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Graphene Oxide/Reduced Graphene Oxide Aerogels

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Abstract

In this chapter, we will discuss aerogels based on graphene oxide/reduced graphene oxide—promising composite materials, based on 2D carbon nanoparticles, with a certain architecture that prevents aggregation of graphene layers with a highly developed surface that have a high potential technological realization as materials for supercapacitors, sensors, batteries, and actuators. This chapter describes the existing methods for producing composite aerogels based on graphene oxide/reduced graphene oxide, the structural features of these materials, the most relevant studies in the areas of surface modification, architectural control, improvement of mechanical properties, and the most interesting applications. It has been shown that such materials have relatively high specific surface values and a high degree of exfoliation of graphene layers, but an urgent need is to improve them, which is due to the fragility of graphene aerogels and composite materials based on them, as well as the need to modify the surface to control porosity.

Keywords: graphene oxide aerogels, reduced graphene oxide aerogels, self-gelation, cross linking, hydrothermal synthesis, highly porous materials, carbon based materials

1. Introduction

At present, one of the most urgent topics in science is the creation of aerogels based on reduced graphene oxide. Their high porosity, characterized by low material density and high specific surface area, as well as the ability to conduct electric current attracts the attention of various groups of scientists. The work on the creation of such materials has been conducted for the past 20 years. A number of materials developed during this time and approaches to their production form a serious prospect for the use of these materials as supercapacitors, gas sensors, electric batteries, and actuators. The increased interest in graphene oxide as a

precursor of such materials is due to its ability to form stable colloidal dispersions in polar solvents (such as water) and also to transform into a reduced electrically conductive graphene-like form under chemical or thermal treatment. In addition, the ability of such materials to multi-cyclic deformations, flexibility, and elasticity attracts special interest of researchers. The rapid growth of publication activity in this theme in recent years is partly due to the need for the development of portable electronic devices, in particular, energy storage devices that are included in the everyday life of each person. In the development of aerogels based on reduced graphene oxide, the authors are striving to increase the electrical conductivity, the specific surface area, the mechanical strength, elasticity, and durability of these materials. The part of the science effort was aimed at studying the methods of obtaining aerogels from reduced graphene oxide. It has been shown that the main and most effective methods for the formation of superporous ultralight structures are self-gelation of graphene oxide containing systems, hydrothermal-assisted formation of aerogels, cross-linking of a structure, followed by freeze drying or supercritical drying. Each of the described methods has its advantages and disadvantages, which are effectively being used to achieve the target parameters of synthesized materials. To improve the obtained structures and give them new properties, the surface of graphene-like sheets is being modified in various ways: various polymeric materials are being introduced into the structure, the surface is being decorated with metal particles, the materials are being doped with nitrogen, etc. The application of these approaches made it possible to significantly improve the mechanical, electrophysical, catalytic, and sorption properties of aerogels and allow obtaining materials with controlled architecture and unique morphology of the surface. The latest achievements in this area will be discussed in this chapter.

2. Synthesis of reduced graphene oxide aerogels

Unique structures and attractive properties of reduced graphene oxide (rGO)-based 3D materials were the reasons to establish a number of approaches for fabrication of those materials with controlled regular structure. The main methods of organization of such structures are self-gelation of graphene oxide (GO) containing systems, hydrothermal-assisted formation of aerogels, and cross-linking of a structure. Almost all these methods need a support of freeze drying or supercritical drying due to ability to prevent stacking of graphene oxide/reduced graphene oxide sheets during drying process. The absence of mobility of the GO/RGO layers and the fixation of the dispersion structure make it possible to obtain materials with a high porosity, a high specific surface area, and a high degree of exfoliation of the graphene-like sheets in the final material.

As a rule, freeze drying of the samples leads to the formation of a large number of macropores. This is due to the fact that during the freezing of the sample, ice crystals are formed, which displace part of the material from its volume, which leads to local structural irregularities and the formation of macropores in place of the crystals after they are removed from the matrix during the drying process. It is clear that the size of the ice crystals is highly dependent on the freezing speed of the material, but even the use of liquid nitrogen for freezing does not avoid macroporosity due to the low thermal conductivity of nitrogen. Supercritical drying leads to

the formation of a uniform microporous structure. Both approaches lead to the formation of ultralight porous structures with highly developed morphology, but each of them has its advantages. For example, the presence of macropores provides a large number of diffusion paths for various molecules and ions, which is an undoubted advantage for a number of applications.

Various organic and inorganic reducing agents are used. Zhang et al. used L-ascorbic acid to obtain a mechanically strong and electrically conductive aerogel [1]. The authors showed that, in contrast to other reducing agents (NaBH_4 , LiAlH_4 , hydrazine), the reduction with L-ascorbic acid does not lead to the formation of reaction by-products that significantly affect the uniformity of the structure of the synthesized aerogel. NaHSO_3 , vitamin C, Na_2S , ammonia boron trifluoride, sodium ascorbate, and hydroquinone have also been used by various investigators to form aerogels based on reduced graphene oxide [2, 3]. Aerogels based on reduced graphene oxide have also been obtained using a new inexpensive, environmentally friendly reducing medium that combines oxalic acid and sodium iodide [4]. The materials showed a low density, high porosity structure, and electrical conductivity. Yang et al. have developed a light, environmentally friendly, mild method of forming aerogel by thermal evaporation of a suspension of graphene oxide in the presence of NaHCO_3 [5]. This approach is based on in-situ reduction to form an rGO aerogel. The aerogel based on the reduced graphene oxide was also synthesized using the hypophosphorous acid reduction process and I_2 [6]. He showed a large surface area of $830 \text{ m}^2/\text{g}$. Typically, the reduction with chemical agents is carried out in a liquid medium; however, in work [7], an interesting approach was first proposed for the reduction of the aerogel of graphite oxide with hydrazine vapor at room temperature after drying. The authors showed that the reduction has explosive character, and the resulting material practically does not differ from the material obtained by thermal shock reduction at 600°C (Figure 1). Also, various organic amines are used as reducing agents.

2.1. Gelation of graphene oxide followed by drying

The simplest and most effective way to produce three-dimensional materials from graphene-like sheets is to obtain a hydrogel from graphene oxide, followed by removal of the solvent by drying. It is known that a stable dispersion of graphene oxide is formed at a certain concentration [8] due to the optimal ratio of the forces of electrostatic repulsion due to the huge number of oxygen-containing functional groups on the basal plane of the particles and the van der Waals interaction of monolayers. Gelation of suspensions occurs when the balance between these forces is violated and leads to the stratification of the particles of graphite oxide on the monolayers of graphene oxide (Figure 2).

The process of gel formation depends on many factors: van der Waals interaction, n-n stacking, the formation of hydrogen bonds, and electrostatic interaction [9]. The most important factor is also the concentration of suspensions, but the data on the optimal concentration are quite different. It has been shown that the optimal concentrations of gelation when exposed to ultrasound in a suspension of GO are 30 mg/ml and $0.075\text{--}0.125 \text{ mg/ml}$ in different cases [10], but the aerogel obtained in the second case had a weak mechanical strength. In the work of Bai et al. [11], the optimal concentration was 4 mg/ml . Such a strong difference in the results, in our opinion, is due to several factors. The first of these is the method for obtaining

