

Article

Immobilization of Exfoliated g-C₃N₄ for Photocatalytical Removal of Organic Pollutants from Water

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Abstract: Graphitic carbon nitride (g-C₃N₄) was synthesized from melamine and exfoliated by thermal treatment. Exfoliated g-C₃N₄ particles were immobilized by electrophoretic deposition from an ultrasonically treated ethanolic suspension aged up to 12 weeks. During the aging of the suspension, the separation of particles bigger than 10 μm was observed. The separated stable part of the suspension contained particles with a relatively uniform size distribution, enabling the fabrication of g-C₃N₄ films that were stable in a stirred aqueous solution. Such stable immobilized particles of exfoliated g-C₃N₄ are reported for the first time. The photocatalytic activity of such layers was evaluated using aqueous solutions of Acid Orange 7 (AO7) and 4-chlorophenol (4-CP). The photocatalytic decomposition of AO7 was faster in comparison with the decomposition of 4-CP. Mineralization was observed in the case of AO7, but not in the case of 4-CP, where the decrease of 4-CP concentration is due to 4-CP polymerization and the formation of a dimer, C₁₂H₈Cl₂O₂. This indicates that the use of g-C₃N₄ as a photocatalyst for oxidative degradation of organic compounds in water is limited.

Keywords: exfoliated g-C₃N₄; electrophoresis; acid orange 7; 4-chlorophenol; photocatalysis; mineralization



Citation: Rusek, J.; Paušová, Š.; Praus, P.; Krýsa, J. Immobilization of Exfoliated g-C₃N₄ for Photocatalytical Removal of Organic Pollutants from Water. *Catalysts* **2021**, *11*, 203. <https://doi.org/10.3390/catal11020203>

Academic Editor: Sami Rtimi

Received: 21 December 2020

Accepted: 29 January 2021

Published: 3 February 2021

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1. Introduction

Different sustainable energy sources and technologies for cleaning water and air are currently being investigated in order to protect the environment. Photocatalysis is considered a promising technology for energy harvesting, conversion, and storage, as well as a method for the oxidative decomposition of harmful compounds from water and air [1,2]. Graphitic carbon nitride (g-C₃N₄) is a conjugated polymer, which recently drew a lot of attention as a metal-free and UV- and visible light-responsive photocatalyst in the field of solar energy conversion and environmental remediation. This is due to its appealing electronic band structure (band gap energy: 2.7 eV [3]) and earth-abundant nature. g-C₃N₄ can be prepared by different methods such as PVD and CVD, or by thermal condensation of nitrogen-rich precursors, such as cyanamide, dicyandiamide, melamine, urea, and so forth [4–8].

The main disadvantage of g-C₃N₄ is the high recombination rate of photo-induced species, which highly decreases the photocatalytic performance of this photocatalyst. The preparation of nanosized morphologies such as nanosheets by delamination of this layered compound can diminish this drawback [9]. These nanosheets of g-C₃N₄ can be obtained by physical or chemical exfoliation. The first reported g-C₃N₄ nanosheets were prepared by thermal exfoliation [10], leading to an increase of surface area, improvement of electron migration, and increased lifetime of photo-induced electrons and holes. Ultrasonic exfoliation is another type of physical exfoliation; however, this type of exfoliation has low efficiency [9]. g-C₃N₄ can also be exfoliated by a chemical method, via redox reactions using different oxidants [11,12].

Exfoliated g-C₃N₄ exhibits higher photocatalytic activity and can be used in different applications such as water or air cleaning [13–15]. For these applications, g-C₃N₄ can be used in the form of suspensions or films. Another type of application is H₂ production [16]; however, the powdered material is quite limiting for this type of application, so a strong focus is devoted to the preparation of thin films. The ex situ preparation from exfoliated g-C₃N₄ material is a very challenging task due to the low particle size homogeneity of prepared particles, which leads to low mechanical stability of prepared films [17].

Many works showing the photocatalytic activity of g-C₃N₄ using different model pollutants like amoxicillin [4], methylene blue [13,18], Rhodamine B [19], tetracycline, ciprofloxacin, salicylic acid, ibuprofen [20], Acid Orange 7 [21,22], or 4-chlorophenol [23] were already published. These works show that the ability of bulk g-C₃N₄ to remove the organic compounds is low, and modification of the surface, doping, or composite preparation is needed to increase the degradation rate of organic compounds. Only two works describe the ability of g-C₃N₄ to mineralize organic compounds (e.g., dyes and 4-chlorophenol) [22,23].

In the present work, powder g-C₃N₄ was synthesized by the thermal treatment of melamine, further thermally exfoliated, and then immobilized on a glass support. Immobilization of the powder material was performed by the electrophoretic technique from ethanolic suspensions. As far as we know, this technique of g-C₃N₄ immobilization has not been thoroughly studied before, and only a few publications deal with this method of immobilization, mainly for the preparation of photoelectrodes for photoelectrochemical water splitting [24,25]. Photocatalytic activity of prepared layers was measured using 4-chlorophenol (4-CP) and Acid Orange 7 (AO7) dye as model aqueous pollutants. Besides monitoring of the pollutant decay, the content of total organic carbon was also measured to evaluate the ability of g-C₃N₄ to mineralize organic pollutants, which is reported very rarely.

