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Three-dimensional graphitic carbon nitride functionalized graphene composites (g-C$_3$N$_4$@G) were grown using a simply one-step hydrothermal reduction. The super-capacitive properties of the as-formed 3D g-C$_3$N$_4$@G were evaluated in a symmetrical supercapacitor. It is found that the 3D g-C$_3$N$_4$@G exhibit high specific capacitance of 264 F·g$^{-1}$ and good cycling stability.

**Introduction**

Electrochemical supercapacitors (ECs) have attracted increasing attentions, especially in the fields of electrochemical energy storage and conversion due to their high power capability and long cycle-life. ECs can be divided into two types, electric double layer capacitors (EDLCs) and the pseudo-capacitors. The electrodes for EDLCs capacitor are usually the materials with high surface area through the separation of electronic and ionic charges at the electrode-electrolyte interface. While the pseudo-capacitors are based on redox active electrode materials (e.g., metal oxides, conducting polymers, and carbons rich in oxygen and nitrogen containing surface functional groups) that operate through fast and reversible surface or near-surface Faradic reactions. To achieve a high performance of ECs, the electrode materials are allowed to possess large specific surface area, high conductivities, low fabrication cost, abundant resource and satisfactory electrochemical stability. Among the various kinds of electrode materials applied into ECs, carbon-based materials with high effective surface area and excellent conductivity have received much attentions recently.

Graphene with a 2D monolayer structure of sp$^2$-bonded carbon atoms has many advantages over other carbon materials such as large specific surface area, outstanding electrical, mechanical and thermal properties. As is well known graphene can be used as a versatile building block for self-assembly into specific architectures, which is essential for converting the remarkable microscopic characteristics of graphene sheet into macroscopic properties of practical significance. It was found that the combination of g-C$_3$N$_4$ with graphene could improve the conductivity and electrocatalytic performance of g-C$_3$N$_4$, which has been explored as a metal-free material for electrocatalysis.

In this work, we have reported a rational assembly of g-C$_3$N$_4$ and graphene into 3D interconnected networks by a facile one-step hydrothermal method. The resulting well-defined 3D g-C$_3$N$_4$@G induces the hierarchical architecture, thus facilitate the charge transfer and provide multi-way electron transfer which can effectively accelerate the electrochemical process to achieve high energy storage.

**Experimental**

**Preparation of Graphene Oxide**

Graphene Oxide (GO) was prepared by oxidation of natural graphite powder according to a modified Hummers’ method. Briefly, graphite (3g) was added to concentrated sulfuric acid (70 mL) under stirring at room temperature, then sodium nitrate (1.5 g) was added, and the mixture was cooled to 0 °C. Potassium permanganate was added slowly to keep the temperature of the suspension lower than 20 °C under vigorous agitation. The reaction system was transferred to a 35-40 °C water bath for about 0.5 h, forming a thick paste. 140 mL water was added and keep agitation for 15min, then an additional 500 mL of water was added and followed by a slow addition of 20 mL of H$_2$O$_2$ (30 %), turning the color of the solution from dark brown to yellow. The mixture was filtered and washed with 1:10 HCl aqueous solution (250 mL) to remove metal ions followed by repeated washing with water and centrifugation to remove the acid. The resulting solid was dispersed in water by ultrasonication for 1 h to make a GO aqueous dispersion (0.5 wt. %). Finally, the obtained brown
Preparation of g-C₃N₄

This preparation used melamine as the precursor, which was carbonized at 600 °C for 2 h in a quartz tube furnace and treated with concentrated sulfuric acid. And then, the as-produced g-C₃N₄ was exfoliation with an excess of KMnO₄ at 50 °C for 2h, H₂O₂ (30 %) was added to remove the surplus of KMnO₄ from the sphere of the reaction. Finally, the product was purified by dialysis and freeze-drying for further use.