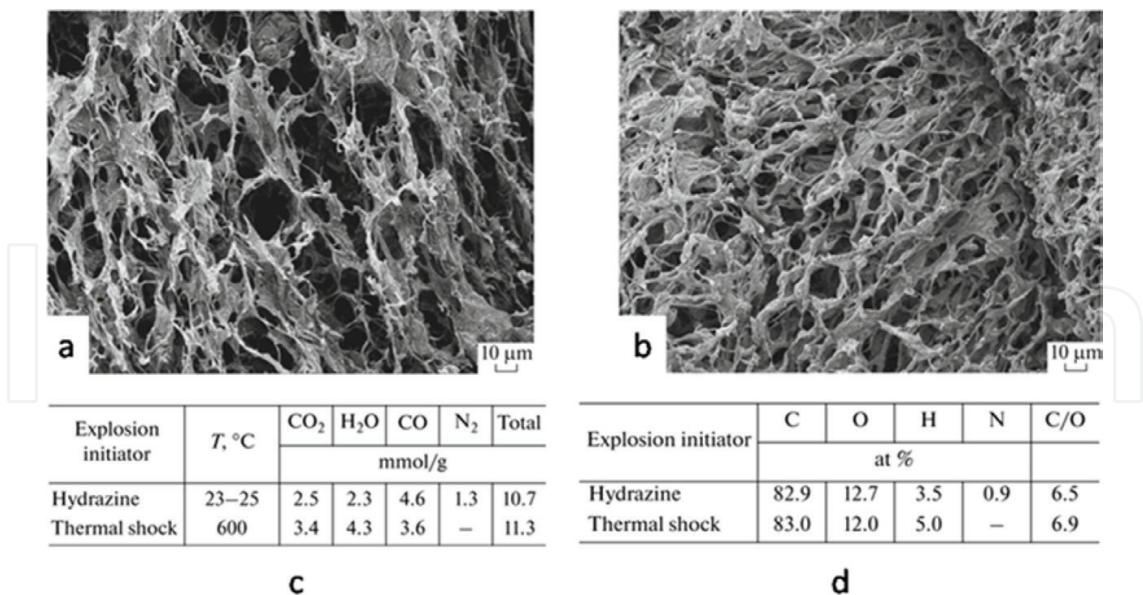


Figure 1. Micrographs of materials obtained by explosive reduction of graphite oxide aerogel by (a) thermal shock and (b) hydrazine vapor. (c) Gaseous products of explosive reduction of graphite oxide aerogel by thermal shock and by hydrazine vapor. (d) Comparison of the elemental compositions of materials obtained by explosive reduction of graphite oxide aerogel by thermal shock and by hydrazine vapor [7].

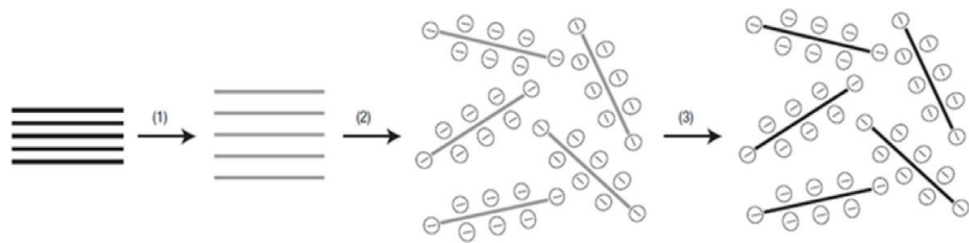


Figure 2. Scheme showing the chemical route to the synthesis of aqueous graphene dispersions. 1, Oxidation of graphite (black blocks) to graphite oxide (lighter colored blocks) with greater interlayer distance. 2, Exfoliation of graphite oxide in water by sonication to obtain GO colloids that are stabilized by electrostatic repulsion. 3, Controlled conversion of GO colloids to conducting graphene colloids through deoxygenation by hydrazine reduction [8].

a dispersion of graphene oxide. In the case where the critical gelling concentration is high, the dispersion is typically prepared by redispersing the sample of graphite oxide (in the form of a film or powder) air dried at an elevated temperature (typically $T = 60^{\circ}\text{C}$). As practice shows, this method leads to the staking of monolayers and their redispersion is greatly hampered, which leads to a significant decrease in the ability to form a spatial grid and to gel. On the contrary, if the dispersion is prepared bypassing the drying stage of the product under such conditions (for example, by purifying the product from acids by dialysis), the self-gelation of dispersion occurs at substantially lower concentrations, even in the absence of ultrasonic treatment. The second factor is the size of the basal plane of the particles of graphene oxide, which is rarely taken into account in the processes of self-gelation of GO dispersions. This is due to the fact that it is rather difficult to obtain particles of graphene oxide with a given basal plane size. It is clear that the interaction of particles of different sizes should be completely different, but there are no dependencies of this kind in the scientific literature. The third factor

is, at times, quite a noticeable difference, including in the chemical composition, of the graphene oxide itself (**Figure 3**), obtained from different types of graphite [12].

2.2. Hydrothermal-assisted formation of reduced graphene oxide aerogel

Hydrothermal synthesis is a method of obtaining various chemical compounds and materials using physicochemical processes in closed systems that occur in aqueous solutions at temperatures above 100°C and pressures above 1 atm. In graphene systems, this process is realized at temperatures close to the effective reduction temperature of graphene oxide (200°C), using various reagents that can influence the structure and chemical composition and target physical properties of aerogels.

One stage hydrothermal synthesis of aerogel from reduced graphene oxide (**Figure 4a–f**) was first proposed by Xu et al. [13]. The work shows that the aerogel obtained by this method is mechanically strong (after 12 hours of hydrothermal treatment at T = 180°C, the sample demonstrated an elastic modulus of 290 ± 20 kPa), could support 100 g of weight with little deformation, and has good electrical conductivity (4.9 ± 0.2 mS/cm), thermal stability, and high specific capacity (160 ± 5 F/g). It should be noted that the initial concentration of hydrogel

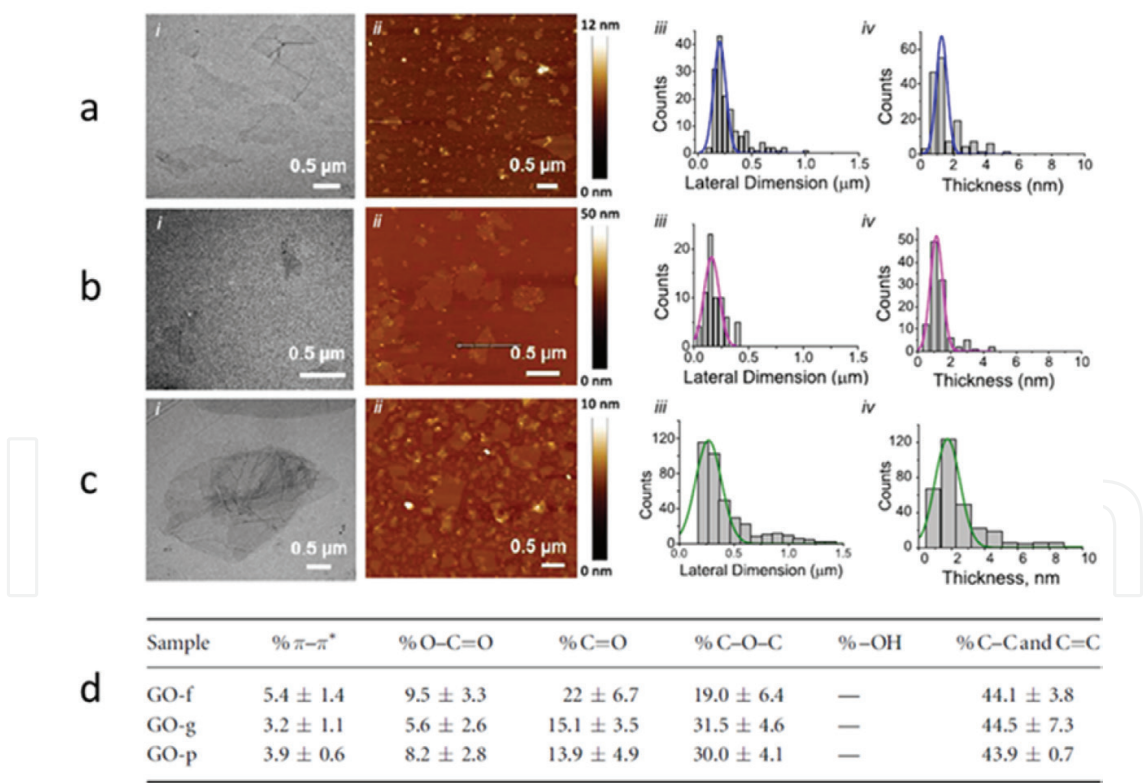


Figure 3. Structural characterization of (a) GO-f, (b) GO-g, and (c) GO-p. TEM analysis (i), AFM height imaging (ii), lateral size distribution (iii), and thickness distribution (iv). The analysis in (iii) and (iv) was based on counting approximately 100 sheets captured in several AFM images. (d) Quantification of $\pi-\pi^*$, carboxylic groups (O—C=O), carbonyls (C=O), epoxides (C—O—C), hydroxyls (C—OH), and graphitic structure (C—C and C=C) by high resolution C1s XPS spectra for GO-f, GO-g, and GO-p [12]. Three different GO thin sheets were synthesized from three starting graphite material: flakes (GO-f), ground (GO-g), and powder (GO-p).

