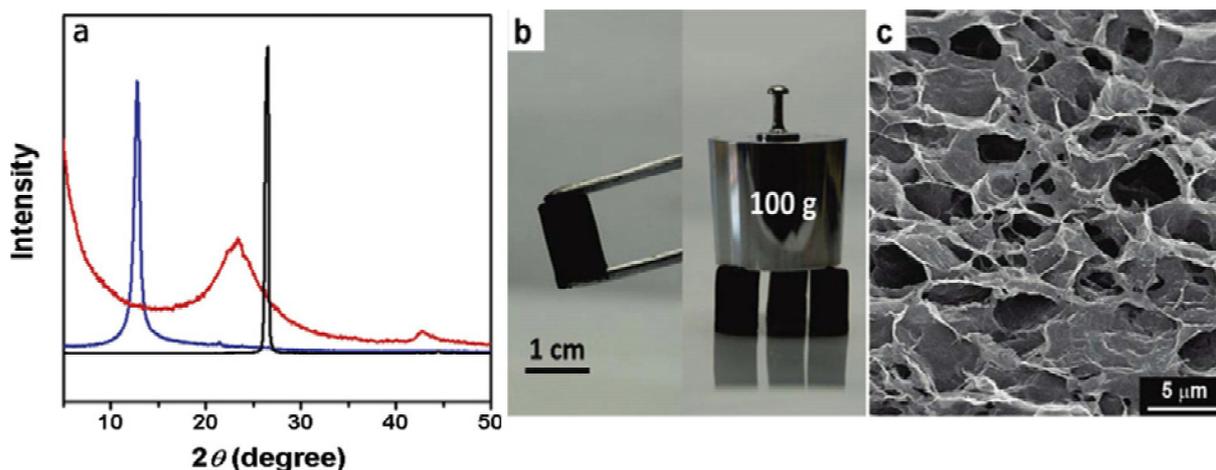
dation of graphite powder with strong oxidants. In general, three major methods were developed to synthesize GO from graphite, including Hummer and Offeman's method [38], Staudenmaier's method [39], and Brodie's method [40]. Among these methods, the modified Hummers method is commonly accepted due to its inexpensive and simple operation compared with the others. Our group also reported the modified Staudenmaier's method early in 2010 [41].

### 2.1. The chemical reduction

GNS tend to aggregation or restack because of abundant hydrophilic functional groups of its edges and basal planes. Several experiments demonstrated that the reduction of GO promoted self-assembly of GNS [9]. Generally speaking,  $\pi$ -conjugated system from graphene sheets is recovered by chemical reduction, which was confirmed by X-ray diffraction (Fig. 1a). More importantly,  $\pi$ - $\pi$  stacking interactions between flexible graphene sheets play an important role for self-assembly of GNS.

Self-assembly is a powerful technique for achieving nanostructural building blocks into monoliths. A hydrothermal synthesis is demonstrated as a simple and efficient method for constructing graphene-based hydrogel [9]. In this method, they realized self-assembly of reduced graphene oxide (rGO) sheets into 3D graphene architectures with hierarchical structure and novel properties. The prepared self-assembled graphene hydrogel (SGH) have many performances, such as excellent mechanical property (Fig. 1b), a well-defined and interconnected 3D porous network (Fig. 1c), a wonderful thermally stability (25-100 °C) and high specific capacitance (175 F·g<sup>-1</sup>). In addition, SGH can also be obtained via hydrothermal treatment with divalent metal ion (Ca<sup>2+</sup>, Co<sup>2+</sup>, or Ni<sup>2+</sup>) using polyvinyl alcohol as a strengthening agent [33]. Poly (N-isopropylacrylamide) (PNIPAAm) is also successfully interpenetrated graphene hydrogel via a hydrothermal method [42].

Hydrothermal synthesis technology, as a traditional and convenient method, needs conditions of high temperature and high pressure, and the mixtures are absolutely sealed. It is beneficial to improve gel rate and keep gel integrality. However, high temperature and high pressure not only need expensive equipment and energy but also are not suitable for large-scale preparation. So it is urgent to develop a facile and feasible strategy to achieve self-assembly graphene nanosheets.



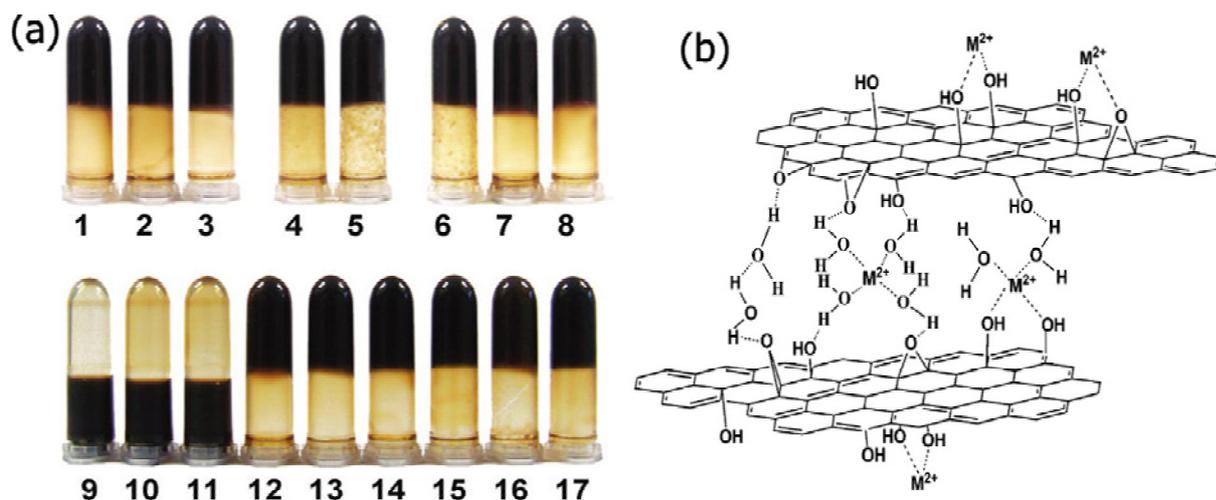
**Fig. 1.** (a) XRD patterns of natural graphite (black), GO (blue), and freeze-dried SGH (red); (b) Photographs of a strong SGH allowing easy handling and supporting weight; (c) A SEM image of the SGH interior microstructures. Reprinted with permission from [Y.-X.Xu, K.-X.Sheng, C.Li, and G.-Q.Shi, Self-assembled graphene hydrogel via a one-step hydrothermal process. *American Chemical Society Nano*, Volume 4, 4325 (2010)]. Copyright (2010) by American Chemical Society Publishing Group.