Preparation of 3D g-C₃N₄@G

3D g-C₃N₄@G was prepared by hydrothermal reduction of GO sheets and g-C₃N₄ in their mixed aqueous dispersion. According to experiment and data comparison as shown in the supporting information, 2 mg g-C₃N₄ was dispersed into 15 mL homogeneous GO aqueous (3 mg mL⁻¹) under stirring in a beaker. Then the mixture was transferred to the Teflon-lined autoclave at 180 °C for 12 h, the 3D-structure was finally obtained through lyophilization for following experiments.

Fabrication of g-C₃N₄@G supercapacitors

All the components were directly assembled into a layered structure without using a binding agent or conducting additive. The two slices of g-C₃N₄@G electrodes (ca. 0.5 mm × 2 mm × 2 mm), that cut from the as-prepared cylindrical g-C₃N₄@G sample, were separated by a piece of filter paper soaked with 0.1 M LiClO₄ electrolyte and thus assembled in a symmetrical two-electrode configuration with gold flakes of 0.3 × 0.5 cm as the current collector to fabricate a symmetrical supercapacitor.

Electrochemical Measurements

Electrochemical performances of the supercapacitor were tested with galvanostatic charge-discharge and cyclic voltammetry (CV) on a CHI 760 potentiostat, CH Instruments, Inc. All of the experiments were carried out in a two-electrode system. The potential range for CV measurements and galvanostatic charge/discharge tests have been performed in a potential range between 0 and 1 V, the electrochemical impedance spectra (EIS) were taken at the open-circuit potential in the frequency range of 0.01-10⁵ Hz with a modulating amplitude of 5 mV. The capacitance C was calculated by using the equation: C = I/(dV/dt), where I and dV/dt are the discharge current and the slope of the discharge curve. The mass-specific capacitances (Cₘ) was derived from the equation: Cₘ = 2C/m, m is the mass of one electrode. The energy density (E) and Power density (P) of the g-C₃N₄@G supercapacitor depicted in the Ragone plot was calculated by the equation E=0.5CₘΔV² and P=E/Δt, where Δt was the discharge time, ΔV was the voltage change within the discharge time.

Characterization

The morphology of the samples was explored by JSM-7001F Field-emission scanning electron microscope (FE-SEM) and JEM-2010 high resolution transmission electron microscopy (HR-TEM). The X-ray diffraction (XRD) analysis was carried on a D8 advance X-ray diffractometer with Cu Kα radiation (λ=1.5418 Å). FT-IR spectrum is recorded from KBr pellets in range 400-4000 cm⁻¹ on a Nicolet-360 FT-IR spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was performed on the ESCALAB 250 photoelectron spectrometer (ThermoFisher Scientific) with Al Kα (1486.6 eV) as the X-ray source set at 150 W and a pass energy of 30 eV for high-resolution scan.

Conductivities of the samples were measured by a conventional four-probe technique. Nitrogen sorption measurements were carried out with a Quantachrome Autosorb-IQ gas adsorption analyzer at 77 K.

Results and Discussion

The process for the fabrication of 3D g-C₃N₄@G is illustrated in Figure 1a. The hydrothermal treatment process allows formation of g-C₃N₄ grafted graphene basal plane with a loosely 3D structure with a density of 13.2 mg cm⁻³ as shown in Figure 1b and 1c similar to that of common 3D graphene (Figure S1). The enlarged SEM image in Figure 1d reveals that g-C₃N₄ in the composites are uniformly dispersed along graphene basal planes without any obvious aggregates which is further confirmed by the corresponding EDS elemental mapping (Figure 1e). Elemental mappings clearly show that the uniform distribution of N, C, and O elements over the graphene mesh. The conductivity of g-C₃N₄@G (0.38 S·m⁻¹) is comparable to the pristine graphene (0.35 S·m⁻¹). Meanwhile, the nitrogen cryo-adsorption isotherms are shown in (Figure S2), where both 3DG and g-C₃N₄@G composites show a Type IV isotherm characteristics with a wide hysteresis loop indicating the existence of mesopores. Pore size distribution curves reveal a narrow distribution of pores diameters, the specific surface area of g-C₃N₄@G deposition is 320 m²·g⁻¹, which is obviously higher than that of the pristine 3D graphene (208 m²·g⁻¹).

