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Tubular graphitic-C 3 N 4 : a prospective material for energy storage and green photocatalysis

Abstract

We have established a facile and scaleable approach to fabricate tubular graphitic-C₃N₄ using melamine. The construction of the unique tubular morphology is a result of the pre-treatment of melamine with HNO₃. Herein, for the first time, we have explored the electrochemical properties of g-C₃N₄ as an electrode material for supercapacitors. Tubular g-C₃N₄ has significant advantages due to its distinctive morphology, high surface area (182.61 m² g⁻¹) and combination of carbon with nitrogen. Therefore, tubular g-C₃N₄ 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-C₃N₄ maintained a high capacitance retention capability (90%) after 1000 cycles. The photocatalytic activity of tubular g-C₃N₄ was evaluated using the organic dyes such as Methylene Blue (MB) and Methylene Orange (MO) under visible light. Tubular g-C₃N₄ demonstrated good photocatalytic activity and enhanced stability compared to bulk g-C₃N₄. The enhanced performance is because of the high surface area, which contains more active sites for reaction. The encouraging performance of tubular g-C₃N₄ 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.

Keywords

3, c, graphitic, tubular, green, photocatalysis, storage, energy, material, prospective, 4, n

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Tubular graphitic-C₃N₄: a prospective material for energy storage and green photocatalysis†Cite this: *J. Mater. Chem. A*, 2013, **1**, 13949Muhammad Tahir,^a Chuanbao Cao,^{*a} Faheem K. Butt,^a Faryal Idrees,^a Nasir Mahmood,^b Zulfiqar Ali,^a Imran Aslam,^a M. Tanveer,^a Muhammad Rizwan^a and Tariq Mahmood^a

We have established a facile and scaleable approach to fabricate tubular graphitic-C₃N₄ using melamine. The construction of the unique tubular morphology is a result of the pre-treatment of melamine with HNO₃. Herein, for the first time, we have explored the electrochemical properties of g-C₃N₄ as an electrode material for supercapacitors. Tubular g-C₃N₄ has significant advantages due to its distinctive morphology, high surface area (182.61 m² g⁻¹) and combination of carbon with nitrogen. Therefore, tubular g-C₃N₄ 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-C₃N₄ maintained a high capacitance retention capability (90%) after 1000 cycles. The photocatalytic activity of tubular g-C₃N₄ was evaluated using the organic dyes such as Methylene Blue (MB) and Methylene Orange (MO) under visible light. Tubular g-C₃N₄ demonstrated good photocatalytic activity and enhanced stability compared to bulk g-C₃N₄. The enhanced performance is because of the high surface area, which contains more active sites for reaction. The encouraging performance of tubular g-C₃N₄ in supercapacitors and as a photocatalyst points toward it being a prospective material for energy storage that is environmentally clean.

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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 from researchers. Supercapacitors have been found to be reliable sources for energy storage with the combined features of batteries and traditional dielectric capacitors. Their ability to rapidly store and release electrical energy at high power densities and with high rate capabilities makes them promising candidates for energy storage.^{1,2}

Among the transition metal oxides, RuO₂ and MnO₂ are potential candidates for ECs. However, these aforementioned materials suffer from issues such as high cost (RuO₂) and the voltage window of MnO₂ is not appropriate beyond 0.6 V for symmetric capacitors due to electrode dissolution.^{3–6}

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 capacities, 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

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† Electronic supplementary information (ESI) available: SEM images of tubular g-C₃N₄, BET of tubular g-C₃N₄ and bulk g-C₃N₄, charge-discharge curves of bulk g-C₃N₄, and Table S1 and S2 can be found in ESI. See DOI: 10.1039/c3ta13291a

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 TiO_2 as a photocatalyst by Fujishima *et al.* in 1972.¹⁶ Unfortunately, due to its large bandgap (3.2 eV) and charge recombination, the quantum efficiency of TiO_2 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.*¹⁹ reported the use of $\text{g-C}_3\text{N}_4$ 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).¹⁹ $\text{g-C}_3\text{N}_4$ 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 $\text{g-C}_3\text{N}_4$ 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 $\text{g-C}_3\text{N}_4$ and nanostructures of $\text{g-C}_3\text{N}_4$ 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 $\text{g-C}_3\text{N}_4$ nanostructures have a clear advantage over bulk nitrogen doped carbon materials.^{10,11,14} Moreover, the concentration of nitrogen is another important factor to help enhance the specific capacitance of supercapacitors.

