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Rapid photocatalytic degradation of acetaminophen and levofoxacin using g-C₃N₄ nanosheets under solar light irradiation

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Abstract

Rapid photocatalytic performance was targeted through modifying the graphite-like carbon nitride (g-C₃N₄) bulk materials to nanosheet structure via thermal oxidation etching process. Simple thermal oxidation etching treatment was used in order to reduce multilayer g-C₃N₄ structure to nanosheet material. The differences in the obtained sample of g-C₃N₄ nanosheets and pristine g-C₃N₄ were characterised via scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDX), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), Photoluminescence (PL), Fourier-transform infrared spectroscopy (FTIR), UV–vis diffuse reflectance spectroscopy (UV–vis DRS), Brunauer–Emmett–Teller (BET) analysis and particle size analysis. The photocatalytic efficiency was tested for the degradation of acetaminophen and levofoxacin under direct solar irradiation. The results showed some variation in XRD, particle size and BET results indicating that etching process was evolved in reducing the particles size and lowering the layers number in g-C₃N₄ bulk sample. The optical and band gap properties results noticed some variation where the XPS and FTIR spectra showed some modification on g-C₃N₄ nanosheet motif such as the C–H, CO and N pyridinic structure. Accordingly, the photocatalytic degradation of acetaminophen by the g-C₃N₄ nanosheets under solar irradiation was much faster and reached 99% in one hour where in the case of g-C₃N₄ bulk sample the degradation reached only 38% in 4 h. Similarly, levofoxacin degradation with nanosheet sample reached 99% in one hour compare to 16% in presence of the bulk sample. This enhancement can be attributed to multiple factors such as smaller particle size, rich carbon surface and lower band gap exhibited by the g-C₃N₄ nanosheets. This further indicates that the performance of g-C₃N₄ can be further enhanced via this method and can used to treat wastewater contaminated by pharmaceuticals under solar irradiation.

1. Introduction

In the last few decades, a considerable interest has developed regarding the health impact of organic and inorganic pollutants in the environment. Such contamination in our aqueous environment is increasing annually due to the increase in the development and demand. So far, several studies have highlighted the presence of organic pollutants in treated water. Meanwhile, some other studies focused on the possible pathways for those pollutants to reach freshwater in the environment [1–4]. Emerging pollutants can be found in the environment at µg/L to ng/L levels. In general, this includes chemicals such as pharmaceutical compounds and personal care products as well as endocrine disrupting chemicals [5]. Moreover, the presence of some pharmaceutical compounds knowing for causing a serious effect in the health of an organism [6]. Therefore, it is necessary to develop efficient techniques to eliminate and decompose emerging pollutants from water and wastewater as soon as possible.

Implementing the properties of semiconductors materials can be very promising method helps to purify waters and wastewaters [7–9]. To date, several photocatalytic materials such as metal oxides, metal sulphaides,
and Oxy-nitrides, have been utilized to obtain a photocatalytic response [10–13]. Moreover, there is growing interest on non-TiO\textsubscript{2} and non-ZnO photo-catalysts due to their wide band gap [14–17]. Unfortunately, most of photocatalysts material have various problems at present, including very weak light absorption, non-suitable redox potential for photocatalytic reaction, short-term stability and/or high preparation price [18–21]. In contrast, carbonic materials are promising conducting materials due to their high charge mobility. Among these, graphite-like carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) is considered to be an interesting photocatalytic material since Wang and his co-worker published its novel use as an active photocatalyst for hydrogen evolution under irradiation with visible light [22]. Thus, tremendous attention has centred on the use of g-C\textsubscript{3}N\textsubscript{4} for pollutant degradation and chemical synthesis. The graphite carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) nanosheets have a 2D polymer semiconductor structure that is very similar to that of graphene (figure 1 (a)). The band gap of this graphite like carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) photocatalyst was measured to be around 2.7 eV [23–26]. g-C\textsubscript{3}N\textsubscript{4} has attracted world-wide attention due to its interesting properties including a suitable redox potential, band structure located in the visible light region compare to the band structure of TiO\textsubscript{2} which is located in UV region (figure 1 (b)), thermal and chemical stability, and ease of preparation that allows for large-scale production from low-cost precursors. Recently, g-C\textsubscript{3}N\textsubscript{4} was synthesized from urea, thiourea, melamine, cyanamide and dicyanadiamide [27–29].

