Spontaneous assembly of strong and conductive graphene/polypyrrole hybrid aerogels for energy storage†

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Spontaneous assembly of nanoscale building blocks into three-dimensional (3D) frameworks is a vital strategy for practical application in environmental remediation, energy storage/conversion, sensing devices, etc. Herein we report an environmentally friendly, low cost, and easy to scale-up route to synthesize reduced graphene oxide (rGO)-polypyrrole (PPy) hybrid aerogels by applying this novel spontaneous assembly method for the first time. The strong interaction between rGO and PPy, the reaction mechanism, the doping/(conducting) behaviour and the electrochemical energy storage of the resulting hybrid aerogels have been fully characterized by FTIR, Raman, TG, XRD, SEM, TEM, nitrogen sorption tests, CV, EIS, etc. The results show that for the resulting hybrid aerogels, the existence of PPy can significantly enhance the electrochemical capacitance of the rGO aerogels, while the existence of the rGO sheets can greatly enhance the mechanical properties of the PPy assemblies.

Introduction

Aerogels, three-dimensional (3D) porous architectures, can be synthesized from molecular precursors by sol–gel processing or assembling of nanoscale building blocks (e.g. nanoparticles, nanotubes, nanosheets, etc.) with subsequent replacing of the liquids in wet gels with air without collapsing the interconnected microstructure by supercritical fluid drying or freeze drying. Some unique characteristics such as extremely low densities, large open pores and high inner surface areas enable aerogels to be applied in the fields of energy storage/conversion,1–4 catalysis,5–7 environmental remediation,8–11 sensing devices,12–14 and so on. But no aerogel has so far been reported to be prepared by spontaneous assembly of the starting materials in the absence of oxidants, reductants, high temperature, etc.

Among various nanoscale building blocks, graphene is one of the most attractive 2D nanoscale building blocks due to its excellent electronic, mechanical, optical, large-specific-surface-area and bio-compatible properties.15,16 Thus, the studies on the assembly of graphene nanosheets into 3D hydrogel/aerogel have flourished.17–19 However, trenchant conditions, such as high temperatures, high pressures and hazardous chemical agents, are generally involved in various processes. Moreover, the major challenge in graphene-based aerogels is that graphene nanosheets easily form irreversible agglomerates or even graphitic stacking due to strong inter-layer π–π interactions and hydrophobic interactions. Consequently, the inherent properties of pristine graphene nanosheets cannot be exploited thoroughly and the aerogels usually exhibit inferior mechanical properties, which inhibit the application of the graphene-based aerogel, for instance in energy storage and conversion. Although metal salts have been introduced into GO solution to prevent the overlap of reduced graphene oxide (rGO) nanosheets and maximize the specific surface area, this strategy is not very desirable due to its fussy and expensive process.20–22

Pyrrrole (Py) is a heterocyclic aromatic compound comprising a five-membered ring which is used as a monomer in polypyrrole (PPy) synthesis by chemical- or electro-polymerization. PPy has been widely explored for its good conductivity, facile synthesis, low cost, good stability and high redox pseudocapacitive charge storage.23–25 Therefore, PPy is considered as a desired mediator to construct 3D graphene based composites. Lee and co-workers reported that graphene oxide (GO) can be reduced with Py and the oligomers of Py adsorbed on the graphene nanosheets by π–π interactions with the help of heat treatment.26 Bai et al. synthesized the graphene oxide/conducting...
polymer composite hydrogels using GO and Py monomers as the feedstock with ammonia persulfate as an oxidizing agent.\textsuperscript{27} 3D graphene-PPy hydrogels have been created by the one-step self-assembly process in the presence of Cu\textsuperscript{2+}, which helps the realization of the oxidation polymerization of Py meanwhile the newly generated Cu\textsuperscript{2+} ions synchronously reduced GO into graphene for accomplishing the construction of the composite hydrogel.\textsuperscript{28} In addition, graphene-PPy foam synthesized via a multistep route by hydrolytic condensation (cross-linking), polymerization reactions and hydrothermal reduction of GO was reported by Liu and co-workers.\textsuperscript{29} Recently, a new method was created in which 3D porous PPy-G foam was prepared by hydrothermal reduction of GO aqueous dispersion with the Py monomer and consequently \textit{in situ} electro-polymerization of Py.\textsuperscript{24,25} As a result, all these 3D graphene-PPy architectures were prepared through multistep routes and trenchant conditions generally employed in the process of synthesis, which was desirable for neither scale-up nor energy conservation and environment protection.\textsuperscript{30,31}

