Plasma-induced, nitrogen-doped graphene-based aerogels for high-performance supercapacitors

Xue-Yu Zhang\(^1\), Shi-Han Sun\(^1\), Xiao-Juan Sun\(^2\), Yan-Rong Zhao\(^1\), Li Chen\(^3\), Yue Yang\(^1\), Wei Lü\(^1\) and Da-Bing Li\(^2\)

Commonly used energy storage devices include stacked layers of active materials on two-dimensional sheets, and the limited specific surface area restricts the further development of energy storage. Three-dimensional (3D) structures with high specific surface areas would improve device performance. Herein, we present a novel procedure to fabricate macroscopic, high-quality, nitrogen-doped, 3D graphene/nanoparticle aerogels. The procedure includes vacuum filtration, freeze-drying, and plasma treatment, which can be further expanded for large-scale production of nitrogen-doped, graphene-based aerogels. The behavior of the supercapacitor is investigated using a typical nitrogen-doped graphene/Fe\(_3\)O\(_4\) nanoparticle 3D structure (NG/Fe\(_3\)O\(_4\)). Compared with 3D graphene/Fe\(_3\)O\(_4\) structures prepared by the traditional hydrothermal method, the NG/Fe\(_3\)O\(_4\) supercapacitor prepared by the present method has a 153\% improvement in specific capacitance, and there is no obvious decrease in specific capacitance after 1000 cycles. The present work provides a new and facile method to produce large-scale, 3D, graphene-based materials with high specific capacitance for energy storage.

Light: Science & Applications (2016) 5, e16130; doi:10.1038/lsa.2016.130; published online 7 October 2016

Keywords: energy storage; N-doping; plasma; three-dimension

INTRODUCTION

The intrinsic two-dimensional (2D) structure of graphene provides unique physical properties, making it possible to fabricate self-assembled, three-dimensional (3D) architectures\(^1\). Combining functional nanomaterials with 3D graphene structures would enhance their specific applications. Recently, 3D, graphene-based materials have attracted attention due to their porous structure, which provides a high specific surface area and synergetic effects in the composites\(^14\)-\(^19\). The 3D, graphene-based hybrids are becoming candidates for energy storage, such as in Li ion batteries, hydrogen storage and supercapacitors\(^20\)-\(^24\). Several methods have been reported for fabricating 3D, porous, graphene-based structures, including chemical vapor deposition\(^25\), growth assisted by a template\(^26\)-\(^28\) and chemical self-assembly\(^29\)-\(^34\). In spite of the significant development for constructing 3D graphene-based structures, these commonly used fabrication methods are generally multistep, hard to control and involve harmful chemical agents. Therefore, further development for preparing high-quality 3D structures is still highly desirable.

In addition, the capacitance of intrinsic graphene is not sufficient for commercial applications but can be improved by N-doping\(^35\)-\(^39\). The preparation of N-doped graphene sheets by arc discharge/plasma treatment and chemical vapor deposition (CVD) thermal annealing of graphene oxide (GO) with NH\(_3\) have been reported\(^35\),\(^40\),\(^41\). Plasma treatment is an eco-friendly and efficient way to produce N-doped graphene sheets, and several reports have demonstrated N-doping of graphene by plasma\(^42\),\(^43\). However, these reports address 2D structures and are not aimed at energy storage. A method for fabricating high-quality, N-doped, graphene-based, hybrid, 3D structures does not exist.

In this work, we report a novel method for preparing N-doped, 3D, graphene/Fe\(_3\)O\(_4\) nanoparticle aerogel (NG/Fe\(_3\)O\(_4\)), which can be expanded for large-scale production of nitrogen-doped, graphene-based aerogel and various active nanomaterials can be incorporated into the 3D hybrid structures. The high-quality NG/Fe\(_3\)O\(_4\) aerogels are acquired by controllable physical treatment of GO. Compared with the 3D reduced-graphene/Fe\(_3\)O\(_4\) (RGO/Fe\(_3\)O\(_4\)) prepared by the commonly used hydrothermal method, the present method produces greatly improved porous networks and exhibits significantly enhanced supercapacitor performance. The present work provides a new and facile method to produce high-quality, 3D, graphene-based materials for application in energy storage.