As a facile and feasible strategy, chemical reduction method is developed by using mild reduction agents, such as sodium ascorbate,  $\text{NaHSO}_3$ ,  $\text{Na}_2\text{S}$ , Vitamin C and HI, etc. For example, sodium ascorbate, as a kind of inexpensive and green materials, was used to achieve cylindrical SGH by Sheng's group [43]. The obtained SGHs have a higher specific capacitance of  $240 \text{ F}\cdot\text{g}^{-1}$  than those by the hydrothermal methods ( $175 \text{ F}\cdot\text{g}^{-1}$ ). Compared with the hydrothermal synthesis, neither chemical cross-linkers nor high pressures are necessary in the mild chemical reduction process, and the shapes of 3D SGHs could be controlled by changing the types of reactors [32]. HI acid, as a reducing reagent, was also added to GO solution to achieve a higher level of reduction of GO [44,45]. However, concentrated HI is highly toxic and not suitable for large-scale preparation of graphene-based materials. To overcome this disadvantage, Zhang with co-workers presented [46] a reaction system with oxalic acid (OA) and sodium iodide (NaI), and obtained GO suspension with ultralow concentration ( $0.1 \text{ mg}\cdot\text{mL}^{-1}$ ) for preparation of 3D graphene assemblies with low density, highly porous structures. Recent studies indicated that mercaptoacetic acid and mercaptoethanol [17] were demonstrated to not only efficiently restore  $\pi$ - $\pi$  conjugated structure but also accomplish in situ self-assembling of rGO. The rGO aerogels by freeze drying process have high porosity that is beneficial for ion absorption. For instance, a facile one-step simultaneously in situ self-assembly of GO sheets was investigated by Cong et al. [13]. The method is proved to be a versatile to induce

macroscopic assembly of rGO sheets with the functional metal oxide [47-49]. The resulting GHA exhibits outstanding capability for removal of pollutants. Therefore, mild chemical reduction strategy is a facile reduction-induced self-assembly method owing to its simplicity and scalability.

## 2.2. The cross-linking agents

**Hydrogen bonds.** GO sheets bring various hydrophilic oxygenated functional groups, while graphene itself is hydrophobic. So GO sheets can form a stable dispersion in water as an amphiphilic macromolecule [50]. However, GO dispersion is instable in a strong acidic aqueous medium due to the insufficient mutual repulsion [51]. If the pH value of the GO solution decreases, electrostatic repulsion is weakened and hydrogen bonding force is enhanced because of the protonation of carboxyl groups. Therefore, increasing the bonding force or weakening the repulsion force is an effective way to obtain stable GO gelation. Cross-linking agents were largely explored to promote gelation of GO sheets by increasing the bonding force between GO sheets. There are several cross-linkers including hydroxyl (PVA) [28], oxygen-containing (PEO, HPC, etc.) [50] (Fig. 2a) or nitrogen functional groups (ethylenediamine [30], polyamines [52]). These polymers can blend with adjacent GO sheets by forming hydrogen bonds, and provide additional bonding force in the process of gelation. Interestingly, some of the GO/polymer composite hydrogels are pH-sensitive. In addition, some small quaternary ammonium salts,

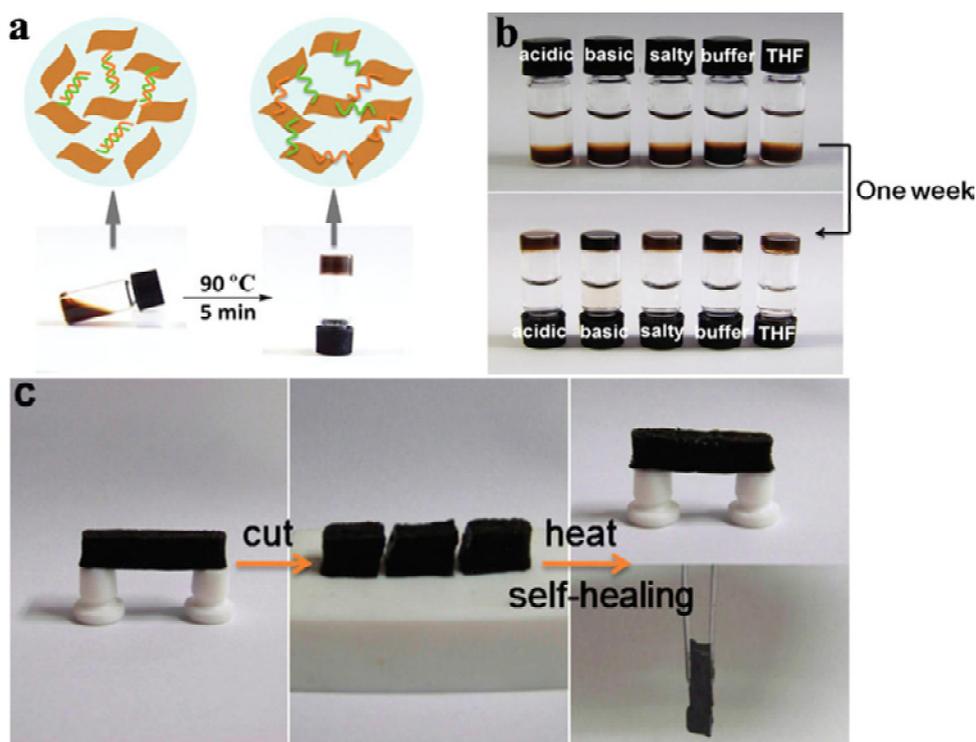


**Fig. 2.** (a) Photographs of 5 mg mL<sup>-1</sup>GO solutions mixed with different cross-linkers: **1**, 0.5 mg mL<sup>-1</sup> PVP; **2**, 1 mg mL<sup>-1</sup> HPC; **3**, 1 mg mL<sup>-1</sup> PEO; **4**, 0.1 mg mL<sup>-1</sup> PDDA; **5**, 0.2 mg mL<sup>-1</sup> PEI; **6**, 0.3 mg mL<sup>-1</sup> CTAB; **7**, 1.9 mg mL<sup>-1</sup> TMAC; **8**, 0.3 mg mL<sup>-1</sup> melamine; **9**, 20 mM Li<sup>+</sup>; **10**, 20 mM K<sup>+</sup>; **11**, 20 mM Ag<sup>+</sup>; **12**, 15 mM Mg<sup>2+</sup>; **13**, 9 mM Ca<sup>2+</sup>; **14**, 3 mM Cu<sup>2+</sup>; **15**, 3 mM Pb<sup>2+</sup>; **16**, 3 mM Cr<sup>3+</sup>; **17**, 3 mM Fe<sup>3+</sup>. Reprinted with permission from [H. Bai, C. Li, X. -L. Wang, and G. -Q. Shi, On the Gelation of Graphene Oxide. *The Journal of Physical Chemistry C*, Volume **115**, 5548 (2011)]. Copyright (2011) by American Chemical Society Publishing Group (b) Schematic illustration of the formation of gel-like rGO with divalent ion linkage. M<sup>2+</sup> represents the divalent ion (Ca<sup>2+</sup>, Ni<sup>2+</sup>, or Co<sup>2+</sup>). Reprinted with permission from [X. Jiang, Y.-W. Ma, J.-J. Li, Q.-L. Fan, and W. Huang, Self-assembly of reduced graphene oxide into three-dimensional architecture by divalent ion linkage. *The Journal of Physical Chemistry C*, Volume **114**, 22464 (2010)]. Copyright (2010) by American Chemical Society Publishing Group.

such as cetyltrimethyl ammonium bromide (CTAB), melamine and tetramethyl ammonium chloride (TMAC), could also promote the formation of GO hydrogels [50] (Fig. 2a).