Herein we have developed a spontaneous assembly method to construct rGO-PPy hybrid aerogel at room temperature, which is environmentally friendly and easy to scale-up. The redox reaction between GO and Py resulted in reduction of GO and polymerization of Py in the meantime without addition of any other oxidation or reduction agents. Various mass ratios of GO to Py have been studied for the formation of rGO-PPy hybrid hydrogels, and the specific surface area, thermal stability, electrical conductivity and mechanical properties of the corresponding hybrid aerogels have also been studied. As a supercapacitor electrode material, the rGO-PPy aerogel shows high specific capacitance (304 F g\textsuperscript{-1}) at a current density of 0.5 A g\textsuperscript{-1} in an aqueous electrolyte. The work presented here, to the best of our knowledge, is the first report on the spontaneous assembly of the hybrid aerogels in the absence of any other oxidant as well as reductant with extremely mild conductions. Our work might also give inspiration to synthesize more hybrid aerogels based on graphene and any other conducting polymer such as polyaniline, polythiophene, \textit{etc.} and the resulting hybrid aerogels might find broad application in the fields including energy storage, industrial catalysis, water purification, \textit{etc.}

**Experimental**

**Materials**

Graphite (crystalline powder, 400 mesh), P\textsubscript{2}O\textsubscript{5}, K\textsubscript{2}S\textsubscript{2}O\textsubscript{7}, 30% H\textsubscript{2}O\textsubscript{2}, HCl and H\textsubscript{2}SO\textsubscript{4} were purchased from Sinopharm Chemical Reagent Company. These chemicals were of analytical grade and were used without further purification. The Py monomer was purchased from Qiangsheng Chemical Reagent Company and was further purified by vacuum distillation and then stored at 0 °C before use. GO was prepared from graphite powder by a modified Hummers method reported in our previous study.\textsuperscript{32}

**Synthesis of rGO-PPy hybrid hydrogels/aerogels**

rGO-PPy hybrid hydrogels were synthesized via an \textit{in situ} polymerization method. Typically, different amounts of purified Py were added to 4 mL 8 mg mL\textsuperscript{-1} GO suspension under stirring and dispersed by ultrasonication to obtain a homogeneous solution. Then the reaction mixture was kept under ambient conditions (\textsim 25 °C) for three days to obtain rGO-PPy hydrogel, which was defined as the aging process. After aging, the hydrogel was washed with ethanol to remove impurities in the hydrogel network by the solvent-exchange process, and then supercritically dried with CO\textsubscript{2} (40 °C, 10 MPa) for 12 hours to obtain rGO-PPy hybrid aerogel. To investigate the effect of synthetic conditions, the aerogels with the initial mass ratios of GO to Py of 100:1, 50:1, 40:1, 30:1, 20:1, 15:1, 9:1, 7:1, 5:1, 3:1, 1:1, 1:3, 1:5, 1:7, 1:9, 1:10, 1:20 and 1:30 were synthesized, which were named GP100, GP50, GP40, GP30, GP20, GP15, GP9, GP7, GP5, GP3, GP1, PG3, PG5, PG7, PG9, PG10, PG20, and PG30 respectively. For comparison, rGO aerogel reduced with l-ascorbic acid with the initial GO concentration of 8 mg mL\textsuperscript{-1} and polypyrrole aerogel were also prepared by the method as reported in ref. 32 and 33.

**Electrochemical investigation on the rGO-PPy hybrid aerogels**

Electrochemical performances of the products were investigated in a three-electrode test system using an electrochemical workstation (Chenhua, CHI 660D) with a platinum wire and a saturated calomel electrode (SCE) as the counter electrode and the reference electrode, respectively. 6 M KOH aqueous solution was used as the electrolyte. The CV curves were scanned from 5 mV s\textsuperscript{-1} to 50 mV s\textsuperscript{-1} within −1 to 0 V potentials. The galvanostatic charge–discharge tests were carried out at current densities of 0.5 A g\textsuperscript{-1}, 1 A g\textsuperscript{-1}, 2 A g\textsuperscript{-1}, 5 A g\textsuperscript{-1}, 10 A g\textsuperscript{-1}, respectively. The EIS was recorded in the frequency range of 0.01 Hz to 100 MHz. The working electrode was made by pressing the as-prepared rGO-PPy hybrid aerogel into Ni foam with a size of 1.5 cm × 1.5 cm under a pressure of 5 MPa without addition of any binders and other conductive additives. The rGO and PPy aerogel electrodes were prepared by the same procedure.

