Oxidized graphitic carbon nitride nanosheets as an effective adsorbent for organic dyes and tetracycline for water remediation

Mahdieh Yousefi^{a,b,†}, Silvia Villar-Rodil^{b,†}, Juan I. Paredes^{b,*}, Alireza Z. Moshfegh^{a,c,*}

^aInstitute for Nanoscience and Nanotechnology, Sharif University of Technology, Azadi Avenue, P. O. Box 14588–8969, Tehran, Iran

^bInstituto Nacional del Carbón, INCAR-CSIC, C/Francisco Pintado Fe 26, 33011 Oviedo, Spain

^cDepartment of Physics, Sharif University of Technology, Azadi Avenue, P. O. Box 11155–9161, Tehran, Iran

[†] These authors contributed equally to the work.

* Corresponding author: paredes@incar.csic.es

* Corresponding author: moshfegh@sharif.edu

Abstract

Graphitic carbon nitride (g-C₃N₄) is promising as adsorbent for water remediation as its chemical structure allows a variety of mechanisms to interact with wastewater pollutants. However, several issues, such as low specific surface area and insufficient dispersibility in water, have to be tackled to achieve a competitive performance in such use. Previous attempts to improve the features of g-C₃N₄ as an adsorbent have relied on carbon doping and exfoliation in the solid phase by thermal expansion. Here, we demonstrate that exfoliation in the liquid phase by a combination of oxidation and sonication allows preparing g-C₃N₄-based materials with improved dispersibility in water, increased exposed surface, and abundance of surface functional groups. The obtained oxidized g-C₃N₄ adsorbents exhibited high adsorption capacities which were remarkable towards organic dyes (~70–600 mg/g) and excellent in the case of the antibiotic tetracycline (895 mg/g) in aqueous solution. The present results should open new opportunities for the use of oxidized g-C₃N₄ materials as adsorbents for water remediation.

Keywords: nanostructured materials; oxidation; scanning electron microscopy, SEM; electron emission spectroscopy

1. Introduction

The isolation of graphene, the first two-dimensional (2D) material, in 2004 [1] and the subsequent discovery of its outstanding physical properties [2] triggered a revolution in the field of materials science in search of other 2D materials [3]. The great research interest of 2D materials lies on their unique electronic, optical or mechanical properties derived from reduced dimensionality that provide them with prospective applications in many fields, such as, electronics, photonics, energy conversion and storage, and catalysis, among others [4]. Furthermore, an intrinsic characteristic of 2D materials, their high surface area, enhances surface activity [5], which is beneficial to many applications where phenomena such as adsorption, charge storage or catalysis are implied. In analogy with the case of graphene, one of the most popular strategies in the quest for new 2D materials has been the exfoliation of parent layered materials [5]. Like graphite, these materials consist of planar layers with strong intra-layer chemical bonding joined together by weak interlayer interactions, lending themselves to exfoliation by weakening the interlayer adhesion. Exfoliation in the liquid phase, usually accomplished by oxidation, sonication, ion intercalation or ion exchange, is a particularly attractive route for the production of 2D nanosheets due to its versatility and scalability [5].

Among different layered materials, the polymeric semiconductor graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), which is the most stable polymorph of carbon nitride [6], has attracted significant attention in recent years. $g\text{-C}_3\text{N}_4$ is a graphene analogue with *ABA* stacking of hexagonal planar sheets of tris-*s*-triazine units connected by tertiary amines [7] [see Fig. S1a of the Supplementary Material (SM)]. This material is commonly synthesized by polyaddition/polycondensation of nitrogen-rich organic precursors [6]. Although a promising candidate for several applications in many fields, such as catalysis [6,8], photocatalysis [9–15] and energy conversion and storage [16,17,18], some features of bulk $g\text{-C}_3\text{N}_4$, such as high recombination rate of photogenerated charges [19], low specific surface area, and low dispersibility [20,21] limit its actual use. Down-sizing to two dimensions has been undertaken as a strategy to improve both the performance and processing of $g\text{-C}_3\text{N}_4$ in different applications. Specifically, $g\text{-C}_3\text{N}_4$ has been exfoliated in the liquid-phase by several different methods, namely, sonication in different solvents [22–24], acid [25–27] and alkali treatment [28] and oxidation [29–31].

There are a variety of techniques for removing organic pollutants from wastewater, mainly based on oxidation [32] and adsorption [33] processes, each of which having its own advantages and drawbacks [34]. Oxidation processes, including photocatalysis [35,36], microwave catalysis [32,37], photodegradation, Fenton, photo-Fenton, ultrasonication and ozonation, transform organic pollutants into non-toxic substances. These processes allow removing large amounts of contaminants, being at the same time effective disinfection methods. However, they have the disadvantages of implying the formation of by-products (the oxidized/degraded pollutant) [34] and relatively high operational costs [32]. Adsorption on suitable adsorbent materials, on the other hand, affords elimination of contaminants in large amounts at moderate cost without generation of by-products [34,38–40]. Microwave irradiation has been combined with both oxidation and adsorption techniques for enhanced pollutant removal [32].

