Tubular graphitic-C$_3$N$_4$: a prospective material for energy storage and green photocatalysis

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Abstract
We have established a facile and scaleable approach to fabricate tubular graphitic-C\textsubscript{3}N\textsubscript{4} using melamine. The construction of the unique tubular morphology is a result of the pre-treatment of melamine with HNO\textsubscript{3}. Herein, for the first time, we have explored the electrochemical properties of g-C\textsubscript{3}N\textsubscript{4} as an electrode material for supercapacitors. Tubular g-C\textsubscript{3}N\textsubscript{4} has significant advantages due to its distinctive morphology, high surface area (182.61 m\textsuperscript{2} g\textsuperscript{-1}) and combination of carbon with nitrogen. Therefore, tubular g-C\textsubscript{3}N\textsubscript{4} demonstrated a good specific capacitance of 233 F g\textsuperscript{-1} at a current density of 0.2 A g\textsuperscript{-1} in 6 M KOH electrolyte. Furthermore, tubular g-C\textsubscript{3}N\textsubscript{4} maintained a high capacitance retention capability (90\%) after 1000 cycles. The photocatalytic activity of tubular g-C\textsubscript{3}N\textsubscript{4} was evaluated using the organic dyes such as Methylene Blue (MB) and Methylene Orange (MO) under visible light. Tubular g-C\textsubscript{3}N\textsubscript{4} demonstrated good photocatalytic activity and enhanced stability compared to bulk g-C\textsubscript{3}N\textsubscript{4}. The enhanced performance is because of the high surface area, which contains more active sites for reaction. The encouraging performance of tubular g-C\textsubscript{3}N\textsubscript{4} in supercapacitors and as a photocatalyst points toward it being a prospective material for energy storage that is environmentally clean. The Royal Society of Chemistry.

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Tubular graphitic-C$_3$N$_4$: a prospective material for energy storage and green photocatalysis†

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We have established a facile and scaleable approach to fabricate tubular graphitic-C$_3$N$_4$ using melamine. The construction of the unique tubular morphology is a result of the pre-treatment of melamine with HNO$_3$. Herein, for the first time, we have explored the electrochemical properties of g-C$_3$N$_4$ as an electrode material for supercapacitors. Tubular g-C$_3$N$_4$ has significant advantages due to its distinctive morphology, high surface area (182.61 m$^2$ g$^{-1}$) and combination of carbon with nitrogen. Therefore, tubular g-C$_3$N$_4$ demonstrated a good specific capacitance of 233 F g$^{-1}$ at a current density of 0.2 A g$^{-1}$ in 6 M KOH electrolyte. Furthermore, tubular g-C$_3$N$_4$ maintained a high capacitance retention capability (90%) after 1000 cycles. The photocatalytic activity of tubular g-C$_3$N$_4$ was evaluated using the organic dyes such as Methylene Blue (MB) and Methylene Orange (MO) under visible light. Tubular g-C$_3$N$_4$ demonstrated good photocatalytic activity and enhanced stability compared to bulk g-C$_3$N$_4$. The enhanced performance is because of the high surface area, which contains more active sites for reaction. The encouraging performance of tubular g-C$_3$N$_4$ in supercapacitors and as a photocatalyst points toward it being a prospective material for energy storage that is environmentally clean.