**Instrumentation**

The FT-IR spectra were acquired using a Nicolet 6700 Fourier Transform Infrared Spectrometer (FT-IR, Nicolet 6700, Thermo Fisher Scientific). The specimens for FT-IR measurements were prepared by grinding the rGO-PPy aerogel and KBr together, and then compressed into thin pellets under 10 MPa. Raman spectra were recorded using a LabRAM HR Raman Spectrometer (LabRAM HR, Horiba-JY) fitted with a 632.8 nm laser. The crystal structure was characterized by X-ray diffraction (XRD, D8 Advance, Bruker AXS). A field emission scanning electron microscope (FESEM, Hitachi S-4800), X-ray Energy Dispersive Spectrometer (EDS, Apollo 40SDD) and transmission electron microscope (TEM, Tecnai G2 F20 S-Twin) were used to investigate the morphology and microstructure of...
the samples. The pore structure of the samples was analyzed using a Surface Area Analyzer (Micrometrics, ASAP 2020 HD88). The Brunauer–Emmett–Teller (BET) method and the Barrett–Joyner–Halenda (BJH) model were utilized to determine the BET specific surface area (SSA) and the pore size distribution, respectively. Thermogravimetric analysis (TGA) was performed on a TG 209 F1 thermogravimetric analyser (NETZSCH, TG 209 F1 Iris). The heating rate was set to 10 °C min$^{-1}$ under N$_2$ and the analytical temperature region was set from ambient temperature to 900 °C. The conductivity of rGO-PPy aerogels was evaluated using a four point probe tester (Hengci, ST-2258A). Nano Indenter (Agilent Technologies, G200) was used to explore the mechanical properties of rGO-PPy aerogels.

**Results and discussion**

The procedure for fabricating the rGO-PPy aerogels is illustrated in Fig. 1a. Two important steps are included, namely the synthesis of rGO-PPy hydrogels, and subsequent supercritical CO$_2$ drying. The GO aqueous suspension (4 mL, 8 mg mL$^{-1}$) was mixed uniformly with different amounts of the Py monomer by ultrasonication for about 10 min. Ambient temperature ($\sim$25 °C) aging was performed to obtain rGO-PPy hydrogel. During the aging process, the Py monomer reduced GO to rGO and itself was oxidized to PPy. Three days later, the rGO-PPy hydrogel was obtained which was consequently washed with plenty of water to get rid of unpolymerized Py, followed by solvent-exchange with an alcohol. Supercritical CO$_2$ drying of the hydrogel was the final step to acquire the corresponding rGO-PPy aerogel. The densities of the obtained rGO-PPy aerogels were in the range of 28 to 45 mg cm$^{-3}$ (see Fig. S11a†). To obtain rGO-PPy hydrogels, the optimal mass ratios of GO to Py monomer should be below 40 : 1 as shown in Fig. 1b and the stable rGO-PPy hydrogels evaluated by a tube inversion method were seldom observed if mass ratios of GO to Py monomer should be below 40 : 1. The above phenomenon has demonstrated that much less reductant, Py, is needed to reduce GO and to induce the assembly of rGO to the 3D network than l-ascorbic acid as the reductant. With the Py amount increasing, the obtained rGO-PPy hydrogels shrank to some extent due to the higher degree of reduction of GO by the excess Py monomer and some PPy with low polymerization degree would diffuse out of the network, which made the reaction solution become yellow (Fig. S11b†).