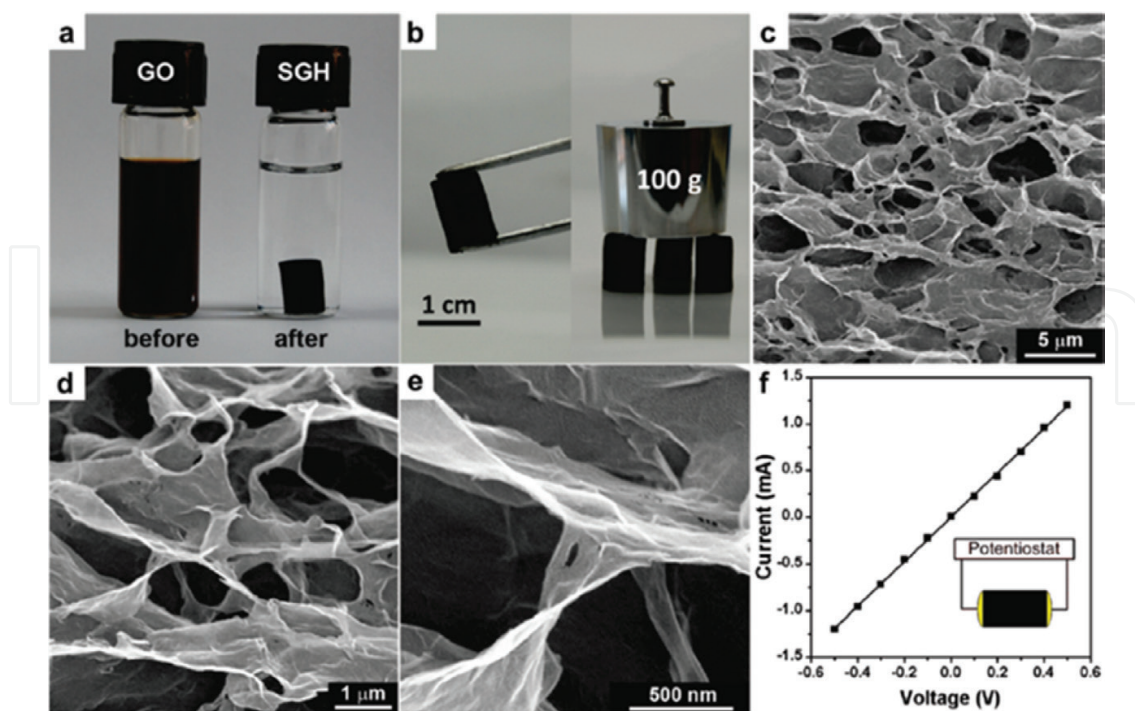


Figure 4. (a) Digital photographs of a homogeneous GO aqueous dispersion with a 2 mg/mL concentration before and after hydrothermal reduction at 180°C for 12 h; (b) photos of a strong self-assembled graphene hydrogel; (c–e) SEM images with different magnifications of the strong self-assembled graphene hydrogel interior microstructures; and (f) room temperature I - V curve of the strong self-assembled graphene hydrogel exhibiting Ohmic characteristic by the two-probe method for the conductivity measurements [13].

oxide graphene was only 0.5–2 mg/mL, which was enough to the self-gelation of GO dispersion. It is also shown that the concentration of dispersion of graphene oxide is an important factor affecting the process of aerogel structure formation and its final properties. A study of the dependence of rGO aerogel properties on the time of hydrothermal reaction showed that with increasing thermal treatment time both mechanical and electrophysical characteristics of aerogel are improved.

Using the features of a closed environment allows the in-situ modification of rGO aerogels [14]. In his work, a method for forming a three-dimensional structure of reduced graphene oxide with noble metals was developed by hydrothermal reaction of a suspension of graphene oxide containing noble metal salts and glucose. The obtained material, containing Pt in the structure (**Figure 5d–f**), demonstrated high catalytic activity. Other authors have shown that using a hydrothermal reduction process for graphene oxide in the presence of divalent metal ions (Ni^{2+} , Ca^{2+} , Co^{2+}), an aerogel of rGO decorated with metallic nanoparticles (**Figure 5a–c**) can be obtained in-situ [15]. A lot of work is devoted to the processes of decorating the particles of reduced graphene oxide in aerogels with various metal oxides. In particular, the great attention of researchers is attracted to Fe_3O_4 [16–18]. Special attention is also paid to the process of doping rGO aerogels with nitrogen. Doping with nitrogen by introducing into the system organic amines, ammonia, amino acids, and other nitrogen-containing compounds, at the stage of hydrothermal treatment, leads to a