**Multi-valent metal ions.** Many researchers reported developed strategies for achieving self-assembly of GO sheets by metal ions that were found to promote gelation of GO sheets. Moreover, investigations on a variety of metal ions (e.g., K<sup>+</sup>, Li<sup>+</sup>, Ag<sup>+</sup>; Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>) indicated that monovalent ions couldn't reduce gelation whereas divalent and trivalent ions could promote GO self-assembly (see, e.g., Fig. 2). The phenomenon mainly ascribe to these metal ions interacting with individual GO by a bonding force. For instance, noble-metal salts and glucose were added into the dilute suspension of GO, and promoted GO self-assembly into 3D architectures via a hydrothermal process [10]. Meanwhile, different macroscopic sizes of the samples can be obtained by different volumes of the container. On the other hand, the concentration of GO was also investigated that influence the pore density and size. Metal ions play an important role by formation of chemical and hydrogen bonds between the interconnected water, divalent metals and oxygen-containing groups on GO.

**Biomacromolecules.** Biomacromolecules are confirmed as another class of compounds that have the capability of interacting with GO sheets. As early as 2010, GO/DNA composite self-assembled hydrogels (GO/DNA SH) were fabricated by Xu and coworkers [35]. Some reports observed that the DNA chains were attached on the surfaces of GO sheets via  $\pi$ - $\pi$  stacking interactions [53-55]. Fig. 3a exhibits the procedure of preparing self-assembled GO/DNA composite hydrogel (GO/DNA SH) and possible gelation mechanism. The as-prepared GO/DNA SH is provided with the unique characteristics: (i) It is undamaged in a variety of harsh conditions, from strong acid (pH 2) to strong basic (pH13) even if in organic solvents (THF) (Fig. 3b).(ii) It also exhibits excellent capacity of adsorbing dye agents and self-healing (Fig. 3c). This phenomenon is ascribed to the massive presence of hydroxyl, epoxide, and carboxylic groups at the basal planes and edges of GO. Moreover, the oxygen-containing groups facilitate aqueous dispersions of GO, and stabilize gelation molecules [56]. Fluorenylmethyloxycarbonyl, one of peptide based hydrogelators, was reported to form GO/peptide based supramolecular hydrogels [57]. The study demonstrated that GO got well dispersed within the hydrogel system because of aromatic  $\pi$ - $\pi$  stacking interactions between the large



**Fig. 3.** (a) The procedure of preparing GO/DNA SH and the proposed gelation mechanism; (b) Effects of pH, NaCl, buffer, and organic solvent on GO/DNA SH stability; (c) Self-healing process of the as-prepared free-standing GO/DNA SH. Reprinted with permission from [Y.-X. Xu, Q. Wu, Y.-Q. Sun, H. Bai and G.-Q. Shi, Three-Dimensional Self-Assembly of Graphene Oxide and DNA into Multifunctional Hydrogels. *American Chemical Society Nano*, Volume 4, 7359-7360 (2012)]. Copyright (2012) by American Chemical Society Publishing Group.

aromatic surface of GO and aromatic moieties of the gelator peptides.

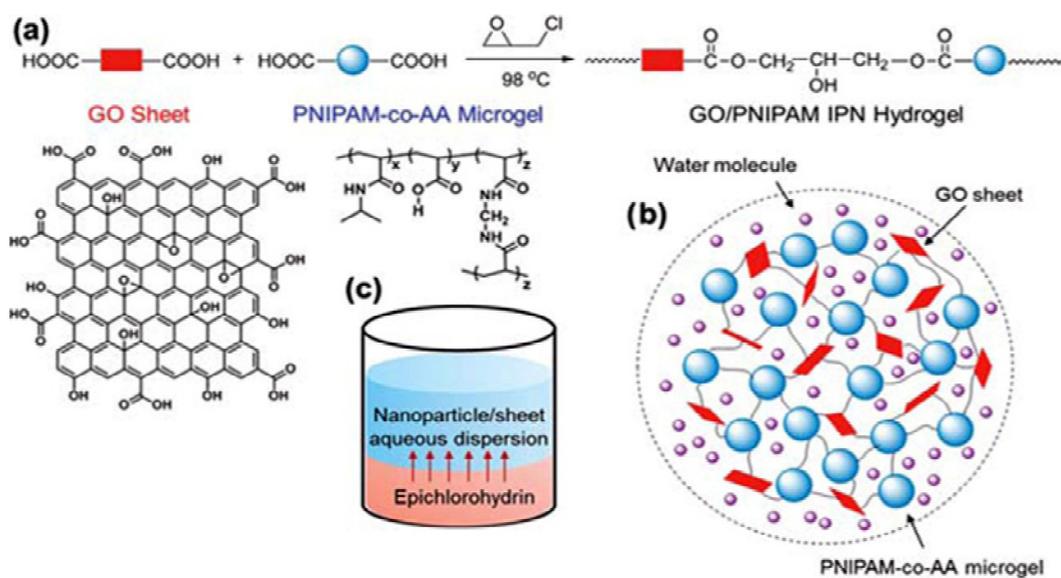
In addition, chitosan (CS), as a kind of an inexpensive natural biomaterial, play the role of a cross-linking agent by a strong electrostatic interaction and hydrogen bonds with GO sheets in GO-CS composites hydrogels [36], which exhibit excellent absorption capacities toward organic dyes, anionic and heavy metal ions from water contaminants.

### 2.3. The polymerization strategy

Sol-gel polymerization was used to fabricate a variety of mesoporous materials, such as graphene aerogels, carbon nanotube foams, and carbon aerogels [16,58-59]. Compared with the weak interaction between GO sheets in the cross-linking methods, polymerization provides covalent bonds between GO sheets [16]. For instance, a thermal- and pH-responsive GO/poly (N-isopropylacrylamide) (PNIPAM) hydrogel was prepared by a facile one-step strategy [Fig. 4] [60]. GO sheets were cross-linked with PNIPAM-co-acrylic acid microgels in water [61] via the reaction between carboxyl groups and epichlorohydrin (ECH) to form covalent bonding. The acquired composite hydrogel exhibited dual

thermal- and pH- responsive features with good reversibility. Remarkable electrical conductivities ( $0.87 \text{ S cm}^{-1}$ ) and low densities ( $\sim 10 \text{ mg cm}^{-3}$ ) were found in these graphene 3D aerogels. Meng's group also reported that a modified sol-gel polymerization was applied to fabricate graphene/carbon composite aerogels [62]. They found that alkali-treated GO can be act as a solid base catalyst to induce the polymerization of resorcinol with formaldehyde. The prepared aerogels has significantly enhancement in both the surface area and the electrical ( $763 \text{ m}^2 \text{ g}^{-1}$  and  $0.53 \text{ S cm}^{-1}$ , respectively). The outstanding characteristics give it much probability in super capacitors.

Frontal polymerization (FP) progresses through a self-heating as a driving force, and then it is continuously moving through the reaction zone, and ultimately completes the overall polymerization conversion [63]. FP was first discovered as a new method for synthesizing PNIPAM nanocomposite hydrogels by Alzari et al. [64]. The resulted hydrogel is a thermo-responsive hydrogel that exhibit a particular rheological behavior. The  $G'$  modulus and complex viscosity of hydrogels were increased with the increasing of the graphene contents. However,



**Fig. 4.** (a) Formation of GO/PNIPAM interpenetrating hydrogel networks via the reaction between ECH and carboxyl groups in GO sheets and PNIPAM-co-AA microgels. Reprinted with permission from [S.-T. Sun and P.-Y. Wu, A one-step strategy for thermal- and pH-responsive graphene oxide interpenetrating polymer hydrogel networks. *Journal of Materials Chemistry*, Volume 21, 4095 (2011)]. Copyright (2011) by Royal Society of Chemistry Publishing Group.