To understand the interactions between Py and GO, the FT-IR absorption spectra of PPy, GO, rGO and rGO-PPy aerogel (PG5) were acquired and compared as shown in Fig. 2a. For the curve of GO, the peaks located at 1735, 1043, 1226 and 1056 cm$^{-1}$ correspond to carbonyl C=O stretching vibration, carboxy C=O stretching vibration, C–OH stretching vibration, and epoxy C=O stretching vibration, respectively. The peak around 1616 cm$^{-1}$ can be assigned to the aromatic C=C stretching vibration. After chemical reduction (the curve of rGO), the peaks for oxygen-containing groups of GO are reduced significantly or entirely vanished. The remaining peaks at 1731, 1573 and 1222 cm$^{-1}$ are attributed to the carbonyl C=O, aromatic C=C and residual –OH. The results are in agreement with a previous report. The characteristic peaks of PPy located at 1540 and 1450 cm$^{-1}$ are due to the symmetric and anti-symmetric ring-stretching modes, respectively. The bands at 1040 and 1300 cm$^{-1}$ are attributed to C–H band in-plane vibration and C–N stretching vibrations, respectively. Meanwhile, the peaks near 1170 and 893 cm$^{-1}$ indicate the doping state of PPy and the bands at 783 and 964 cm$^{-1}$ verify the presence of the polymerized pyrrole.33,37,38 For the sample PG5, the above mentioned typical vibration band related to the oxygen-containing groups of GO are reduced significantly or vanished and several new bands located at 1562, 1461, 1041 and 1365 cm$^{-1}$ appear at the same time which adhere to the stretching vibration band of PPy rings and the C–N stretching vibration of Py, but shift a little bit to the higher wavenumber direction, which probably is due to the π–π interaction between rGO nanosheets and aromatic PPy rings. The peaks at 782 cm$^{-1}$ and 960 cm$^{-1}$ in the curve of PG5 are relatively weak due to the low polymerization degree of PPy. In addition, the peaks related to the doping state of PPy in the PG5 demonstrate that PPy is doped by protons dissociating from GO. These results indicate that GO nanosheets are reduced by Py and the Py monomer is polymerized by the oxygen-containing groups of GO during the formation of the rGO-PPy hydrogels. However the doping level of PPy is limited due to the finite

![Fig. 1](image-url) Fig. 1 (a) Schematic illustration of the formation mechanism of the rGO-PPy aerogels and (b) the effect of the mass ratio of GO to Py on the hydrogel formation.

![Fig. 2](image-url) Fig. 2 (a) FT-IR spectra and (b) XRD patterns of GO, PPy, rGO-PPy and rGO reduced by l-ascorbic acid.
dissociation of carboxyl groups located on the edges of GO nanosheets, which corresponds to the relatively low electrical conductivity of the rGO-PPy hybrid aerogels as shown in Fig. SI2.†

Raman spectroscopy measurements further confirm the polymerization of Py by GO nanosheets as shown in Fig. SI3.† The Raman spectrum of GO displays two bands located at 1353 cm\(^{-1}\) and 1593 cm\(^{-1}\). These two bands could be assigned to the D and G bands for the carbon material. The D band corresponds to the first-order zone boundary phonons existing in a deformed graphene, whereas the G band corresponds to the in-plane bond-stretching motion of C–sp\(^2\) atoms. The Raman spectrum of rGO aerogel reduced by L-ascorbic acid shows D and G bands at 1324 and 1582 cm\(^{-1}\) respectively. However, the intensity of the D band at 1324 cm\(^{-1}\) increases obviously, which indicates the significant decrease of the size of the in-plane sp\(^2\) domains.\(^{39,40}\) The Raman spectrum of Py shows a band at around 1574 cm\(^{-1}\), corresponding to the C=C backbone stretching of Py. The band at 1326 cm\(^{-1}\) is attributed to the ring stretching mode of Py. The peak at 1043 cm\(^{-1}\) is attributed to the C–H in-plane deformation. The bands located at about 983 and 933 cm\(^{-1}\) correspond to ring deformations associated with the dication (bipolaron) and the radical cation (polaron), respectively.\(^{30,35,41,42}\) The Raman spectrum of the PG5 aerogel shows the characteristic bands of Py and an enhanced intensity of the band around 1330 cm\(^{-1}\), which indicates strong interactions between Py and rGO nanosheets.