The graphite-like carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) semiconductor can be prepared following a relatively simple process. It can be synthesized via thermal polycondensation of conjoint monomers to obtain a typical mass polymer either in a low vacuum system or under a high pressure [30–32]. Moreover, several research groups have successfully prepared carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) under ambient pressure in a semi-closed system, which is more convenient from an industrial point of view [33, 34]. However, enhancement of g-C\textsubscript{3}N\textsubscript{4} photocatalytic performance is targeted from researchers and one way to do so is to transfer the g-C\textsubscript{3}N\textsubscript{4} bulk material to nanosize materials. To the best of our knowledge no systematic investigation has been done on the degradation of Acetaminophen and levofloxacin via g-C\textsubscript{3}N\textsubscript{4} nanosheets obtained via thermal oxidation process. We report here, the enhancement of the photocatalytic degradation of Acetaminophen and levofloxacin with the help of g-C\textsubscript{3}N\textsubscript{4} nanosheets obtained from g-C\textsubscript{3}N\textsubscript{4} bulk materials via thermal oxidation process under solar light irradiation.

2. Experimental section

2.1. Materials and preparation

The melamine powder was purchased from Sigma-Aldrich (M2659 ALDRICH) and was used in the synthesis of g-C\textsubscript{3}N\textsubscript{4} without further purification. The preparation of the g-C\textsubscript{3}N\textsubscript{4} bulk was performed with help of a muffle furnace via direct heating of the melamine powder in a semi-closed system. 1 g of melamine powder was placed into an alumina crucible with a cover. Direct heating was applied to increase the temperature from room temperature to 550 °C at heating rate of 20 °C min\textsuperscript{−1} under a nitrogen flow for 25 min. For the g-C\textsubscript{3}N\textsubscript{4} nanosheet, 0.2 g of the bulk sample heated at 550 °C for 12 h without nitrogen as represented in Scheme 1. The
n数值heet samples were left to cool to room temperature, and then the product was collected for further analysis.

2.2. Characterization
X-ray diffraction (XRD) measurements were conducted for the as-prepared g-C₃N₄ 12h and g-C₃N₄ 3h samples to identify the crystal phases on the benchtop x-ray diffractometer (MiniFlex600) with graphite monochromatized Cu Kα radiation (λ = 1.540 Å). The morphology of the resulting samples was examined using a field emission scanning electron microscope (FESEM; JSM-7800F, JOEL, Japan). A maximum working voltage of 15 kV and 10 mm of working distance were used during the measurement. X-ray photoelectron spectroscopy (XPS) measurements were conducted using multi-probe x-ray photoelectron spectroscopy (XPS) (Omicron Nanotechnology, Germany). The XPS measurements were analysed as individual components using the Casa XPS software (Casa Software Ltd). The binding energies of the obtained spectra were calibrated with respect to the carbon C 1s peak at 284.6 eV. UV–vis diffuse reflection spectroscopy (UV–vis DRS) was performed on a UV–vis Spectrometer Lambda 650 S (Perkin Elmer), and the infrared spectra were obtained using CARY 600 FTIR (Agilent Technologies). The photo luminance (PL) was performed on a PerkinElmer LS55 spectrometer. Brunauer–Emmett–Teller (BET) surface area analysis was carried out using ASAP2010 under liquid N₂ with 50 P/P₀ points, Micromeritics, USA. The particle sizes were measured using Microtrac particle sizer.