Herein, we have fabricated tubular $\text{g-C}_3\text{N}_4$ 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 $\text{g-C}_3\text{N}_4$ has been used, for the first time, as an electrode material for supercapacitors in KOH electrolyte. The specific capacitance of the tubular $\text{g-C}_3\text{N}_4$ 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 $\text{g-C}_3\text{N}_4$ as a photocatalyst for the degradation of MO and MB. It shows excellent efficiency compared to bulk $\text{g-C}_3\text{N}_4$ 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 $\text{g-C}_3\text{N}_4$ could be a green material for energy storage and photocatalysis. The large surface area and porous structure of tubular $\text{g-C}_3\text{N}_4$ could also be useful for gas separation, water purification, catalyst support and water splitting.²⁶

Experimental section

Fabrication of tubular $\text{g-C}_3\text{N}_4$

1 g of melamine was dissolved in 30 ml of ethylene glycol to make a saturated solution. 60 ml of 0.1 M HNO_3 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 $10^\circ\text{C min}^{-1}$. Bulk $\text{g-C}_3\text{N}_4$ 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 $\text{g-C}_3\text{N}_4$ (85%), activated carbon (10%) and polytetrafluoroethylene (PTFE) (5%) were mixed with ethanol, pasted on to nickel foam ($5 \text{ cm} \times 1 \text{ cm}$) 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, C_0 , 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 $\text{g-C}_3\text{N}_4$

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. 1(a) and (b) clearly show the tubular like growth of

Fig. 1 (a and b) SEM images of tubular $g\text{-C}_3\text{N}_4$ at different magnifications. (c) A TEM image of tubular $g\text{-C}_3\text{N}_4$. (d) A TEM image of a single tube of $g\text{-C}_3\text{N}_4$ (the inset shows an SAED pattern of tubular $g\text{-C}_3\text{N}_4$).

$g\text{-C}_3\text{N}_4$. From the SEM images it is obvious that these tubular like structures are dense and uniform with an average diameter of $0.8\ \mu\text{m}$. It can also be observed that all of the tubes grew to a uniform average length of $20\ \mu\text{m}$. The unique morphology of $g\text{-C}_3\text{N}_4$ was constructed by treating melamine with HNO_3 in the presence of ethylene glycol. HNO_3 probably breaks the electroneutrality of the aromatic ring of melamine and ethylene glycol then polymerizes resulting in the construction of a tubular structure. The role of ethylene glycol is to carbonize and stabilize the tubular morphology of $g\text{-C}_3\text{N}_4$ as ethylene glycol can easily polymerize after the electroneutrality of the aromatic ring is broken and then modify the melamine to form a tubular structure. Furthermore, during the annealing process ethylene glycol enhances the carbon content, stabilizing the phase and unique tubular structure of $g\text{-C}_3\text{N}_4$. Additionally, the formation mechanism of the tubular structure is dependent on controlling the annealing temperature at which breakage of the electroneutrality occurs, providing anchoring sites for ethylene glycol, which then forces melamine to form tubes. During the annealing process movement of the carbonated species occurs from the inside to the outside, which results in the creation of a tubular structure. To further confirm the tubular morphology, TEM studies were carried out and it is clear from the TEM images that $g\text{-C}_3\text{N}_4$ has a tubular morphology. Fig. S1† shows an SEM image of $g\text{-C}_3\text{N}_4$, which confirms that all of the $g\text{-C}_3\text{N}_4$ products have well defined tubular structures. Fig. 1(c) and (d) are delineated TEM images of $g\text{-C}_3\text{N}_4$, which further confirm the tubular like growth of $g\text{-C}_3\text{N}_4$. The inset of Fig. 1(d) shows an SAED pattern of $g\text{-C}_3\text{N}_4$, which can be indexed to the (002) plane of $g\text{-C}_3\text{N}_4$ with an inter planar distance of $0.326\ \text{nm}$ and this correlates well with the XRD results. Due to incomplete condensation and the number of defects present in tubular $g\text{-C}_3\text{N}_4$, sharp diffraction spots are absent.²⁸ Generally, carbon nitride materials exhibit symmetries close to that of scaffolding tri-s-triazine hexagonal structures and their inter grown domains demonstrate graphite-like stacking of C_3N_4 layers. 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.²⁸