g-C₃N₄ shows promise as adsorbent of organic pollutants for water remediation [41–43] to tackle the global environmental issue of organic pollution. In analogy with the case of graphene, the ability of g-C₃N₄ to adsorb aromatic pollutants, such as dyes and drugs, has been related mostly to π - π interactions between the π -conjugated systems of g-C₃N₄ and the adsorbates [41–43]. Consequently, the strategies to improve adsorption have sometimes aimed at the enlargement of g-C₃N₄ π -conjugated system by carbon doping [41,42]. However, the adsorption of organic pollutants on g-C₃N₄ could take place by mechanisms other than π - π interactions, such as hydrogen bonding, electrostatic interactions, etc [38,39]. Indeed, in the same way that hydrogen bonding has been shown to play an important role in the stable colloidal dispersion of g-C₃N₄ in solvents [22], it could be expected to contribute significantly to the adsorption of organic molecules on its surface. Thus, the performance of g-C₃N₄ as an adsorbent could benefit too from the enhancement of hydrogen bonding interactions by the increase of the amount and/or variety of functional groups prone to interact. Another strategy to improve the performance of g-C₃N₄ as adsorbent previously reported in the literature has been the increase of its available surface area by thermal exfoliation in solid phase [44]. In a different context, specifically, in studies dealing with the use of g-C₃N₄ as photocatalyst and not as adsorbent, liquid-phase exfoliation through oxidation [29–31] has proved useful to improve the dispersibility in water and increase the surface

area of bulk g-C₃N₄. This suggests that oxidation of g-C₃N₄ could also be used to produce g-C₃N₄-derived adsorbents with improved features. Furthermore, oxidation could introduce abundant and varied oxygen-containing groups that would increase the possibilities of interaction with adsorbates.

In this work, we report the preparation of g-C₃N₄-derived adsorbents by exfoliation in the liquid phase through a combination of oxidation and sonication, as well as their application for the adsorption of the antibiotic tetracycline and a variety of dyes. The oxidized g-C₃N₄ materials show improved colloidal stability in water and adsorption capability for all the organic pollutants towards their non-oxidized counterpart. In fact, the adsorption capacities of our oxidized g-C₃N₄ materials compare well with those reported in the literature for g-C₃N₄-related materials [29,41–44], being similar to or sometimes superior than most of the reported values for graphene [45–54] and other carbon-based nanosheets [55,56].

2. Materials and methods

2.1. Materials and reagents

The chemicals and reagents used were obtained from Sigma–Aldrich unless otherwise indicated: commercial g-C₃N₄ powder (chemical purity $\geq 99.5\%$, Carbodeon Ltd.), H₂SO₄ (98%), HCl (37%), KMnO₄ ($\geq 99\%$, Aldrich), H₂O₂ (30 wt. %), the dyes methylene blue (MB), methylene green (MG), rose Bengal (RB), rhodamine B (RhB), basic fuchsin (BF), methyl orange (MO), and the drug tetracycline (TC). All these chemicals were used as received, with no further purification. Ultrapure water (Milli-Q; resistivity: 18.2 M Ω cm) was used throughout the study.

2.2. Oxidation of graphitic carbon nitride

Graphitic carbon nitride was oxidized by a modified Hummers method recently reported by Teng et al. [31]. Specifically, 30 mL of concentrated sulfuric acid was added to 1.00 g of bulk g-C₃N₄ powder under continuous stirring at room temperature. Then, 1.2 g of KMnO₄ was slowly added into the mixture under constant stirring. The resulting mixture was left to react under constant stirring for another 2 hours at room temperature (22 °C). Then, the reaction flask was placed in an ice bath and 200 mL of Milli–Q water was added slowly to the suspension, followed by hydrogen peroxide aqueous solution until the color of the suspension changed from brown to milky. After filtration through a

2 μm filtering paper, the precipitate was first washed with ~ 0.5 L of 2% wt. HCl solution, and then with Milli-Q water until the pH reached ~ 6 . To prepare a material with a significantly higher extent of oxidation, the same procedure was carried out with a larger amount of oxidant (3.6 g of KMnO_4) and at higher reaction temperature (60 $^\circ\text{C}$). The products were vacuum-dried at 80 $^\circ\text{C}$ for 8 hours.

2.3. Characterization techniques

The samples were characterized by elemental analysis, UV-Vis absorption spectroscopy, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), powder X-ray diffraction (XRD) and N_2 physisorption. UV-Vis absorption spectra were recorded with a Helios α spectrophotometer (Thermo Spectronic) with an optical path length of 1 cm. Elemental analyses were carried out in a LECO Truspec Micro CHN microanalyses apparatus with an accessory for direct O determination. Prior to the analysis, the samples were dried overnight at 105 $^\circ\text{C}$. ATR-FTIR spectroscopy was accomplished on a Nicolet 8700 spectrometer (Thermo Scientific) with a diamond ATR crystal. XPS measurements were accomplished on a SPECS system at a pressure of 10^{-7} Pa with a non-monochromatic Mg K_α X-ray source operated at 11.81 kV and 100 W. All the g- C_3N_4 samples exhibited charge effects that caused an up-shift in the binding energy of ~ 2 –2.5 eV. Such displacement was corrected a posteriori, using the carbon impurity (adventitious carbon) at 285.0 eV as a reference. Field emission (FE) SEM and STEM images were acquired on a Quanta FEG 650 system (FEI Company) operated at 25 and 20 kV, respectively. Freshly cleaved highly oriented pyrolytic graphite was used as substrate for SEM specimens. The samples were prepared by drop-casting a small volume (~ 20 –40 μL) of diluted g- C_3N_4 dispersion onto the substrate, which was preheated at ~ 50 $^\circ\text{C}$, and then allowing it to dry. Specimens for STEM were prepared by drop-casting ~ 10 μL of washed g- C_3N_4 onto a copper grid (200 square mesh) covered with a continuous carbon film (Electron Microscopy Sciences), which was then allowed to dry. XRD patterns were recorded with a D8 Advance diffractometer (Bruker) at angles (2θ) between 10 and 70 $^\circ$, using Cu K_α radiation ($\lambda = 0.1504$ nm) at a step size of 0.02 $^\circ$ and time per step of 1s. N_2 adsorption-desorption isotherms were recorded at -196 $^\circ\text{C}$ in an ASAP 2420 volumetric apparatus (Micromeritics), after degassing overnight under vacuum at 120 $^\circ\text{C}$. Total pore volumes were calculated from the amount of N_2

adsorbed at $P/P_0=0.95$, using a density of 0.813 g cm^{-3} for liquid N_2 . The specific surface areas were obtained from the adsorption branch of the N_2 isotherms by the standard Brunauer-Emmett-Teller (BET) method in the relative pressure range from 0.05–0.35. The pore size distribution curves were determined from the adsorption branches by the Barrett-Joyner-Halenda (BJH) method. For the colloidal stability tests, aqueous dispersions of the g- C_3N_4 materials were prepared by bath sonication for 5 h of the solids at nominal concentration of 1 mg mL^{-1} and the resulting dispersions were left to stand undisturbed, monitoring the UV-Vis absorbance at the absorption maxima of the supernatant versus time.