The electronic structure and the surface chemistry composition of the as-prepared rGO-PPy aerogels were also investigated by XPS measurements. As shown in Fig. SI4a,† only the peaks corresponding to C 1s (284.5 eV) and O 1s (531.5 eV) signals can be clearly detected in the survey spectrum of the GO. It is worth noting that an additional signal centred at 399.5 eV ascribed to N 1s can be observed for rGO-PPy aerogel (PG5), which is consistent with the EDX analysis mentioned above. Moreover, the O 1s and C 1s peaks of the carbons binding to oxygen atoms of PG5 become significantly weak and the C 1s peak becomes much stronger in comparison with those of GO, which suggests the recovery of the π-conjugated structure. Fig. SI4b† shows the de-convolution C 1s XPS spectrum of GO. Four types of carbon-containing functional groups centred at 284.5, 286.5, 287.3 and 288.7 eV, corresponding to C≡C in aromatic rings, C–O (epoxy and alkox), C=O, and O–C≡O (carboxyl) respectively, are detected.\(^{43-45}\) In the case of PG5 aerogel (Fig. SI4c†), the intensity of all C 1s peaks of carbons binding to oxygen, especially the peak of C–O (epoxy and alkox), decreases dramatically. At the same time, the C–N linkage peak (285.2 eV) can also be detected, which originates from Py in PG5 aerogel.\(^{46,47}\) In addition, a stronger π–π* shake-up satellite peak around 291.5 eV, a characteristic of aromatic or conjugated systems,\(^{48}\) is observed for PG5 rather than for GO, indicating that less defects in the structure are present in PG5 and the π–π interaction exists between rGO and Py in PG5 aerogel. The peak centred about 399.5 eV corresponds to the N 1s region. The symmetric N 1s XPS peak of PG5 (Fig. SI4d†) at 399.5 eV corresponds to “pyrrolic” nitrogen,\(^{49,50}\) which is derived from Py in PG5. The calculated atomic percentage of N in PG5 is 7.37 atom% (8.05 weight%), which is different from the original content of Py (PG5, the ratio of Py to GO is 5, which means the Py content in weight is 83.33% (the N content in weight is 17.41%)). The main reason of the N content decrease is that Py could not be totally polymerized in the reaction process, which is in accordance with the results in Fig. SI1b.†

The XRD patterns reveal crystal forms of pure Py, GO, rGO-PPy aerogel (PG5) and rGO aerogel as shown in Fig. 2b. A broad characteristic peak of Py appears at about 25°, indicating its amorphous nature.\(^{38,51}\) The diffraction peak of GO centred at 10.7° corresponds to the interlayer spacing of 0.77 nm. For rGO reduced by L-ascorbic acid, the diffraction peaks at 22.4° and 42.6° can be attributed to the graphite-like structure (002) and (100), respectively.\(^{52}\) In the case of PG5, the peak located at 10.7° disappears, which indicates the successful reduction of GO with Py acting as a reductant. The peak at 23.1° can be attributed to the diffraction peak of either Py or rGO. The interaction between Py and rGO has induced the peaks to shift from their primary positions. The peak located at 42.6° in the case of the rGO-PPy is a fingerprint peak for graphite, due to the (100) diffraction, indicating the reformation of graphitic microcrystals on the graphene plane due to the reduction of GO by the Py monomer, which is in accordance with the rGO aerogel reduced by L-ascorbic acid.

The field emission scanning electron microscopy (FESEM) images manifest the microstructure of the rGO-PPy aerogels as shown in Fig. 3a, b and SI5.† The rGO-PPy aerogel (PG5) has a microporous 3D network with interconnected pores with a wide size distribution due to randomly self-assembled inter-twisted rGO nanosheets. What is more, the solid walls of the pores are thin, which demonstrates that the stacking of rGO nanosheets is inhibited by Py remarkably. The mesoporous nature of rGO-PPy aerogels is further investigated by the nitro-
gen physisorption measurement. The N$_2$ adsorption isotherm of rGO-PPy aerogel (GP3) [Fig. 3c] is of type IV attributed to monolayer-multilayer adsorption, suggesting the mesoporous nature of the rGO-PPy aerogel. The N$_2$ adsorption–desorption isotherm of rGO-PPy aerogel (GP3) exhibits a hysteresis loop with the character of H4, indicating the presence of slit-like pores.$^{53}$ The hysteresis between the adsorption and desorption branches (at 0.4–0.6 P/P$_0$) further suggests a highly uniform pore size with no pore-blocking effects from narrow pores during desorption,$^{54}$ which conforms to the pore-size distribution plots calculated using the Barrett-Joyner-Halenda (BJH) method from the desorption branch of the isotherm. The pore size is mainly about 3.9 nm as shown in Fig. 3d. The Brunauer–Emmett–Teller (BET) analysis further reveals the specific surface area of rGO-PPy aerogel (GP3) with a value of 408 m$^2$ g$^{-1}$. As comparison, rGO aerogel exhibits a similar adsorption–desorption isotherm but lower BET specific area (167 m$^2$ g$^{-1}$, Fig. SI6†), resulting from stacking and coalescing of rGO nanosheets. The energy dispersive X-ray (EDS) is employed to detect the distribution of PPy within the rGO-PPy aerogels. As shown in Fig. SI7,† carbon, nitrogen and oxygen elements in the rGO-PPy aerogels distribute homogenously, indicating the uniform distribution of PPy on rGO nanosheets.