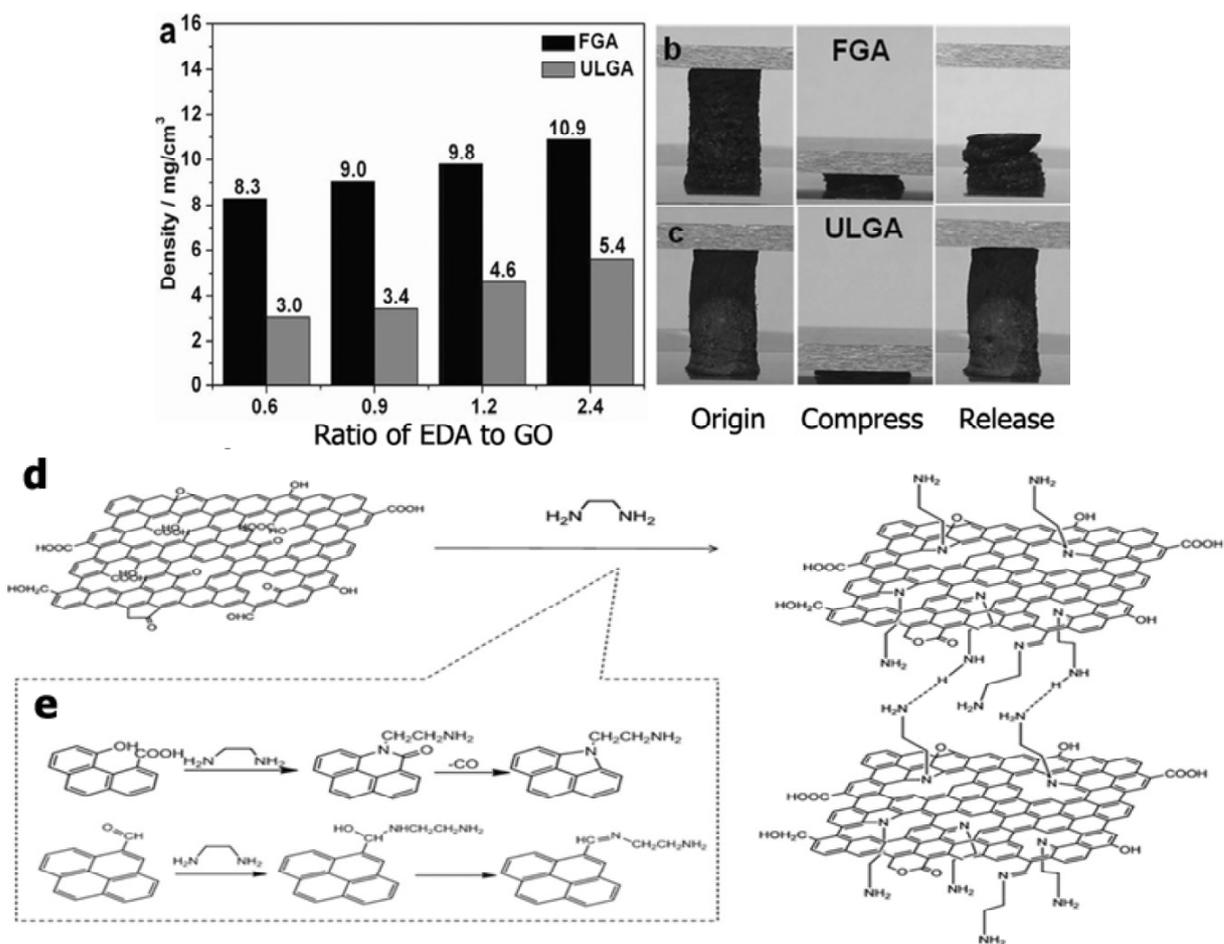
their mechanical strength is not satisfied, meanwhile, a low rate of equilibrium swelling limits its scope of application. To improve the properties of PNIPAM hydrogels, Ma et al. [27] introduced *in-situ* polymerization with GO to prepare a composite hydrogel with improved swelling capability and mechanical behavior. The equilibrium swelling ratios of the GO composite hydrogels are two times larger than that of PNIPAM, and the final water retention of the composite hydrogels is a little higher than that of neat PNIPAM hydrogel. Additionally, an effective method was developed by Shen and his coworkers [65] to prepare GO/polyacrylamide (PAM) composite hydrogels via free radical polymerization. Compared with neat PAM hydrogels, the GO/PAM composite hydrogels have higher rigidity, better tensile and greatly enhanced mechanical and thermal properties.

## 2.4. Nitrogen containing graphene hydrogels

Nitrogen doping can further utilize excellent properties of graphene so that it attracted marvelous attention in the past few years [66,67]. Recently, our group reported synthesis of nitrogen-doped graphene and its electrocatalytic performance toward oxygen reduction reaction [68]. It is confirmed that nitrogen is successfully doped in graphene with the formation of pyridinic N, pyrrolic N, and graphitic N, and the maximum nitrogen content is 6.6% via

X-ray photoelectron spectroscopy. Recently, an ultralight and highly compressible graphene aerogels was constructed using ethylenediamine (EDA) as a weak reducing agent that introduced into GO colloidal solution [30]. A treatment of functionalization-lyophilization-microwave was used to obtain ultralight graphene aerogel (ULGA). Different ratio of EDA to GO gave rise to different density of graphene aerogels (FGA) and ULGA (Fig. 5a). The compressibility experiments were also demonstrated vividly (Figs. 5b and 5c). Similarly, a convenient hydrothermal process for fabricating supercapacitors of nitrogen containing graphene hydrogels using ammonia and different organic amines was first developed by Chen's group [69]. Figs. 5d and 5e demonstrate the progress of controlled assembly of the 3D nitrogen containing graphene hydrogels.

Pyrrole was also used as N-doped reagent of graphene hydrogels because of its conjugated structure and electron-rich N atoms [70]. In the course of reaction progress, pyrrole not only provides N source through hydrogen bonding or  $\pi$ - $\pi$  interactions to anchor on the surfaces of GO but also plays a swelling agent to effectively prevent GO from self-stacking during a hydrothermal process. Polyamine is also used as a very good cross-linker between GO sheets through hydrogen bonding and electrostatic interaction (Figs. 6a and 6b). This tentative molecular interaction was reported in detail by Adhikari et al. [52]. In this method, polyamines were added into rGO dispersion with a mild reducing agent (vitamin



**Fig. 5.** (a) The density of functionalized graphene aerogel (FGA) and ultralight graphene aerogel (ULGA) as a function of EDA to GO ratio. (b) and (c) the digital images showing compressibility of FGA and ULGA, respectively. Reprinted with permission from [H. Hu, Z.-B. Zhao, W.-B. Wan, Y. Gogotsi and J.-S. Qiu, Ultralight and Highly Compressible Graphene Aerogels. *Advanced Materials* Volume **25**, 2221 (2013)]. Copyright (2013) by Wiley Publishing Group. (d) Illustration of the enhancement of the distance between graphene layers by ethylenediamine. (e) the possible reaction pathways for nitrogen doping. Reprinted with permission from [P. Chen, J.-J. Yang, S.-S. Li, Z. Wang, T.-Y. Xiao, Yu. Hong, Qian, S.-H. Yu, Hydrothermal synthesis of macroscopic nitrogen-doped graphene hydrogels for ultrafast supercapacitor. *Nano Energy*, Volume **2**, 253 (2013).] Copyright (2013) by SciVerse ScienceDirect Publishing Group.