2.3. Photocatalytic activity test
Acetaminophen and levofloxacin were chosen as pharmaceutical compounds to test the photocatalytic activity of the as-prepared g-C₃N₄ nanosheet. All photoreaction experiments were carried out in a photocatalytic reactor batch system consisting of a cylindrical borosilicate glass reactor vessel with an effective volume of 500 ml. The activity studies were conducted in an open atmosphere with an air diffuser fixed at the reactor to uniformly disperse the air into the solution. The reaction suspensions were prepared by adding 0.1 g of as-prepared g-C₃N₄ into 250 ml of aqueous Acetaminophen and levofloxacin solution with an initial concentration of 5 mg l⁻¹. Prior to illumination, the reaction suspensions were magnetically stirred for 30 min in dark to ensure adsorption–desorption equilibrium between the photocatalyst and the Acetaminophen and levofloxacin. During illumination, about 6 ml of the suspension solution were taken from the reactor at a scheduled interval. The samples were centrifuged at 8000 revolutions per minute for 5 min and were then filtered to remove the catalyst. The degradation experiments followed by HPLC-UV/Vis Shimadzu Nexera-i series LC-2040 liquid chromatograph (Shimadzu, Japan). The column used was C18 (Waters X 3.9’300 mm, 15–20 μm). The Mobile phase was made from 0.1 M ammonium acetate and acetonitrile (30%–70%). The flow rate was 0.8 ml min⁻¹ and the injection volume was 20 μl. The obtained results analysed with help of Labsolution® software.

3. Results and discussion
3.1. Characterization of g-C₃N₄ nanosheets
g-C₃N₄ bulk material and g-C₃N₄ nanosheet samples were examined via energy dispersive x-ray spectroscopy (EDX) measurements as shown in figure 2(a). The EDX analysis reveals that the main signals obtained from carbon (C) and nitrogen (N). There are some weak signals from the sample holder (Al) and the platinum coating. The morphology of the resulting samples shows the sheet structure, which is a characteristic shape of g-C₃N₄ (figures 2(b) and (c)) [35–37]. Moreover, the g-C₃N₄ nanosheet seems to be softer and fluffier (figure 2(c) inset).
In order to confirm the transformation to the nanosheet structure the TEM analysis were carried out, figures 3 (a1), (a2) and (a3) showed TEM images of the bulk sample, the bulk sample showed darker colour indicating more thickness with clear multilayers structure. In the other hand figures 3(b1), (b2) and (b3) showed the TEM images of the nanosheet sample. The images clearly presented a fine thin sheet of g-C3N4 indicating the nanosheet transformation.

The XRD results for the bulk g-C3N4 and the nanosheets are shown in figure 4. The spectrum of the g-C3N4 semiconductor exhibits two main diffraction peaks, one peak at 27.90° corresponding to the (002) plane typical for the interlayer stacking peak of the C-N conjugated aromatic systems and a second weak diffraction peak at around 13.05° indexed in the (100) plane and representing the interplanar separation of tri-s-triazine units. These diffraction peaks are in good agreement with the g-C3N4 that has been reported in the literature [38]. The position of the diffraction peaks was retained during the treatment process, showing
the existence of the main structure of g-C$_3$N$_4$. However, the overall diffraction intensity was reduced by increasing the etching treatment. The (001) plane peak disappeared and it can be considered because of the reduced structural correlation length prompted by a decrease in the number of layers. This result reflects the formation of the g-C$_3$N$_4$ nanosheets.

Figure 5 presents the Fourier transform infrared (FTIR) spectrum of the as-prepared samples to identify the specific interaction of the functional groups. The result indicates the presence of the graphite-like structure of carbon nitride. The N–H stretching modes and the O–H from water absorbed on the surface are present in the broad peak observed in the range of 3000–3500 cm$^{-1}$. The bands around 1200–1600 cm$^{-1}$ are characteristic of a typical stretching mode of CN heterocycles. In addition, the s-triazine ring mode was observed at 801 cm$^{-1}$. However, there was some broadening in the peak at 3000–3500 cm$^{-1}$, which is indexed to CO vibration.