Introduction

Using fuels for energy, while maintaining a clean environment, is a fundamental necessity of human life. Significant increases in industrial activity and population have inevitably enhanced energy demands. This global energy crisis has further motivated scientists to develop highly efficient and renewable methods for energy production and storage. Electrochemical capacitors (ECs)/supercapacitors have recently attracted great interest due to their easy availability, good polarization properties, large surface area and low cost. 14 Conductive polymers have also shown enhanced capacitive performance, but their poor oxidation stability and mechanical properties still need to be improved. 7–9 Carbon materials (carbon black, activated carbon, carbon nanotubes, carbon onions, graphene, etc.) are the most studied materials for supercapacitors due to their easy availability, good polarization properties, high surface area and low cost. 9 However, they suffer from problems such as oxidation stability, unstable electrical conductivity and low specific conductivities and energies. 10–11 The presence of nitrogen in carbon materials enhances their capacitances, while maintaining the superb cycling ability of their ECs. 12–14 By introducing nitrogen, a carbon material’s electron-donor properties, surface polarity and electric conductivity can all be improved. 12–15 It also enhances the wettability of the material in the electrolyte and, therefore, increases the mass transfer efficiency. 12–15 Despite the advantages of N based carbon materials various issues, such as the complexity and high cost of synthesis methods for doping nitrogen and low surface areas, still needed to be addressed. 11 In this regard, a facile method to produce nitrogen doped carbon materials with large surface areas for the development of high performance supercapacitors is required. Keeping these points in mind, we have synthesized tubular graphitic carbon nitride, as an electrode material for supercapacitors.

Increases in industrial activities are alarming due to various environmental problems. Among these problems, water pollution is an important concern for humans. Organic waste is one
of the main industrial products causing water pollution. Various techniques have been employed to separate these organic pollutants from water. In this concern, photocatalysis under visible light is highly significant and has attracted a lot of interest since the discovery of TiO₂ as a photocatalyst by Fujishima et al. in 1972. Unfortunately, due to its large bandgap (3.2 eV) and charge recombination, the quantum efficiency of TiO₂ is very low, which prevents its practical application. Researchers have been trying to synthesise other photocatalysts, which must be easily separable, nontoxic, facile to fabricate, stable in water and cost effective.16–18

Graphitic carbon nitride, an attractive organic semiconductor, has received worldwide attention since Wang et al. reported the use of g-C₃N₄ as a metal free photocatalyst, which could produce hydrogen from water and absorb more visible light than many oxides due to its bandgap (2.70 eV). g-C₃N₄ possesses a small bandgap, excellent chemical stability, special optical characteristics and a high thermal stability, which make it a promising photocatalyst for the degradation of organic pollutants under visible light. However, the efficiency of g-C₃N₄ is very low due to its low practical surface area and high recombination rate of photogenerated electron–hole pairs. Various techniques have been adopted to improve its efficiency of which composite fabrication with other semiconductors, doping with noble metals and non-metals, the preparation of porous g-C₃N₄ and nanostructures of g-C₃N₄ are worth mentioning.20–25

Nanostructures (tubes, wires, rods, sheets, spheres, etc.) have been found to be more efficient than their bulk counterparts. When used in supercapacitors and as photocatalysts their performances have been found to be better due to their larger specific surface areas and more suitable bandgaps.24,26 A larger specific surface area provides more active sites for reaction, a shorter bulk diffusion length and a stronger redox ability of the charge carriers.25,26 Most nitrogen doped carbon supercapacitor electrodes have been fabricated using nanopowders. In this respect, supercapacitor electrodes prepared using g-C₃N₄ nanostructures have a clear advantage over bulk nitrogen doped carbon materials.19,21,22,23 Moreover, the concentration of nitrogen is another important factor to help enhance the specific capacitance of supercapacitors.

Herein, we have fabricated tubular g-C₃N₄ using a chemical method, keeping all of the aforementioned aspects in mind. This time-saving, facile and low temperature synthesis process has been successfully repeated. The prepared tubular g-C₃N₄ has been used, for the first time, as an electrode material for supercapacitors in KOH electrolyte. The specific capacitance of the tubular g-C₃N₄ supercapacitor was 233 F g⁻¹ at a current density of 0.2 A g⁻¹. The value found is higher than the results reported for other nitrogen-doped carbon materials e.g., MWCNTs, CNTs/N-enriched carbon, N-enriched carbon and ultrathin N-doped graphitic carbon nano-cages. We have also used tubular g-C₃N₄ as a photocatalyst for the degradation of MO and MB. It shows excellent efficiency compared to bulk g-C₃N₄ due to its larger aspect ratio and surface area. The recycling ability and stability of the material were also investigated. In light of the obtained results, we propose that the prepared tubular g-C₃N₄ could be a green material for energy storage and photocatalysis. The large surface area and porous structure of tubular g-C₃N₄ could also be useful for gas separation, water purification, catalyst support and water splitting.26

