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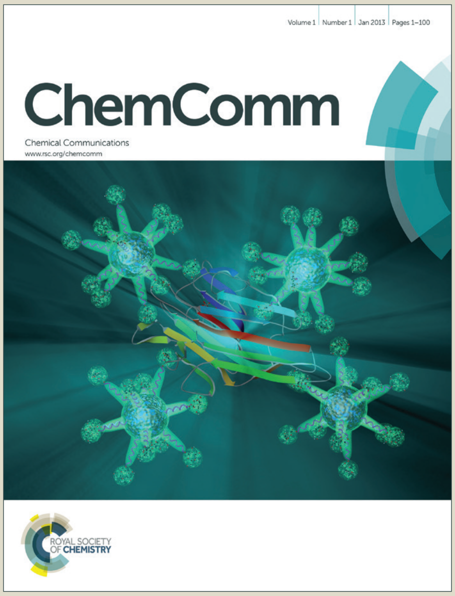

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# Tuning of surface wettability of RGO-based aerogels for varied adsorbates in water using different amino acid[†]

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**The RGO-based aerogels with varied and controllable surface wettability were fabricated using different amino acids. Hydrophobic cys-RGO aerogels prepared by L-cysteine exhibited outstanding adsorption toward oils and organic solvents while hydrophilic lys-RGO aerogels obtained from L-lysine can be used as adsorbents for heavy metal ions in water.**

Aerogels are three dimensional (3D) networks consisting of interpenetrating micropores and mesopores. Among them, RGO-based aerogels have attracted extremely attention due to their peculiar properties including low density, high surface area, large open pores as well as those translated from the RGO building block, which make them attractive in a variety of applications such as solar cells, lithium-ion batteries, various sensors, water purification, and in other systems.[1] RGO-based aerogels with good mechanical and thermal strength have already been reported to fabricate from GO as the starting building block and a variety of cross-linkers, such as water soluble polymers, metal ions, DNA and so on[2] have been applied to promote the assembly of RGO-based hydrogel and aerogels by physical or chemical interactions.

A very important application of the RGO-based aerogels is to be used as adsorbents for sewage treatment. Their peculiar properties enable an easy access and diffusion of the ions and molecules throughout their highly porous structures.[3] For different adsorbates and to meet different adsorption condition in the practical applications, the controlling of the surface wettability of the materials is important. However, so far only a few studies have dealt with the wetting properties of RGO-based aerogels and a facile tuning of the surface wettability of RGO-based aerogels have not yet been reported previously.

In this communication, we demonstrated a simple method to fabricate RGO-based aerogels with varied and controllable surface wettability by using different amino acid as cross linker and reducing agent. The cys-RGO aerogels prepared in the presence of L-cysteine (L-cys) are hydrophobic and exhibit outstanding adsorption capacity toward various oils and organic solvents in water. On the contrary, the lys-RGO aerogels obtained from L-lysine (L-lys) are hydrophilic, which can be used as excellent adsorbents for heavy metal ions in water.

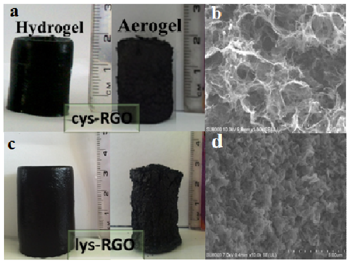
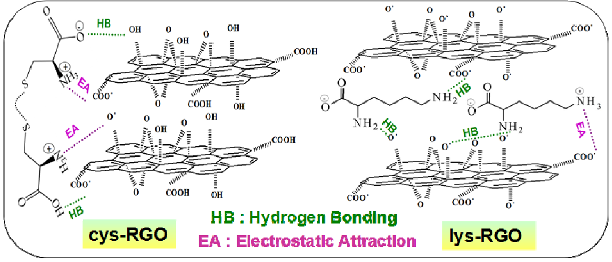


**Fig. 1** Photographs of (a) cys-RGO hydrogel and corresponding aerogel; (b) SEM images of cys-RGO aerogel; Photographs of (c) lys-RGO hydrogel and corresponding aerogel; (d)SEM image of lys-RGO aerogel.