2. Results and Discussion

2.1. Material Characterization

According to the SEM analysis, the as-prepared exfoliated graphitic carbon nitride (Ex-CN) contains huge agglomerates of g-C₃N₄ particles (Figure 1A). These agglomerates consist of particles 1–5 µm in diameter. The presence of g-C₃N₄ was confirmed by XRD analysis (Figure S1 in Supplementary Materials; more Ex-CN characteristics are published in [26]). Ex-CN powder prepared by thermal treatment of melamine contains particles with a wide range of particle size distribution, which was also confirmed by the measurement of hydrodynamic particle size in suspension (5–700 µm, see Table 1). Layers prepared from such a powder showed poor mechanical stability (after immersion in water, Ex-CN powder was washed off the substrate). It was recently shown that the non-uniform particle size distribution frequently results in cracks in both the film and the interface between film and substrate [27]. It is, therefore, necessary to decrease particle size and achieve a more uniform particle size distribution.

Table 1. The influence of ultrasonic treatment on the hydrodynamic particle size of exfoliated g-C₃N₄ (Ex-CN).

Sample	Dx(50) [µm]	Particle Size Range [µm]
Ex-CN as prepared	93	5–700
Ex-CN settled particles from aq. susp. 3 h US and dried *	14	0.5–90
Ex-CN settled particles from eth. susp 3 h US and dried *	12	0.3–80
Ex-CN stable part of aq. susp. 3 h US *	2	0.2–20
Ex-CN stable part of eth. susp 3 h US *	2	0.1–10

* After one week of sedimentation.

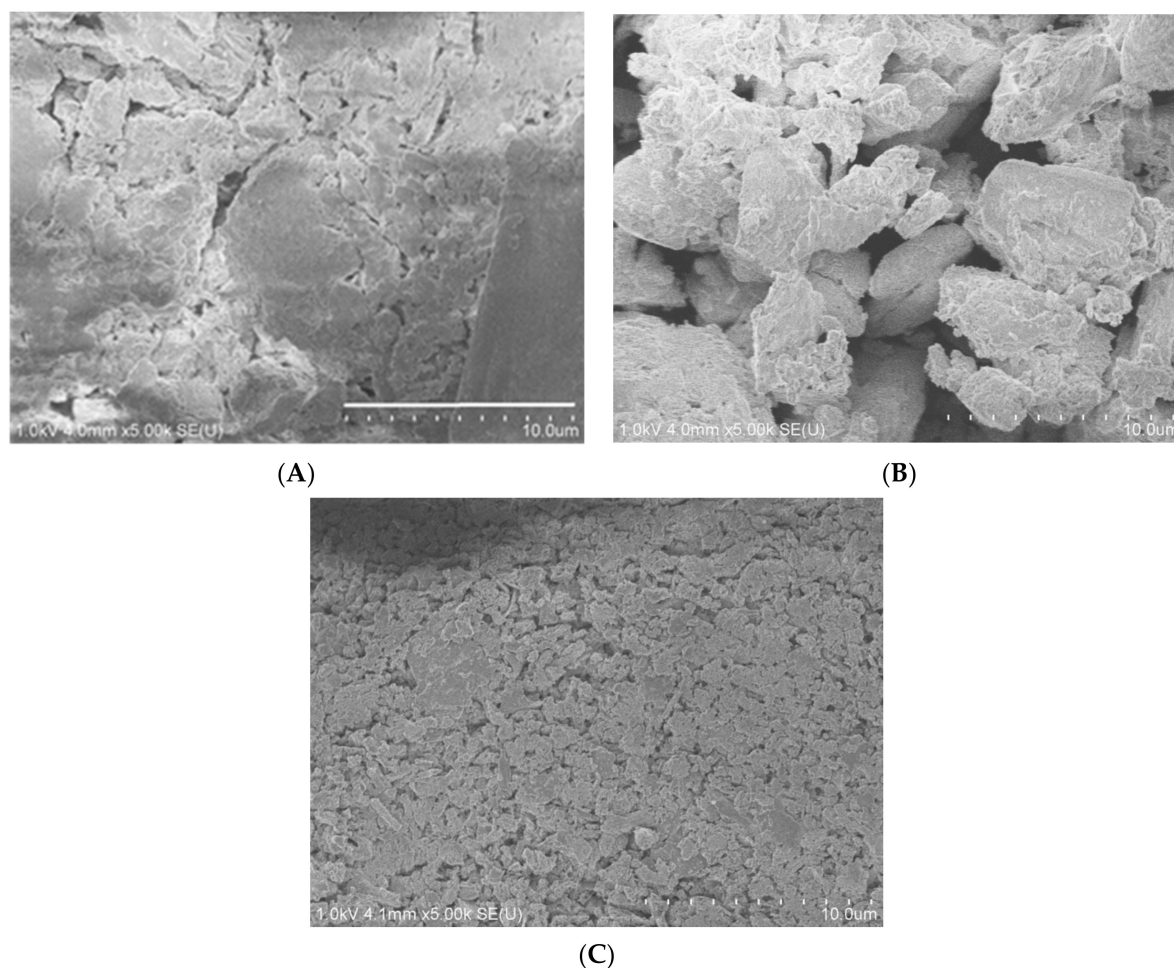


Figure 1. SEM images of as-prepared exfoliated g-C₃N₄ powder (A), settled part of the ultrasonication (US)-treated exfoliated g-C₃N₄ suspension after one-week sedimentation (B), stable part of suspension after one-week sedimentation (C). The scale is the same for all images (10 μm), and in image (A), the scale is highlighted by the white line.