Experimental section

Fabrication of tubular g-C₃N₄

1 g of melamine was dissolved in 30 ml of ethylene glycol to make a saturated solution. 60 ml of 0.1 M HNO₃ was then added to the prepared solution. After stirring for 10 min, the mixture was washed with ethanol and dried at 60 °C for 12 h. As a result a white colored powder was obtained, which was then annealed at 450 °C for 2 h at a heating rate of 10 °C min⁻¹. Bulk g-C₃N₄ was also prepared at 550 °C for comparison purposes.27

The sample was characterized by Scanning Electron Microscopy (SEM, Hitachi S-4800), X-ray Diffraction (XRD Philips X’Pert Pro MPD), X-ray Photoelectron Spectroscopy (XPS, Thermo Scientific, Escalab250Xi) and Transmission Electron Microscopy (TEM, Tecnai G20, JEOL, Japan).

Preparation of the electrodes

Tubular g-C₃N₄ (85%), activated carbon (10%) and polytetrafluoroethylene (PTFE) (5%) were mixed with ethanol, passed on to nickel foam (5 cm × 1 cm) and then dried at 60 °C for 12 h. An Ag/AgCl (in saturated KCl solution) electrode and platinum wire were used as the counter and reference electrode, respectively. The electrochemical behavior of the working electrode was analyzed in 6 M KOH electrolyte using a three-electrode cell.

Photocatalytic tests

For the photocatalytic tests, a 0.1 g sample was dissolved in a 40 ml aqueous solution of MO and MB in a glass beaker. The concentrations of MO and MB were both 10 mg L⁻¹ of water. In order to obtain an adsorption–desorption equilibrium between the photocatalyst and the dyes (MO, MB), the solution was stirred continuously for 30 min in the dark. The solution was then irradiated with visible light. A 500 W xenon lamp was used as a visible light source. After every 15 min, 4 ml of the solution was removed and the UV-absorption measured. Before measurement, the solution was centrifuged in order to remove catalyst particles and avoid interference. The initial concentration, C₀, is the maximum absorption of MB and MO in solution at 610 nm and 463.5 nm, respectively, obtained after the absorption equilibrium is reached, but before light irradiation. For the stability measurements the same materials were removed from the solution and the above mentioned steps were repeated for a second and third time.

Results and discussion

Characterization of the tubular g-C₃N₄

Morphological characterization of the as-synthesized products was carried out using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The SEM images shown in Fig. I(a) and (b) clearly show the tubular like growth of
Furthermore, it is also observed that under an intense electron beam the melon species suffer from structural decomposition, which makes them unsuitable for better quality HRTEM and SAED measurements. An X-ray diffraction (XRD) investigation was performed in order to explore the crystal structure and phase of g-C3N4, as shown in Fig. 2. The XRD pattern of bulk g-C3N4 shows two peaks at 13.1° and 27.3°. The small peak at 13.1° corresponds to the (100) plane with \( d = 0.676 \) nm and the other strong peak at 27.3° corresponds to \( d = 0.324 \) nm, due to the long-range interplanar stacking of the aromatic system and is recognized as the (002) plane of bulk g-C3N4. However, the XRD pattern of tubular g-C3N4 only shows one broad and low intensity peak at 27.1° with an interplanar distance of 0.326 nm, which corresponds to the (002) plane of tubular g-C3N4.\textsuperscript{28–30}