The cys-RGO hydrogels were prepared from GO and L-cys hydrothermally and the examined weight ratio of GO to L-cys ($r_{G/C}$) ranged from 1:0.25 to 1:2. Well shaped hydrogels can be obtained for $r_{G/C}$ ranged from 1:0.5 to 1:2. The hydrogels obtained have a 3D cylindrical morphology in the macroscopic views, which conform to that of the vessel (Fig. S1). The size of the obtained hydrogels vary a little with the ratio of $r_{G/C}$ and for $r_{G/C}$ at 1:2, the obtained cylinder has a diameter of approximately 15 mm and a height of 25 mm (Fig. 1a). Upon freeze dried, the as-prepared hydrogel was dehydrated with almost no shrinkage to maintain the 3D monolithic architecture as cys-RGO aerogel with a density of 13.5 mg/cm$^3$. The SEM image of the cys-RGO aerogel exhibits that the GO nanosheets interconnect to form a three-dimensional porous network on a large scale, with the pore sizes range from 5μm to 20μm (Fig. 1b). The formation of the macropores is probably attributed to the generation of gaseous products during the hydrothermal process. The Brunauer-Emmett-Teller (BET) nitrogen adsorption isotherm reveals that the cys-RGO aerogel exhibits a typical Type II adsorption/desorption isotherms. The BET specific surface area is determined to be approximately 35.67 m$^2$/g (Fig. S2), higher than that of freeze dried RGO-based aerogel (11.8 m$^2$/g) prepared using L-ascorbic acid as a reducing agent and cross linker.[4] The XPS of the as-prepared cys-RGO aerogel in the S 2p region show peaks at 163.6 and 164.8 eV, corresponding to the S $2p_{3/2}$ and S $2p_{1/2}$ of disulfide (Fig. S3a). This suggests that the cys-RGO aerogels are cross-linked by RGO nano-sheets via disulfide bond. The XPS spectra of the aerogel in the C 1s region reveals that the oxygen-bound carbon content decreases from the original 55% in GO to 14.7% in the cys-RGO aerogel, indicating a high degree of GO was reduced during the hydrothermal gelation process (Fig. S3b).[5]The Raman spectrum of cys-RGO aerogel shows that the intensity ratio of the D band and G band in the aerogel ($I_D/I_G$ = 1.29) is higher as compared with that of GO ($I_D/I_G$ = 0.96), indicating that the introduction of defects during the process of cys-RGO aerogel formation (Fig. S4).[6]

Similarly, L-lysine was also used as a cross-linker to build RGO-based hydrogel. Hydrogels can be obtained for the weight ratio of GO to L-lys ($r_{G/L}$) varied from 1:0.25 to 1: 2, (Fig. S5). The optimum condition to shape up integral hydrogel with ~25 mm in diameter and ~40 mm in height is observed at $r_{G/L}$ =1:2 (Fig. 1c). Freeze drying of the lys-RGO hydrogel led to the formation of lys-RGO aerogel without obvious shrinkage. The as-obtained lys-RGO aerogel has an ultralow density of 3 mg/cm$^3$, which is much lower than that obtained from L-cys and the majority of already reported RGO-based aerogels.[7] Unlike the cys-RGO aerogel, the lys-RGO aerogel is composed of interconnected and cross-linked crumpled nanosheet of RGO to form a three-dimensional porous structure with slit-shaped pores. It is worth noting that the as-obtained lys-RGO aerogel exhibits a more fluffy structure as compared to the cys-RGO aerogel, in consistence with its lower density (Fig. 1d). The obvious different morphology observed on cys- and lys-RGO aerogel clearly indicates that the structure of the RGO-based aerogels can be tailored by the addition of different amino acids as the cross-linker. With a more fluffy structure and a lower density, the lys-RGO aerogel is anticipated to have a larger BET specific surface area. However, no valid BET specific surface area can be obtained for the lys-RGO aerogel due to its low thermal stability under vacuum treatment. The thermal unstability of the as-prepared lys-RGO aerogel is clearly shown in its TGA by showing a sharp mass loss of about 18.2 wt.% before 80 °C and the weight loss continues until 500 °C (Fig. S6). Such a sharp weight loss is not observed over the similar cys-RGO aerogel, implying that the heat treatment on the lys-RGO aerogel leads to the collapse of its framework. The XPS spectra of lys-RGO aerogel in the N1s region shows peaks at 399.8 and 401.8 eV, in agreement with the binding energy of the C-N and N-H, and suggests that the lys-RGO aerogel is functionalized with amino groups (Fig. S7a). As compared with that of cys-RGO aerogel, the O-bound C content (21.8 %) in lys-RGO aerogel is higher, indicating a lower reduction degree of RGO in lys-RGO aerogel (Fig. S7b). Accordingly, the $I_D/I_G$ ratio of lys-RGO aerogel (1.03) is also lower than that of cys-RGO aerogel (1.29), indicating that the chemical reduction of GO by L-lys has resulted in RGO with less defects than cys-RGO aerogel (Fig. S4).