The Ex-CN powder was suspended in two different liquids, and the resulting suspensions were treated by ultrasonication (US) for the duration of 3 h. The influence of sonication on the hydrodynamic particle size of exfoliated g-C₃N₄ is shown in Table 1, which contains the values of D(x)50 (medium value of particle size distribution; the particle diameter of 50% of the particles in the cumulative distribution) and the whole range of particle sizes of the measured sample. The curves with the hydrodynamic particle size distribution are shown in Figure S2 in Supplementary Materials. However, even the use of sonication did not lead to the preparation of stable suspensions. After one week, the separation of smaller and bigger particles was observed. The particles with a diameter lower than 20 μm stayed suspended in aqueous suspension; in the case of the ethanolic suspension, particles smaller than 10 μm stayed suspended. The value of D(x)50 was 2 μm in both suspensions. The stable part of the ethanol suspension was then used for the electrophoretic deposition.

After the ultrasonic treatment, the size of the particles decreased; however, sedimentation of larger particles was still observed. After one week, no further sedimentation was observed, and the particle size in the suspension did not change further. Images of settled particles and particles from the stable part of the suspension after one week of sedimentation are shown in Figure 1B,C, respectively. Before the SEM analysis, both parts of the suspension were dried, but we can clearly see that particles from the stable part of the suspension are smaller, and the distribution of their size is more homogeneous. According to SEM analysis, g-C₃N₄ from the settled part of suspension contained particles

of size from 2–30 μm , and the particle size of g-C₃N₄ from the stable part of the suspension was 1–3 μm . This is in very good agreement with the values in Table 1 obtained by the measurement of hydrodynamic particle size. However, the particles tend to re-agglomerate after drying, as documented in Figure 1C, so it is preferable to keep particles suspended in a liquid.

2.2. Electrophoretic Deposition

The suspension of exfoliated g-C₃N₄ particles in ethanol was treated by ultrasonication for 3 h. The main studied parameters were the age of the suspension and the deposition time of the electrophoretic deposition, which determine the deposited amount of catalyst. Suspensions aged 1 h and 16 h after ultrasonication were not suitable for the preparation of mechanically stable layers. The probable reason is that such suspensions still contained large particles. Thus, suspensions treated by US were then left for 1 and 12 weeks to allow bigger particles to settle down. The deposited amounts of g-C₃N₄ on fluorine doped tin oxide (FTO) glass support (shown in Table 2) were measured to follow the influence of suspension aging, and thus the reproducibility of suspension preparation. It was found that the amount of g-C₃N₄ depends on the deposition time, but it is the same for 1 and 12 weeks of suspension aging.

Table 2. Dependence of deposited amount of Ex-CN US on the time of electrophoretic deposition and the age of the Ex-CN US suspension used.

Age of Electrolyte	Deposition Time/s	Deposited Amount/mg cm ^{−2}
1 h	2	0.040 ± 1 *
	5	0.089 ± 1 *
	30	1.356 ± 30 *
One week	5	0.050 ± 1
	30	0.201 ± 4
	50	0.265 ± 3
Twelve weeks	5	0.049 ± 1
	30	0.206 ± 4
	50	0.264 ± 3
	70	0.305 ± 4 *

* Layers were not mechanically stable after immersion into water.

The stability of layers in aqueous solution under stirring in the dark was monitored by the naked eye, and also by the measurement of the UV–vis spectra of aqueous solution in which layers were immersed. After 4 h, we found that for 1 and 12 weeks of aging, no difference in UV–vis spectra was observed, and stable layers were prepared. This suggests that for the fabrication of stable films, the g-C₃N₄ suspension has to contain particles smaller than 10 μm (see Table 1). However, when the amount of deposited g-C₃N₄ exceeded 0.3 mg cm^{−2}, particles of g-C₃N₄ started to peel off after immersion into water. The amounts of deposited g-C₃N₄ for suspensions aged 1 and 12 weeks were very similar. This suggests that after the initial sedimentation of bigger particles, the suspension is stable, and that the particle size of g-C₃N₄ in suspensions does not differ significantly after 12 weeks of aging. The images of the prepared thin layers of g-C₃N₄ using 1-hour- and 1-week-aged electrolyte are shown in Figure 2.