An X-ray diffraction (XRD) investigation was performed in order to explore the crystal structure and phase of $g\text{-C}_3\text{N}_4$, as shown in Fig. 2. The XRD pattern of bulk $g\text{-C}_3\text{N}_4$ shows two peaks at 13.1° and 27.3° . The small peak at 13.1° corresponds to the (100) plane with $d = 0.676\ \text{nm}$ and the other strong peak at 27.3° corresponds to $d = 0.324\ \text{nm}$, due to the long-range interplanar stacking of the aromatic system and is recognized as the (002) plane of bulk $g\text{-C}_3\text{N}_4$. However, the XRD pattern of tubular $g\text{-C}_3\text{N}_4$ only shows one broad and low intensity peak at 27.1° with an interplanar distance of $0.326\ \text{nm}$, which corresponds to the (002) plane of tubular $g\text{-C}_3\text{N}_4$.^{28–30}

X-ray photoelectron spectroscopy (XPS) was performed to investigate the elemental composition and chemical states of tubular $g\text{-C}_3\text{N}_4$. The high resolution N1s spectrum of $g\text{-C}_3\text{N}_4$ has three peaks at $398.54\ \text{eV}$, $399.43\ \text{eV}$ and $400.4\ \text{eV}$, as shown in Fig. 3(a). The first two peaks can be attributed to $\text{sp}^3\ \text{C-N}$ bonds while the third one is due to a $\text{N-sp}^2\text{C}$ bond, which proves that there is bonding between the nitrogen and carbon atoms.^{31,32} The high resolution spectrum of C1s can be resolved into two peaks. The first peak at $288.16\ \text{eV}$ confirms the existence of C-N-C coordination, whereas the second peak at $284.92\ \text{eV}$ is related to surface adventitious carbon.³³ The N/C ratio of tubular $g\text{-C}_3\text{N}_4$ is calculated to be 1.25, which is consistent with previously reported results.^{28–30,33}

The optical properties of tubular $g\text{-C}_3\text{N}_4$ and bulk $g\text{-C}_3\text{N}_4$ were investigated using PL and UV spectroscopy. A xenon lamp was used to excite the materials. The PL spectra of tubular $g\text{-C}_3\text{N}_4$ and bulk $g\text{-C}_3\text{N}_4$ are shown in Fig. 4(a). The emission peaks of bulk $g\text{-C}_3\text{N}_4$ and tubular $g\text{-C}_3\text{N}_4$ are observed at $456.19\ \text{nm}$ and $435.19\ \text{nm}$, respectively. These peaks correspond to the bandgap of the respective sample and belong in the blue-violet light region, indicating the existence of a π state in tubular $g\text{-C}_3\text{N}_4$.³³ This might be attributed to a quantum

Fig. 2 XRD patterns of tubular $g\text{-C}_3\text{N}_4$ and bulk $g\text{-C}_3\text{N}_4$.

Fig. 3 High resolution XPS spectra of tubular g-C₃N₄: (a) N1s and (b) C1s.

Fig. 4 (a) PL spectra of tubular g-C₃N₄ and bulk g-C₃N₄. (b) UV spectra and bandgaps of tubular g-C₃N₄ and bulk g-C₃N₄.

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.³³ To further confirm the bandgap, UV studies were carried out and the UV spectra of tubular g-C₃N₄ and bulk g-C₃N₄ along with their corresponding bandgaps, are shown in Fig. 4(b). The bandgaps of tubular g-C₃N₄ and bulk g-C₃N₄ 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-C₃N₄ and bulk g-C₃N₄ 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-C₃N₄ (182.61 m² g^{−1}) is much higher than that of bulk g-C₃N₄ (10.12 m² g^{−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-C₃N₄ 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^{−1} and 0.5 A g^{−1}. The discharge time of tubular g-C₃N₄ is longer at a current density of 0.2 A g^{−1} compared to that at a higher current density of 0.5 A g^{−1}.