MATERIALS AND METHODS

Preparation of GO and Fe\(_3\)O\(_4\) nanoparticles

A modified Hummers method was used to prepare GO. Fe\(_3\)O\(_4\) nanoparticles (NPs) were prepared by FeCl\(_3\)-6H\(_2\)O (58 mg) and FeCl\(_2\)-4H\(_2\)O (21.5 mg), which were added to 30 ml deionized water and deoxygenated for 15 min with nitrogen gas. After heating...
to 80 °C, NH₃·H₂O (600 μl, 20 wt%) was injected rapidly and kept stirring for 1 h. The resulting Fe₃O₄ NPs were separated from the reaction mixture with a magnet after cooling to room temperature.

**Preparation of NG/Fe₃O₄**

A GO solution, including appropriate Fe₃O₄ NPs, was stirred for 1 h to obtain the GO/Fe₃O₄ suspension. Then, the GO/Fe₃O₄ suspension was deposited onto Ni-foam by vacuum filtration, followed by freeze-drying. Finally, the GO/Fe₃O₄ composites were reduced and nitrogen-doped simultaneously by hollow cathode (HCD) plasma discharge for 15 min in Ar and N₂ (Figure 1). The as-prepared sample was denoted as NG/Fe₃O₄. A schematic view of the HCD system used for the plasma treatment and the plasma experiment parameters are shown in Supplementary Fig. S1 and Table S1, respectively.

**Hydrothermal synthesis of RGO/Fe₃O₄**

For comparison, RGO/Fe₃O₄ fabricated by the commonly used hydrothermal method was prepared, and the electrochemical behavior was investigated. The GO/Fe₃O₄ suspension was kept in an autoclave at 180 °C for 12 h, followed by freeze-drying. A paste, including the active materials (RGO/Fe₃O₄), conductive carbon black and polyvinylidene fluoride, was used to prepare test electrodes on Ni-foam.

**Characterization and electrochemical measurements**

X-ray diffraction (XRD) measurements were performed with CuKa radiation (D-MAX II A, λ=0.15406 nm). A VG ESCALAB MKII (Thermo Scientific, Waltham, MA, USA) was used for the X-ray photoelectron spectroscopy (XPS) investigation. Transmission electron microscopy (TEM) images were acquired by a JEOL2010 (JEOL, Tokyo, Japan). Fourier transform infrared spectroscopy (FTIR) curves were obtained on a VERTEX 70 (Bruker, Ettlingen, Germany). The electrical conductivity of NG/Fe₃O₄ and RGO/Fe₃O₄ aerogel samples was determined via the four-probe method at room temperature. An IVIUMSTAT (Ivium, Eindhoven, Netherlands) electrochemical workstation was used for the electrochemical investigations, and the electrolyte was 6 M KOH. The galvanostatic charge−discharge was measured under different current densities between −1.0 and 0 V. The cyclic voltammetry (CV) was measured at different scan rates (5, 20, 100 and 200 V s⁻¹) between −1.0 and 0 V. The electrochemical impedance spectroscopy was acquired from 100 kHz to 0.01 Hz by applying a signal of 14.14 mV.