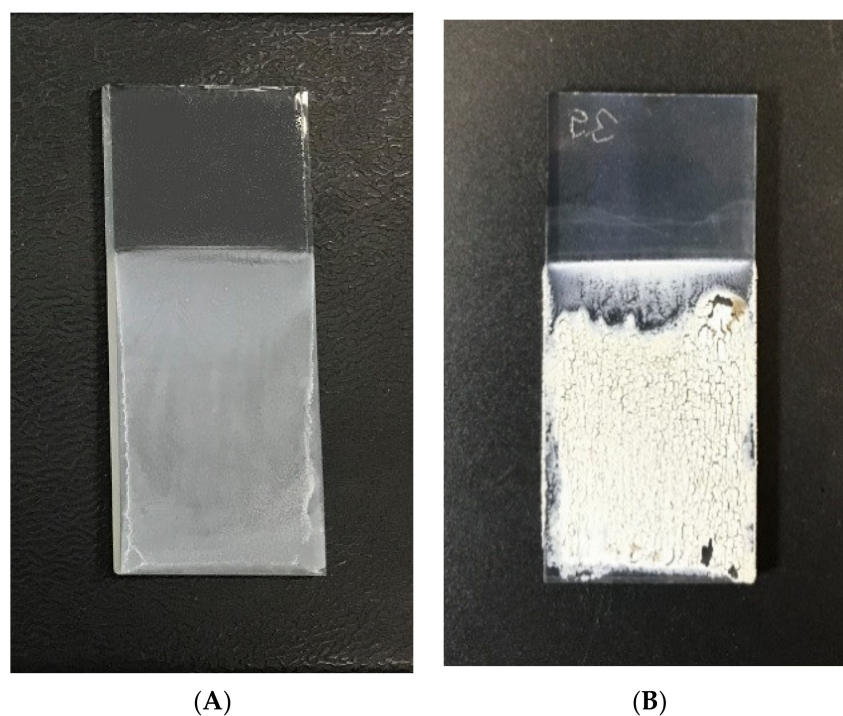


Figure 2. Top view on g-C₃N₄ layers. The suspension prepared from US-treated g-C₃N₄ after one week of sedimentation (A) and a fresh suspension (B) were used for electrophoretic deposition (applied potential, 50 V; time, 30 min).

Figure 3A,B show the SEM images of FTO glass and Ex-CN US particles deposited on FTO glass. Even particles of g-C₃N₄ are clearly visible on the FTO glass, but they do not cover the surface of the FTO glass entirely due to the small g-C₃N₄ content (0.05 mg cm^{−2}). The range of the hydrodynamic particle size in 1-week-aged suspension is relatively small (1–10 nm, see Table 1). The SEM morphology of the deposited layer is in agreement and shows the presence of particles of various sizes below 5 μm.

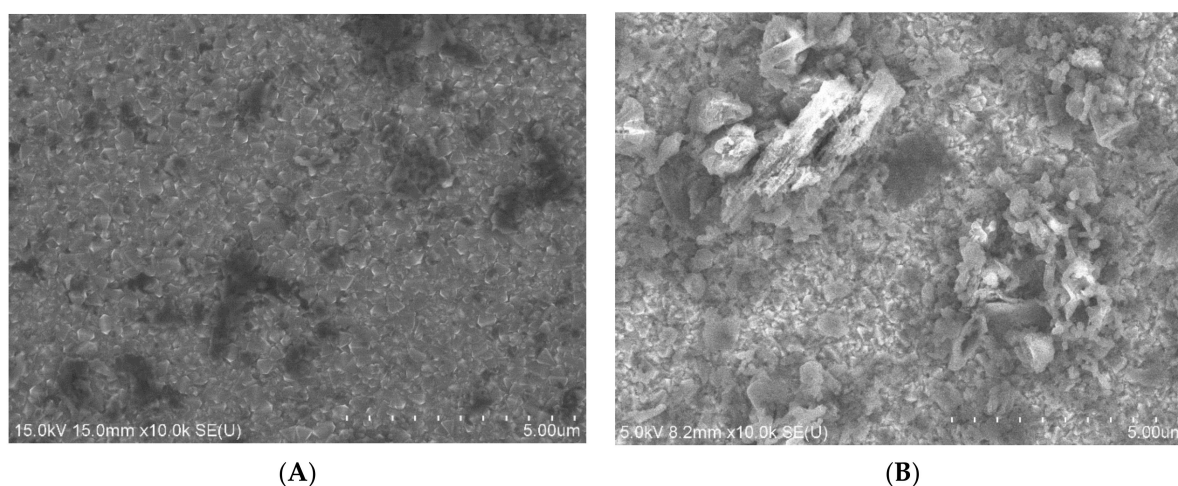


Figure 3. SEM images of (A) FTO glass substrate and (B) US-treated exfoliated g-C₃N₄ particles (0.050 mg cm^{−2}) on FTO glass deposited by electrophoresis from the stable part of a suspension aged one-week.

2.3. Photocatalytic Activity

$g\text{-C}_3\text{N}_4$ layers were deposited on a conductive substrate by electrophoresis. Therefore, we performed measurements of the open circuit potential (OCP) in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$. Figure 4 shows the time dependence of OCP in the dark and under illumination. Upon irradiation, OCP shifts negatively, and after about 30 s, a steady-state value is reached. After turning the illumination off, the OCP value decays, and eventually reaches its initial dark value. The decrease of OCP when the electrode is illuminated is due to excess electrons generated in the film. This shift of OCP (about 15 mV) is not as large as for anatase sol-gel TiO_2 films (about 330 mV) [28] or thermal rutile TiO_2 films (about 400 mV) [18], but indicates that $g\text{-C}_3\text{N}_4$ behaves as an n-type semiconductor.