Fig. 5(b) shows the last five charge–discharge curves of tubular g-C₃N₄. The discharge time for the 1000th cycle is very close to that for the 1st discharge at both current densities, which proves the excellent capacitance retention of tubular g-C₃N₄. Specific capacitance (*C*) values for tubular g-C₃N₄ and bulk g-C₃N₄ are given in Fig. 5(c). The specific capacitance is calculated from the charge–discharge curves according to eqn (1):³⁴

Fig. 5 (a) The first five charge–discharge curves of tubular g-C₃N₄ within a potential window of −0.2 to 1.0 V and at current densities of 0.2 A g^{−1} and 0.5 A g^{−1}. (b) The last five charge–discharge curves of tubular g-C₃N₄ within a potential window of −0.2 to 1.0 V and at current densities of 0.2 A g^{−1} and 0.5 A g^{−1}. (c) The specific capacitance at current densities of 0.2 A g^{−1} and 0.5 A g^{−1} for tubular g-C₃N₄ and bulk g-C₃N₄. (d) The efficiency of tubular g-C₃N₄ at current densities of 0.2 A g^{−1} and 0.5 A g^{−1}.

$$C = (It)/(mV) \quad (1)$$

where *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^{−1} at a current density of 0.2 A g^{−1} for the 1st cycle and 212 F g^{−1} for the 1000th cycle, which shows the high cycling stability of tubular g-C₃N₄. Similarly, tubular g-C₃N₄ maintains its high specific capacitance even at a higher current density of 0.5 A g^{−1}, where it is 204 F g^{−1} for the 1st cycle and 182 F g^{−1} for the 1000th cycle. However, in comparison to tubular g-C₃N₄, bulk g-C₃N₄ shows a very low specific capacitance. At the lower current density of 0.2 A g^{−1} the capacitance is only 81 F g^{−1}, while it is 70 F g^{−1} at a current density of 0.5 A g^{−1}. This indicates that the higher surface area of the tubular g-C₃N₄ nanostructures is advantageous for supercapacitor electrodes. The highly stable cycling life of tubular g-C₃N₄ is further confirmed by the efficiency of tubular g-C₃N₄, as shown in Fig. 5(d). The efficiency of tubular g-C₃N₄ decreases from 100% to 91% after 1000 cycles at a current density of 0.2 A g^{−1} and to 90% at a current density of 0.5 A g^{−1}. This demonstrates the high stability of tubular g-C₃N₄. Tubular g-C₃N₄ shows a better performance than many other carbon based materials, such as those listed in Table S1.†^{37–50} The electrode composed of tubular g-C₃N₄ has a high porosity and large surface area that allows a continuous charge distribution.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-C₃N₄ that increases its electron donor–acceptor characteristics.³⁵ The higher nitrogen content in tubular g-C₃N₄ is helpful for

enhancing the capacitance as it can improve the wettability with the electrolyte and, therefore, increase the mass transfer efficiency.^{36,37} It also provides a large additional pseudo-capacitance as well.^{36,37} Xu *et al.* reported that an increased nitrogen content in porous carbon increased the pseudo-capacitance, as a result the overall capacitance was improved.³⁶ However, in order to investigate the exact mechanism for the higher specific capacitance of tubular g-C₃N₄ further studies are needed.

Photocatalytic performance

The photocatalytic response of tubular g-C₃N₄ 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-C₃N₄ successfully degraded MB within only 75 min, while bulk g-C₃N₄ 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-C₃N₄ requires 255 min to completely degrade MO. Tubular g-C₃N₄ 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

Fig. 7 Plots of $\ln(C_0/C)$ vs. time for tubular g-C₃N₄ and bulk g-C₃N₄ for the degradation of MB and MO.

position of the initial peak is observed. The relationship between $\ln(C_0/C)$ and time for tubular g-C₃N₄ and bulk g-C₃N₄ 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-C₃N₄ 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-C₃N₄ over bulk g-C₃N₄ is shown in Fig. 8(a), in which first order rate constants k (min⁻¹) of tubular g-C₃N₄ and bulk g-C₃N₄ for the degradation of MB and MO are compared. The first order rate constants were calculated using following equation:

$$\ln(C_0/C) = kt \quad (2)$$

Tubular g-C₃N₄ has a k value of 0.02116 min⁻¹ for MB and 0.0067 min⁻¹ for MO, as shown in Fig. 8(a). The k value of tubular g-C₃N₄ shows a significant improvement of the photodegradation properties when compared to bulk g-C₃N₄. Tubular g-C₃N₄ 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.

Fig. 6 (a) Photodegradation of MB using tubular g-C₃N₄. (b) Photodegradation of MB using bulk g-C₃N₄. (c) Photodegradation of MO using tubular g-C₃N₄. (d) Photodegradation of MO using bulk g-C₃N₄.

Fig. 8 (a) First order rate constants, k (min⁻¹), of tubular g-C₃N₄ and bulk g-C₃N₄ for the degradation of MB and MO. (b) Stability test results for tubular g-C₃N₄.

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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