2.4. Dye/drug adsorption experiments

For the dye/drug adsorption measurements, 5 mg of the g- C_3N_4 material was added to 5 mL of water and sonicated for 5 h (J.P. Selecta Ultrasons system, 40 kHz, power $\sim 20 \text{ W L}^{-1}$). Then, 10 mg of dye/drug was added and the mixture was sonicated for 10 min to dissolve the dye/drug at initial concentration of 2 mg mL^{-1} . To ensure the attainment of adsorption equilibrium, the mixture was stirred for 24 h at room temperature (22°C) and $\text{pH}\approx 6$, after which the adsorbent was separated from the solution by centrifugation. The adsorbed amounts were then calculated from the difference between the initial and equilibrium concentration of the dye/drug in the supernatant. The concentrations were determined with UV–Vis absorption spectroscopy, from the measured absorbance at the absorption maxima characteristic of the dyes/drug, namely, the peaks located at wavelength of 664 nm for MB, 660 nm for MG, 560 nm for RB, 555 nm for RhB, 542 nm for BF, 465 nm for MO, and 357 nm for TC. To measure the TC isotherm, the same protocol was followed but using different initial TC concentrations.

For their regeneration, the adsorbents were separated from the adsorption medium by decantation, which was speeded by centrifugation. The aqueous supernatant was exchanged by ethanol and the adsorbent was re-dispersed in ethanol by ultrasonication for 10 min. The adsorbate was desorbed from the material by successive precipitation/re-dispersion cycles in fresh ethanol. The desorption of the dye/drug was monitored by measuring the UV-vis absorbance of the supernatant. Typically, three such precipitation/re-dispersion cycles in ethanol were done to remove the adsorbate, followed by three washing (precipitation/re-dispersion) cycles in water, to remove the

ethanol. After regeneration, the adsorbent was re-used in the same adsorption conditions described above.

3. Results and discussion

3.1. Preparation and characterization of oxidized g-C₃N₄ powders

With a view to using g-C₃N₄ as adsorbent for water remediation, we tried to improve some of its characteristics, such as colloidal stability in water, exposed surface area as well as the number and variety of surface functional groups. To this end, we have undertaken oxidation of g-C₃N₄ by a modified Hummers method [31]. After preliminary tests with a range of oxidation conditions (different oxidation temperatures and amounts of oxidant), we have chosen two different oxidation protocols – milder (room temperature, 1.2 g of KMnO₄) and harsher (60 °C, 3.6 g of KMnO₄) – to produce materials with significantly different oxidation extents. The starting material and those oxidized at milder and harsher conditions will be henceforth designated as g-C₃N₄, g-C₃N₄ ox RT and g-C₃N₄ ox 60, respectively. The yields in weight percent were ~60% and ~20%, for g-C₃N₄ ox RT and g-C₃N₄ ox 60, respectively.

The color of g-C₃N₄ powder transformed from the starting deep yellow into pale yellow after mild oxidation and into almost white after the harsher one (see Fig. 1a). This change in color can be related to a decrease in the size of the π -conjugated domains with oxidation that increases the energy gap between valence and conduction band and blue-shifts the optical band gap of the material. SEM was conducted to examine the morphology of the oxidized samples. Figs. 1b–d show representative micrographs of the starting, non-oxidized materials and the samples oxidized at different temperatures. The starting g-C₃N₄ powder consists of particles with lateral dimensions of several micrometers and layered morphology (Fig. 1b) [22]. Upon oxidation, the lamellar shape is retained, but the lateral dimension of the particles decreases (Figs. 1c and d).

Figure 1. (a) Digital photograph of, from left to right: the starting $\text{g-C}_3\text{N}_4$ powder, $\text{g-C}_3\text{N}_4$ oxidized at room temperature and at $60\text{ }^\circ\text{C}$. (b–d) Representative FE-SEM images of the starting $\text{g-C}_3\text{N}_4$ powder (b), $\text{g-C}_3\text{N}_4$ oxidized at room temperature (c) and at $60\text{ }^\circ\text{C}$ (d).

The introduction of oxygen in the materials was confirmed by the elemental analysis results, which are gathered in Table 1. Indeed, while the starting bulk $\text{g-C}_3\text{N}_4$ powder lacked oxygen, the oxidized materials displayed significant amounts of such element. The considerable amount of H (equivalent to $\sim 19\text{ at. } \%$) found in the starting $\text{g-C}_3\text{N}_4$ material comes from the incomplete condensation of the material (see Fig S1 of the SM), as has been previously reported in the literature [6]. The elemental analysis results added up approximately $100\text{ wt}\%$ within experimental error, which indicated that no other elements than C, N and H (and O, in the case of the oxidized materials) were present in the analyzed samples.