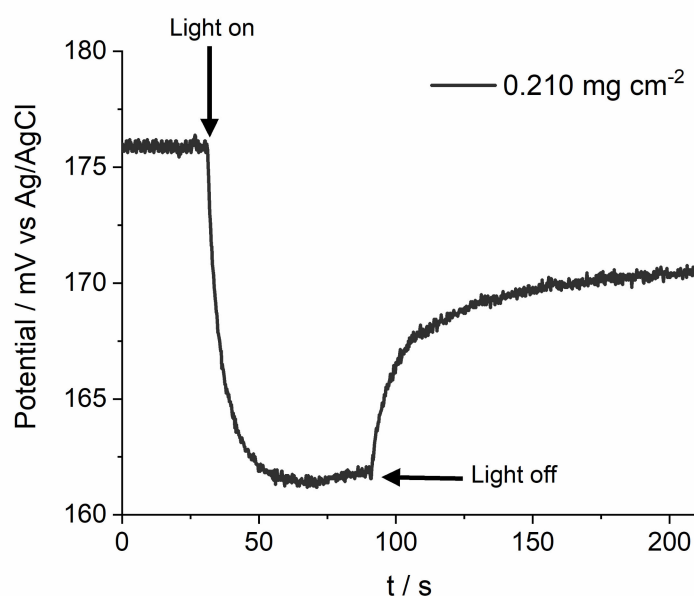


Figure 4. Open circuit potential of $g\text{-C}_3\text{N}_4$ layer (content 0.210 mg cm^{-2}) on FTO glass. Electrolyte $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$, 1.5 G simulated solar light, light irradiance 100 mW cm^{-2} .

The immobilized Ex-CN layers prepared by electrophoresis on FTO glass showed good mechanical stability in an aqueous solution (e.g., no changes in layer integrity were observed after 4 h of stirring). The photocatalytic activity was tested using two different model pollutants (AO7 and 4-CP) with an initial concentration of $10^{-4} \text{ mol dm}^{-3}$.

The influence of the deposited amount of $g\text{-C}_3\text{N}_4$ and the age of the ethanol suspension of $g\text{-C}_3\text{N}_4$ on photocatalytic degradation of azo dye AO7 is shown in Figure 5 (one-week-aged suspension) and Figure S3 in Supplementary Materials (twelve-weeks-aged suspension). The degradation curves of AO7 under irradiation for various contents of $g\text{-C}_3\text{N}_4$ in the layer are shown in Figure 5, together with the decay of the AO7 concentration measured by UV-vis spectroscopy in the dark for the layer with the highest content of $g\text{-C}_3\text{N}_4$ (0.263 mg cm^{-2}). The adsorbed amount of AO7 after 4 h was very small (about 1%). The degradation rate of AO7 under irradiation increases with the increasing amount of $g\text{-C}_3\text{N}_4$ in the layers; however, there is a limit in the maximum $g\text{-C}_3\text{N}_4$ content because of the stability of prepared layers. When the layers contain more than 0.3 mg cm^{-2} of $g\text{-C}_3\text{N}_4$, their mechanical stability is poor.

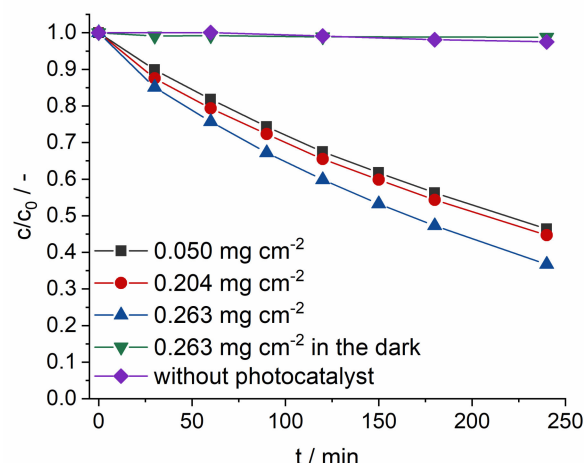


Figure 5. Acid Orange 7 concentration (measured by UV-vis spectroscopy) decrease under light (without photocatalyst and for 3 contents of g-C₃N₄) and in the dark. A one-week-aged suspension was used for layer deposition on FTO glass, and the light source was UV Sylvania Lynx-S BLB, with a broad maximum at 365 nm. The initial concentration of AO7 was 10^{−4} mol dm^{−3}.

It was found that the age of the suspension does not have a significant influence on the photocatalytic efficiency of prepared layers. Using layers containing the highest possible mechanically stable amount of g-C₃N₄, the removed amounts of AO7 were 63% and 62% after 4 h, for a one-week- and twelve-weeks-aged suspension, respectively. This suggests that it is possible to use variously aged (from 1 week to 12 weeks) suspensions for the deposition without reducing the photoactivity of the prepared layer.