Figure 1. (a) Progress on preparation of 3D g-C₃N₄@G; (b)
belonging to the (002) peak of graphitic carbon planes, indicating that observed in graphene is a characteristic deformation of triazole ring modes. The peak at 27.3 eV corresponds to C1N coordination of g-C3N4. As shown in Figure 3b, the high-resolution C 1s spectrum exhibits the chemical relationships of the carbon. The peak at 288.3 eV belongs to C-C coordination, and the peak centered at 288.3 eV corresponds to C-N coordination of g-C3N4. The high-resolution N 1s spectrum (Figure 3c) reveals the typical nitrogen status including pyridine (398.8 eV), pyrrolic (400.5 eV), and graphitic (401.1 eV) N species, which are also reflected by C-N-C peak in the C 1s spectrum of g-C3N4@G (Figure 3b).

Figure 3d shows the XRD patterns of the original g-C3N4, pristine graphene, and g-C3N4@G. The g-C3N4 and pristine graphene XRD patterns are overlapped by graphene, the peaks at ca. 800 cm−1 and ca. 1571 cm−1 belonging to g-C3N4 can still be recognized. The corresponding high-resolution C 1s spectrum and C N 1s spectrum; (d) XRD patterns of the original g-C3N4, pristine graphene, and g-C3N4@G; (e) FT-IR spectrum of the 3DG and g-C3N4@G, respectively; (f) Raman spectrum of the 3DG and g-C3N4@G.

The electrochemical performance of g-C3N4@G were measured in a two-electrode configuration. To ascertain the origin of the exceptional performance of the g-C3N4@G-based supercapacitor, we also tested the electrochemical performance of the pristine graphene for comparison. A symmetric supercapacitor was approximated constructed by first sandwiching the membrane that soaked with 0.1 mol·L−1 of LiClO4 between two identical pieces of g-C3N4@G, and then encapsulating the device with porous polyethylene terephthalate (PET) membranes (Figure 3a). The CV curves of g-C3N4@G capacitor with the potential range from 0 to 1.0 V (vs. Ag/AgCl) exhibit almost rectangular-like shape indicating a good charge transport within the g-C3N4@G electrodes as shown in Figure 4b, the scan rate is 10, 30, 50, and 100 mV·s−1, respectively. The galvanostatic charge/discharge curves with different current densities of 0.4, 1.0, 2.0, 3.0, and 4.0 A g−1 were shown in Figure 4c, no obvious IR drop was observed on the start of all discharge curves, indicating that all the devices had a small internal series resistance and efficient extraction of stored energy. The specific capacitance of the g-C3N4@G was calculated to be about 264 F g−1 at a current density of 0.4 A g−1 based on the charge-discharge curves, which is the best value the survey of supercapacitors based on 3DG has recorded (Table 1). Notably, the capacitance...
of g-C_{3}N_{4}@G electrode was about twice as high as the 3D pristine graphene electrode at a range of current densities from 1.0 to 4.0 A·g\(^{-1}\) (Figure 4c). This essentially implies g-C_{3}N_{4}@G have a larger active surface areas and faster electron transfer rate in comparison with the control electrode.

Electrochemical impedance spectroscopy (EIS) was also performed to further evaluate the electrochemical performance of devices based on 3DG and g-C_{3}N_{4}@G, respectively. Both devices show characteristics approaching the ideal capacitive behavior (Figure 4f). The high-frequency intercept with the real axis is the equivalent series resistance (R_s), representing the sum of the electrolyte solution resistance, the intrinsic resistance of the active material and the contact resistance at the electrode/electrolyte interface.\(^{25}\) It is clearly observed that the g-C_{3}N_{4}@G has a slightly lower R_s value than that of 3DG from the magnified high-frequency region in the inset image. The power density and energy density are calculated by using the charge-discharge data. Figure 4g shows the Ragone plot for g-C_{3}N_{4}@G based supercapacitor. The energy density is nearly 30 W·h·kg\(^{-1}\) and the power density is 4.0 kW·kg\(^{-1}\) at a current density of 4.0 A·g\(^{-1}\), these results indicate that the supercapacitor based on g-C_{3}N_{4}@G material can operate with higher power density and energy density.\(^{27}\)