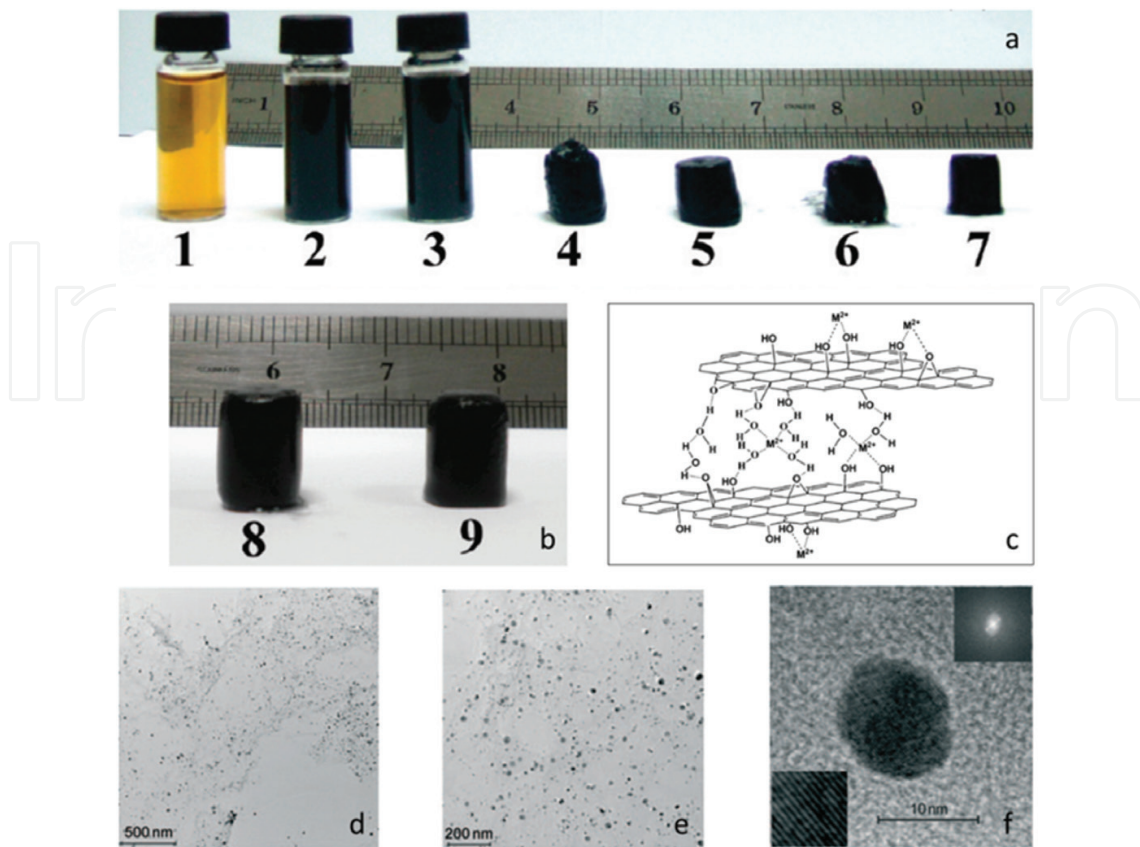


Figure 5. (a) Digital photographs of the GO before and after hydrothermal treatment: (1) GO, (2) rGO, and (3) rGO mixed with Ca²⁺ (m_{Ca}/m_{GO} is 0.003) suspensions as well as the gel-like rGO cylinders assembled by Ca²⁺. Various m_{Ca}/m_{GO} were used: (4) 0.005, (5) 0.010, (6) 0.050, and (7) 0.100. (b) Photographs of the gel-like rGO samples assembled by (8) Ni²⁺ and (9) Co²⁺ with metal-ion/GO weight ratio of 0.010 [15]. (c) Schematic illustration of gel formation of rGO with divalent ion (M²⁺) linkage. (d–f) TEM images of graphene oxide decorated with Pd nanoparticles [14].

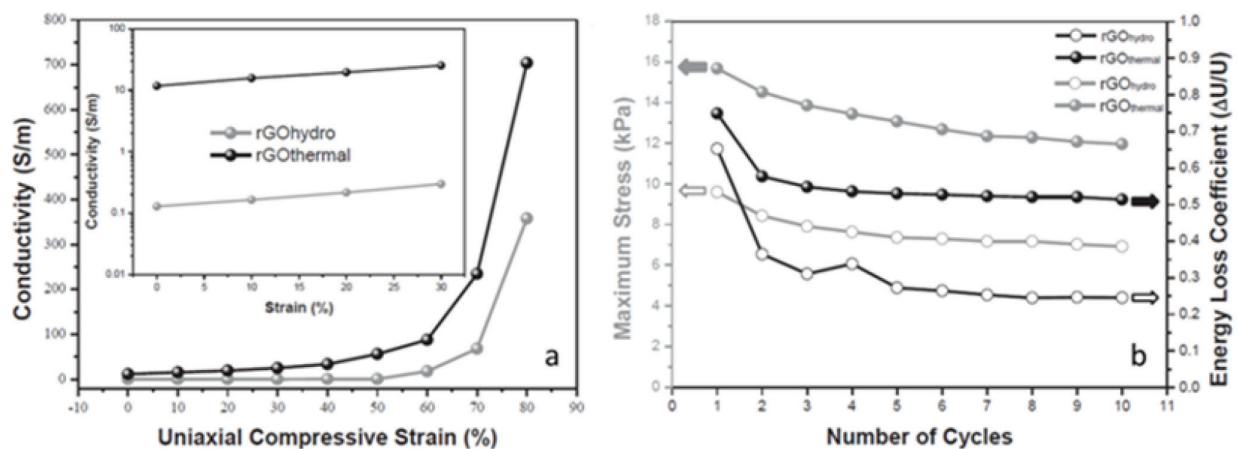


Figure 6. (a) Electrical conductivity of rGOhydro (prepared by hydrothermal synthesis) and rGOthermal (prepared by thermal annealing) aerogels when compressed along the axial direction. (b) Maximum stress (left pointing arrows) and energy loss coefficient (right pointing arrows) of rGO thermal aerogel during 10 cycles [23].

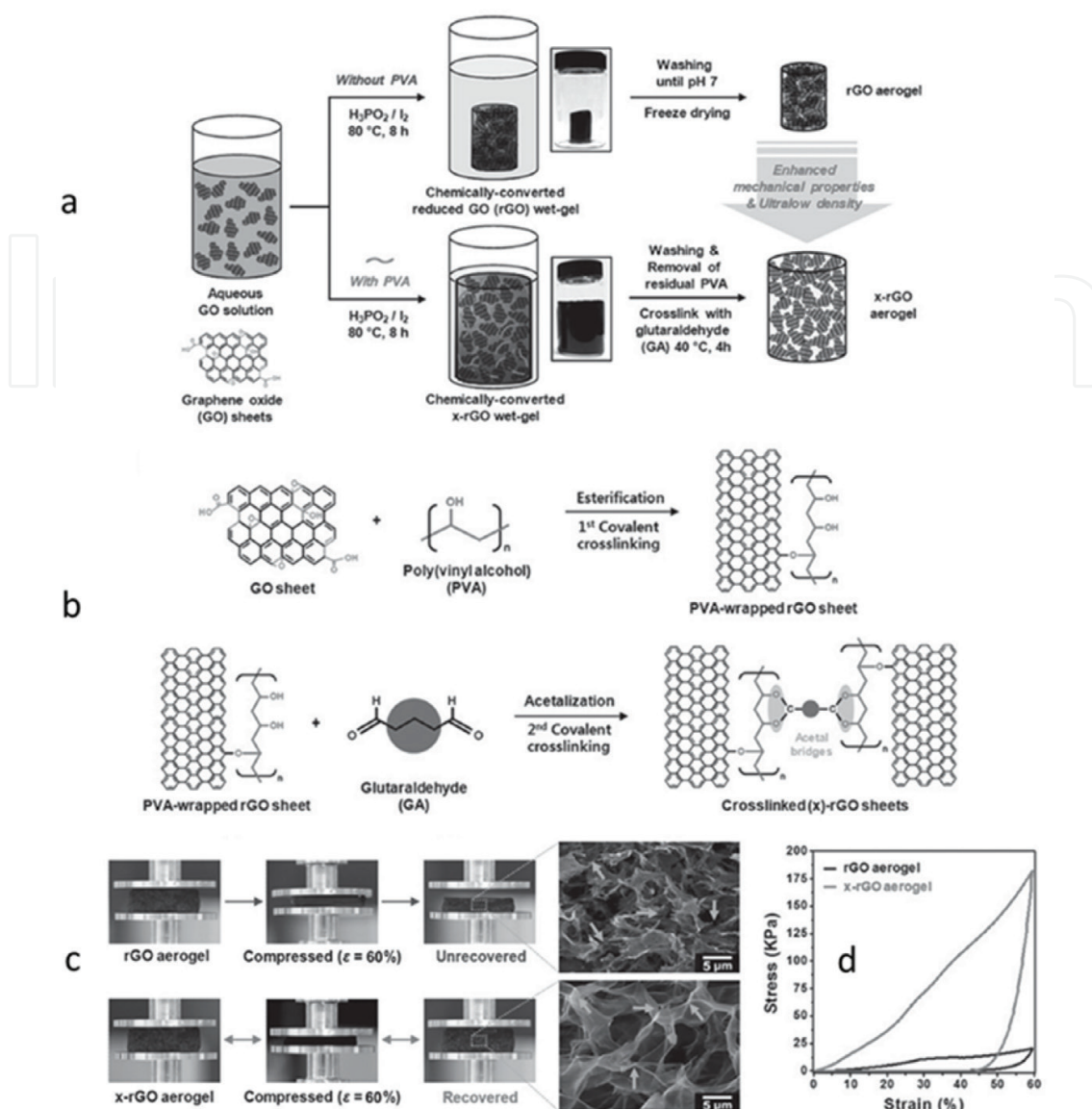


Figure 7. (a) Illustration of the different steps for fabricating the rGO (chemically converted reduced GO) aerogel and x-rGO (cross-linked rGO) aerogel. Insets at center: Digital photographs depict the as-prepared chemically converted rGO wet-gel and x-rGO wet-gel (top and bottom, respectively) after the self-assembly process. (b) A possible cross-linking mechanism between PVA-wrapped rGO sheets and Glutaraldehyde. PVA-bonded rGO sheets were covalently cross-linked by an acetal oxygen bridge through esterification reaction. (c) Digital photographs and SEM images (from left to right) of rGO and x-rGO aerogels after compression with 60% strain. Arrows indicate the material areas of deformed and recovered after the compression for rGO and x-rGO aerogels, respectively. (d) Compressive stress-strain curves were plotted with 60% strain for rGO and x-rGO [25].

significant increase in the electrophysical characteristics of aerogels from reduced graphene oxide [19–21], improves electrocatalytic properties [22], and also contributes to obtaining a more regular structure of the aerogel itself.