Table 1. Elemental analysis of the starting $\text{g-C}_3\text{N}_4$ and $\text{g-C}_3\text{N}_4$ oxidized in different conditions:

Sample	H	C	N	O
	(wt%)	(wt%)	(wt%)	(wt%)
$\text{g-C}_3\text{N}_4$	1.7	34.5	63.3	-
$\text{g-C}_3\text{N}_4$ ox RT	2.5	32.1	55.8	10.3
$\text{g-C}_3\text{N}_4$ ox 60	3.1	28.9	51.3	15.5

To obtain additional information on the chemical modifications undergone by the materials upon oxidation, the samples were further analyzed by ATR-FTIR and XPS. The ATR-FTIR spectrum of the starting material (Fig. 2, black trace) confirmed that its structure comprised both triazine cycles (in fully condensed g-C₃N₄ planes) and uncondensed amine groups (see Fig. S1a of the SM). Specifically, typical s-triazine ring vibrations were found at 1573 and 1542 cm⁻¹ (doubly degenerated band assigned to quadrant stretching), 1460 and 1405 cm⁻¹ (double semicircle stretching), and ~800 cm⁻¹ (out-of plane bending by sextants) [57]. In addition, primary amines were detected by the presence of bands at 3246 cm⁻¹ (asymmetric N-H stretching) and 3180 cm⁻¹ (symmetric N-H stretching), as well as strong NH₂ scissoring deformation band at 1639 cm⁻¹ [22,57]. One of the most noticeable changes upon oxidation (blue and red traces in Fig. 2) was the broadening of the band centered at ~3200 cm⁻¹, due to appearance of intense O-H stretching bands of carboxyl (3400–2400 cm⁻¹) and hydroxyl groups (3400–3300 cm⁻¹). The spectra in the 1700–1000 cm⁻¹ range, which showed well-defined and distinguishable bands for the starting material, blurred in the case of the oxidized samples due to overlapping of the bands coming from their varied and abundant functional groups. However, the characteristic band of s-triazine units at ~800 cm⁻¹ is clearly visible throughout the series.

Figure 2. ATR-FTIR spectra for the non-oxidized, starting bulk material (black trace), g-C₃N₄ oxidized at room temperature (blue trace) and at 60 °C (red trace).

More detailed information on the chemical transformation of the materials upon oxidation was obtained by XPS analysis. The survey XPS spectra (not shown) confirmed that no elements other than C, N and O (H is not detectable by this technique) were present in the samples. Fig. 3 shows the background-subtracted, deconvoluted high resolution XPS C 1s, N 1s and O 1s core level spectra for g-C₃N₄ ox RT (blue trace) and g-C₃N₄ ox 60 (red trace). The spectra of the non-oxidized, starting bulk material (black trace) are given as a reference. In the case of bulk g-C₃N₄, the main carbon and nitrogen species found at 288.2 and 398.7 eV, in the C 1s and N 1s spectra, respectively, were assigned to C and N bonded in sp² hybridization in the triazine cycles [6] (see Fig. S1a of the SM), while the wide bands found about 6 eV higher in binding energy were assigned to their corresponding $\pi \rightarrow \pi^*$ satellite bands [22]. The N 1s signal at 400.1 eV was assigned to sp³-hybridized, tertiary N in the form of N bridges amongst triazine units (see Fig. S1a of the SM). Primary and secondary amines were expected to be present due to the incomplete condensation of the structure (see the elemental analysis above and Fig. S1a of the SM). Although neutral amines are seldom included in the usual deconvolution scheme for N 1s of g-C₃N₄ [6], such omission could be related to the fact that they go unnoticed as their signal, which would be located at ~399.5 eV [58], overlaps with that corresponding to tertiary amines in the bridges. The peak at ~401.2 eV was assigned to quaternary N in positively charged amino functions [6,22]. Indeed, positively charged nitrogen could result from ionization of the sample during the XPS experiment [58]. The latter assignments were also supported by the fact that XPS bands corresponding to neutral or both neutral and charged amines have been reported for substances which have a close structural relation with g-C₃N₄, such as aniline [59], melamine [60] or melamine resin [58].

Figure 3. Background-subtracted and deconvoluted high resolution XPS N 1s (a), C 1s (b), and (c) O 1s core level spectra for the non-oxidized, starting bulk material (black trace), g-C₃N₄ oxidized at room temperature (blue trace) and at 60 °C (red trace).

A gradual diminution of the relative amount of triazine cycles, and thus of the size of π -conjugated domains, with the degree of oxidation was observed (see Figs. 3a and b). In the N 1s spectra (Fig. 3a), no signal arose in the range where oxidized nitrogen species such as pyridine-N-oxides (402.9 eV) or nitrogen oxides (405.3 eV) would be expected [61], suggesting that the oxygen-containing species introduced were bonded to carbon rather than to nitrogen atoms. Indeed, new signals appeared in the C 1s spectra (Fig. 3b), which are indicative of hydroxyl formation (C in oxidation state +1, singly bonded to oxygen found at ~286.4 eV) and carboxyl groups (C in oxidation state +3 located at 289.4 eV) [62]. The presence of carbonyl groups (C in oxidation state +2 located at ~288 eV), whose signal would overlap with the main C 1s signal for g-C₃N₄, which is that of C doubly bonded to N, could not be discarded from the C 1s spectra. Indeed, the O 1s spectra of the oxidized materials (Fig. 3c) supported the presence of carbonyls in sample g-C₃N₄ ox RT, the components found at ~530.5, ~532 and ~533.5 eV being assigned to C=O in carbonyl, O-H in hydroxyl and O-H in carboxyl groups, respectively [63,64]. On the molecular level, the acid hydrolysis of the tertiary N bridges to yield primary and secondary amines could make carbon available to form oxygen-containing groups (see Fig. S1b in the SM).