Figure 6 shows the decay of 4-CP concentration under irradiation for layers with 0.049–0.267 mg cm^{−2} of g-C₃N₄, and in the dark for the layer with 0.267 mg cm^{−2} of g-C₃N₄. An example of the 4-CP solution chromatogram before and after 4 h of irradiation is shown in Supplementary Materials as Figure S4. The results of detailed analysis of the reaction mixture are shown below. As with AO7, the concentration decay (see Figures 5 and 6) is faster for layers with a higher content of g-C₃N₄. This can be explained by the increased amount of absorbed UV light, as can be seen in Figure S5 (in Supplementary Materials) showing the UV-Vis spectra of immobilized layers of different g-C₃N₄ contents.

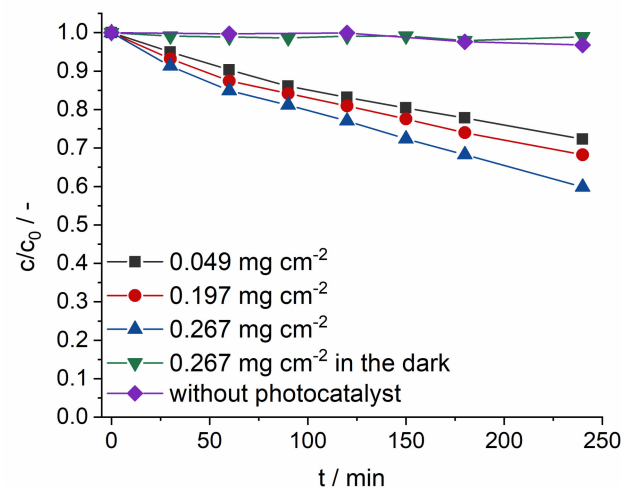


Figure 6. 4-chlorophenol concentration (measured by HPLC) decrease under light (without photocatalyst and for 3 contents of g-C₃N₄), and for 0.267 mg cm^{−2}, in the dark. A one-week-aged suspension was used for layer deposition on FTO glass; the light source was a UV Sylvania Lynx-S BLB, with a broad maximum at 365 nm. The initial concentration of 4-CP was 10^{−4} mol dm^{−3}.

In the case of 4-CP, the degradation rate was lower than for AO7. With the most active layer, about 40% of 4-CP was removed in 4 h (while for AO7, it was more than 60% in 4 h). The adsorbed amount of 4-CP after 4 h was also about 1%, the same as in the case of AO7.

g-C₃N₄ shows semiconductor-like light absorption with suitable bandgap energy (2.77 eV [26]) for the photocatalytic reaction under UV or visible light irradiation up to 447 nm. However, not only is the value of the band gap important, but so are the positions of conduction (CB) and the valance band (VB). The position of CB of g-C₃N₄ is very negative (~ -1.27 V vs. NHE at pH 7 [29]), which indicates that carbon nitride has strong reductive properties, but the position of the VB (1.39 V vs. NHE at pH 7 [29]) is lower than the potential for the $\bullet\text{OH}/\text{OH}^-$ couple, which means that no formation of $\bullet\text{OH}$ takes place on the surface of g-C₃N₄. This was confirmed by electron paramagnetic resonance (EPR) spectroscopy in our previous work [15].

The exfoliated g-C₃N₄ shows different but significant efficiency for removal of AO7 and 4-CP. For the highest content of g-C₃N₄, the calculated degradation rate is $1.04 \times 10^{-9} \text{ mol cm}^{-2} \text{ min}^{-1}$ and $4.81 \times 10^{-10} \text{ mol cm}^{-2} \text{ min}^{-1}$ for AO7 and 4-CP, respectively. The measurement of total organic carbon removal would show the ability to mineralize those two organic compounds. The initial concentration of dissolved organic carbon (DOC) for AO7 was 19.4 mg dm^{-3} , and for 4-CP 9.0 mg dm^{-3} , which corresponds to the initially used concentration of both compounds ($10^{-4} \text{ mol dm}^{-3}$). After 24 h of irradiation, in the case of the AO7 solution, the DOC concentration decreased to 16.8 mg dm^{-3} , while in the case of the 4-CP solution, it remained almost the same (8.94 mg dm^{-3}). This shows a significant difference in the ability of g-C₃N₄ to mineralize these two organic compounds.