Moon et al. developed highly elastic and conductive N-doped monolithic graphene aerogels, using hexamethylenetetramine as a reducing agent, a nitrogen source, and a dispersion stabilizer of reduced graphene oxide [23]. To produce this material, hydrothermal synthesis was used, followed by annealing at $T = 1000^\circ C$. The developed material showed good mechanical properties

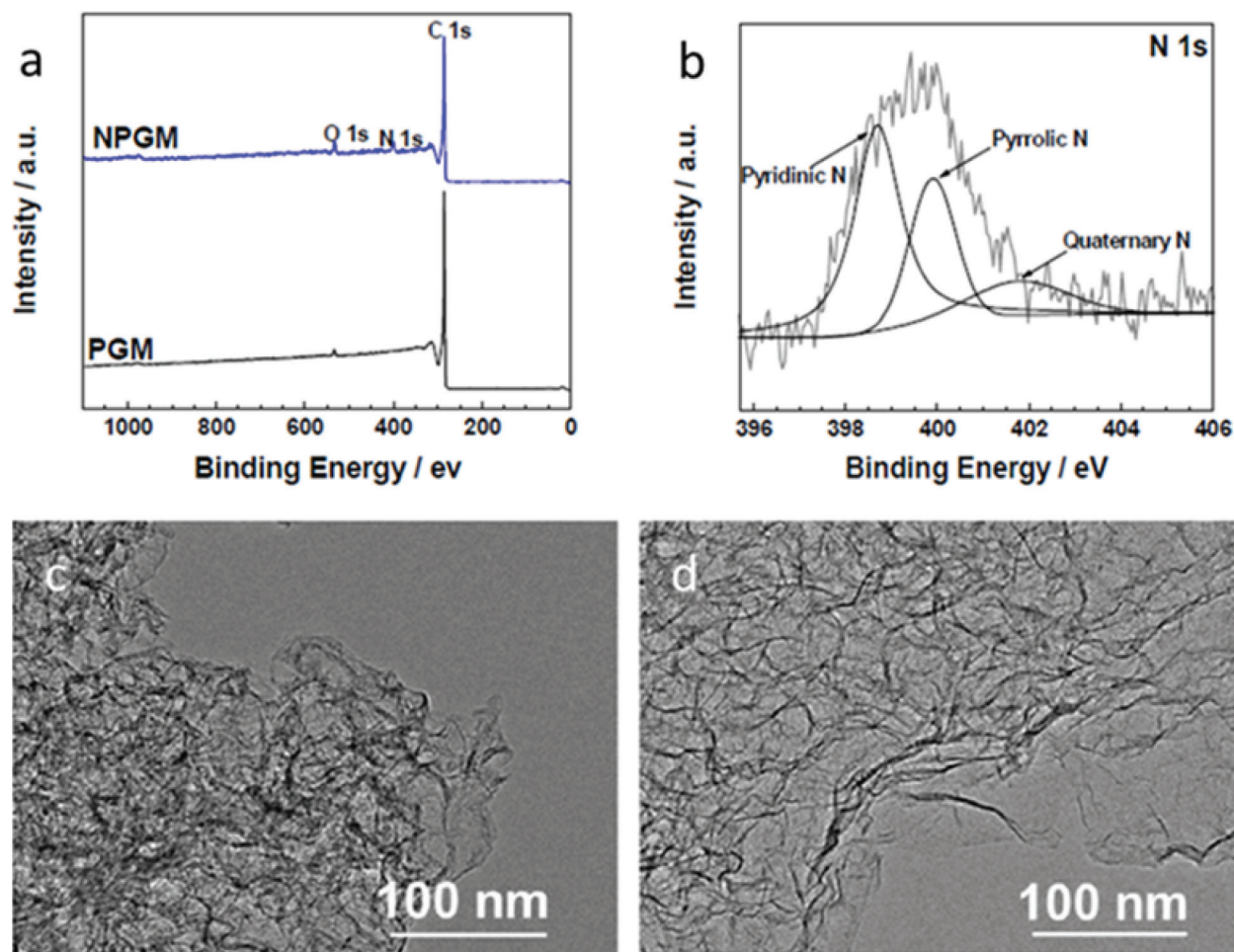


Figure 8. (a) XPS full spectrum of NPGM (nitrogen-doped porous graphene material) and PGM (porous graphene material). (b) N1s spectrum of NPGM. TEM images of NPGM (c) and PGM (d) [27].

(**Figure 6b**) and record electrical conductivity of 704 S/m for aerogels based on the reduced graphene oxide (**Figure 6a**). It has also been reported that ammonia is an effective agent for the production of nitrogen-doped aerogels [24]. The authors showed that when ammonia is introduced into the hydrothermal synthesis reactor, the degree of doping of the reduced graphene oxide is sufficiently high (8.4 atomic %) and the material has a high specific surface area of 830 m²/g.

2.3. Polymer-assisted aerogel formation

Polymer-assisted aerogel formation with a cross-linking approach consists of the use of polymer components capable of binding to monolayers of graphene oxide, creating steric hindrances for stacking layers into stacks and reducing the available surface. The first version of this approach is the chemical bonding of polymer chains to graphene oxide particles. Reversibly deformable, highly elastic and strong aerogels based on reduced graphene oxide [25] have been developed using this method (**Figure 7**). Poly(vinyl alcohol) and glutaraldehyde were used as cross-linking components. The scheme of the processes is shown in the figure. Hypophosphorous acid and iodine were used as reducing agents. It is important to note that in addition to the high porosity of 92.16% and the low density of 10.6 mg/cm³, the