XRD patterns of the materials were acquired to investigate the effect of oxidation on the crystalline structure of g-C₃N₄. The diffractograms are shown in Fig. 4. The starting, non-oxidized, g-C₃N₄ powder displayed two characteristic diffraction peaks at ~12° and ~27°, which correspond to the in-plane periodicity of the hole-to-hole distance of nitride pores in the crystal (100) and interlayer, graphite-like stacking (002), respectively [20]. Upon oxidation, both peaks widened due to the decrease in crystallinity of the material. In the most oxidized material (red trace), the (100) peak weakened until almost disappearing, suggesting a notable increase in the disorder of the oxidized layers.

Figure 4. XRD patterns of the non-oxidized, starting bulk material (black trace), g-C₃N₄ oxidized at room temperature (blue trace) and at 60 °C (red trace).

An increase in surface area against the starting, non-oxidized material was expected if only for the decrease in particle size observed upon oxidation (see Figs. 1b–d). To confirm this, N₂ adsorption/desorption isotherms were measured for the g-C₃N₄ powders and the results are shown in Fig. 5a. The starting g-C₃N₄ powder showed a type II isotherm according to the IUPAC classification [65], which is typical of non-porous materials, while the oxidized materials showed type IV isotherms, with hysteresis loops in the higher relative pressure range, which are indicative of the presence of mesoporosity. The fact that the hysteresis loop extends to the highest relative pressure range (0.8–1) indicates the existence of macroporosity as well [66]. Indeed, the pores size distributions shown in Fig. 5b confirm the presence of both meso

and macroporosity. The total pore volume increased from $0.06 \text{ cm}^3 \text{ g}^{-1}$ for the starting $\text{g-C}_3\text{N}_4$ to $0.22 \text{ cm}^3 \text{ g}^{-1}$ ($\text{g-C}_3\text{N}_4$ ox RT) and $0.14 \text{ cm}^3 \text{ g}^{-1}$ ($\text{g-C}_3\text{N}_4$ ox 60) for the oxidized powders. Thus, as previously reported for $\text{g-C}_3\text{N}_4$, oxidation promoted a significant development of porosity [30,31], mostly in the mesopore range, as confirmed by the comparison of the pore size distribution for the non-oxidized, starting material with those of the oxidized materials (see Fig. 5b). The hysteresis loop belongs to type H3 according to the IUPAC classification [65], which is characteristic of adsorption on agglomerated lamellar structures such as those shown by these materials (see Figs. 1c and d). As expected, the BET specific surface area increased from $25 \text{ m}^2 \text{ g}^{-1}$ for the starting $\text{g-C}_3\text{N}_4$ to $73 \text{ m}^2 \text{ g}^{-1}$ and $42 \text{ m}^2 \text{ g}^{-1}$ for the oxidized powders $\text{g-C}_3\text{N}_4$ ox RT and $\text{g-C}_3\text{N}_4$ ox 60, respectively. However, we note that the materials tested for the application as sorbents here were not the agglomerated powders, i. e., the starting $\text{g-C}_3\text{N}_4$ commercial powder or the powders obtained after its oxidation, but rather the colloidal aqueous dispersions of nanosheets obtained after sonication of those powders. Thus, the BET surface of the dry agglomerated powder is hardly expected to be representative of the behavior of the thin nanosheets in colloidal dispersion as the van der Waals attraction will cause the re-stacking of the nanosheets during the drying process [21], and thus decrease the surface exposed for adsorption.

Figure 5. (a) N_2 adsorption–desorption isotherms (full symbols: adsorption; empty symbols: desorption) at -196°C and (b) corresponding pore size distributions of bulk $\text{g-C}_3\text{N}_4$ (black squares), $\text{g-C}_3\text{N}_4$ oxidized at room temperature (blue squares) and at 60°C (red squares).

3.2. Preparation and characterization of oxidized g-C₃N₄ dispersions

The introduction of oxygen-containing functional groups in g-C₃N₄ was expected to promote hydrophilicity, improving the colloidal stability of its aqueous dispersions, and thus facilitating its practical use in water remediation. Aqueous dispersions of both non-oxidized and oxidized g-C₃N₄ were prepared by bath sonication of the solids at nominal concentration of 1 mg mL⁻¹ for 5 h. Fig. 6a shows the UV-Vis extinction spectra of aqueous dispersions of g-C₃N₄ (black trace), g-C₃N₄ ox RT (blue trace) and g-C₃N₄ ox 60 (red trace). The three of them showed two main spectral features at ~230 and 320 nm, which were respectively assigned to $\pi \rightarrow \pi^*$ transitions from C=N structures in the tris-s-triazine unit, and to the $n \rightarrow \pi^*$ transitions from nitrogen lone pairs, either belonging to the extended tris-s-triazine structure or to the amine groups at the edges [22,67] (see Fig. S1a of the SM).

Figure 6. (a) UV-Vis absorption spectra of aqueous dispersions of non-oxidized g-C₃N₄ (black trace), g-C₃N₄ oxidized at room temperature (blue trace) and at 60 °C (red trace). (b) Absorbance retention of the aqueous g-C₃N₄ dispersions over time (same color code as (a)).

As a test of the colloidal stability of the different materials, their dispersions were left to stand undisturbed and the UV-Vis absorbance at the absorption maxima of the supernatant (located at ~320 nm, for g-C₃N₄ and g-C₃N₄ ox RT and at 230 nm, for g-C₃N₄ ox 60), which is linearly correlated with the concentration of dispersed material, was monitored versus time. The results are gathered in Fig. 6b and they confirm the improvement of colloidal stability upon oxidation. Indeed, while the non-oxidized bulk

powder quickly sediments over the first few hours after bath sonication, retaining less than 25% of its initial absorbance after 3 days, the oxidized materials retain more than 75% after the same time. This allows a reasonable time window for processing. In fact, three weeks after their preparation, the non-oxidized powder fully sedimented while more than 40% of the oxidized powders remained in dispersion.

