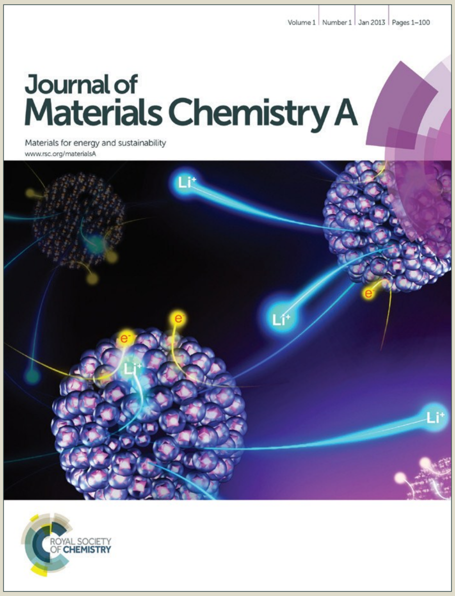
Journal of Materials Chemistry A

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

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Journal Name

ARTICLE

Dopamine-mediated fabrication of ultralight graphene aerogels with low volume shrinkage

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Large volume shrinkage and high temperature are the frequently encountered problems during preparation of graphene aerogels via hydrothermal reactions. Here we report dopamine-mediated fabrication of ultralight graphene aerogels (UGAs) with low volume shrinkage at mild temperature of hydrothermal reaction. The UGAs were fabricated by hydrothermal reaction of the graphene oxide (GO)/dopamine colloidal solutions at 85 °C in the presence of dopamine followed by freeze-drying and pyrolysis. The interaction between GO and dopamine in the aqueous phase, the effects of various parameters on formation of the UGAs, the roles of dopamine in hydrothermal reactions as well as the wettability and electrical conductivity of the UGAs were investigated using a wide range of analytical techniques. The GO concentration, dopamine concentration, and the temperature and time of hydrothermal reaction have great influences on formation of the UGAs. The addition of dopamine forms crosslinking points among the GO sheets and results in partial reduction of GO in the hydrothermal reaction. In addition, the N atoms of dopamine were doped into the graphene sheets. The UGAs feature low volume shrinkage (8.3 %), ultralow density (3.5 mg cm^{-3}), excellent superhydrophobicity/superoleophilicity (CA_{water} ~ 155.5° and CA_{oil} ~ 0°), very high absorbency for organic liquids (134.0 ~ 282.9 g g^{-1}) as well as excellent fire retardant property and high conductivity (3.07 S cm^{-1}). All these merits make the UGAs very promising materials for absorption of organic pollutants, sensors and energy storage, etc.

1. Introduction

3D porous carbon materials in forms of foam,[1] sponge[2] and aerogel[3] have received significant attention recently in many fields including oil absorption, catalysts, sensors and supercapacitors[4] due to their outstanding advantages such as low density, low thermal conductivity and high electrical conductivity, etc. Various 3D carbon materials with novel properties have been successfully created using different building blocks like carbon nanofibers, carbon nanotubes, graphene and biomass.[5] Compared with other 3D carbon materials composed of nanofibers and nanotubes, graphene aerogels (GAs) not only maintain unique structural merits of graphene sheets but also explore outstanding properties including lower density, excellent electrical conductivity and mechanical strength as well as extraordinary absorption properties. A variety of methods such as hydrothermal reaction,[4c, 6] chemical reduction[7] and thermal reduction[8] have been used to fabricate GAs. Compared with the other methods, hydrothermal reaction of graphene oxide (GO) is the frequently used strategy because of its simplicity and high availability of GO. For example, Sui *et al.* prepared nitrogen-doped graphene aerogels (NGAs) with high nitrogen level and excellent electrical conductivity via hydrothermal reaction at 180 °C.[4c] However, hydrothermal reactions of GO for the preparation of GAs were often carried out at high temperature, which resulted in serious volume shrinkage of the prepared GAs. To address these problems, various reagents including sodium ascorbate, ethylenediamine and sodium iodide have been used to assist the hydrothermal reactions of GO.[7, 8b] Sheng *et al.* fabricated high performance graphene hydrogels by hydrothermal reaction of GO dispersions with sodium ascorbate at 90 °C.[7b] Hu *et al.* prepared ultralight GAs with high compressibility via hydrothermal reaction of GO at 95 °C in the presence of ethylenediamine followed by lyophilization and microwave reduction.[8b] Although the temperature of hydrothermal reaction has been decreased to some extent, the volume shrinkage of the as-prepared GAs is still large. All these push us to explore a facile approach to fabricate multifunctional GAs with low volume shrinkage at mild temperature.