**RESULTS AND DISCUSSION**

Figure 1 shows the experimental procedures of the hydrothermal synthesis of NG/Fe₃O₄. The GO/Fe₃O₄ mixed suspension was deposited onto Ni-foam by vacuum filtration, followed by freeze-drying. Finally, the GO/Fe₃O₄ composites were reduced and nitrogen-doped simultaneously by plasma treatment. Using the hydrothermal method, a gel-like cylinder of RGO/Fe₃O₄ was constructed, as shown in Figure 2a. The formation of a 3D porous network with micrometer-sized pores was confirmed by scanning electron microscopy (SEM), as shown in Figure 2b and 2c. However, as in the commonly used hydrothermal methods, the aggregation of graphene sheets during hydrogel formation was inevitable due to the reduction-induced strong π-stacking interaction between graphene sheets, which is originally prohibited by the oxygen-containing surface groups of GO. The network walls of RGO/Fe₃O₄ show a tendency of layered aggregation, even though the decoration of Fe₃O₄ NPs as spacers on graphene nanosheets partially prevents the aggregation. Compared with hydrothermally prepared RGO/Fe₃O₄, NG/Fe₃O₄ exhibits greatly improved 3D architectures. The SEM image of NG/Fe₃O₄ (Figure 2d) is highly transparent, and the bone of the Ni-foam could be observed clearly. The 3D porous networks are directly formed on the bone by vacuum filtration and freeze-drying. Figure 2e and 2f shows that very thin graphene sheets make up the walls of NG/Fe₃O₄. The average size of the pores is several tens of microns, which is larger than that of RGO/Fe₃O₄.

For RGO/Fe₃O₄ nanostructures, a paste including RGO/Fe₃O₄, conductive carbon black and polyvinylidene fluoride was used to prepare test electrodes on Ni-foam. For comparison, a Ni-foam electrode decorated by RGO/Fe₃O₄ was directly prepared by the hydrothermal process without further addition of conductive carbon black and polyvinylidene fluoride, as follows: A Ni-foam electrode was soaked in the GO/Fe₃O₄ suspension and kept in an autoclave at 180 °C for 12 h, followed by freeze-drying, which resulted in the formation of an RGO/Fe₃O₄-decorated, Ni-foam electrode (RGO/Fe₃O₄@Ni-foam) produced by the hydrothermal process, as shown in Supplementary Fig. S2c. The microstructure of the RGO/Fe₃O₄@Ni-foam was similar to that of the RGO/Fe₃O₄, as shown in Figure 2a-2c. In addition, Supplementary Fig. S2d and S2e reveals that the scrolled 3D structures are covered on the Ni bones and have similar morphology to that of RGO/Fe₃O₄, and the aggregation of graphene sheets during hydrogel formation was observed. This result indicates that the preparation method of the aerogel plays a key role in avoiding the aggregation tendency in the reduction process. The larger pore sizes and thinner pore walls increased the specific surface area of NG/Fe₃O₄ (92 m² g⁻¹) compared to that of RGO/Fe₃O₄ (55 m² g⁻¹) based on the BET results (Supplementary Fig. S3). These properties of NG/Fe₃O₄ are directly related to the potential applications from adsorbents to supercapacitors.

Both samples had similar TEM images, and the nanosized Fe₃O₄ particles were anchored on graphene uniformly, suggesting efficient assembly between the graphene sheets and the NPs (Supplementary Fig. S4 and Figure 2g). In this work, the diameters of the Fe₃O₄ particles were in the range of 10−15 nm. The density and size of the Fe₃O₄ particles in the NG/Fe₃O₄ and RGO/Fe₃O₄ samples were almost identical. Figure 2h shows the XRD curves of Fe₃O₄, NG/Fe₃O₄ and RGO/Fe₃O₄. For all three samples, the main diffraction peaks were assigned to (111), (311), (220), (422), (440), and (511) of the crystal planes of Fe₃O₄, consistent with the Fe₃O₄ JCPDS card, which suggests that the chemical constitution of Fe₃O₄ was retained after the hydrothermal synthesis and plasma treatment. The sharp diffraction peak at 10.3° in GO, as shown in Supplementary Fig. S5, was replaced by a broad peak between 20° and 30°, which results from the (002) reflection of the graphene of NG/Fe₃O₄ and RGO/Fe₃O₄, indicating that GO was reduced by the hydrothermal and plasma treatment.
Figure 2i summarizes the FTIR spectra of GO, NG/Fe$_3$O$_4$ and RGO/Fe$_3$O$_4$. GO exhibits typical oxygen-related functional groups. The peaks at 1053 and 1226 cm$^{-1}$ are attributed to the C–O and phenolic C–OH vibrations, whereas that of 1725 cm$^{-1}$ is originated from the C=O vibration.$^{44-46}$ For RGO/Fe$_3$O$_4$ and NG/Fe$_3$O$_4$, an Fe–O related peak at 570 cm$^{-1}$ was observed,$^{47}$ which indicates a C–O–Fe linkage between the graphene nanosheets and the Fe$_3$O$_4$ NPs.