![Figure 4](image)

**Figure 4.** (a) Schematic illustration of g-C_{3}N_{4}@G supercapacitor device; (b) CV curves with different scan rates and (c) galvanostatic charge-discharge curves for g-C_{3}N_{4}@G at different discharge current densities; (d) The galvanostatic charge-discharge curves of graphene and g-C_{3}N_{4}@G with the currents density of 1.0 A·g\(^{-1}\); (e) Capacitance at different current densities of g-C_{3}N_{4}@G and graphene; (f) Nyquist plots of g-C_{3}N_{4}@G and graphene measured at open-circuit conditions, high-frequency region of the plots are shown enlarged in the inset image; (g) Ragone plot of g-C_{3}N_{4}@G based supercapacitor.

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Table 1. Direct comparison of the specific capacitance (C_m) of different 3DG-based materials supercapacitors
interaction between the ions and electrode is reduced resulting in a reduction in capacitance. It can be seen that the specific capacitance values after 1000 charge-discharge cycles was obvious higher than its initial status at all the current densities, this may be caused by the fact that the g-C$_3$N$_4$@G was activated for being long time charge-discharge.

The cycling stability of the supercapacitor is also an important parameter to evaluate its potential for practical applications. Figure 5d illustrates the temporal evolution of the specific capacitance of g-C$_3$N$_4$@G supercapacitor over consecutive charge-discharge cycles. Interestingly, the specific capacitances increases at the first several hundred cycles, then gradually decrease and eventually stabilize. The increase of during initial cycles can be attributed to the activation process that allows the trapped ions to diffuse out. There is no obvious degradation could be observed during the cycling experiment even after 10000 charge-discharge cycles, indicating that our g-C$_3$N$_4$@G supercapacitor has a good long-term electrochemical stability.

![Figure 5](image_url)

**Figure 5.** (a) CV curves of supercapacitors based on the g-C$_3$N$_4$@G after 1000 charge-discharge cycles with the current density at 3.0 A g$^{-1}$; scan rates are 10 mV s$^{-1}$, 30 mV s$^{-1}$, 50 mV s$^{-1}$ and 100 mV s$^{-1}$, respectively; (b) The galvanostatic charge-discharge curves of g-C$_3$N$_4$@G supercapacitor after 1000 charge-discharge cycles at different discharge currents: 0.4, 1.0, 2.0, 3.0, and 4.0 A g$^{-1}$; (c) The capacitance of g-C$_3$N$_4$@G supercapacitor after 1000 charge-discharge cycles; (d) The capacitance of g-C$_3$N$_4$@G supercapacitor under the cycling tests for 10000 charge-discharge cycles at a current density 4.0 A g$^{-1}$.

**Conclusions**

In summary, g-C$_3$N$_4$@G have been prepared by a simply one-step hydrothermal reduction and showed promising electrochemical performances as electrode materials for supercapacitor. The results showed that the existence of g-C$_3$N$_4$ was advantageous in that it could decrease the aggregation of graphene, leading to a capacity improvement and better cycle performance. Capacitance values of 264 F g$^{-1}$ have been achieved representing a more than 75% improvement over that of the supercapacitor made from pure 3DG electrodes (152 F g$^{-1}$). The reported 3D composites materials are much desirable for electrode materials in supercapacitors.

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**Notes and references**

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†Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/
‡Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

One-step strategy to graphitic-C3N4 functionalized graphene composites as advanced three-dimensional supercapacitor electrode materials.
36x28mm (300 x 300 DPI)