Dopamine, like L-3,4-dihydroxyphenylalanine in the adhesive proteins of mussel, can polymerize and deposit on all kinds of substrates.[9] The integration of dopamine and graphene has recently been successfully explored to create novel materials. Gao *et al.* prepared polydopamine-functionalized graphene hydrogels as reusable adsorbents for water purification.[9d] Dopamine serves as both reductant and surface modifier. Song *et al.* fabricated ultralight NGAs by

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† Electronic Supplementary Information (ESI) available: [Digital images, viscosity, zeta potentials, SEM images, EDX analysis, FTIR spectra, XPS spectra and TGA analysis]. See DOI: 10.1039/x0xx00000x

hydrothermal reaction of the pH 8.0 GO/dopamine solution at 180 °C.[10] However, the hydrothermal reaction at 180 °C resulted in large volume shrinkage of the NGAs.

Herein, we report fabrication of ultralight graphene aerogels (UGAs) by dopamine-mediated hydrothermal reaction of GO in a mild acidic condition at 85 °C, followed by freeze-drying and pyrolysis. Compared with the previously reported GAs, the UGAs obtained in this study have the following advantages. (1) The UGAs were prepared at mild temperature with very small volume shrinkage. (2) The UGAs feature low density, excellent superhydrophobicity, extremely high absorbency for oils, excellent fire-resistance and high conductivity, which make them promising materials for absorption of organic pollutants, sensors and energy storage, etc.

2. Experimental

2.1 Materials

Graphite was supplied by Asbury Graphite Mills, Inc, United States. Dopamine hydrochloride (98%) was purchased from Shanghai DEMO Medical Tech Co., China. H_2SO_4, $NaNO_3$, $KMnO_4$, H_2O_2, HCl, triethylamine, ethylenediamine, sodium sulfite, chloroform, dichloromethane, *n*-hexane, toluene, ethanol, petroleum ether, vacuum pump oil and Oil Red O were purchased from China National Medicines Corporation Ltd. All the chemicals were analytical grade and used as received without further purification.

2.2 Preparation of UGAs

GO was prepared by a modified Hummers method.[11] The UGAs were prepared according to the following procedure. Typically, an appropriate amount of GO aqueous solution was dispersed in water by ultrasonication for 2 h in order to dilute and strip the GO sheets thoroughly. Then, 0.5 mL of dopamine aqueous solution (20 mg mL^{-1}) was added into 5.75 mL of the GO dispersion (3.27 mg mL^{-1}), and stirred for 2 min to form a uniform pH 2.0 solution. Subsequently, the solution was sealed in a 45 mL teflon-lined autoclave and maintained at 85 °C for 12 h to transform the brown aqueous solution into a black nitrogen doped-graphene hydrogel. Finally, the hydrogel was freeze-dried to form the NGA, which was further calcined in an N_2 atmosphere at 1000 °C for 2 h to form the UGA.