The geometrical morphology of PPy is further displayed in TEM and HR-TEM images as shown in Fig. 4 (and Fig. SI8†). For GO nanosheets, leaf-like transparent sheets with wrinkles are observed in Fig. 4a. Furthermore, according to the HR-TEM results, clearly plates can be seen in Fig. 4b. The selected area electron diffraction (SAED) pattern (the inset of Fig. 4b) shows only diffraction rings, indicating the disordered nature of GO. As shown in Fig. 4c and d, PPy in the form of plate-like nanoparticles with different sizes disorderedly anchors onto rGO nanosheets, which could be ascribed to the polymerization of Py with different oxygen-containing groups with different oxidizing abilities randomly attached on GO nanosheets. The SAED pattern of rGO-PPy aerogel (PG5) shows several bright spots and some amorphous circles, which are derived from rGO and amorphous PPy respectively. The comparison between GO and PG5 indicates that GO is reduced by Py and Py is polymerized by oxygen-containing groups of GO simultaneously. What is more, the geometrical morphology of PPy also proves that slit-like pores in the GP3 are constructed by plate-like PPy nanoparticles.

The thermal stabilities of GO, rGO, PPy and the rGO-PPy aerogel (PG5) are shown in Fig. 5a. It can be seen from this figure that all the products show different mass losses below 100 °C due to de-intercalation of water absorbed in the products. In the case of pure PPy, nearly 21.24% weight loss occurs at around 200 °C, ascribed to the decomposition of PPy chains.$^{55,56}$ 14.19% of its mass is maintained at 900 °C. As for GO, it displays a steep weight loss at around 189 °C, ascribed to the decomposition of labile oxygen-containing groups of GO, similar results were reported by Fang et al.$^{57}$ With the increment of temperature, the residual oxygen-containing groups with high bond energy decompose gradually. A 51.04% mass loss has been detected when the temperature rises to 900 °C. rGO shows a weight loss about 18.59% at 100–500 °C due to the removal of oxygen-containing groups by l-ascorbic acid, illustrating a much higher thermal stability in comparison with GO. The remaining small fraction of stable oxygen-containing groups on the rGO nanosheets is removed during the TG heating scan. 51.1% initial mass of rGO is reserved at 900 °C. The TG curve of PG5 is seriously different from pure GO and pure PPy. 23.84% of mass loss for PG5 at 100–500 °C replaces the steep weight loss of 38.14% for GO at the same temperature, which can be ascribed to that some oxygen-containing groups of GO are removed by Py. 59.13% of PG5 in weight still remained at 900 °C, indicating that it is much more stable than the individual GO, PPy and even rGO aerogel reduced by l-ascorbic acid. The possible reasons for high thermal stability of PG5 are as follows. Firstly, most oxygen-containing groups of GO are removed by the Py monomer and Py is oxidatively polymerized by GO simultaneously. Secondly, the sandwich-like structure of PG5 inhibits the thermal decomposition of rGO and PPy. Thirdly, the strong doping interaction between PPy and protons dissociating from rGO,
which is confirmed from the FT-IR and Raman results, increases the energy for decomposing rGO and PPy.

The mechanical properties of rGO-PPy aerogel (PG5) and rGO aerogel are investigated by the nanoindentation test. Fig. 5b shows the storage modulus and loss modulus of PG5 aerogel and rGO aerogel. For both PG5 and rGO aerogels, all the storage modulus values are higher than the loss modulus values over the entire range of frequencies, indicating an elastic rather than a viscous response of the composite aerogels under the small-deformation oscillation and that both rGO-PPy aerogel and rGO aerogel have a permanent cross-linked network. The storage modulus of 12.2 MPa for PG5 aerogel is much higher than the value of 6.36 MPa for rGO aerogel, which shows that rGO-PPy aerogel exhibits better elastic response performance than rGO aerogel. On the other hand, the mechanical performance of PG5 is much more outstanding than that of other aerogels. These remarkable mechanical properties of rGO-PPy aerogel can be attributed to the factors as follows: (a) the strong π–π interaction between rGO nanosheets and PPy chains; (b) PPy acting as a cross-linker in the rGO-PPy aerogels with a sandwich-like structure; (c) the doping reaction between PPy chains and protons dissociated from rGO nanosheets; (d) the excellent mechanical properties of the rGO nanosheets themselves.