X-ray photoelectron spectroscopy (XPS) was performed to investigate the elemental composition and chemical states of tubular g-C3N4. The high resolution N1s spectrum of g-C3N4 has three peaks at 398.54 eV, 399.43 eV and 400.4 eV, as shown in Fig. 3(a). The first two peaks can be attributed to sp\(^3\) C–N bonds while the third one is due to a N–sp\(^2\)C bond, which proves that there is bonding between the nitrogen and carbon atoms.\textsuperscript{21,32} The high resolution spectrum of C1s can be resolved into two peaks. The first peak at 288.16 eV confirms the existence of C–N–C coordination, whereas the second peak at 284.92 eV is related to surface adventitious carbon.\textsuperscript{33} The N/C ratio of tubular g-C3N4 is calculated to be 1.25, which is consistent with previously reported results.\textsuperscript{28–30,31}

The optical properties of tubular g-C3N4 and bulk g-C3N4 were investigated using PL and UV spectroscopy. A xenon lamp was used to excite the materials. The PL spectra of tubular g-C3N4 and bulk g-C3N4 are shown in Fig. 4(a). The emission peaks of bulk g-C3N4 and tubular g-C3N4 are observed at 456.19 nm and 435.19 nm, respectively. These peaks correspond to the bandgap of the respective sample and belong in the blue-violet light region, indicating the existence of a \( \pi \) state in tubular g-C3N4.\textsuperscript{31} This might be attributed to a quantum
confinement effect that has shifted the conduction and valence bands. Another possible explanation is that it may be due to better packing and electronic coupling.\textsuperscript{33} To further confirm the bandgap, UV studies were carried out and the UV spectra of tubular g-C\textsubscript{3}N\textsubscript{4} and bulk g-C\textsubscript{3}N\textsubscript{4} along with their corresponding bandgaps, are shown in Fig. 4(b). The bandgaps of tubular g-C\textsubscript{3}N\textsubscript{4} and bulk g-C\textsubscript{3}N\textsubscript{4} are 2.85 eV and 2.7 eV, respectively. These values are in good agreement with the PL studies.

The surface areas of tubular g-C\textsubscript{3}N\textsubscript{4} and bulk g-C\textsubscript{3}N\textsubscript{4} were determined using the Brunauer–Emmett–Teller (BET) equation in the relative pressure range of 0.04–0.32. The surface area of tubular g-C\textsubscript{3}N\textsubscript{4} (182.61 m\textsuperscript{2} g\textsuperscript{–1}) is much higher than that of bulk g-C\textsubscript{3}N\textsubscript{4} (10.12 m\textsuperscript{2} g\textsuperscript{–1}), as shown in Fig. S3, which provides larger spaces to accommodate more charge storage and exposes more active sites for the photochemical reaction.

**Electrochemical measurements**

The electrochemical properties were first delineated using galvanostatic charge–discharge curves. Fig. 5(a) shows the first five charge–discharge curves of tubular g-C\textsubscript{3}N\textsubscript{4} in 6 M aqueous KOH using a three electrode cell in a potential window of –0.2 to 1.0 V at current densities of 0.2 A g\textsuperscript{–1} and 0.5 A g\textsuperscript{–1}. The discharge time of tubular g-C\textsubscript{3}N\textsubscript{4} is longer at a current density of 0.2 A g\textsuperscript{–1} compared to that at a higher current density of 0.5 A g\textsuperscript{–1}.