2.3 Characterization

The micrographs of the samples were taken using a field emission scanning electron microscope (SEM, JSM-6701F, JEOL) and a field emission transmission electron microscope (TEM, TECNAI-G2-F30, FEI). Before SEM observation, all samples were fixed on copper stubs and coated with a layer of gold film (~ 7 nm). The energy dispersive X-ray (EDX) analysis was done on the attachment to SEM. For TEM observation, the samples were prepared as follows. A drop of the solution was put on a copper grid and dried in the open atmosphere. The X-ray diffraction (XRD) patterns were obtained on X'pert PRO diffractometer with working conditions Cu Kα, 30 mA and 40 kV ($\lambda = 1.54060$ Å). The scanning was made at room temperature between 3 and 40° in 2θ with a scanning speed of 0.02° per second. The Fourier transformed infrared (FTIR) spectra of the samples were recorded by a Thermo Nicolet NEXUS TM spectrophotometer using KBr pellets. The surface chemical composition of the samples was analyzed via X-ray photoelectron spectroscopy (XPS) using a VG ESCALAB 250 Xi spectrometer equipped with a Monochromated AlKa X-ray radiation source and a hemispherical electron analyzer. The spectra were recorded in the constant pass energy mode with a value of 100 eV, and all binding energies were calibrated using the C1s peak at 284.6 eV as the reference. Rheological tests of the samples were measured using a Physica MCR301 rheometer (Anton Paar, Germany) at 25 °C and atmospheric pressure. Zeta potentials of samples were measured on a Malvern ZEN3600 Zeta voltmeter (Britain). Measurement of contact angle (CA) of water was performed using a Contact Angle System OCA20 (Dataphysics, Germany). The syringe was positioned in a way that the water drop (7 μL) could contact surface of the samples before leaving the needle. A minimum of six readings were recorded for each sample. Thermogravimetric analysis (TGA) was carried out using a STA 6000 simultaneous thermal analyzer (PerkinElmer Instrument Co., Ltd. USA) in the range of 25 to 1000 °C at a rate of 10 °C min^{-1} under a N_2 atmosphere. The electrical conductivity of the aerogel was measured using a four-probe resistivity meter (Kund Technology Co. Ltd. Guangzhou, China). The specific surface areas of samples were analyzed using an Accelerated Surface Area and Porosimetry System (Micromeritics, ASAP2020, Atlanta, USA) using N_2 as an adsorbate at -196 °C. The specific surface area was calculated by the BET method. Total pore volume was obtained from the volume of N_2 held at the relative pressure $P/P_0 = 0.95$.

3. Results and discussion

3.1 Design and preparation of UGAs

The UGAs were fabricated by hydrothermal reaction of the GO/dopamine colloidal solutions in a mild acidic condition at 85 °C in the presence of dopamine followed by freeze-drying and pyrolysis (Fig. 1a). Dopamine serves as both reductant and nitrogen source. First, an aqueous solution of dopamine was added into the GO solution and stirred for 2 min to form a homogeneous GO/dopamine colloidal solution (pH 2.0). The GO solution quickly became sticky once dopamine was added, which indicates interaction between GO and dopamine. Then, the brown colloidal solution was cured in a Teflon-lined autoclave at 85 °C for 12 h to form a black graphene hydrogel. The resultant hydrogel exhibited very small volume shrinkage (8.3 %). Without dopamine, the hydrogel could not be formed at 85 °C and only a seriously contracted hydrogel was formed with increasing the temperature to 150 °C. Serious contraction of graphene hydrogels in the process of hydrothermal reaction is the frequently observed phenomenon.[3c, 4c, 6, 12] We also studied the effects of other reductants including triethylamine, ethylenediamine and sodium sulfite on volume shrinkage of the graphene hydrogels. It was found that the hydrogels prepared with these reductants were either very fragile or exhibited serious volume shrinkage (Fig. S1). Finally, the UGAs with a density of less than 3.5 mg cm^{-3} were obtained after freeze-drying of the hydrogels followed by calcination in an N_2 atmosphere at 1000 °C for 2 h. The density of the UGAs is lower than many of the aerogels based on CNTs, graphene and biomass,[13] and only slightly larger than the ultra-flyweight CNTs/graphene aerogel (0.16 mg cm^{-3}) and the FIBER aerogel (0.12 mg cm^{-3}) (Table S1).[14] A piece of the UGA can stand stably on cotton fibers and no deformation of the cotton fibers was observed.

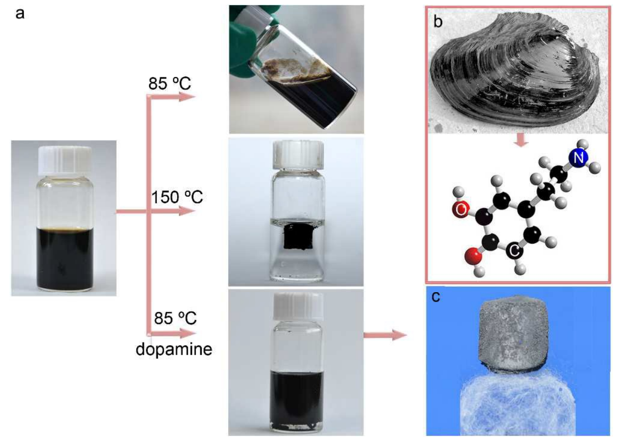

Fig. 1 (a) Preparation of graphene hydrogels under different conditions, (b) image of mussel and chemical formulas of dopamine, and (c) image of the UGA on cotton fibers.