The XPS surveys of GO/Fe$_3$O$_4$, RGO/Fe$_3$O$_4$ and NG/Fe$_3$O$_4$ are shown in Figure 3a. For all three samples, peaks corresponding to the C 1s and O 1s were observed. Compared with GO/Fe$_3$O$_4$, the O 1s peak intensities of RGO/Fe$_3$O$_4$ and NG/Fe$_3$O$_4$ decreased, suggesting an increased C/O ratio after reduction by the hydrothermal process and plasma treatment, and the oxygen-related functional groups were efficiently removed. This hypothesis was confirmed by the deconvoluted C 1s spectra (Figure 3b). The weak signals of C–O and C=O in RGO/Fe$_3$O$_4$ compared with that of GO/Fe$_3$O$_4$ suggest that most of the GO was reduced, and the residual oxygen-related functional groups resulted from the incomplete reduction during the hydrothermal process. However, the oxygen-related peaks in the NG/Fe$_3$O$_4$ were nearly invisible, which indicates that the plasma treatment was more efficient for the reduction of 3D GO-based hybrids than the hydrothermal method. The formation of Fe$_3$O$_4$ in RGO/Fe$_3$O$_4$ and NG/Fe$_3$O$_4$ was further confirmed by the Fe 2p spectra (Figure 3c).

Two characteristic peaks corresponding to Fe 2P$_{1/2}$ and 2P$_{3/2}$ at approximately 724.8 and 711.3 eV were observed, which is consistent with the XRD results. The survey spectra in Figure 3a indicate the presence of nitrogen in both RGO/Fe$_3$O$_4$ and NG/Fe$_3$O$_4$. For RGO/Fe$_3$O$_4$, the introduction of nitrogen is attributed to the reduction agents used in the hydrothermal process, and the nitrogen in NG/Fe$_3$O$_4$ results from N$_2$ plasma treatment. The analysis of the N chemical bonding is shown in Figure 3d, and the N 1s peak can be deconvoluted into three components. The pyridinic and pyrrolic N at 398.2 and 400.1 eV correspond to the N atoms of the π-conjugated system.$^{35,48,49}$ The graphitic N at 401.7 eV corresponds to the N atoms...
replacing the C atoms inside graphene sheets, which could be observed clearly for NG/Fe3O4 but was nearly invisible for RGO/Fe3O4, as shown in Figure 3d. The first two types of N atoms located in the π-conjugated system account for most of the N in graphene and contribute one or two p-electrons. The graphitic N atoms can be considered to be threefold coordinated sp2 N in the hexagonal rings of graphene, which plays an important role in regulating the electronic properties of graphene in electrochemical systems48,49. According to our results, the graphitic N doping is difficult to achieve by the hydrothermal method, and plasma treatment is crucial to achieve a high-quality, N-doping, graphene-based aerogel.