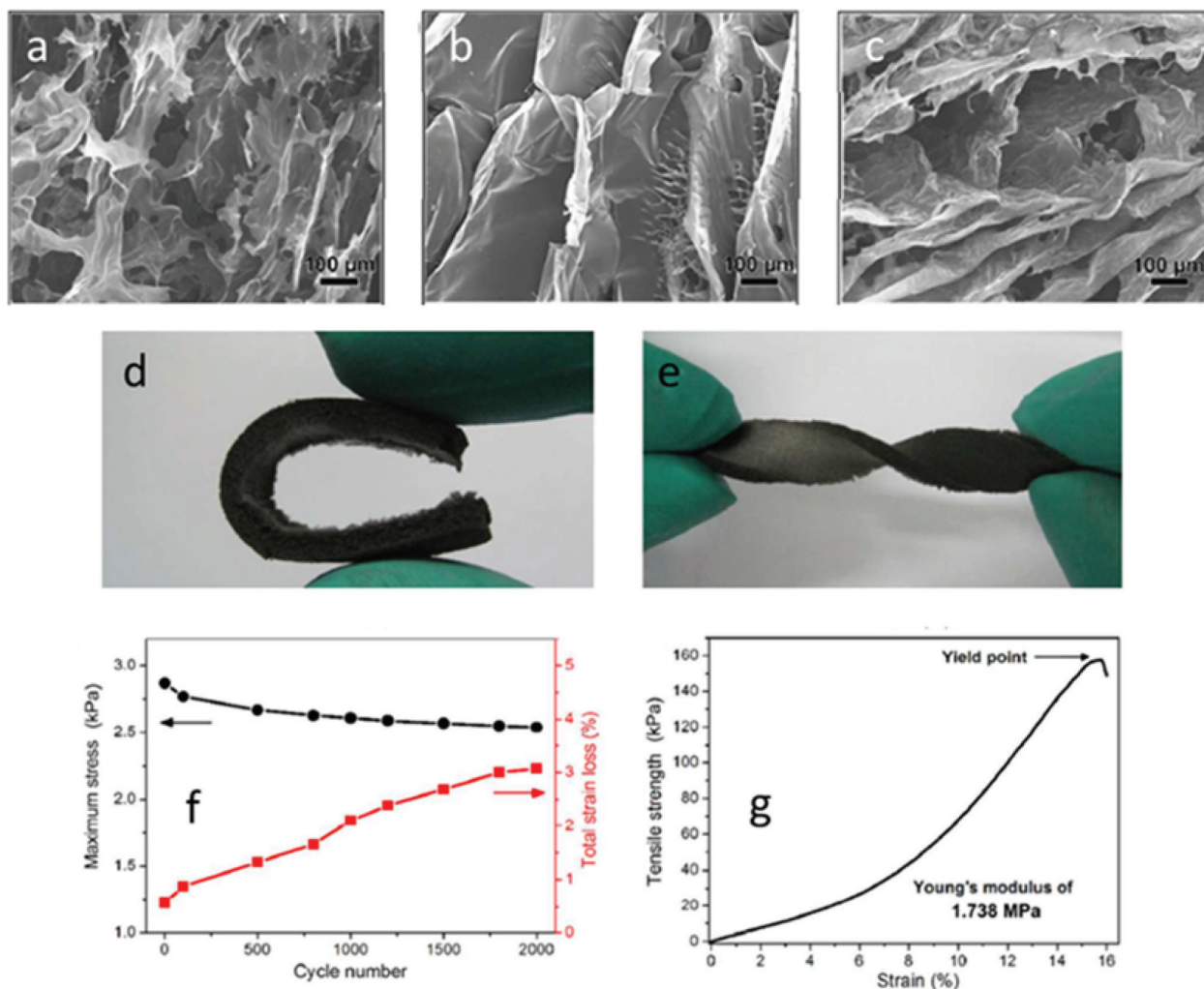


Figure 9. (a–c) SEM image of rGO aerogel, PI monolith, and rGO/PI nanocomposite, respectively. (d, e) Digital images show the high-level deformation of bend and torsion of rGO/PI nanocomposite. (f) Retention of maximum stress at 50% strain and total loss during 2000 cycles. (g) Tensile σ - ϵ curve for the rGO/PI [30].

combination of polymer chains and graphene oxide layers led to the mechanical strength of the material, whose structure was not fundamentally changed even after deformation by 60% (**Figure 7c**). Therefore, x-rGO aerogel exhibits 8.6 times higher compressive stress as compared with rGO aerogel (**Figure 7d**).

The second cross-linking option is the use of sol-gel technology, which is the preparation of a sol followed by its conversion to a gel-colloid system consisting of a liquid dispersion medium enclosed in a spatial grid formed by the connected particles of the dispersed phase. For the first time to produce aerogels based on reduced graphene oxide, this technology was applied by Worsley et al. [26]. The authors proposed the use of polymerization of resorcinol and formaldehyde in the presence of sodium carbonate in an aqueous dispersion of graphene oxide. The obtained material showed an increased electrical conductivity (~ 102 S/m) compared to the reduced graphene oxide (~ 0.5 S/m), as well as a high specific surface area of 584 m²/g. Later Sui et al. also obtained an rGO aerogel with a high degree of nitrogen doping (5.8 atomic %), having

a surface area of 1170 m²/g [27] by sol-gel technology (**Figure 8**). The material was synthesized by freeze-drying an rGO/melamine-formaldehyde hydrogel and subsequent thermal treatment.

A third option for the formation of cross-linked aerogels is the polymerization of monomers in-situ in the presence of a dispersion of graphene oxide. Various polymers such as pyrrole [28] and aniline [29] have been used for this approach. Zhao et al. proposed a unique approach to the production of aerogel by hydrothermal reaction of graphene oxide with pyrrole, followed by electrochemical pyrrole polymerization [30]. The material showed excellent resistance to high loads without significant structural deformation and loss of elasticity. Qin et al. have developed a unique superelastic aerogel consisting of reduced graphene oxide and polyimide [30]. For its preparation, the introduction of a water-soluble polyamido acid into a dispersion of graphene oxide followed by lyophilization and thermal annealing was used. This aerogel showed extremely low density, excellent flexibility, the possibility of multiple reversible deformations (even after 2000 cycles), and good electrical conductivity (**Figure 9**). Li et al. proposed a utilization of in-situ polymerization of acrylamide to create rigid 3D structures based on reduced graphene oxide [31].

3. Applications of reduced graphene oxide aerogels

The first and the most developing direction of applications is the use of such aerogels as active electrode materials for supercapacitors. The supercapacitor is an electrochemical device for storage of electric energy on the surface of highly porous materials with an organic or inorganic electrolyte. At the heart of the work of supercapacitors, there are two processes—the formation of a double electrical layer at the material/electrolyte boundaries and electrochemical reactions on the surface of the electrode material, leading to the appearance of pseudocapacitance [32]. Both processes occur on the surface of the material during the charge/discharge of the device, so the energy capacitance of these devices is highly dependent on the surface area of the aerogels used. The combination of an electrically conductive three-dimensionally connected structure and good electrical conductivity of graphene-like materials makes them extremely attractive for this application. The high specific surface area of aerogels based on the reduced graphene oxide provides high capacity on a double electrical layer. To introduce a pseudocapacitive component, the aerogel surface is ordinarily decorated with transition metal oxides (Mn, V, etc.) capable of participating in redox reactions during charge/discharge of the device, making a significant contribution to the overall capacitance value [33–36]. Also interesting is the direction in the creation of flexible supercapacitors. In the framework of this direction, in addition to the reduced graphene oxide, various polymers are introduced into the aerogel, such as glucose [37], polyvinyl alcohol [25], polyaniline [38], etc.

The second, but not less interesting and intensively developing, direction is the use of aerogels based on reduced graphene oxide for rechargeable lithium-ion batteries. Graphene-like materials are the most widespread anode materials in commercial Li-ion batteries [39, 40]. The main role of rGO aerogel is to facilitate the multidimensional electronic transport routes and to reduce transport spaces between the electrode and the electrolyte. The consequence

of this is an increase in the performance of the batteries and their cyclic stability. Sometimes, rGO aerogels containing metal, metal oxide, and metal sulfide are used as hybrid materials for the cathode of Li-ion batteries [41]. Similar structures containing Fe_3O_4 [42, 43] and Fe_2O_3 [39] show promising capacities ($900\text{--}1100 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$) with good cyclicity. SnO_2 is also used as an integral part of the FOG aerogel for this application [44]. Batteries with this material also show high performance ($600\text{--}1200 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$) [45].

Three-dimensional electroconductive structures of rGO aerogels are an excellent platform for creating electrochemical sensors, strain gauge sensor, and biosensors. Introduction to the structure of metals, oxides, and hydroxides of metals provides high sensitivity and electrochemical stability [46]. Ultraelastic aerogels based on rGO and carbon nanotubes were fabricated for use in a strain gauge sensor with adjustable voltage/pressure measurement [47]. The sensitivity is adjusted by changing the aerogel density. In the compression test, the measurement coefficient was 230 and 125% for deformations of 30 and 60%, respectively. The aerogel containing gold nanoparticles in its structure was used for the electrochemical determination of hydroquinone and o-dihydroxybenzene [48]. The detection limit is $1.5 \times 10^{-8} \text{ M}$ for hydroquinone and $3.3 \times 10^{-9} \text{ M}$ for o-dihydroxybenzene.