In accordance with the reduction of GO to RGO, the diffaraction peak at 10.2° in the XRD patterns for both cys-RGO and lys-RGO aerogels disappears (Fig. S8). Accordingly, the FT-IR spectra of both cys-RGO and lys-RGO aerogels show much weaker peaks at 1730 cm$^{-1}$ and 1385 cm$^{-1}$ as compared with those of GO, indicating that the hydroxyl and carboxyl groups on GO surface have been successfully reduced during the aerogel formation process (Fig. S9). All these characterizations confirmed that the RGO-based aerogels have been successfully obtained.



**Scheme 1** Interactions between GO and L-cysteine (or L-lysine).

The formation of the cys-RGO aerogel and lys-RGO aerogel using different amino acids was depicted in Scheme 1. Since the mixture of L-cys and GO has a pH value of about 3.8, L-cys exists mainly as +1 cation with protonated amino group as well as the zwitterion in the solution. Most of the carboxyl groups on the surface of GO is deprotonated in this pH value since the isoelectric point (IEP) of GO is lower than 2.[8] Therefore, the existences of the electrostatic attraction and the hydrogen bonds between L-cys and GO together with the π-π stacking between GO make GO gellable and the formation of interconnected 3D hydrogels. During the hydrothermal process, GO can be partially reduced to RGO by L-cys. On the contrary, L-lys is a basic amino acid and the pH value of the mixture of L-lys and GO is about 10.8. At this pH value, L-lys exists mainly as anion with deprotonated carboxyl group while a small fraction of L-lys exsits in the form of zwitterion. There still exists electrostatic attraction between the protonated amino group on the side chain of lysine and the de-protonated carboxyl group on GO surface. Besides this, additional hydrogen bond between the amino groups in lysine and the carboxyl groups of GO and the π-π stacking also help to form 3D lys-RGO hydrogel. Since L-lys is larger as compared with L-cys, the dimension of the as-formed lys-RGO aerogel is much bigger than that of the cys-RGO aerogel and is less dense.

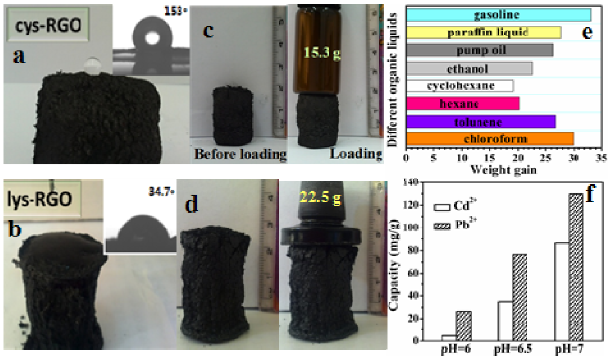


**Fig. 2** Photograph of a water droplet supported on (a)cys-RGO and (b) lys-RGO aerogel (Inset: water contact angle of the aerogel); Photographs of (c)cys-RGO and (d) lys-RGO aerogel; (e) Adsorption capacities of the cys-RGO aerogel towards different organic solvents in terms of their weight gain; (f) Adsorption toward Cd$^{2+}$ and Pb$^{2+}$ over the lys-RGO aerogel at different pH.

It was found that the contact angles of all the prepared cys-RGO aerogels are hydrophobic while all the lys-RGO aerogels are hydrophilic. The contact angle of the prepared cys-RGO aerogels varied from 98.8° to 153.0° with different $r_{G/C}$ ratio (Fig. S10a). A superhydrophobic surface with the contact angle of 153.0° can be obtained when the $r_{G/C}$ ratio was 1:2 (Fig. 2a). A similar variation in the contact angles from 84.0° to 34.7° with $r_{G/L}$ ratio from 1:0.5 to 1:2 was also observed over the as-prepared lys-RGO aerogels (Fig. 2b and S10b). This indicates that the tuning of the surface wettability of RGO-based aerogels can be simply realized by using different type and varied amount of amino acid as cross linkers. The different surface wettability exhibited by two types of aerogels is not hard to understand since the amino acid used in the formation of cys-RGO aerogel (L-cys) contains hydrophobic thiol group while that used in the formation of lys-RGO aerogel (L-lys) contains hydrophilic amino group. The capability of controlling the surface wettability of RGO-based aerogels is important for their applications as adsorbents. In addition to this, both types of aerogels exhibit high mechanical strength, which can be attributed to the superior mechanical properties of the cross-linked RGO structure. The cys-RGO aerogel can support 15.3 g counterpoise without any deformation of its size and shape, more than 255 times of its own weight (Fig. 2c). The lys-RGO aerogel can bear even more weight (22.5 g), which is 375 times of its own weight (Fig. 2d). The stress-strain ($\sigma - \varepsilon$) curves (Fig. S11) shows that for cys-RGO aerogel, the linear-elastic regime is at $\varepsilon < 57\%$ with an elastic modulus over 0.26 MPa, while that of lys-RGO aerogel is at $\varepsilon < 49\%$ with an elastic modulus over 0.45 MPa. The high mechanical strength of aerogels is important for their application since it can sustain the harsh condition during the practical applications.