A typical three-electrode method was used in this work to investigate the electrochemical behavior. The working electrodes were prepared from RGO/Fe3O4 and NG/Fe3O4. The CV curves of RGO/Fe3O4 and NG/Fe3O4 are shown in Figure 4a and 4b. The specific capacitances \( C (F g^{-1}) \) can be calculated from the CV curves using the following equation:

\[
C = \frac{\int I dv}{\nu m V}
\]  

where \( V, I, m \) and \( \nu \) are the potential window (V), the current (A), the mass of the active materials (g) and the scan rate (mV s\(^{-1}\)), respectively. Figure 4c summarizes the specific capacitance of the two samples as a function of the scan rate. The NG/Fe3O4 electrode reached a maximum of 386 F g\(^{-1}\) at 5 mV s\(^{-1}\), which is much higher than that of the RGO/Fe3O4 electrode (253.3 F g\(^{-1}\)). Due to the \textit{in situ} preparation of the RGO/Fe3O4@Ni-foam electrode, the specific capacitance at 5 mV s\(^{-1}\) was 267 F g\(^{-1}\), which was slightly improved compared with that of the RGO/Fe3O4 electrode but was still far behind the NG/Fe3O4 electrode. The galvanostatic charge–discharge lines of the NG/Fe3O4 electrode exhibit an almost symmetric triangular shape (Figure 4d), indicating a high reversibility in the charge and discharge cycle50–52. Figure 5a shows the Nyquist plots of the NG/Fe3O4 and RGO/Fe3O4 electrodes. For both samples, the Nyquist plots consist of two distinct parts: a linear part at low frequency and a semicircle part at high frequency. The two samples exhibit similar plots. In the high-frequency part (inset of Figure 5a), the charge transfer resistance (Rct) was calculated as 0.9 and 0.85 \( \Omega \) for the NG/Fe3O4 and RGO/Fe3O4 electrodes, respectively. The bulk electrical conductivity of the NG/Fe3O4 aerogel sample was 174 S m\(^{-1}\), three times greater than that of RGO/Fe3O4 (55 S m\(^{-1}\)). Although the conductive agent (conductive carbon black in this work) was absent in the preparation progress of the NG/Fe3O4 electrode, the Rct of the NG/Fe3O4 electrode has a similar value to that of the RGO/Fe3O4 electrode, which is also lower than in some previous studies44,53, indicating the excellent conductivity of NG/Fe3O4. The NG/Fe3O4 electrode shows excellent cycling stability, as shown in Figure 5b, and there is no obvious decrease in capacitance after 1000 cycles, which is crucial for commercial applications of supercapacitors54–56. The addition of pseudocapacitor materials is an efficient way to improve the performance of graphene-based supercapacitors. Two very important pseudocapacitor materials are transition metal compounds and conducting polymers. Generally, supercapacitors based on conducting polymers have higher specific capacitance than transition metal compounds; however, their cyclic stability is often poor57. Transition metal compounds have improved cyclic stability, but the weaknesses of the transition metal compounds are poor mechanical strength and low electrical conductivity. An efficient strategy to improve supercapacitor performance would be a combination of

**Figure 3** (a) XPS surveys of GO/Fe3O4, RGO/Fe3O4 and NG/Fe3O4; (b) XPS C 1s spectrum of the GO, RGO/Fe3O4 and NG/Fe3O4 samples; (c) XPS Fe 2p spectrum of the NG/Fe3O4 samples; (d) XPS N 1s spectrum of the NG/Fe3O4 and RGO/Fe3O4 samples.

**Figure 4** (a) CV curves of the RGO/Fe3O4 and NG/Fe3O4 electrodes. The capacitance at 5 mV s\(^{-1}\) was 386 F g\(^{-1}\) for NG/Fe3O4 but was nearly invisible for RGO/Fe3O4, as shown in Figure 3d. The first two types of N atoms located in the π-conjugated system account for most of the N in graphene and contribute one or two p-electrons. The graphitic N atoms can be considered to be threefold coordinated sp2 N in the hexagonal rings of graphene, which plays an important role in regulating the electronic properties of graphene in electrochemical systems48,49. According to our results, the graphitic N doping is difficult to achieve by the hydrothermal method, and plasma treatment is crucial to achieve a high-quality, N-doping, graphene-based aerogel.