In the technique, actuators are transducers that convert an input signal (electrical, optical, mechanical, pneumatic, etc.) into an output signal (usually in motion) that acts on the control object. Devices of this type include electric motors; electric, pneumatic, or hydraulic actuators; relay devices; comb drives; DMD mirrors; electroactive polymers; robotic grasping mechanisms, drives for their moving parts, including solenoid actuators and voice coils; and many others. Recently, the actuators have been intensively studied as potential devices in flexible displays, soft robotics, and haptic devices. rGO-based aerogels are ideal candidates for such devices, because they have high porosity, are ultra-light, flexible, and resilient. To be able to act on the aerogel with magnetic forces, magnetic nanoparticles of Fe_3O_4 were introduced into it [49]. This material demonstrated great magnetic field-induced actuations of 52 and 35% along the radial and axial directions, respectively. Also, several works on actuators based on materials with shape memory are known. Li et al. developed an actuator based on an aerogel from rGO and trans-1,4-polyisoprene, which showed a strain of 80% at 10 V [31].

4. Conclusion

Aerogels based on reduced graphene oxide are promising materials and attracting the interest of many researchers due to unique physicochemical properties. High specific surface area, extremely low density, high porosity, uniqueness of structure, and good electrical conductivity make these materials indispensable in many applications. Main researches are carried out in the direction of surface modification with various materials in order to improve the mechanical, electrophysical, and structural properties of these materials, and the variety and number of articles in this field testify to the incredible promise of materials based on graphene-like particles. However, there are a number of problems that need to be overcome in order to bring most of the developments beyond the scope of laboratory research. First, it is necessary

to develop simple methods for obtaining regular structures based on reduced graphene oxide, suitable for real use. Secondly, special attention needs to be given to a detailed study of the mechanisms of the structure formation of such materials, since at the moment many of the processes are only described, but not explained theoretically. Third, one of the main factors is the high cost of graphene-like materials, which means that efforts should be made to develop cheaper methods for the synthesis of GO and rGO. However, despite the fact that in the near future the researchers will have to solve a number of the problems described above, one can say unambiguously that materials based on graphene-like particles are among the most promising for revolutionary changes in technology, science, and the life of all mankind.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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References

- [1] Zhang X, Sui Z, Xu B, Yue S, Luo Y, Zhan W, et al. Mechanically strong and highly conductive graphene aerogel and its use as electrodes for electrochemical power sources. *Journal of Materials Chemistry*. 2011;**21**:6494-6497. DOI: 10.1039/C1JM10239G
- [2] Chen W, Yan L. In situ self-assembly of mild chemical reduction graphene for three-dimensional architectures. *Nanoscale*. 2011;**3**:3132-3137. DOI: 10.1039/C1NR10355E
- [3] Wu ZS, Winter A, Chen L, Sun Y, Turchanin A, Feng X, et al. Three-dimensional nitrogen and boron co-doped graphene for high-performance all-solid-state supercapacitors. *Advanced Materials*. 2012;**24**:5130-5135. DOI: 10.1002/adma.201201948

- [4] Zhang L, Chen G, Hedhili MN, Zhang H, Wang P. Three-dimensional assemblies of graphene prepared by a novel chemical reduction-induced self-assembly method. *Nanoscale*. 2012;4:7038-7045. DOI: 10.1039/C2NR32157B
- [5] Yang S, Zhang L, Yang Q, Zhang Z, Chen B, Lv P, et al. Graphene aerogel prepared by thermal evaporation of graphene oxide suspension containing sodium bicarbonate. *Journal of Materials Chemistry A*. 2015;3:7950-7958. DOI: 10.1039/C5TA01222H
- [6] Si W, Wu X, Zhou J, Guo F, Zhuo S, Cui H, et al. Reduced graphene oxide aerogel with high-rate supercapacitive performance in aqueous electrolytes. *Nanoscale Research Letters*. 2013;8:247. DOI: 10.1186/1556-276X-8-247
- [7] Gudkov MV, Gorenberg AY, Shchegolikhin AN, Shashkin DP, Mel'nikov VP. Explosive reduction of graphite oxide by hydrazine vapor at room temperature. *Doklady Physical Chemistry*. 2018;478(1):11-14. DOI: 10.1134/S0012501618010037
- [8] Li D, Müller MB, Gilje S, Kaner RB, Wallace GG. Processable aqueous dispersions of graphene nanosheets. *Nature Nanotechnology*. 2008;3:101-105. DOI: 10.1038/nnano.2007.451
- [9] Chabot V, Higgins D, Yu A, Xiao X, Chen Z, Zhang J. A review of graphene and graphene oxide sponge: Material synthesis and applications to energy and the environment. *Energy & Environmental Science*. 2014;7:1564-1596. DOI: 10.1039/c3ee43385d
- [10] Qin SY, Liu XJ, Zhuo RX, Zhang XZ. Microstructure-controllable graphene oxide hydrogel film based on a pH-responsive graphene oxide hydrogel. *Macromolecular Chemistry and Physics*. 2012;213:2044-2051. DOI: 10.1002/macp.201200281
- [11] Bai H, Li C, Wang X, Shi G. On the gelation of Graphene oxide. *Journal of Physical Chemistry C*. 2011;115:5545-5551. DOI: 10.1021/jp1120299
- [12] Jasim D, Lozano N, Kostarelos K. Synthesis of few-layered, high-purity graphene oxide sheets from different graphite sources for biology. *2D Materials*. 2016;3:014006. DOI: 10.1088/2053-1583/3/1/014006
- [13] Xu Y, Sheng K, Li C, Shi G. Self-assembled graphene hydrogel via a one-step hydrothermal process. *ACS Nano*. 2010;4:4324-4330. DOI: 10.1021/nn101187z
- [14] Tang Z, Shen S, Zhuang J, Wang X. Noble-metal-promoted three-dimensional macroassembly of single-layered graphene oxide. *Angewandte Chemie, International Edition*. 2010;49:4603-4607. DOI: 10.1002/anie.201000270
- [15] Jiang X, Ma Y, Li J, Fan Q, Huang W. Self-assembly of reduced graphene oxide into three-dimensional architecture by divalent ion linkage. *Journal of Physical Chemistry C*. 2010;114:22462-22465. DOI: 10.1021/jp108081g
- [16] Cong HP, Ren XC, Wang P, Yu SH. Macroscopic multifunctional graphene-based hydrogels and aerogels by a metal ion induced self-assembly process. *ACS Nano*. 2012;6:2693-2703. DOI: 10.1021/nn300082k
- [17] Wu ZS, Yang S, Sun Y, Parvez K, Feng X, Müllen K. 3D nitrogen-doped graphene aerogel-supported Fe₃O₄ nanoparticles as efficient electrocatalysts for the oxygen reduction