The previous results demonstrated that the current oxidized g-C₃N₄ materials could be suspended in water with good colloidal stability (see Fig. 6b). However, the characteristics of the dispersed object were not known and had to be elucidated. For their use as adsorbents, it would be in principle desirable that the materials retained their lamellar morphology after oxidation and ultrasonic processing. Fig. 7 shows representative STEM images of the objects that were observed for dried g-C₃N₄ aqueous dispersions, which confirmed this point. Indeed, the dispersions were seen to be mostly constituted by thin platelets transparent to the electron beam, with lateral dimensions in the micrometer and submicrometer range, which were interpreted to be few-layer sheets of the corresponding materials. STEM revealed that the smooth surface of the starting material (Fig. 7a) became porous after oxidation. Indeed the g-C₃N₄ ox RT was gauze-like, constituted by very loosely weaved sheets (Fig. 7b), while g-C₃N₄ ox 60 consisted of sheets of fluffy appearance with a great number of voids and pores (Fig. 7c). The appearance and growth of holes throughout the structure upon oxidation would be consistent with the breaking of C–N bonds to yield amines and carboxyls (see Fig. S1b of the SM), which, in high extents, would lead to the release of small fragments of molecular nature. The latter would in turn explain the aforementioned decreasing yields with oxidation.

Figure 7. Representative STEM images of nanosheets deposited from aqueous dispersions of (a) non-oxidized g-C₃N₄, (b) g-C₃N₄ oxidized at room temperature and (c) at 60 °C.

3.3. Dye/drug adsorption of oxidized g-C₃N₄ dispersions

Given the improved dispersion in water, the abundance of functional groups and the increased exposed surface, the oxidized g-C₃N₄ materials seemed ideal as molecular adsorbents in the aqueous phase. To probe their potential, we examined their performance as adsorbents for several dyes and for the antibiotic TC (see Fig. S2 in the SM for their chemical structures). Both anionic (MO and RB) and cationic dyes (MB, MG, RhB and BF) were examined. Fig. 8a shows the adsorption capacity of non-oxidized and oxidized g-C₃N₄ towards the different dyes and TC in aqueous solution measured at room temperature and pH≈6. A comparison of the adsorption capacities of of graphene- and g-C₃N₄-related materials from the literature is also provided in Table 2. The adsorption capacity for every adsorbate was observed to increase significantly with oxidation (see Fig. 6a), yielding values that compared well or improved those previously reported in the literature for g-C₃N₄-related materials [29,41–44] (see Table 2). Even in a more general context, including graphene and other carbon-based adsorbents, the current materials, particularly g-C₃N₄ ox 60, perform remarkably for RhB and exceedingly well in the case of TC. Specifically, g-C₃N₄ ox 60 displays an adsorption capacity of 895 mg/g for TC, which outrates those previously reported for other adsorbents, such as graphene oxide (313 mg/g) [45], carbon-doped spray dried C₃N₄ granules (70 mg/g) [41], and even activated carbon (375.4–672.0 mg/g) [68].

Figure 8. (a) Adsorption capacities of non-oxidized g-C₃N₄ (black bars), g-C₃N₄ oxidized at room temperature (blue bars) and at 60 °C (red bars) for different dyes and the drug tetracycline (TC) in aqueous solution at room temperature. **(b)** TC adsorption isotherm at room temperature for g-C₃N₄ oxidized at 60 °C.

Table 2. Adsorption capacities at equilibrium reported for some common adsorbents and g-C₃N₄-related materials towards different substances from the aqueous phase. The adsorption experiments were typically carried out under continuous stirring at room temperature and pH~6.

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Reference
Graphene oxide	TC	313	45
Graphene oxide/activated carbon hybrid		449 (i)	46
Carbon-doped spray dried C ₃ N ₄ granules		70	41
g-C ₃ N ₄		417	This work
g-C ₃ N ₄ ox RT		711	This work
g-C ₃ N ₄ ox 60		895	This work
Ordered mesoporous carbon	MB	378	55
Halide-based anodic graphene		360	47
Graphene-like porous		469	48

carbon nanostructure

Hemin/graphene hydrogel		100	49
Graphene oxide/activated carbon composite		99.45 (ii)	50
Oxidized g-C ₃ N ₄		45 (iii)	29
Carbon-doped g-C ₃ N ₄		58	42
Mesoporous g-C ₃ N ₄		72	44
g-C ₃ N ₄		34	This work
g-C ₃ N ₄ ox RT		72	This work
g-C ₃ N ₄ ox 60		98	This work
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Ordered mesoporous carbon	MG	436	55
Activated carbon		452	56
g-C ₃ N ₄		170	This work
g-C ₃ N ₄ ox RT		201	This work
g-C ₃ N ₄ ox 60		317	This work
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Graphene modified by graphene quantum dots	RB	562	51
g-C ₃ N ₄		36	This work

g-C ₃ N ₄ ox RT			250	This work
g-C ₃ N ₄ ox 60			451	This work
Graphene		RhB	179	51
Graphene modified by graphene quantum dots			497	51
Halide-based graphene	anodic		343	47
Hollow spheres/graphene aerogel	carbon hybrid		441.5	52
Hemin/graphene hydrogel			350	49
g-C ₃ N ₄			202	This work
g-C ₃ N ₄ ox RT			482	This work
g-C ₃ N ₄ ox 60			602	This work
Halide-based graphene	anodic	BF	355	47
Polyacrylamide/graphene oxide aerogel			1034.3	53
Graphene/ β -cyclodextrin composite			425.8	54

g-C ₃ N ₄			84	This work
g-C ₃ N ₄ ox RT			181	This work
g-C ₃ N ₄ ox 60			192	This work
Halide-based graphene	anodic	MO	923	47
Graphene-like carbon nanostructure	porous		418	48
Graphene modified by graphene quantum dots			193	51
Hemin/graphene hydrogel			40	49
graphene/ β -cyclodextrin composite			328.2	54
Hollow carbon spheres/graphene hybrid			344.1	52
g-C ₃ N ₄			192	This work
g-C ₃ N ₄ ox RT			221	This work
g-C ₃ N ₄ ox 60			294	This work

(i) From the data on adsorption.