**Figure 5** (a) Nyquist plots of the NG/Fe3O4 and RGO/Fe3O4 electrodes. For both samples, the Nyquist plots consist of two distinct parts: a linear part at low frequency and a semicircle part at high frequency. The two samples exhibit similar plots. In the high-frequency part (inset of Figure 5a), the charge transfer resistance (Rct) was calculated as 0.9 and 0.85 \( \Omega \) for the NG/Fe3O4 and RGO/Fe3O4 electrodes, respectively. The bulk electrical conductivity of the NG/Fe3O4 aerogel sample was 174 S m\(^{-1}\), three times greater than that of RGO/Fe3O4 (55 S m\(^{-1}\)). Although the conductive agent (conductive carbon black in this work) was absent in the preparation progress of the NG/Fe3O4 electrode, the Rct of the NG/Fe3O4 electrode has a similar value to that of the RGO/Fe3O4 electrode, which is also lower than in some previous studies44,53, indicating the excellent conductivity of NG/Fe3O4. The NG/Fe3O4 electrode shows excellent cycling stability, as shown in Figure 5b, and there is no obvious decrease in capacitance after 1000 cycles, which is crucial for commercial applications of supercapacitors54–56. The addition of pseudocapacitor materials is an efficient way to improve the performance of graphene-based supercapacitors. Two very important pseudocapacitor materials are transition metal compounds and conducting polymers. Generally, supercapacitors based on conducting polymers have higher specific capacitance than transition metal compounds; however, their cyclic stability is often poor57. Transition metal compounds have improved cyclic stability, but the weaknesses of the transition metal compounds are poor mechanical strength and low electrical conductivity. An efficient strategy to improve supercapacitor performance would be a combination of

**Figure 3** (a) XPS surveys of GO/Fe3O4, RGO/Fe3O4 and NG/Fe3O4; (b) XPS C 1s spectrum of the GO, RGO/Fe3O4 and NG/Fe3O4 samples; (c) XPS Fe 2p spectrum of the NG/Fe3O4 samples; (d) XPS N 1s spectrum of the NG/Fe3O4 and RGO/Fe3O4 samples.
transition metal compounds in highly conductive 3D graphene frameworks. In the present work, we further developed the commonly used hydrothermal method and have shown that plasma-treated NG/Fe3O4 would greatly enhance supercapacitor performance. Due to the non-toxicity, easy redox reactions and low cost of Fe3O4, it has become a good candidate as a pseudocapacitor material, although its theoretical specific capacitance is lower than that of some other transition metal compounds, such as MnO2, RuO2 and V2O5.20,58-60. Table 1 summarizes the performances of supercapacitors prepared with similar 3D systems 20,58,59,61-67. For 3D graphene aerogels prepared by CVD with Ni-foam and integrated with oxides58,59,67, they exhibit large specific surface area and low defects, and these aerogels can be used directly without further reduction. However, the CVD methods generally require rigorous conditions, such as high temperature, templates and dangerous gas. Furthermore, the limited output prevents its expansion for industrialization. In the present work, 3D structures were prepared by in situ plasma reduction, which is a simple and feasible strategy that can be expanded for large-scale production of nitrogen-doped, graphene-based aerogel, and various active nanomaterials can be incorporated into the 3D hybrid structures. In addition, the present method demonstrates competitive specific capacitance compared with CVD methods. Compared with other supercapacitors based on Fe3O4/RGO structures61-64, the present NG/Fe3O4 shows excellent specific capacitance and charge transfer ability. Because of the intrinsic properties of the materials, the specific capacitance of the NG/Fe3O4 electrode is

![Figure 4](a) CV curves of the RGO/Fe3O4 and NG/Fe3O4 electrodes. (b) CV curves of the NG/Fe3O4 electrode. (c) Variation of the specific capacitance against the scan rate for the RGO/Fe3O4 and NG/Fe3O4 electrodes. (d) Galvanostatic charge–discharge curves of the NG/Fe3O4 electrode.