The large BET surface areas and pore volumes, together with excellent mechanical properties, can make these rGO-PPy aerogels viable candidates for use in many fields such as energy storage, catalysis, sensors, etc. It can be seen that the CV curve of rGO aerogel (Fig. 6a) exhibits a typical rectangular shape, implying pure electrical double-layer capacitive behaviour. In contrast, the CV curve of GP3 aerogel displays a box-like shape combined with a pair of redox peaks in the potential range of −0.7 to −0.5 V. Fig. SI9a† shows the CV curves of GP3 aerogel, pure PPy and GO; there is no redox peak in the potential range of −0.7 to 0.5 V for pure PPy and GO and the areas covered by the CV curves of pure and GO are much smaller than that of GP3. The phenomenon above demonstrates that the redox peaks appearing in GP3 CV curves is caused by the PPy doped with protons dissociating from rGO and indicates the coexistence of both the electrical double-layer capacitance and pseudo-capacitance. With the increase of the PPy content in rGO-PPy hybrid aerogels, the intensity of the redox peaks shows the tendency of monotonically increasing and decreasing in sequence and GP3 exhibits the highest redox peak current, which manifests that GP3 realizes the best synergistic effect between rGO and PPy. Fig. 6b shows the typical CV curves of the GP3 aerogel at various scan rates. With an increase in scan rate, the current response increases accordingly. The CV curves retain their shape with small distortions, which implies that the GP3 aerogel electrode has good rate performance and low internal resistance. Fig. SI9b† shows the galvanostatic charge–discharge curves of GP3, rGO, GO and pure PPy at the current density of 0.5 A g⁻¹. It can be seen that GP3 aerogel exhibits nonsymmetric triangular shape, which is also the signal of the existence of pseudo-capacitance besides the electric double layer capacitance. The specific capacitances calculated from the slope of the charge discharge curves are 304 F g⁻¹ and 230.8 F g⁻¹ at current densities of 0.5 A g⁻¹ and 1 A g⁻¹ respectively, which are higher than the performance of supercapacitors made of graphene aerogels prepared by one-step hydrothermal processing and by L-ascorbic acid reduction. This electrochemical performance enhancement could be ascribed to two factors, namely the redox peaks of PPy and the porous surface morphology of GP3 aerogel. In order to further investigate the synergistic effect between PPy and rGO, we evaluated the specific capacitances of rGO-PPy aerogels with different mass ratios of GO to Py and rGO as shown in Fig. 6c. The specific capacitances of all the samples decrease with the increase in the current density, which can be attributed to the required time for ionic migration in the material. The specific capacitance of rGO aerogel is much lower than that of rGO-PPy aerogels at the same current density, which is attributed to that the self-aggregation of rGO in the reduction process makes the rGO aerogel provide less access for the electrolyte. The increase in the specific surface area of the rGO-PPy hybrid aerogels in comparison with rGO aerogel is the main reason for the improved capacitance performance, which is consistent with the BET specific area evaluated above. The pseudo-capacitance conferred by PPy in rGO-PPy aerogels also plays an important role in enhancing the capacitance. For rGO-PPy aerogels, there is an initial increase in the values of the specific capacitance with an increase of the Py amount added in the reaction mixture as shown in Table S11.† GP3 aerogel shows the highest specific capacitance compared with other rGO-PPy aerogel electrodes, attributing to the best synergy of rGO and PPy. The highest BET specific surface area and pseudo-capacitance provided by PPy result in the highest specific capacitance of GP3.
Electrochemical impedance spectroscopy (EIS) analysis was carried out in a frequency range of 0.01–10 kHz to investigate the charge-transfer resistance and the ion diffusion rate of the obtained rGO-PPy aerogels and rGO aerogel as shown in Fig. 6d. These results provide important clues to understand the mechanism behind the different supercapacitive performances exhibited by the above aerogels. The Nyquist plots of all aerogels are composed of semicircles in the high frequency region and a straight line in the low frequency region. The equivalent circuit model of all Nyquist plots exhibits that the whole capacitor circuit is constructed by \( R_s \), \( R_{ct} \), CPE and \( Z_w \) as shown in the insert of Fig. 6d. \( R_s \) is the internal resistance, representing the sum of the electrolyte solution resistance, the intrinsic resistance of the active material and the contact resistance at the electrode–electrolyte interface, in which the electrolyte solution resistance is commonly predominant. \( R_{ct} \) in the Nyquist plot is equal to the value of the intercept of the semicircle with the Y-axis. \( R_{ct} \) is the charge-transfer resistance, which corresponds to the semicircular portion in the high frequency range. \( R_{ct} \) in the Nyquist plot is related to charge transfer through the three electrode–electrolyte interface.