Fig. 5(b) shows the last five charge–discharge curves of tubular g-C\textsubscript{3}N\textsubscript{4}. The discharge time for the 1000\textsuperscript{th} cycle is very close to that for the 1\textsuperscript{st} discharge at both current densities, which proves the excellent capacitance retention of tubular g-C\textsubscript{3}N\textsubscript{4}. Specific capacitance (C) values for tubular g-C\textsubscript{3}N\textsubscript{4} and bulk g-C\textsubscript{3}N\textsubscript{4} are given in Fig. 5(c). The specific capacitance is calculated from the charge–discharge curves according to eqn (1):\textsuperscript{34}

\[
C = \frac{(I \times \Delta t)}{(m \times \Delta V)}
\]

where \(\Delta t\) is the discharge time of the capacitor, \(I\) is the discharge current, \(m\) is the mass of the working electrode and \(V\) is the potential window. The calculated specific capacitance is 233 F g\textsuperscript{–1} at a current density of 0.2 A g\textsuperscript{–1} for the 1\textsuperscript{st} cycle and 212 F g\textsuperscript{–1} for the 1000\textsuperscript{th} cycle, which shows the high cycling stability of tubular g-C\textsubscript{3}N\textsubscript{4}. Similarly, tubular g-C\textsubscript{3}N\textsubscript{4} maintains its high specific capacitance even at a higher current density of 0.5 A g\textsuperscript{–1}, where it is 204 F g\textsuperscript{–1} for the 1\textsuperscript{st} cycle and 182 F g\textsuperscript{–1} for the 1000\textsuperscript{th} cycle. However, in comparison to tubular g-C\textsubscript{3}N\textsubscript{4}, bulk g-C\textsubscript{3}N\textsubscript{4} shows a very low specific capacitance. At the lower current density of 0.2 A g\textsuperscript{–1} the capacitance is only 81 F g\textsuperscript{–1}, while it is 70 F g\textsuperscript{–1} at a current density of 0.5 A g\textsuperscript{–1}. This indicates that the higher surface area of the tubular g-C\textsubscript{3}N\textsubscript{4} nanostructures is advantageous for supercapacitor electrodes. The highly stable cycling life of tubular g-C\textsubscript{3}N\textsubscript{4} is further confirmed by the efficiency of tubular g-C\textsubscript{3}N\textsubscript{4}, as shown in Fig. 5(d). The efficiency of tubular g-C\textsubscript{3}N\textsubscript{4} decreases from 100% to 91% after 1000 cycles at a current density of 0.2 A g\textsuperscript{–1} and 90% at a current density of 0.5 A g\textsuperscript{–1}. This demonstrates the high stability of tubular g-C\textsubscript{3}N\textsubscript{4}. Tubular g-C\textsubscript{3}N\textsubscript{4} shows a better performance than many other carbon based materials, such as those listed in Table S1.\textsuperscript{37–39} The electrode composed of tubular g-C\textsubscript{3}N\textsubscript{4} has a high porosity and large surface area that allows a continuous charge distribution.\textsuperscript{34} Thus, the high specific capacitance can be attributed to the large BET surface area as it increases the electrode–electrolyte contact area and makes ion transport more feasible. Additionally, the excellent specific capacitance is due to the higher nitrogen content in tubular g-C\textsubscript{3}N\textsubscript{4} that increases its electron donor–acceptor characteristics.\textsuperscript{35} The higher nitrogen content in tubular g-C\textsubscript{3}N\textsubscript{4} is helpful for
enhancing the capacitance as it can improve the wettability with the electrolyte and, therefore, increase the mass transfer efficiency.\textsuperscript{36,37} It also provides a large additional pseudo-capacitance as well.\textsuperscript{36,37} Xu \textit{et al.} reported that an increased nitrogen content in porous carbon increased the pseudo-capacitance, as a result the overall capacitance was improved.\textsuperscript{36} However, in order to investigate the exact mechanism for the higher specific capacitance of tubular g-C\textsubscript{3}N\textsubscript{4} further studies are needed.