![Figure 5](a) EIS of the RGO/Fe3O4 and NG/Fe3O4 electrodes, with insets showing the high-frequency parts and the equivalent circuit diagram used for fitting the EIS data. (b) Cycle performance of the NG/Fe3O4 electrode at a current density of 2 A g⁻¹. The inset shows the first 10 cycles of galvanostatic charge–discharge. EIS, electrochemical impedance spectra.
still lower than that of MnO₂/RGO and RuO₂/RGO electrodes\(^{20,38,59}\). However, the present method is a simple and feasible one compared with the traditional hydrothermal process and CVD method. The active nanomaterials can be further expanded for other compounds of transition metals, such as Co, Ni, Mn, Mo and V. The dip-coating and plasma treatment strategy works well for the 3D NG/Fe₃O₄ system and would also be effective for other compounds of transition metals. The properties of some other materials, such as cobalt oxide and Ni(OH)₂, which have ‘battery’ electrochemical behavior, are not compared\(^{68}\).

**CONCLUSIONS**

In conclusion, we have developed a plasma treatment approach to fabricate 3D NG/Fe₃O₄ nanostructures as high-performance supercapacitor electrode materials. During the plasma process, the GO of the GO/Fe₃O₄ materials was reduced and N-doped. The as-prepared NG/Fe₃O₄ electrode exhibited good electrochemical performance, especially high specific capacitance, excellent stability and low charge transfer resistance. As a mature, simple, efficient, low-cost and environmentally friendly method, plasma treatment is a promising process for the preparation and modification of energy storage materials.

**ACKNOWLEDGEMENTS**

The authors are grateful for funding by the National Natural Science Foundation of China (grant nos. 61322406, 61376020, 11474035 and 61574021).

---

**Table 1** Summary of the capacitive performance of the supercapacitors based on similar structures

| Sample            | Fabrication method                  | \(C_s\) (F g\(^{-1}\)) | \(R\) (Ω) | \(T\)  | \(C\) (%) | Ref                        |
|-------------------|-------------------------------------|------------------------|-----------|--------|----------|-----------------|
| NG/Fe₃O₄         | Freeze-drying/plasma reduction and doping | 386              | 0.9       | 1000   | 97       | Present work    |
| MnO₂/RGO         | Dip coating                          | 450                 | 6.5       | 10 000 | 90       | 20               |
| MnO₂/CNT/GE/N-foam | CVD                                 | 251                 | 1.25      | 3000   | 82       | 58               |
| RuO₂/CNT/GE/N-foam | CVD/dip coating                     | 502.7               | 1.02      | 8000   | 106      | 59               |
| Fe₃O₄/G            | 2D sandwich-like sheet grown on GO/RGO | 349              | —         | 1000   | —        | 61               |
| Fe₃O₄/RGO           | Hydrogen reducing                  | 262                 | —         | 1000   | —        | 62               |
| Fe₃O₄/RGO           | Hydrothermal                        | 220                 | 1.62     | 3000   | —        | 63               |
| Fe₃O₄/GS            | Vacuum filtration/ heat treatment   | 368                 | —         | 1000   | —        | 64               |
| RGO/porous         | Electrochemical exfoliation         | 325                 | 3.6       | 5000   | 98       | 65               |
| 3D-RGO            | Hydrothermal polymerization/ carbonization | 225            | —         | 5000   | 94       | 66               |
| GE/N-foam         | CVD                                 | 180                 | 0.93      | 2000   | 100      | 67               |

Abbreviations: \(C_s\), retention rate of \(C_s\) after the cycle life test; \(C\), specific capacitance; CNT, carbon nanotube; GE, graphene; GS, graphene sheet; \(T\), internal resistance obtained from the electrochemical impedance spectra measurements; \(l\), cycles of the cycle life test.
Supplementary Information for this article can be found on the Light: Science & Applications' website (http://www.nature.com/lsa).