3.2 Interaction between GO and dopamine in aqueous phase

In order to study the interaction between GO and dopamine in the aqueous phase before the hydrothermal reaction, the rheological properties of the GO/dopamine colloidal solutions with different dopamine concentration were shown in Fig. 2. The viscosity of the GO/dopamine colloidal solutions is much larger than that of the GO aqueous solution in the entire shearing process, which means formation of crosslinking points among the GO sheets by the addition of dopamine (Fig. 2a). In addition, the initial viscosity of the GO/dopamine colloidal solutions increases from 267 to 320 mPa·s with increasing the dopamine concentration, indicating formation of more crosslinking points at a high dopamine concentration (Fig. S2). The viscosity of the GO/dopamine colloidal solutions diminishes evidently with increasing the shear rate while the shear stress gradually increases (Fig. 2b). This result indicates transformation from the Newtonian to the non-Newtonian fluid and shear thinning behavior of the colloidal solution because of partly dissociation of the weak crosslinking points among the GO sheets.[15] Moreover, the concentration of dopamine has great influence on the viscoelastic properties of the GO/dopamine colloidal solution. Oscillatory measurements revealed that the storage modulus (G′) of the GO/dopamine colloidal solutions is higher than their loss modulus (G″) over the entire tested range of angular frequency (Fig. 2c), indicating an elastic rather than a viscous response of the colloidal solution due to the crosslinked sheets of GO.[6, 16] In addition, G′ and G″ increase with increasing the dopamine concentration from 0 to 1.60 mg mL^{-1}, and then decrease significantly with further increasing the dopamine concentration to 3.20 mg mL^{-1}. Moreover, G′ of all the solutions exhibited a linear stage at the angular frequency range of 0.1 to 25 rad s^{-1}. With further increasing the angular frequency, the GO solution showed an evident decrease of G′, whereas G′ of the GO/dopamine solutions remained constant or even showed an increase at a higher dopamine concentration. These results further confirmed that the crosslinking degree between the GO sheets increased with increasing the dopamine concentration.[6, 17]

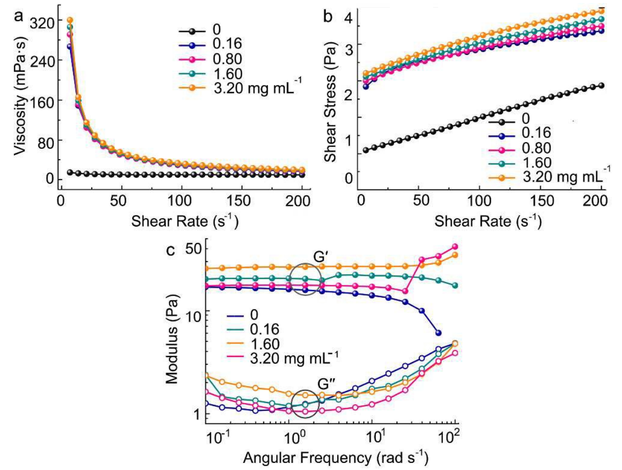

Fig. 2 (a, b) Steady, and (c) dynamic rheological behavior of the GO/dopamine colloidal solutions with different dopamine concentration.

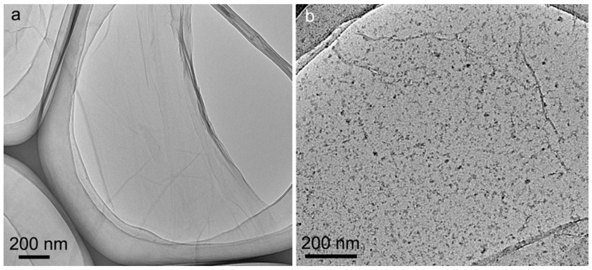

Fig. 3 TEM images of (a) GO and (b) GO/dopamine (1.60 mg mL^{-1} dopamine) colloidal solutions.