(ii) Experimental adsorption capacity (not calculated through Langmuir model).

(iii) Calculated from data on removal efficiencies (knowing the initial concentration of adsorbate, mass of sorbent and total volume) after adsorption equilibration in the dark (i. e., in the absence of photocatalytic processes).

An adsorption isotherm was measured for the adsorbent/adsorbate pair which yielded the best adsorption capacity, i. e., g-C₃N₄ ox 60/TC (see Fig. 8b). The amount of dye adsorbed at equilibrium steadily increased with equilibrium concentration of dye in aqueous solution, reaching a plateau at ~1 mg mL⁻¹, which suggests that TC adsorbs as monolayer, rather than as multilayer.

After adsorption, the adsorbents could be easily separated from the adsorption medium and regenerated for their further use (see Experimental Section for details). The TC adsorption process was repeated for five times to test the reusability of the adsorbents. Fig. 9 shows the percentage of the adsorption capacity for TC retained by g-C₃N₄ ox RT (blue bars) and at 60 °C (red bars). Compared to the TC adsorption of the first cycle, the adsorption efficiency of both g-C₃N₄ ox RT and g-C₃N₄ ox 60 after 5 adsorption-desorption cycles was only reduced by ~10 %, which indicates that they are not only efficient but recyclable adsorbents for TC removal.

Figure 9. Histogram for the reusability of g-C₃N₄ oxidized at room temperature (blue bars) and at 60 °C (red bars) as adsorbent for the drug tetracycline (TC) in aqueous solution at room temperature.

As for the reasons for the enhancement of the performance of g-C₃N₄ as adsorbent upon oxidation, the improvement of the dispersibility in water, desirable as it

is for the processing of the current materials, cannot be held responsible. Indeed, as the adsorption was measured over the first 24 h after preparation of the dispersions and under continuous stirring (see Experimental Section for details), the measurement conditions minimized the differences in colloidal stability between the non-oxidized and the oxidized materials. In contrast, the changes in the surface chemistry confirmed by XPS (see Fig. 3), which determine the type and strength of the adsorbent-adsorbate interactions, must play a critical role in such improvement. Unlike the case of graphene, where the π -conjugated system is the preponderant chemical environment, and thus adsorption is expected to rely almost exclusively on π - π interactions between the π clouds of graphene and the adsorbate, the chemical structure of g-C₃N₄ (see Fig. S1a in the SM) lends itself to a range of possible interactions. Apart from π - π interactions, these mechanisms include hydrogen bonding, acid-base and electrostatic interaction (see Fig. S3 in the SM). However, given that the chemical structure of all the g-C₃N₄ materials and adsorbates studied here contain a π -conjugated system of a greater or lesser extent (see Fig. S2 of the SM), this being the common factor among all of them all, π - π interactions must play a role in the significant adsorption measured in all cases. In fact, the adsorption of some of the substances examined here, such as MB and TC, has been previously suggested in the literature to rely exclusively on π - π interactions with the aromatic moieties of g-C₃N₄ [41,42]. Basing on that assumption, enlarging the π -conjugated system of g-C₃N₄ by, for instance, carbon doping, has been adopted as a strategy to increase its adsorption capacity [41,42]. However, in the case of our materials, although the relative amount of aromatic, triazine moieties diminished with the extent of oxidation (see the XPS results above), adsorption capacity increased (see Fig. 8a). This suggests that, although π - π interactions do play a role, they are not the sole adsorption mechanism, and that increasing the adsorption capacity of g-C₃N₄ does not necessarily involve an enlargement of its π -conjugated system. Indeed, the adsorption capacities of our oxidized g-C₃N₄ materials were twice and ten times larger for MB [42] and for TC [41] (g-C₃N₄ ox 60), respectively, than the corresponding values reported for carbon doped materials obtained with more complex protocols involving relatively high temperatures [41,42]. Indeed, the adsorption capacity for MB was similar (g-C₃N₄ ox RT) or higher (g-C₃N₄ ox 60) to the highest previously reported adsorption capacity for g-C₃N₄-related materials [44].

Electrostatic interactions could also play a role in the adsorption mechanism. Indeed, g-C₃N₄ dispersions are colloiddally stabilized by electrostatic repulsion of the charged nanosheets [20,21]. However, the fact that there was not a clear bias in favor of cationic (MB, MG, RhB and BF) or anionic dyes (MO and RB) and that the most remarkable performance of all three materials was obtained for a neutral species (TC) suggests that electrostatic interaction was not a critical factor for the adsorption process under the present conditions.

As g-C₃N₄ has a weakly basic character conferred by its nitrogen-rich chemical structure [20], acid-base interactions could influence the adsorption of adsorbates susceptible to them, such as those tested here. The introduction of oxygen-containing functionalities in the oxidized g-C₃N₄ materials, such as carboxyls (see XPS results above) would be expected to introduce some slightly acidic character too. According to the pKa values of the adsorbates, namely: 2.6, 11.2 (MB); 3.40, 3.76 (MO); 3.9, 4.7 (RB) [69]; 4.1 (MG) [70]; 11.7 (BF) [71]; 3.1 (RhB) [72]; 3.3 (TC) [73], while MO, RB, MG, RhB and TC display slightly acidic character, BF is basic, and MB is amphoteric. There seems to be a slightly detrimental effect on adsorption for the basic dyes (MB and BF), suggesting that the interaction between the basic functional groups of g-C₃N₄ materials and the acidic groups in most adsorbates enhance their adsorption.