According to Momeni et al. [30], AO7 can undergo two mechanisms during the electrochemical degradation, oxidative and reductive, which means that the degradation of AO7 occurs even without the formation of $\bullet\text{OH}$. As possible reaction intermediates of AO7 degradation via the oxidative route, 4-nitrosobenzenesulfonate and 1-iminonaphthalen-2(1H)-one were identified in the literature; for the reductive route, 4-aminobenzenesulfonate and 1-aminonaphthalene-2-ol were identified [31]. These products can be further degraded into organic compounds containing organic molecules of lower molecular weights, and also into CO₂, which is in agreement with a decrease of organic carbon in AO7 solution (about 13% in 24 h). Therefore, we can say that although the decrease of AO7 concentration after 4 h is about 63%, the decrease of total organic carbon (TOC) after 4 h is only about 2%, which means that the rate of mineralization is much lower than the rate of AO7 degradation. Similarly, Jiang et al. [22] observed mineralization only for g-C₃N₄ activated by HCl in the presence of peroxymonosulfate; for non-activated g-C₃N₄, no mineralization was shown, and only concentration decay of AO7 was observed. The case of 4-CP is different; values of TOC are within the error range of the measurement technique, so we can assume that the concentration of organic carbon is constant, and the 4-CP is only transformed into another type of organic compound. According to Cui et al. [23], 4-CP can undergo dechlorination, and the mineralization ability of 4-CP depends on the surface structure of g-C₃N₄; they observed negligible TOC removal by bulk and exfoliated g-C₃N₄, but mesoporous g-C₃N₄ has shown the ability to mineralize 4-CP. We observed the formation of an organic compound with the summary formula C₁₂H₈Cl₂O₂. This compound was detected by GC/MS analysis. The structure of this compound is shown in Figure S6B in Supplementary Materials. Reactive species formed under irradiation on the surface of g-C₃N₄ most likely attack the O–H bond, creating reactive radicals that can form organic compounds with higher molecular weight via a dimerization reaction. To confirm that this compound is not formed just by the catalysis of 4-CP in the presence of g-C₃N₄, we performed a 16 h measurement in the dark and under UV irradiation. The results shown in Figure S6A,B (in Supplementary Materials) indicate that this organic compound is formed only under UV irradiation, and that g-C₃N₄ has catalytic properties only under illumination.

3. Experimental

3.1. Materials, Chemicals, Synthesis of Catalyst

Melamine ($\geq 99\%$) was purchased from Sigma Aldrich. Triply distilled water was used for all experiments. Methanol (LC-MS grade, Fisher Scientific, Waltham, MA, USA) was used for HPLC analysis. Acid Orange 7 (Sigma-Aldrich, St. Louis, MO, USA) and 4-chlorophenol (Sigma, USA), serving as the model compounds, were used without further purification. Bulk graphitic carbon nitride was synthesized by thermal treatment of melamine at $550\text{ }^{\circ}\text{C}$ for 4 h; exfoliated graphitic carbon nitride (Ex-CN) was then prepared by thermal treatment of bulk $\text{g-C}_3\text{N}_4$ at $500\text{ }^{\circ}\text{C}$ for 2 h with a temperature increase of $10\text{ }^{\circ}\text{C min}^{-1}$.

3.2. Preparation of Layers

Layers of Ex-CN were prepared by electrophoretic deposition on a transparent conductive glass substrate (FTO glass; i.e., glass covered by a layer of fluorine-doped tin oxide). To decrease the particle size of prepared exfoliated $\text{g-C}_3\text{N}_4$, ultrasonic treatment (Bandelin Sonorex digitec DT 52 H, operating frequency 35 kHz) of a suspension in ethanol was used for 3 h. This suspension of Ex-CN US (2.5 g dm^{-3}) was used for electrophoresis, employing FTO glass (TEC7 Sigma Aldrich, 5×2.5 or $3.5 \times 1.5\text{ cm}^2$) electrodes.

The electrophoretic deposition of exfoliated $\text{g-C}_3\text{N}_4$ particles on FTO glass was performed at room temperature ($22\text{ }^{\circ}\text{C}$). The distance between both electrodes was 2 cm. A high voltage DC source (Statron 3250.4, 0–150 V/0–0.2 A, Switzerland) was used as an electrical power source. Measured data were recorded by a UT61C digital multimeter (range of $600\text{ }\mu\text{A}$ –10 A) and analyzed by UNI-T software. Layers of $\text{g-C}_3\text{N}_4$ were deposited on the cathode at a voltage of 50 V. This value was selected based on our previous experience with electrodeposition of TiO_2 particles [32] and further optimization. The electrophoretic deposition was performed after 1 h, 16 h, 1 week, and 12 weeks.

3.3. Characterization and Activity Evaluation

Scanning electron microscopy (SEM) was performed using a Hitachi S-4800 field emission scanning electron microscope (FESEM) (Hitachi, Japan). Measurement of hydrodynamic particle size of selected samples was performed using a MasterSizer 3000 (Malvern Instruments, Malvern, UK).

Measurement of the photocatalytic activity of immobilized exfoliated $\text{g-C}_3\text{N}_4$ was performed using AO7 and 4-CP as model pollutants. Tests were performed in small, stirred reactors with a volume of 25 mL. Samples with a deposited $\text{g-C}_3\text{N}_4$ layer were fixed vertically in the reactor and at right angles to the horizontal light source, comprising two 11 W fluorescent lamps (Sylvania Lynx-S BLB), with a broad maximum at 365 nm. The irradiated surface area was 9.6 cm^2 , and the temperature was kept at $20\text{ }^{\circ}\text{C}$. At first, a test in the dark was performed to determine the adsorbed amount of the model compounds on the photocatalyst. Then a fresh layer was used to determine the concentration decay of 4-CP due to the UV irradiation. After a given time in the dark or under UV irradiation, the reaction mixture was analyzed by UV-Vis spectroscopy using a Cecil Instruments CE 2021 UV/Vis spectrophotometer for the AO7 analysis. For the 4-CP analysis, HPLC was employed, using a Shimadzu chromatographic system with an LC-10ADvp pump and an SPD-M10Avp diode array detector (wavelength range of 200–800 nm); the column used was a LiChrospher 100 RP-18e ($5\text{ }\mu\text{m}$), the mobile phase was a mixture of methanol and distilled water (60:40), and the flow rate of mobile phase was 1 mL min^{-1} . TOC measurements were performed using a TOC-L (Shimadzu, Japan). Reaction intermediates were followed by gas chromatography (GC) connected with mass spectroscopy (MS), using a 7890 GC System with a 7010 GC/MS Triple Quad (Agilent Technologies, USA). The GC column was an HP-ULTRA 2, and the carrier gas was helium with a constant flow of 1.5 mL min^{-1} . MS used the ionization technique with an EI @ 70 eV , with the temperature of the ionization source set to $230\text{ }^{\circ}\text{C}$ and a scanning range of 29–450 Da with a rate of 5 scans s^{-1} . For