The interaction between GO and dopamine was further investigated by TEM (Fig. 3) and zeta potentials (Table S2). The GO sheets are very large and have some wrinkles. In the GO/dopamine colloidal solution, a large number of polydopamine nanoparticles with an average size of ~ 9 nm were formed, which were homogenously enwrapped in the GO sheets (Fig. 3b). This is because of covalent grafting of polydopamine nanoparticles on the GO sheets.[9c, 18] The GO colloidal solution displays a zeta potential of −54.8 mV due to the negatively charged carboxylate groups. The zeta potential gradually increases to −23.6 mV with increasing the dopamine concentration, which is because of existence of quaternary ammonium salt in the GO/dopamine colloidal solution.

Furthermore, the zeta potential of the corresponding graphene hydrogel dramatically changed from negative to positive (+17.4 mV) owing to oxidation of dopamine on the GO sheets and the partial reduction of GO in the hydrothermal reaction.[19]

3.3 Effects of various parameters on formation of NGAs

The concentration of dopamine has great influence on formation of the graphene hydrogels. Without dopamine, graphene hydrogel cannot be formed at 85 °C and only the hydrogel with large volume shrinkage was formed at 150 °C (Fig. 4a and Table S3). The volume of the graphene hydrogel decreased with increasing the dopamine concentration from 0.08 to 0.80 mg mL^{-1}. Although the volume shrinkage was low for the graphene hydrogels prepared with a dopamine concentration of less than 0.80 mg mL^{-1} (Fig. 4a), the corresponding NGAs are fragile (Fig. S3). This phenomenon indicates that the interaction between GO sheets is too weak to form intact NGAs at low dopamine concentrations. The volume of the hydrogel increased with further increasing the dopamine concentration from 0.80 to 3.20 mg mL^{-1} and the intact NGAs were obtained owing to the strong interaction between GO sheets via dopamine. According to the previous reports,[6b, 8b] in the hydrothermal process at high temperature (e.g., 150 °C), GO sheets were partially reduced and the reduced GO sheets tend to overlap with each other. Therefore, large volume shrinkage of graphene hydrogels often occurred in the common hydrothermal reactions. However, dopamine could form crosslinking points with the GO sheets and partially reduce them. Thus, the graphene hydrogels can be formed at lower temperature (85 °C) in this study, which reduced overlapping of the GO sheets and decreased volume shrinkage of the NGAs. The NGA exhibited a well-defined and interconnected 3D network microstructure with pore sizes ranging from several micrometers to a few tens of micrometers (Fig. 4b-c). The walls of these pores are composed of unfolded graphene sheets. There is no big difference in morphology between NGA and GA observed via SEM except for the large volume shrinkage of the GA (Fig. S4). In addition, the specific surface area of the NGA is lower than that of GA owing to the existence of polydopamine in the NGA (Table S4).

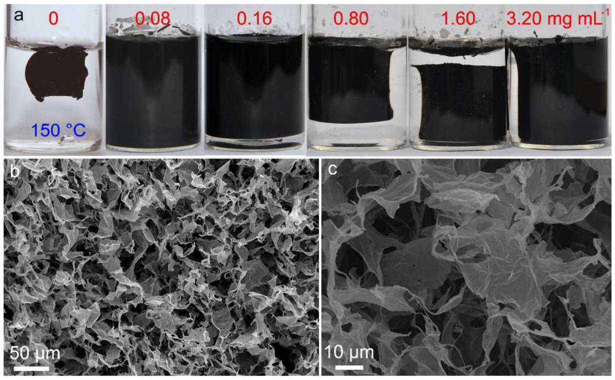

Fig. 4 (a) Images of the graphene hydrogels with different dopamine concentration and (b, c) SEM images of the NGA with a dopamine concentration of 1.60 mg mL^{-1}.