### 3.2. Optical properties of nanosheets

The UV–vis diffuse reflectance spectroscopy (UV–vis DRS) was conducted to assess the optical properties of the g-C$_3$N$_4$ samples. Figure 6(a) illustrates the main absorption results for g-C$_3$N$_4$ bulk and g-C$_3$N$_4$ nanosheet. The optical absorption edge of g-C$_3$N$_4$ bulk occurs at 390 nm and then red shifted to a longer wavelength for g-C$_3$N$_4$ nanosheets.
The effect of longer thermal oxidation treatment is consistent with the reported results [39, 40]. Moreover, the g-C₃N₄ nanosheet sample is more efficient than g-C₃N₄ bulk sample in absorbing near UV and visible range up to 470 nm. The spectra exhibit a long absorption tail for g-C₃N₄ nanosheet sample, and this can be attributed to structural defects formed for the sample treated for a longer time. The Tauc plot was used to calculate the optical band gap [41]. The Tauc plots (the curve of \((\alpha h\nu)^{1/2}\) versus \(E\) where \(E\) is the energy in eV and \(\alpha\) is the absorption) are shown in figures 6(b) and (c). The band gap value of g-C₃N₄ was calculated to be 2.7 eV for g-C₃N₄ nanosheet and 2.8 eV for g-C₃N₄ bulk sample.

Figure 7(a) investigates the chemical composition of the constituent elements of the g-C₃N₄ obtained via XPS analysis. The XPS spectra reveal that the elements mainly present are carbon, nitrogen and some oxygen. The high-resolution spectra of carbon and nitrogen peaks are shown in figure 7(b). The binding energies at 286.7, 288.4 and 289.2 eV are indexed to carbon from C–NH₂, C–N and C=N respectively while, the binding energies at 397.1, 397.1 and 400.3 eV are attributed to nitrogen from C=N–C, N–(C)₃ and C–N–H respectively. Moreover, some changes occurred for carbon and nitrogen peaks. Low intensity core levels peaks detected indicating the surface modification of the sample. Two peaks appeared at binding energies 284.27 and 290.2 eV which could be attributed to C–C or C–H carbons while the other peak at 290.2 eV can be assigned to CO resulting from etching process and adsorbed on the sample surface [42, 43]. This result is compatible with broadening observed in the FTIR result. For the nitrogen, the peak at binding energy 393.6 eV can be assigned to edge type N pyridinic which was reported previously for sample prepared at higher energy [44–46]. The amount
of each element and the carbon to nitrogen ratio (C/N) (wt%) are shown in table 1. There was a slight increase in the C/N ratio. This enhancement may indicate a carbon-rich surface which may enhance the photocatalytic activity by promoting charge carrier separation [47].

The photoluminescence emission (PL) spectra of as obtained g-C3N4 samples are shown in figure 8(a). The PL measurement was performed at room temperature for the g-C3N4 bulk and g-C3N4 nanosheet samples at excitation wavelengths of 360 nm. The main emission peak is located at about 450 nm for both samples. The emission peak addressed the photo-generated electron-hole pairs process in the g-C3N4. Moreover, the emission intensity indicates the rate of photo generated electron-hole pairs. The spectra show that the g-C3N4 nanosheet has a higher intensity compared to that for the g-C3N4 bulk. The decrease in the intensity can be explained by the electron trapping process that occurs within the bulk material due to a crystal mismatch, which prevents electron-hole mobility. Moreover, the formation of nanosheets promoted the charge mobility as reported earlier [48]. Moreover, The Commission Internationale de l’Eclairage (CIE) chromaticity diagram of nanosheet and bulk sample presented in figure 8(b). The CIE (x, y) coordinate of both samples located at (0.17, 0.18 which further confirm that the PL emission is covering the blue-violet.

| Content (%) | C   | N   | O   | C/N |
|-------------|-----|-----|-----|-----|
| g-C3N4 bulk | 42.23 | 56.92 | 0.65 | 0.74 |
| g-C3N4 nanosheet | 43.68 | 55.54 | 0.78 | 0.78 |

Figure 8. (a) The comparison of photoluminescence (PL) spectra of g-C3N4 (b) corresponding 1931 (CIE) chromaticity diagram.