- reaction. *Journal of the American Chemical Society*. 2012;**134**:9082-9085. DOI: 10.1021/ja3030565
- [18] Xu X, Li H, Zhang Q, Hu H, Zhao Z, Li J, et al. Self-sensing, ultralight, and conductive 3D graphene/iron oxide aerogel elastomer deformable in a magnetic field. *ACS Nano*. 2015;**9**:3969-3977. DOI: 10.1021/nn507426u
- [19] Chen P, Yang JJ, Li SS, Wang Z, Xiao TY, Qian YH, et al. Hydrothermal synthesis of macroscopic nitrogen-doped graphene hydrogels for ultrafast supercapacitor. *Nano Energy*. 2013;**2**:249-256. DOI: 10.1016/j.nanoen.2012.09.003
- [20] Leea JW, Kob JM, Kim J-D. Hydrothermal preparation of nitrogen-doped graphene sheets via hexamethylenetetramine for application as supercapacitor electrodes. *Electrochimica Acta*. 2012;**85**:459-466. DOI: 10.1016/j.electacta.2012.08.070
- [21] Wang T, Wang L, Wu D, Xia W, Zhaoa H, Jia D. Hydrothermal synthesis of nitrogen-doped graphene hydrogels using amino acids with different acidities as doping agents. *Journal of Materials Chemistry. A*. 2014;**2**:8352. DOI: 10.1039/c4ta00170b
- [22] Suhaga D, Singhb A, Chattopadhyayc S, Chakrabartid S, Mukherjee M. Hydrothermal synthesis of nitrogen doped graphene nanosheets from carbon nanosheets with enhanced electrocatalytic properties. *RSC Advances*. 2015;**5**(50):39705-39713
- [23] Moon IK, Yoon S, Chun KY, Oh J. Highly elastic and conductive N-doped monolithic graphene aerogels for multifunctional applications. *Advanced Functional Materials*. 2015;**25**:6976-6984. DOI: 10.1002/adfm.201502395
- [24] Sui ZY, Meng YN, Xiao PW, Zhao ZQ, Wei ZX, Han BH. Nitrogen-doped graphene aerogels as efficient supercapacitor electrodes and gas adsorbents. *ACS Applied Materials & Interfaces*. 2015;**7**:1431-1438. DOI: 10.1021/am5042065
- [25] Hong JY, Bak BM, Wie JJ, Kong J, Park HS. Reversibly compressible, highly elastic, and durable graphene aerogels for energy storage devices under limiting conditions. *Advanced Functional Materials*. 2015;**25**:1053-1062. DOI: 10.1002/adfm.201403273
- [26] Worsley MA, Pauzauskie PJ, Olson TY, Biener J, Satcher JH, Baumann TF. Synthesis of graphene aerogel with high electrical conductivity. *Journal of the American Chemical Society*. 2010;**132**:14067-14069. DOI: 10.1021/ja1072299
- [27] Sui ZY, Wang C, Yang QS, Shu K, Liu YW, Han BH, et al. A highly nitrogen-doped porous graphene—An anode material for lithium ion batteries. *Journal of Materials Chemistry A*. 2015;**3**:18229-18237. DOI: 10.1039/C5TA05759K
- [28] Zhao Y, Liu J, Hu Y, Cheng H, Hu C, Jiang C, et al. Highly compression-tolerant supercapacitor based on polypyrrole-mediated graphene foam electrodes. *Advanced Materials*. 2012;**25**:591-595. DOI: 10.1002/adma.201203578
- [29] Tai Z, Yan X, Xue Q. Three-dimensional graphene/polyaniline composite hydrogel as supercapacitor electrode. *Journal of the Electrochemical Society*. 2012;**159**:A1702-A1709. DOI: 10.1149/2.058210jes

- [30] Qin Y, Peng Q, Ding Y, Lin Z, Wang C, Li Y, et al. Lightweight, superelastic, and mechanically flexible graphene/polyimide nanocomposite foam for strain sensor application. *ACS Nano*. 2015;**9**:8933-8941. DOI: 10.1021/acsnano.5b02781
- [31] Li C, Qiu L, Zhang B, Li D, Liu CY. Robust vacuum-/air-dried graphene aerogels and fast recoverable shape-memory hybrid foams. *Advanced Materials*. 2016;**28**:1510-1516. DOI: 10.1002/adma.201504317
- [32] Zhai Y, Dou Y, Zhao D, Fulvio PF, Mayes RT, Dai S. Carbon materials for chemical capacitive energy storage. *Advanced Materials*. 2011;**23**:4828-4850. DOI: 10.1002/adma.201100984
- [33] Liu Y, He D, Wu H, Duan J, Zhang Y. Hydrothermal self-assembly of manganese dioxide/manganese carbonate/reduced graphene oxide aerogel for asymmetric supercapacitors. *Electrochimica Acta*. 2015;**164**:154-162. DOI: 10.1016/j.electacta.2015.01.223
- [34] Wu Y, Gao G, Wu G. Self-assembled three-dimensional hierarchical porous V₂O₅/graphene hybrid aerogels for supercapacitors with high energy density and long cycle life. *Journal of Materials Chemistry*. 2015;**A3**:1828-1832. DOI: 10.1039/C4TA05537C
- [35] Yu G, Hu L, Vosgueritchian M, Wang H, Xie X, McDonough JR, et al. Solution-processed graphene/MnO₂ nanostructured textiles for high-performance electrochemical capacitors. *Nano Letters*. 2011;**11**:2905-2911. DOI: 10.1021/nl2013828
- [36] He Y, Chen W, Li X, Zhang Z, Fu J, Zhao C, et al. Freestanding three-dimensional graphene/MnO₂ composite networks as ultralight and flexible supercapacitor electrodes. *ACS Nano*. 2013;**7**:174-182. DOI: 10.1021/nn304833s
- [37] Lee WSV, Peng E, Choy DC, Xue JM. Mechanically robust glucose strutted graphene aerogel paper as a flexible electrode. *Journal of Materials Chemistry*. 2015;**A3**:19144-19147. DOI: 10.1039/C5TA06072A
- [38] Lv P, Tang X, Zheng R, Ma X, Yu K, Wei W. Graphene/polyaniline aerogel with super-elasticity and high capacitance as highly compression-tolerant supercapacitor electrode. *Nanoscale Research Letters*. 2017;**12**:630. DOI: 10.1186/s11671-017-2395-z
- [39] Xiao L, Wu D, Han S, Huang Y, Li S, He M, et al. Self-assembled Fe₂O₃/graphene aerogel with high lithium storage performance. *ACS Applied Materials & Interfaces*. 2013;**5**:3764-3769. DOI: 10.1021/am400387t
- [40] Ren L, Hui KN, Hui KS, Liu Y, Qi X, Zhong J, et al. 3D hierarchical porous graphene aerogel with tunable meso-pores on graphene nanosheets for high-performance energy storage. *Scientific Reports*. 2015;**5**:14229. DOI: 10.1038/srep14229
- [41] Zhou G, Li F, Cheng HM. Progress in flexible lithium batteries and future prospects. *Energy & Environmental Science*. 2014;**7**:1307-1338. DOI: 10.1039/C3EE43182G
- [42] Chen W, Li S, Chen C, Yan L. Self-assembly and embedding of nanoparticles by in situ reduced graphene for preparation of a 3D graphene/nanoparticle aerogel. *Advanced Materials*. 2011;**23**:5679-5683. DOI: 10.1002/adma.201102838

- [43] Wei W, Yang S, Zhou H, Lieberwirth I, Feng X, Müllen K. 3D graphene foams cross-linked with pre-encapsulated Fe₃O₄ nanospheres for enhanced lithium storage. *Advanced Materials*. 2013;25:2909-2914. DOI: 10.1002/adma.201300445
- [44] Yao X, Guo G, Ma X, Zhao Y, Ang CY, Luo Z, et al. In situ integration of anisotropic SnO₂ heterostructures inside three-dimensional graphene aerogel for enhanced lithium storage. *ACS Applied Materials & Interfaces*. 2015;7:26085-26093. DOI: 10.1021/acsami.5b07081
- [45] Wang R, Xu C, Sun J, Gao L, Yao H. Solvothermal-induced 3D macroscopic SnO₂/nitrogen-doped graphene aerogels for high capacity and long-life lithium storage. *ACS Applied Materials & Interfaces*. 2014;6:3427-3436. DOI: 10.1021/am405557c
- [46] Yan X, Yao W, Hu L, Liu D, Wang C, Lee CS. Progress in the preparation and application of three-dimensional graphene-based porous nanocomposites. *Nanoscale*. 2015;7:5563-5577. DOI: 10.1039/C5NR00030K
- [47] Lv P, Yu K, Tan X, Zheng R, Ni Y, Wang Z, et al. Super-elastic graphene/carbon nanotube aerogels and their applications as a strain-gauge sensor. *RSC Advances*. 2016;6:11256-11261. DOI: 10.1039/C5RA20342B
- [48] Juanjuan Z, Ruiyi L, Zaijun L, Junkang L, Zhiguo G, Guangli W. Synthesis of nitrogen-doped activated graphene aerogel/gold nanoparticles and its application for electrochemical detection of hydroquinone and o-dihydroxybenzene. *Nanoscale*. 2014;6:5458-5466. DOI: 10.1039/c4nr00005f
- [49] Xu L, Xiao G, Chen C, Run L, Mai Y, Sun G, et al. Superhydrophobic and superoleophilic graphene aerogel prepared by facile chemical reduction. *Journal of Materials Chemistry A*. 2015;3:7498-7504. DOI: 10.1039/C5TA00383K