\( Z_w \) is the Warburg resistance related to the ion diffusion/transport in the electrolyte, which fits to the linear part in the mid-frequency region. A constant phase element is used instead of the pure capacitance due to the depressed semicircle. The results of fitting are shown in Fig. SI10,† which demonstrates that the equivalent circuit model is reasonable. The Nyquist plot of rGO aerogel shows a small semicircle in the high frequency region and the value of \( R_s \) and \( R_{ct} \) of the rGO electrode are 0.3362 \( \Omega \) and 2.125 \( \Omega \) respectively, which could be ascribed to the little residual oxygen-containing groups. All of rGO-PPy samples exhibit an obvious semicircle in the high frequency region, demonstrating that rGO-PPy has larger interfacial charge-transfer resistance than rGO aerogel. Calculated using the Zview software, the charge transfer resistance of GP3 is 7.814 \( \Omega \), which is smaller than 37.94 \( \Omega \) of GP5, attributing to that GO is further reduced by Py. While the charge transfer resistance increases gradually with the increment of Py monomer which is further polymerized in the undoped state (as shown in Table SI2†). The lowest \( R_{ct} \) of GP3 could be explained by the synthetic mechanism of the rGO-PPy aerogels. The resistance of rGO-PPy aerogel is reduced by reducing GO to rGO by the Py monomer, while the polymerization of Py to PPy induces the rise of the resistance for the rGO-PPy aerogel due to the lack of further doping by protons. The rGO-PPy aerogel with the lowest resistance is prepared at an appropriate mass ratio of GO to Py that GO could be reduced by the Py monomer and the polymerized PPy doped with protons anchored on rGO nanosheets. The straight line in the high frequency region of GP3 leans more towards the imaginary axis than that of others, demonstrating its higher specific capacitance. To investigate the electrochemical stability of rGO-PPy aerogel, galvanostatic charge–discharge cycling was performed at a current density of 1 A g\(^{-1}\) (Fig. SI11†). GP3 shows an initial specific capacitance value of 230.8 F g\(^{-1}\). At the initial charge–discharge cycling, a decrease of the specific capacitance is observed, resulting from the structural change of PPy such as decomposition of the PPy main chain during the repeated charge/discharge cycles in a strong basic environment. After 50 cycles, the specific capacitance of GP3 drops down to 134 F g\(^{-1}\), which is 58.26% of the initial specific capacitance value. The decrease in GP3 capacitance could be ascribed to the decomposition of PPy chains with a low degree of polymerization in the strong basic environment. The retained capacitance is provided by rGO, thanks to its superior chemical and electrochemical stability. This indicates that Py is polymerized by oxygen-containing groups of GO and GO is reduced by Py at the same time, which is the key to synthesize rGO-PPy aerogels. The electrochemical measurements not only investigate the energy storage capabilities of rGO-PPy aerogels but also further illuminate the reaction mechanism between GO and Py monomer. We believe that the rGO-PPy aerogel based supercapacitor can be further optimized for the best performance by adjusting the synthetic parameters, annealing the resulting products, etc.

Conclusions

rGO-PPy hybrid aerogels were prepared by an in situ redox polymerization (i.e. spontaneous assembly) method without adding any other reductants or oxidizing agents. The obtained hybrid aerogels exhibited excellent mechanical properties and outstanding electrochemical supercapacitor performance, considerably higher than the rGO counterpart reduced by L-ascorbic acid. High mechanical properties are ascribed to the strong π–π interaction between PPy and rGO and the doping reaction of the protons dissociated from rGO into the PPy main chain. The method might pave the way to prepare various rGO-conducting polymer hybrid aerogels with potential application in many fields.

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Notes and references