The concentration of GO, and the temperature and time of hydrothermal reaction also have significant influences on formation of the graphene hydrogels. Fig. S5 shows images of the graphene hydrogels with GO concentrations ranging from 0.5 to 3 mg mL^{-1}. Clearly, all the GO/dopamine colloidal solutions successfully form macroscopic assemblies, and the volume of the hydrogels increase with increasing the GO concentration. With a hydrothermal reaction of 12 h, the NGAs can be formed when the temperature is not less than 85 °C, or else the products are viscous and shapeless (Fig. S6). It is also unable to form intact NGA at 85 °C when the time of the hydrothermal reaction is less than 12 h (Fig. S7). It should be noted that the NGA can also be formed after kept at room temperature for 20 days in presence of 3.20 mg mL^{-1} dopamine. Hydrothermal reaction at 85 °C can shorten formation of the NGA to 12 h. Moreover, pH of the GO/dopamine solution has an obvious impact on formation of the hydrogel (Fig. S8). With increasing pH of the GO/dopamine colloidal solution adjusted with ammonia from 4 to 10, the as-prepared products gradually became sticky liquids rather than hydrogels.

3.4 Roles of dopamine in hydrothermal reactions and formation of UGAs

The FTIR spectra of GO, GO/dopamine before hydrothermal reaction, NGA and UGA are shown in Fig. 5a. After the introduction of dopamine, the band at 1503 cm^{-1} (shearing vibration of N-H of amide group) and 1283 cm^{-1} (stretching vibration of C-OH in phenolic) appeared, indicating polymerization of dopamine in the GO/dopamine solution.[20] In the spectrum of the NGA, the characteristic bands at 3224 cm^{-1} (stretching vibration of -OH) and 1503 cm^{-1} (shearing vibration of N-H of amide group) disappeared after hydrothermal process. In addition, the intensity of the bands at 1713 cm^{-1} (stretching vibration of C=O of amide) and 1575 cm^{-1} (stretching vibration of N-H in-plane)[21] gradually increased with increasing the dopamine concentration (Fig. 5b). The changes in the FTIR spectra indicate that the oxygen-containing groups of GO sheets were partly reduced and dopamine was oxidized. After pyrolysis, only the bands at 1630 cm^{-1} (stretching vibration of C=C) and 1127 cm^{-1} (stretching vibration of C-N) remained in the spectrum of the UGA, demonstrating that most of functional groups were eliminated and GO sheets were completely reduced. The changes in the FTIR spectra also indicate that N atoms have been doped into defects in the hexagonal-ring of the graphene backbones, which is due to formation of covalent bonds between N atoms of dopamine and C atoms on the GO sheets.[22]

The surface chemical composition of the NGA was analyzed using XPS and EDX (Figs. 5c and S9). The XPS spectrum of the NGA shows prominent C 1s (284.8 eV) and O 1s (532.7 eV) peaks along with a weak N 1s peak (401 eV) corresponding to an N content of 4.36 %. The result is consistent with the N content obtained from the EDX spectrum (Table S5). Compared to GO, there is an obvious increase in the C/O atomic ratio from 2.3 to 3.4 on the surface of the NGA according to their XPS spectra, indicating partial reduction of GO by dopamine in the hydrothermal process. Meanwhile, the N 1s spectrum of the

NGA reveals the presence of pyridinic N (398.2 eV), pyrrolic N (399.7eV) and graphitic N (401.6 eV),[1b, 4c, 8c] which confirms that N atoms merged into the carbon-carbon bonds of the graphene sheets during dopamine-mediated formation of the NGA (Fig. S10a). Pyridinic N contributes to the π system and pyrrolic N is located in a π conjugated system. The graphitic N atoms substitutes the C atoms in the graphene layers (Fig. 6).[5c] In the XPS spectrum of the UGA, the weak N 1s peak is still detectable, but the N content decreased from 4.36% to 1.98% after pyrolysis. In addition, compared to the C 1s spectrum of the NGA, the peak at 285.8 eV was weakened in the C 1s spectrum of the UGA owing to complete removal of the C-O group via further reduction of GO in the pyrolysis process (Fig. S10b-c). All these data further confirms that a part of N atoms of dopamine have been doped into the graphene backbones whereas the other N atoms in the NGA have been removed in the pyrolysis process.