Porous carbon materials have been widely used as adsorbents for pollutants in water.[9] In particular, porous hydrophobic RGO-based aerogels have been fabricated for oil absorption due to its light weight, high surface area and large open pores. Since cys-RGO aerogel is hydrophobic, its adsorption capabilities for various classes of organic liquids in water were investigated. The cys-RGO aerogels show the adsorption capacity of 19-33 times of its own weight for various oils and organic solvent (Fig. 2e), which is comparable to other typical carbonaceous adsorbents such as graphene foam (10-37 times), graphene sponge (20-86 times) and graphene/α-FeOOH aerogel (13-27 times).[10] Besides this, the cys-RGO aerogel exhibited good recyclability. Even after eight gasoline-adsorbing and drying recycles, it still maintained a high adsorption capacity (91% of the first use) (Fig. S12a).These results demonstrated that the cys-RGO aerogels can be employed as excellent adsorbents for various kinds of oils and organic solvents.

Heavy metal ions in water are of great concern due to their extreme toxicity, biological undegradability and tendency to be accumulated in organisms or food chain. Adsorption is one of the most promising and widely used methods to remove these heavy metal ions from water. A number of materials like active carbon and zeolites have already been used in adsorbing heavy metal ions from aqueous solutions. However, these adsorbents suffer from low adsorption capacities and low removal efficiencies. Due to their large surface area, intercalating and ion exchange properties inherited from RGO, hydrophilic lys-RGO aerogels would be suitable for using as an adsorbent for heavy metal ions in water. The adsorption capability of lys-RGO aerogels toward $Cd^{2+}$ and $Pb^{2+}$ was studied (Fig. 2f). As shown in Fig. 4c, the adsorption toward the heavy metal ions by lys-RGO aerogels occurred from low acidic to neutral pH condition and was highly pH dependent. No precipitation of metal hydroxide occurred during the entire adsorption process. The maximum adsorption occurred at pH=7 and the adsorption capacities for $Pb^{2+}$ and $Cd^{2+}$ are 129.5 and 86.5 mg/g respectively. These values are much higher than those reported previously for GO (22.6 mg/g for $Pb^{2+}$ and 20 mg/g for $Cd^{2+}$) and activated carbon (22.85 mg/g for $Pb^{2+}$ and 33.57 mg/g for $Cd^{2+}$).[11]The enhanced adsorption capability toward heavy metal ions of the lys-RGO aerogel with increased pH value indicates that the adsorption is due to the electrostatic interactions between metal ions and negatively charged GO as well as the ion exchange between the proton and the metal ions. As shown in supporting Fig. S12b, the lys-RGO hydrogel has an isoelectric point (IEP) of 5.2 and its zeta-potentials decreases with increasing pH. Therefore with the increasing of pH value, the negative charge on the surface of RGO aerogel increases, which results in enhanced electrostatic attraction between RGO aerogel and the heavy metal ions. In addition to this, an ion-exchange mechanism between heavy metal ions and proton as well as the coordination interaction between metal ions and deprotonated carboxyl groups may be responsible for their adsorption. At low acidic condition, protons can compete with metal ions for adsorption sites on RGO aerogel, resulting in a low level of adsorbed heavy metal ions. Besides this, no obvious loss of adsorption capacity over lys-RGO aerogel was observed in three consecutive runs, indicating that the lys-RGO aerogel has a high stability during the adsorption process (Fig. S12c).

In summary, the RGO-based aerogels with varied and controllable surface wettability were fabricated hydrothermally from GO and different amino acids as cross linker and reducing agent. Hydrophobic cys-RGO aerogels can selectively adsorb organic pollutants in water while the hydrophilic lys-RGO aerogels can be used as adsorbents for heavy metal ions in water. The capability of the formation of the RGO-based aerogels with tunable surface wettability is important considering their applications as adsorbents toward different absorbates in water.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, photographs of RGO hydrogels with different amino acids concentration, BET, XPS, Raman, TGA, XRD, IR and other characterizations. See DOI: 10.1039/c000000x/

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