analysis, the organic compounds were collected via direct immersion of SPME fiber 65 μm DVB/PDMS.

Open circuit potential was measured with an Ag/AgCl (3 mol dm^{-3} KCl) as a reference electrode [33]. The electrolyte was 0.1 mol dm^{-3} Na_2SO_4 . As a light source, a solar simulator (150 W Xe arc lamp (Newport, USA) with an AM1.5G filter, irradiance 1 sun (100 mW cm^{-2})) was used. The irradiated area was 0.45 cm^2 .

4. Conclusions

Exfoliated $\text{g-C}_3\text{N}_4$ particles were immobilized by electrophoretic deposition from an ethanolic suspension. For the fabrication of stable films, the particle size of $\text{g-C}_3\text{N}_4$ particles has to be smaller than 10 μm , and the amount of deposited $\text{g-C}_3\text{N}_4$ should not exceed 0.3 mg cm^{-2} . The photocatalytic activity of such layers was evaluated using two types of model compounds. It was proved that it is possible to use variously aged (1–12 weeks) suspensions for the electrophoretic deposition without reducing the photoactivity of the prepared layer. With increasing layer thickness, higher photocatalytic efficiency was observed; however, the layer thickness is limited by the mechanical stability of prepared layers. The successful immobilization of exfoliated $\text{g-C}_3\text{N}_4$ particles in layers that are stable in a stirred reactor is shown here for the first time.

The photocatalytic decomposition of the dye AO7 was faster in comparison with the decomposition of 4-CP. Mineralization was observed only in the case of AO7; the decrease of DOC after 24 h was 13%. After 4 h of irradiation, the decrease of AO7 concentration measured by HPLC was more than 60%, while the decrease of DOC was only about 2%. On the other side, no mineralization was observed in the case of 4-CP. The decrease of 4-CP concentration without the decrease of DOC could be due to 4-CP polymerization and the formation of a dimer ($\text{C}_{12}\text{H}_8\text{Cl}_2\text{O}_2$). That the decrease of organic carbon does not follow the decrease of 4-CP concentration is an important and not yet published observation. It indicates that the use of $\text{g-C}_3\text{N}_4$ as a photocatalyst for oxidative degradation of organic compounds in water is limited.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2073-4344/11/2/203/s1>, Figure S1: XRD patterns of bulk and exfoliated $\text{g-C}_3\text{N}_4$, Figure S2: Particle size distribution of as prepared exfoliated $\text{g-C}_3\text{N}_4$ and exfoliated $\text{g-C}_3\text{N}_4$ treated in EtOH in ultrasonic bath for 3 h, Figure S3: AO7 concentration (measured by UV-vis spectroscopy) decrease under light (for 3 contents of $\text{g-C}_3\text{N}_4$), Figure S4: HPLC analysis of the initial solution of 4-CP (A) and the reaction mixture after 4 h irradiation in the presence of immobilized exfoliated $\text{g-C}_3\text{N}_4$ photocatalyst (0.206 mg cm^{-2}) (B), Figure S5: UV-vis spectra (transmittance) of FTO glass and layers of exfoliated $\text{g-C}_3\text{N}_4$ (of different content) on FTO glass, Figure S6: GC/MS analysis of 4-CP solution after 16 h in dark (A) and after 16 h irradiation (B) in the presence of exfoliated $\text{g-C}_3\text{N}_4$ photocatalyst.

Author Contributions: Conceptualization, P.P. and J.K.; methodology, J.R. and Š.P.; formal analysis, J.K. and Š.P.; investigation, J.R. and Š.P.; resources, P.P. and J.K.; data curation, J.R. and Š.P.; writing—original draft preparation, Š.P. and J.K.; writing—review and editing, J.K. and Š.P.; visualization, J.R. and Š.P.; supervision, J.K.; project administration, P.P. and J.K.; funding acquisition, P.P. and J.K. All authors have read and agreed to the published version of the manuscript.

Funding: The authors acknowledge the financial support from the Czech Science Foundation (project number 19-15199S).

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank to J. Kosina (UCT Prague) for GC/MS analysis. The SEM analysis provided by the Research Infrastructure NanoEnvicZ, supported by the Ministry of Education, Youth, and Sports of the Czech Republic, under Project No. LM2018124, is acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

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