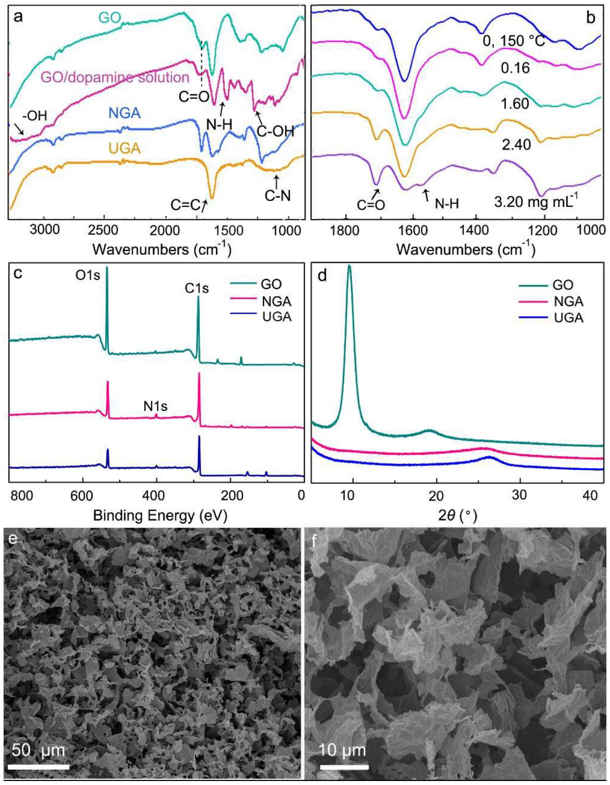

Fig. 5 FTIR spectra of (a) GO, GO/dopamine before hydrothermal reaction, NGA and UGA, (b) NGAs with different dopamine concentration, (c) XPS spectra of GO, NGA and UGA, (d) XRD patterns of GO, NGA and UGA, (e, f) SEM images of UGA.

The structural changes from GO to the UGA owing to the introduction of dopamine were also confirmed by their XRD patterns (Fig. 5d). The strong characteristic peak of GO at 2θ = 9.54° corresponding to a interlayer spacing distance of about 8.30 Å is due to oxygen-containing groups and intercalated water molecules on the GO sheets.[4d] This peak disappeared in the XRD pattern of NGA, and a new weak broad peak attributed to partial reduction of GO appeared at 2θ = 25.9° with a spacing distance of ~3.34 Å, which is in accordance with the XPS results. The UGA shows a peak at 26.2°, which indicates a further decrease of the interlayer spacing distance of graphene sheets owing to removal of the residual oxygen-containing functional groups and the N atoms between the GO sheets during pyrolysis of the NGA. Whereas the N atoms merged into the carbon-carbon bonds of the graphene sheets are still present in the graphene layers after pyrolysis (Fig. 5c). Pyrolysis has changed the NGA to UGA, but has no obvious influence on volume of the sample. The UGA still keep the pore morphology of the NGA (Fig. 5e-f).

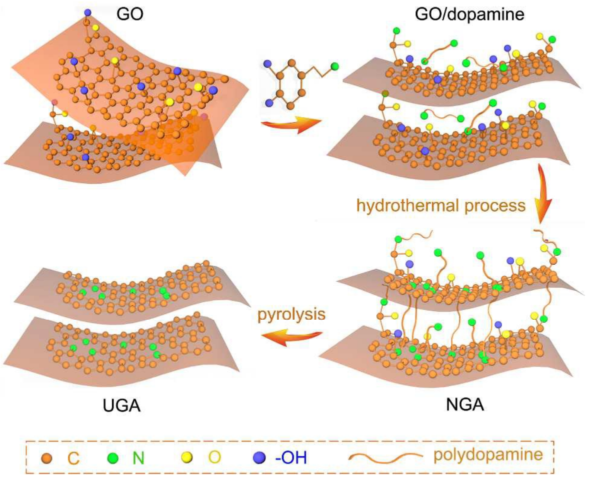

Fig. 6 Schematic illustration of the effects of dopamine during formation of the UGA.