C) to produce stable supramolecular hydrogels. Additionally, the hybrid hydrogels deposited noble metal (Au, Ag, and Pt) nanoparticles were also obtained. Such as rGO hybrid hydrogels matrix with Au nanoparticles was successfully utilized as an efficient catalyst for the reduction of aromatic nitro to amino group (Fig. 6c).

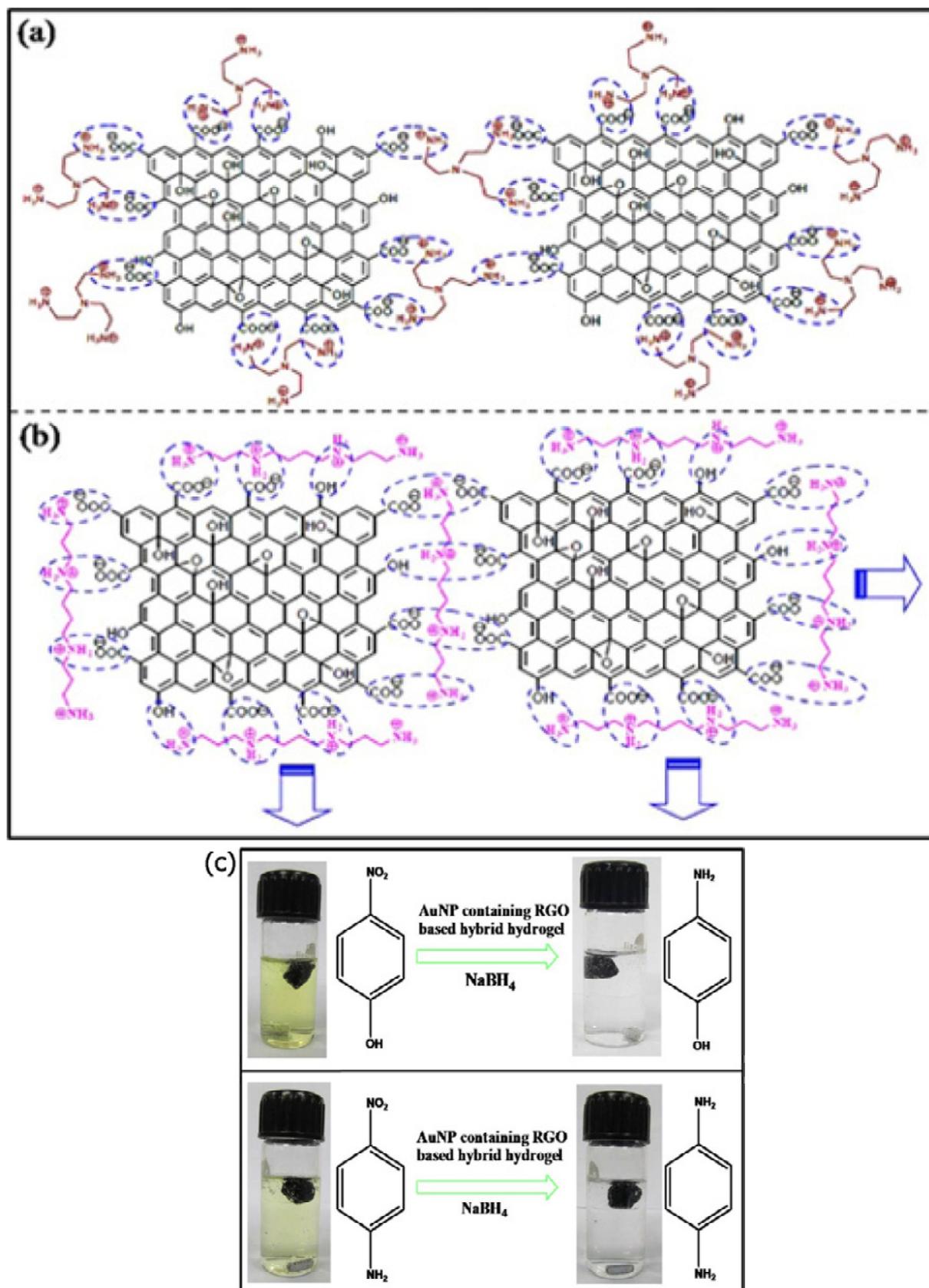
## 2.5. Other methods

Except for the above strategies, there are other approaches for efficiently fabricating GHA, such as supramolecular hybrid hydrogels from noncovalently functionalized graphene with block copolymers [29], TiO<sub>2</sub>-graphene hydrogels [71], synergistically self-assembled carbon aerogels [72] and a pH-respon-

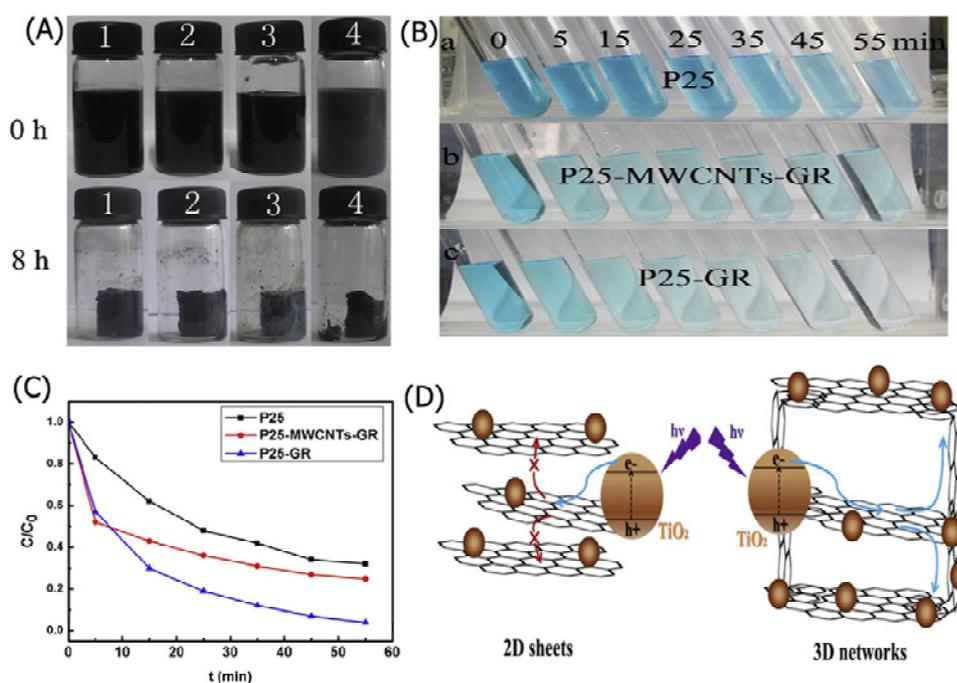
sive GO hydrogel [73]. Notably, these methods are involved in a new possible gelation mechanism, an easier preparation technique, or a more environmental-friendly process, even a new approach for ultraflyweight materials.

A supramolecular route for constructing hybrid hydrogel was proposed by Liu's group [29]. GO nanosheets modified with  $\beta$ -cyclodextrins reacted with block copolymers poly-(N, N-dimethylacrylamide)-b-poly (N-isopropylacrylamide) to form supramolecular hybrid hydrogels by noncovalent interaction.