Another possible interaction between the g-C₃N₄-based adsorbents and the adsorbates is hydrogen bonding. Both non oxidized and oxidized g-C₃N₄ contain abundant functional groups which are liable to form hydrogen bonds. Specifically, the former possesses edges saturated by primary or secondary amines (see Fig. S1a of the SM), while the latter is rich in both nitrogen and oxygen-containing functional groups (see XPS results above). Indeed, the fact that hydrogen bonding has been found to be a key factor for the dispersibility of g-C₃N₄ [22], and also for that of reduced graphene oxide [74] and other nanostructured materials with high content of oxygen-containing functional groups [75], suggests that it could be critical as well in the performance of the g-C₃N₄-based adsorbents studied here. Hence, a possible reason for the improvement in adsorption capacity with the oxidation extent is the increased amounts of functional groups (carboxylic groups in particular) indicated by the higher content in heteroatoms (see Table 1). In a similar line of reasoning, it is not surprising that the chemical structure of TC, the adsorbate for which the highest adsorption capacities were

obtained, outstands amongst those of the studied pollutants for being richer in functional groups prone to hydrogen bonding, e. g., hydroxyl groups (see Fig. S2 in the SM). The greater strength of hydrogen bonds involving O-H groups against those involving N-H could partly explain the better performance of the oxygen-rich oxidized g-C₃N₄ adsorbents against non-oxidized g-C₃N₄. The same argument could justify as well the higher capacity for TC among all the examined adsorbates. Indeed, in previous studies on the sorption of tetracycline and other antibiotics, the adsorption mechanisms has been found to be primarily driven by specific interactions, specifically, hydrogen-bonding [76,77].

The equilibrium adsorption experimental data can be fitted to different models in order to investigate the adsorption mechanism. Here, we used three different models, namely, Langmuir, Freundlich and Temkin models [78] to fit the experimental TC adsorption isotherm (see Fig. 8b):

- The Langmuir adsorption theory assumes that the surface of the adsorbent is uniform, consisting of equivalent adsorption sites; the adsorbate forms a monolayer on the surface of the adsorbent; and there are no interactions between adsorbed species.
- The Freundlich model is commonly used to describe adsorption on heterogeneous surfaces and allows for interactions between adsorbate molecules. This model is not limited to monolayer coverage alone, describing multilayer adsorption as well.
- The Temkin model explicitly takes into account adsorbent–adsorbate interactions and the effects of adsorbate-adsorbate interactions on the adsorption process.

These three models are described by the following equations, respectively:

$$q_e = \frac{q_m C_e}{1 + k_L C_e} \quad (1)$$

$$q_e = k_F C_e^{1/n} \quad (2)$$

$$q_e = \frac{RT}{b} \ln(k_T C_e) \quad (3)$$

where c_e is the concentration of the pollutant in water at equilibrium, q_e is the corresponding amount of adsorbate adsorbed per unit mass of adsorbent, k_L , k_F , k_T are adsorption constants of Langmuir, Freundlich, and Temkin models, respectively, q_m is the amount of adsorbate per unit mass of adsorbate that constitutes a monolayer in the Langmuir model, n is the Freundlich linearity index, and b is the Temkin constant related to the heat of adsorption (J/mol), T is the absolute temperature (K), R is the gas constant (8.314 J/mol K).

Traditionally, these equations were linearized as $1/q_e$ vs. $1/C_e$, $\ln q_e$ vs. $\ln C_e$ and q_e vs. $\ln C_e$, respectively, to make the fitting easier. However, the evolution of computer technology in the last decades currently allows direct non-linear fitting. Indeed, the isotherm was fitted using the non-linear fitting tool from OriginPro software. The fitting curves of the experimental data for TC adsorption onto g-C₃N₄ ox 60 to these three models are shown in Fig. 10, with indication of their R^2 correlation coefficients. None of the fittings were of excellent quality, but the correlation coefficients were within the range reported in similar studies [78]. The lower R^2 value found for Freundlich model (Fig. 10b) supports monolayer coverage of the adsorbent. The higher R^2 value found for Temkin model (Fig. 10c) suggests a predominance of strong adsorbate-adsorbent interactions [79], such as hydrogen bonding, as discussed above.

Figure 10. Fitting of experimental tetracycline adsorption isotherm on g-C₃N₄ ox 60 at RT to (a) Langmuir, (b) Freundlich, and (c) Temkin models (red squares: experimental data; dotted black lines: fitted curves).

4. Conclusions

We have demonstrated that liquid-phase exfoliation by a combination of oxidation and ultrasonic treatment is an efficient method to improve the features of g-C₃N₄ as an adsorbent for molecular adsorption from water. Testing of the g-C₃N₄ materials as adsorbents for organic dyes and the antibiotic tetracycline revealed a performance better for every adsorbate than that previously reported for g-C₃N₄-related materials. In fact, the obtained materials bear comparison with a wider range of adsorbents, such as graphene and other carbon-based materials. Furthermore, in the case of rhodamine B and tetracycline, come of the oxidized g-C₃N₄ materials yield outstanding adsorption capacities, as high as 602 mg/g and 895 mg/g, respectively. We have discussed the different possible adsorbate-adsorbent interactions and concluded that hydrogen bonding must play an important role in the adsorption process. We believe that this work will place g-C₃N₄ materials in a better position as competitive adsorbents for water remediation.

Supplementary Material. Chemical structure of g-C₃N₄ and the adsorbates assayed in the adsorption measurements. Possible adsorbate/g-C₃N₄-derived adsorbent interaction mechanisms.

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