3.5 Wettability and electrical conductivity of UGAs

The UGA is superhydrophobic with a water CA of ~155.5° (Fig. 7a-b). Although a 7 µL water drop is spherical shape on the surface of the UGA, an oil drop of the same volume could be quickly absorbed by the aerogel (CA_{oil} ~ 0°), indicating superhydrophobic/superoleophilic property and selective oil absorption of the aerogel. The superhydrophobic/superoleophilic property and the 3D porous structure of the UGA endow it with excellent oil/water separation efficiency and very high oil absorbency. The UGA can be used to selectively absorb oils from water (Fig. 7c), which makes it a very promising material in treating oily waste water. When a piece of the UGA was placed on the surface of an oil/water mixture, the floating oil dyed with Oil Red O could be completely absorbed by the aerogel. The absorbency of the UGA for various organic liquids is in the range of 134 to 282.9 g g^{-1}, depending on density, viscosity and surface tension of the organics (Fig. 7d). The absorbency of the UGA for organic liquids is higher than most of the reported 3D porous carbon materials.[23] The absorbed organics are stored in the abundant pores of the aerogel. The absorbency of the UGA for *n*-hexane remained in the range 160-175 g g^{-1} after repeated used for 10 times, indicating high reusability (Fig. S11). When directly ignited by open flame, the UGA showed fire retardant property. The burned UGA still kept its skeleton intact even after exposed to the flame for 20 min (Fig. 7e). No weight loss was detected at temperature below 720 °C according to the TGA curve of the

UGA whereas GO and NGA showed significant weight losses in the temperature range of 210 ~ 690 °C due to decomposition of the amino- and oxygen-containing groups (Fig. S12). In addition, the UGA is electrically conductive with a conductivity of 3.07 S cm^{-1}, which is higher than most of the previously reported carbon aerogels (Table S1). A light-emitting diode was illumined when linked to a circuit using the UGA (Fig. 7f).

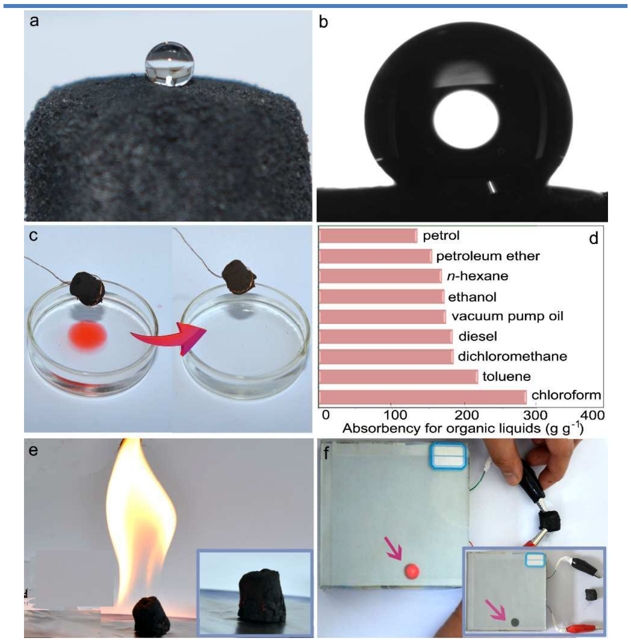

Fig. 7 (a, b) Images of the UGA with a water drop (7 μL) on the surface, (c) removal of *n*-hexane on the surface of water using the UGA, (d) absorbency of the UGA for various organic liquids, (e) image of directly burning the UGA with open flame, and (f) a circuit constructed with the UGA. Oil in (c) was dyed with Oil Red O. The inset in (e) is the image of the UGA after exposed to the flame for 20 min.

4. Conclusions

In summary, we have successfully fabricated multifunctional UGAs with low volume shrinkage through hydrothermal reactions of the GO/dopamine colloidal solutions at mild temperature followed by freeze-drying and pyrolysis. The volume and density of the UGAs are controllable simply by regulating the GO concentration, dopamine concentration, and the temperature and time of hydrothermal reactions. The addition of dopamine forms crosslinking points among the GO sheets and results in partial reduction of GO in the hydrothermal reaction. In addition, the N atoms of dopamine were doped into the graphene sheets. The UGAs feature low volume shrinkage, ultralow density, excellent superhydrophobicity/superoleophilicity, very high absorbency for organic liquids as well as excellent fire retardant property and high conductivity. All these merits make the UGAs very promising materials for potential applications in many fields such as absorption of organic pollutants, sensors and energy storage.

Acknowledgements

We are grateful for financial support of the "Hundred Talents Program" of the Chinese Academy of Sciences and the National Natural Science Foundation (51503212).

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Ultralight graphene aerogels with low volume shrinkage are fabricated at mild temperature of hydrothermal reaction with the help of dopamine.