Low temperature (below 100 °C) synthesis of 3D GHA was seldom reported [74-76]. However, a green, low temperature and simple preparation was designed by Hou's group [71]. They synthesized



**Fig.6.** Tentative Molecular Interaction between GO Sheets and Polyamines [(a) Tris (aminoethyl) amine and (b) Spermine]. (c) Schematic representation of AuNP containing rGO-based hybrid hydrogel catalyzed hydrogenation reactions. Reprinted with permission from [B. Adhikari, A. Biswas and A. Banerjee, Graphene Oxide-Based Hydrogels to Make Metal Nanoparticle-Containing Reduced Graphene Oxide-Based Functional Hybrid Hydrogels. *American Chemical Society Applied Materials & Interface*, Volume 4, 5474-5480 (2012)]. Copyright (2012) by American Chemical Society Publishing Group.



**Fig. 7.** (a) Photographs of initial solutions (0 h) containing GO (1), MWCNTs and GO (2), MWCNTs, P25, and GO (3), P25 and GO (4), respectively, and the obtained hydrogel after the 8 h room-temperature reaction. (b) Photographs of MB solutions with different photocatalyst at a given time interval (c) The corresponding concentration changes of MB during the photo degradation. (d) Schematic diagrams for illuminating the charge behavior at interfaces in 2D P25–GNS and 3D P25–graphene networks. Reprinted with permission from [C.-Y. Hou, Q.-H. Zhang, Y.-G. Li, H.-Z. Wang, P25–graphene hydrogels: room-temperature Synthesis and application for removal of methylene blue from aqueous solution. *Journal Of Hazardous Materials*, Volume **205-206**, 230-233 (2012)]. Copyright (2012) by SciVerse ScienceDirect Publishing Group.

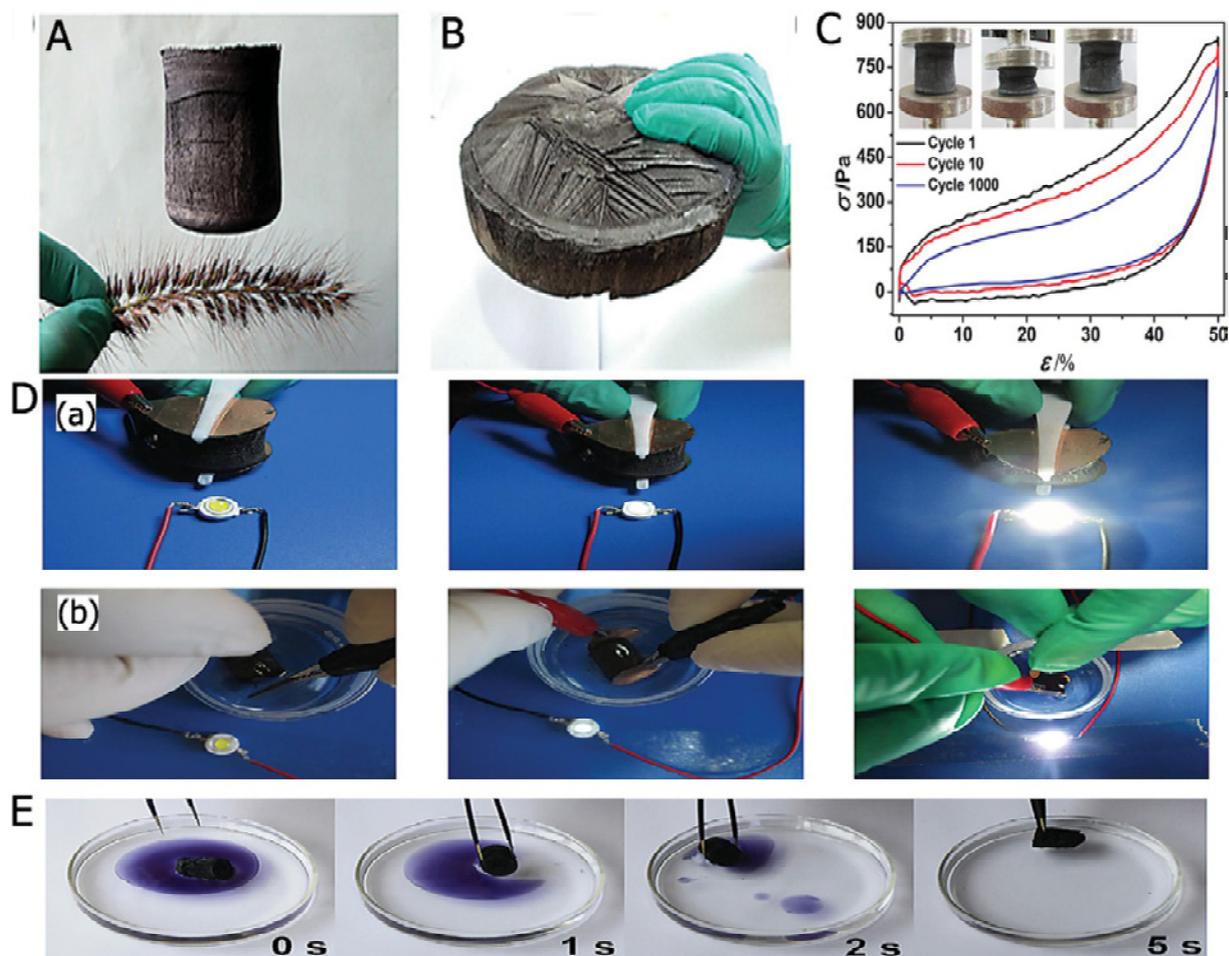
chemically bonded TiO<sub>2</sub> (P25)-graphene composites hydrogels under room-temperature. Multi-walled carbon nanotubes (MWCNTs) or P25 nano-particles functional hydrogels were also acquired at the same condition (Fig. 7a). Fig. 7b shows the phenomenon of photodegradation of methylene blue (MB) under UV light irradiation. P25–graphene sample shows obviously improvement compared with pure P25 and P25-MWCNTs-graphene. Under UV light irradiation, P25-MWCNTs-graphene decomposed about 96% of the initial dyes in less than 1 h (Fig. 7c). The maximum adsorption capacity of methylene blue is 87.63 mg g<sup>-1</sup>. Generally, this phenomenon ascribed to its porous stereo-structure compared to 2D P25–GNS (Fig. 7d).

Ultra-flyweight assembled carbon aerogels (Fig. 8a) with density low to 0.16 mg cm<sup>-3</sup> were made by Sun and coworkers [72]. It is worth mentioning that a “sol-cryo” technology was used to obtain the carbon aerogels with desired densities and shapes such as rods, cylinder, and papers. Moreover, the prepared ultra-flyweight aerogel (UFA) can be easily manufactured in a large-scale (Fig. 8b). A serial of experiments demonstrated that the synergistic

effect between graphene cell walls and carbon nanotube ribs contributed to the good elasticity of UFAs (Fig. 8c). The composites were pressure-responsive, and had fine conductivity and excellent absorption capacity (Fig. 8d and 8e). In addition, a milder, greener and simpler method was reported to achieve GO self-assembly with a critical gel concentration of 30 mg ml<sup>-1</sup>[73]. The GO hydrogel was obtained via directly sonicate GO aqueous for rapidly dispersion without adding any processing steps.