**Photocatalytic performance**

The photocatalytic response of tubular g-C\textsubscript{3}N\textsubscript{4} under visible light was tested using MB and MO. Fig. 6 shows how the peak intensity of the dyes (MO and MB) changes over the degradation time. Tubular g-C\textsubscript{3}N\textsubscript{4} successfully degraded MB within only 75 min, while bulk g-C\textsubscript{3}N\textsubscript{4} required 120 min. Furthermore, for the photodegradation of MO, an initial peak for the MO solution was observed at 463.5 nm. The intensity of this peak continuously decreases with increasing irradiation time and after 165 min no peak for MO was observed. The same amount of bulk g-C\textsubscript{3}N\textsubscript{4} requires 255 min to completely degrade MO. Tubular g-C\textsubscript{3}N\textsubscript{4} shows a good improvement for the photodegradation of MO due to its larger surface area and higher aspect ratio.

There are two possible mechanisms through which a dye can be photodegraded. In one the peak intensity of the dye is decreased, while the position of the main absorption peak remains constant. In the other the main absorption peak is shifted from its initial position as the peak intensity of the dye is decreased. MB follows the first path, while photodegradation of MO follows the second. The main absorption peak of MO is shifted from 463.5 nm to 438.5 nm, while the intensity of the peak decreases from 0.93 to 0.05. The main peak of MB is decreased from 0.96 to 0.07, while no significant change in position of the initial peak is observed. The relationship between \(\ln(C_0/C)\) and time for tubular g-C\textsubscript{3}N\textsubscript{4} and bulk g-C\textsubscript{3}N\textsubscript{4} is shown in Fig. (7), where \(C_0\) is the initial concentration of MB or MO and \(C\) is concentration of the dye at time \(t\). The curve for tubular g-C\textsubscript{3}N\textsubscript{4} is linear; the ratio of \(\ln(C_0/C)\) increases at a constant rate with increasing time.

A clear demonstration of the superiority of tubular g-C\textsubscript{3}N\textsubscript{4} over bulk g-C\textsubscript{3}N\textsubscript{4} is shown in Fig. 8(a), in which first order rate constants \(k\) (min\textsuperscript{-1}) of tubular g-C\textsubscript{3}N\textsubscript{4} and bulk g-C\textsubscript{3}N\textsubscript{4} for the degradation of MB and MO are compared. The first order rate constants were calculated using following equation:

\[
\ln\left(\frac{C_0}{C}\right) = kt
\]

Tubular g-C\textsubscript{3}N\textsubscript{4} has a \(k\) value of 0.02116 min\textsuperscript{-1} for MB and 0.0067 min\textsuperscript{-1} for MO, as shown in Fig. 8(a). The \(k\) value of tubular g-C\textsubscript{3}N\textsubscript{4} shows a significant improvement of the photodegradation properties when compared to bulk g-C\textsubscript{3}N\textsubscript{4}. Tubular g-C\textsubscript{3}N\textsubscript{4} was recycled 3 times for the degradation of both MB and MO. As shown in Fig. 8(b), the material was found to be stable. For the recycling process the same amount of catalytic powder was separated, washed and then used to degrade the same concentration of each dye. Both took almost the same time without any significant loss of efficiency.
Conclusion

We have reported a facile, green and very competent approach to fabricate tubular g-C3N4 with a high surface area (182.61 m² g⁻¹) and specific capacitance (233 F g⁻¹ at a current density of 0.2 A g⁻¹). For the first time, we have used tubular g-C3N4 as an electrode for supercapacitors in KOH electrolyte. Tubular g-C3N4 showed an excellent specific capacitance, which was greater than most other nitrogen doped carbon materials for supercapacitors. Tubular g-C3N4 also showed a good photocatalytic response under visible light. The calculated rate constants were found to be larger than those in earlier reported results. A high specific capacitance and good photodegradation ability indicate that tubular g-C3N4 is a prospective material for clean environmentally friendly energy storage. Our results provide a new outlook in the search for energy storage schemes using tubular g-C3N4 as a functional material that can be fabricated by an economical large scale method. Due to its high surface area and large aspect ratio tubular g-C3N4 could be a good candidate for hydrogen production via water splitting.

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Notes and references