3.3. Particles size and BET analysis
The reduction of g-C3N4 multilayers structure (bulk) to few layered g-C3N4 nanosheets was followed by size particles analysis with help of particle sizer. The particle size distribution are showing in figures 9(a) and (b), where the average particle size were 4967 and 1783 nm for g-C3N4 bulk and g-C3N4 nanosheet respectively. This decline in the particle size is attributed to thermal oxidation etching process. Moreover, the BET surface area and porosity of the samples has been analyzed and the result showed a type 3 shape of isotherms according to the IUPAC classification (figure 9(c)). This result indicate the occurrence of slightly mesoporous-like structure due to the aggregation of sheets to form the bulk g-C3N4, leaving pores in between [49]. The BET surface area has been found to be 94.243 and 30.106 m² g⁻¹ where the BJH adsorption surface area of pores found to be around 123.0573 and 37.8759 m² g⁻¹ for g-C3N4 bulk and g-C3N4 nanosheet respectively. This decreases and the decline indicating the transformation of the multilayers of g-C3N4 bulk to a few layers of g-C3N4 nanosheets where significantly low amount of surface area available for nitrogen adsorption due to the overlap of the single layer of nanosheets [50].
3.4. Evaluation of the photocatalytic activity

Acetaminophen and Levoﬂoxacin were chosen as a pollutant to determine the photocatalytic activity of the as-obtained catalysts on pharmaceuticals. In general, Acetaminophen and Levoﬂoxacin used as a model because they are largely used for medication and they are hardly degraded in the environment. A control experiment used to check the degradation of these compounds in the absence of the catalyst (figure 10). Figures 10(a) and (b) showed the HPLC-UV–vis chromatogram of acetaminophen (5 mg l−1) and normalized degradation rate under solar light irradiation. The photocatalytic degradation of acetaminophen by the g-C3N4 nanosheets under solar irradiation was much faster and reached 99% in one hour where in the case of g-C3N4 bulk sample the degradation reached only 38% in 4 h. Similarly, levoﬂoxacin degradation with nanosheet sample reached 99% in one hour compare to 16% in presence of bulk sample as shown in figures 10(c) and (d).

4. Conclusions

In this work, photocatalytic enhancement has been achieved for degradation of pharmaceutical compounds via g-C3N4 nanosheets, which was obtained via direct heating of melamine, followed by thermal oxidation etching process. The g-C3N4 bulk material obtained and used for the comparison purposes. As a result, the g-C3N4 nanosheet sample show very rapid photocatalytic activity under solar irradiation compare to bulk sample. This enhancement on the photocatalytic activity can be attributed to multiple factors such as smaller particle size, rich carbon surface and high surface area exhibited by the g-C3N4 nanosheets. The g-C3N4 nanosheets have very good potential be used in advanced water and wastewater treatment to eliminate pharmaceuticals to a very low level under solar light irradiation.
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Figure 10. (a), (b) HPLC-UV–vis chromatogram of acetaminophen (5 mg l−1) and degradation rate with g-C3N4 nanosheets under solar light irradiation (catalyst dosage 100 mg, solution volume 250 ml, source of light solar) (c), (d) HPLC-UV–vis chromatogram of levofloxacin (5 mg l−1) degradation with g-C3N4 nanosheets under solar light irradiation (catalyst dosage 100 mg, solution volume 250 ml, source of light solar).
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