### 3. APPLICATIONS OF GHA FRAMEWORK

GHA can be made by different strategies, which endow them with different properties, such as good mechanical strength, excellent electrical conductivity, thermal stability, improved adsorption capability toward dye, oil or inorganic ion and interconnected stereo-structure micropores/mesopores. These properties facilitate GHA to be used in various fields, such as environmental protection, biomedicine and energy sources.

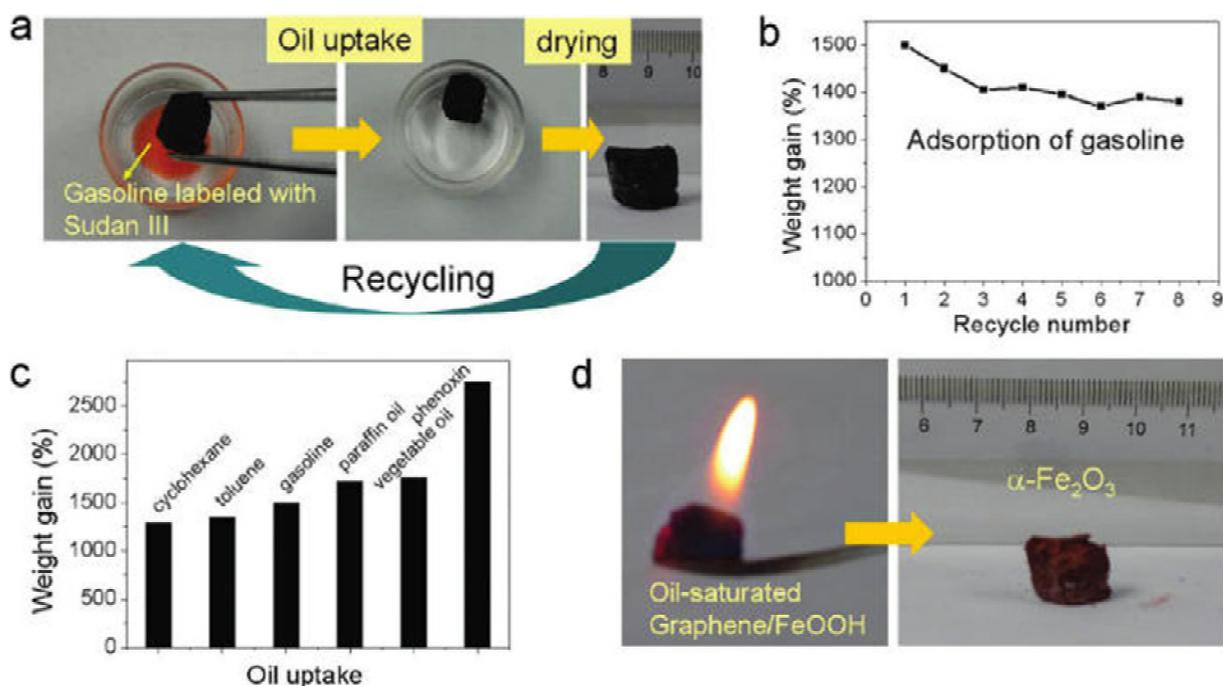


**Fig. 8.** (a) A 100 cm<sup>3</sup> UFA cylinder standing on a lower like dog's tail; (b) A 1000 cm<sup>3</sup> UFA cylinder (21 cm in diameter and 3 cm in thickness). (c) Stress-strain curves of several selected cycles on a UFA during repeated compression. Inset, Photographs of the UFA under fatigue test for 1000 cycles. (d) (a) A circuit constructed with the UFA as lightweight conductive bulk. (b) The circuit constructed with the UFA as ultralight conductive bulk filled with n-hexane. (e) Absorption process of toluene on water by the UFA within 5 s. Reprinted with permission from [H.-Y. Sun, Z. Xu, and C. Gao, Multifunctional, Ultra-Flyweight, Synergistically Assembled Carbon Aerogels. *Advanced Materials*, Volume **25**, 2555-2558 (2013)]. Copyright (2013) by Wiley Publishing Group.

### 3.1. Environmental protection

With the development of industry and agricultural activities, environment pollution is gradually threatening ecological balance and human health, especially toxic gases, heavy metal ions and organic pollutants in air and water. Although various methods have been developed to deal with polluted water [77-80], it is urgent to develop more simple, inexpensive and green methods to prepare adsorption reagents. Adsorption is one of the main strategies to purify water because of its ease of operation and low cost [77,78]. In the past half decade, graphene-based aerogels aroused tremendously hot point due to its good adsorbability. For instance, macroscopic multifunctional GHAs were produced

by Cong and coworkers [13] through a metal ion induced self-assembly process. The graphene/metal oxide aerogels were superhydrophobic and had lots of stable porous structures, so that they exhibited high excellent adsorption capacity and regeneration properties toward oils and nonpolar organic solvents (Figs. 9a and 9c). Interestingly, after the oil-saturated graphene/ $\alpha$ -FeOOH aerogel was burnt, a 3D hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> monolith was obtained (Fig. 9d). In addition, the adsorption capacities of the graphene/ $\alpha$ -FeOOH hydrogel toward Cr (VI) or Pb (II) were confirmed. The calculated maximum adsorption value for Cr (VI) or Pb (II) was 139.2 and 373.8 mg g<sup>-1</sup>, respectively. According to the previous report, mesoporous  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and active carbon toward Cr (VI) was only 15.6 mg g<sup>-1</sup> [77] and 69 mg



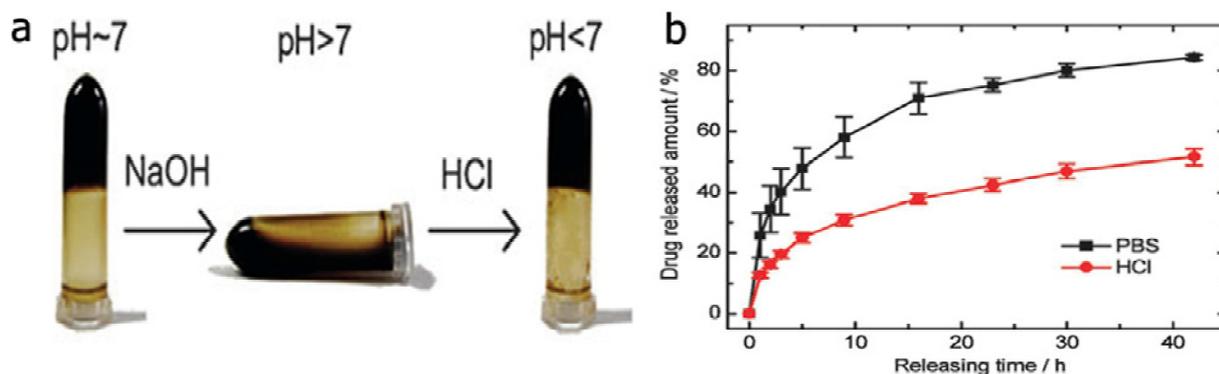
**Fig.9.** (a) Photographs showing the process of the graphene/ $\alpha\text{-FeOOH}$  aerogel adsorbing gasoline. (b) Regeneration capacity of the aerogels for adsorbing gasoline. (c) Adsorption capacities of the aerogels for a range of organic solvents and oils in terms of its weight gain. (d) Photographs of burning the oil-saturated graphene/ $\alpha\text{-FeOOH}$  aerogel. Reprinted with permission from [H.-P. Cong, X.-C. Ren, P. Wang and S.-H. Yu, Macroscopic multifunctional graphene-based hydrogels and aerogels by a metal ion induced self-assembly process. *American Chemical Society Nano*, Volum **6**, 2699 (2012)]. Copyright (2012) by American Chemical Society Publishing Group.

$\text{g}^{-1}$  [79], respectively. Currently, carbon-based materials were regarded as the staple adsorbents for water purification. These materials usually exhibit high capacity towards a certain type of pollutants. Recently, a broad spectrum adsorbent for water purification was reported by Chen's group [36]. They fabricated GO-CS hydrogels with high adsorption capacity towards cationic dyes, anionic dyes and heavy metal ions. A series of experiments were carried out to show that both maximal adsorption capacities towards cationic methylene blue (MB) and anionic Eosin Y were higher than  $300 \text{ mg g}^{-1}$ . Meanwhile, the adsorption capacities of GO-CS hydrogels toward Cu (II) and Pb (II) ions in the concentration range studied were tested to be  $70 \text{ mg g}^{-1}$  and  $90 \text{ mg g}^{-1}$ , respectively. Nevertheless, Qin and coworkers [73] reported that the GO hydrogels had a superior adsorption ability for organic dye rhodamine B ( $350 \text{ mg g}^{-1}$ ) and anionic chromate  $\text{Cr}_2\text{O}_7^{2-}$  ( $140 \text{ mg g}^{-1}$ ). Recently, our group studied applications of graphene-based materials in environmental protection and detection [80]. GO and rGO can form complexes with some metal ions (such as  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Hg}^{2+}$ , etc.) because of many functional groups covered with GO surface, exhibiting excel-

lent adsorption toward heavy metal ions and organic pollutants due to the high porosity.

### 3.2. Biomedicine

Hydrogels have been used extensively in many biological and clinical applications, including drug delivery [81] and tissue engineering [25]. Similar to traditional hydrogels, some graphene-based hydrogels are biocompatible and pH sensitive, so they are potential candidates for controlled drug release, even used as artificial muscle devices [42]. For instance, GO/poly (vinyl alcohol) (PVA) hydrogel is a pH-sensitive and biocompatible composite [28]. As shown in Fig. 10a, the pH-induced gel-sol transition is reversible, and it is ascribed to the different electrostatic repulsion between GO sheets in different pH conditions. To evaluating the drug releasing ability of GO/PVA composite hydrogels, vitamin  $\text{B}_{12}$  (VB<sub>12</sub>) was chose as a model drug. The plots in Fig. 10b expresses the releasing VB<sub>12</sub> from the GO/PVA composite hydrogels in phosphate buffer (pH = 7.4) and hydrochloric acid (pH = 1.7) solutions, respectively. Obviously, the drug release quantity in phosphate buffer is slightly higher than the



**Fig. 10.** (a) Photographs of the pH-induced gel-sol transition. (b) Profiles of releasing VB12 from a GO/PVA composite hydrogel (r P/G = 1: 10) in PBS (pH = 7.4) and HCl (pH = 1.7) solutions. Reprinted with permission from [H. Bai, C. Li, X.-L. Wang, and G.-Q. Shi, A pH-sensitive graphene oxide composite hydrogel. *Chemical Communication*, Volume **46**, 2378 (2010)]. Copyright (2010) by Royal Society of Chemistry Publishing Group.

release value in hydrochloric acid. So it is deduced that the hydrogels can be used to deliver the drugs to the intestine (pH = 6.8–7.4) without much release in acidic gastric juice (pH = 1–2). Moreover, as mentioned above, GO/DNA composite hydrogels have high mechanical strength, excellent environmental stability, high dye-adsorption capacity, self-healing function and bio-compatibility, which endue it a promising potential candidate material used as the tissue engineering, drug delivery in biomedical field. In a subsequent work, it was discovered that a graphene hydrogel by one-step hydrothermal was also used to drug-delivery, tissue scaffolds because of the inherent biocompatibility [9].

### 3.3. Energy sources

In recent years, the potential applications of GHA were explored in energy source field, such as supercapacitors and lithium ion batteries. Supercapacitors are energy storage devices with the properties of fast and reversible storing and releasing of energy, high power densities, long life and high rate capability [82–84]. The theoretical value of specific capacitances of single-layer graphene was calculated  $550 \text{ F g}^{-1}$  [85]. While, chemically modified graphene-based supercapacitor has specific capacitances of 135 and  $99 \text{ F g}^{-1}$  in aqueous and organic electrolytes, respectively [1]. The values are obviously lower than the theoretical value. Carbon materials, especially GHA, have highly open porous structures and facile routes for electron and electrolyte transportations in the interconnected networks. Thus, carbon materials were usually used as an electrode for supercapacitor [9]. As mentioned above, nitrogen-doped graphene hydrogel show

ultrafast charging rate and much higher power density in contrary to most graphene-based materials [86–89]. In addition, a versatile, ultralight, nitrogen-doped graphene framework was obtained by mixing GO and 5 vol.% pyrrole [70], and its specific capacitance was estimated as  $484 \text{ F g}^{-1}$  approaching the theoretical value of  $550 \text{ F g}^{-1}$ . Up to now, it is the highest value achieved for graphene electrodes. In a word, GHA with superior capacitance may have potential applications as ultrahigh power density capacitors in the vehicle, life and the other devices at high rates.

Rechargeable lithium ion batteries, as electrochemical energy storage and conversion devices, are widely used in various civil and military portable electronic equipment, such as laptop, cell phone, flash-light. As early as 2011, 3D networks of magnetic graphene/ $\text{Fe}_3\text{O}_4$  aerogels was successfully prepared by Chen and coworkers [90], which can be used as anode materials for lithium ion batteries. Such a 3D hybrid showed good performance. When the current density was below  $800 \text{ mA g}^{-1}$ , the capacity was up to  $990 \text{ mA h g}^{-1}$ , and even at a current density of  $1600 \text{ mA g}^{-1}$ , it still remained at  $730 \text{ mA h g}^{-1}$ .

## 4. CONCLUSIONS AND PERSPECTIVES

In this article, we summarized recent progresses on the preparation strategies, formation mechanisms and prospected applications of GHA. To achieve versatile, high-performance graphene-based materials, more investigative should be carried out in the future. Firstly, GO, as a key origin materials for graphene-based gels, has some drawbacks (such

as undefined structure, random distribution of oxygen containing groups on the surface [91]) that adverse to graphene nanosheets self-assemble. Therefore, inexpensive and controlled oxidization /exfoliation protocols for graphite to synthesis GO with one or few layer, a defined shape and number of oxygenated groups are urgently demand. Secondly, graphene-based gels provide with excellent mechanical, wonderful thermally stable, ultra-light, and high specific capacitance. While compared with the traditional soft smart or intelligent hydrogel, it exhibits a discontinuous volume phase transition between a swollen state and a collapsed state, in case it undergoes external stimuli, such as temperature, pH, pressure, and solvent composition [92-94]. Additionally, the slow response of bulky graphene gels is challenging for their being developed technologically. Thirdly, all above achievements are still in the stage of laboratory investigation and few of them have been in commercial production, especially the applications of graphene-based aerogels in environmental protection field, hydrogels in biochemical field and energy sources field. Therefore, a simple, mild, inexpensive, environmental-friendly preparation method of GHA is necessary in the future investigation.

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