Floating Photocatalysts for Effluent Refinement Based on Stable Pickering Cellulose Foams and Graphitic Carbon Nitride (g-C₃N₄)

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ABSTRACT: The transfer of heterogeneous photocatalysis applications from the laboratory to real-life aqueous systems is challenging due to the higher density of photocatalysts compared to water, light attenuation effects in water, complicated recovery protocols, and metal pollution from metal-based photocatalysts. In this work, we overcome these obstacles by developing a buoyant Pickering photocatalyst carrier based on green cellulose nanofibers (CNFs) derived from wood. The air bubbles in the carrier were stable because the particle surfactants provided thermodynamic stability and the derived photocatalytic foams floated on water throughout the test period (4 weeks). A metal-free semiconductor photocatalyst, g-C₃N₄, was facilely embedded inside the foam by mixing the photocatalyst with the air-bubble suspension followed by casting and drying to produce solid foams. When tested under mild irradiation conditions (visible light, low energy LEDs) and no agitation, almost three times more dye was removed after 6 h for the floating g-C₃N₄−CNF nanocomposite foam, compared to the pure g-C₃N₄ powder residing on the bottom of a ca. 2 cm-high water pillar. The buoyancy and physicochemical properties of the carrier material were imperative to render escalated oxygenation, high photon utilization, and faster dye degradation. The reported assembly protocol is facile, general, and provides a new strategy for assembling green floating foams that can potentially carry a number of different photocatalysts.

1. INTRODUCTION

The recent water assessment study indicates that 50% of the current world population is likely to live in a water-stressed area by 2023.¹ UNESCO has frequently reiterated in its reports that around 80% of the global wastewaters are liberated into our natural surroundings without any appropriate refinement.² Among the pollutants identified and studied so far, the textile industries are contemplated as the highest generators of waste streams responsible for water pollution. About 280,000 tons of textile dyes are released per annum pandemically.³ These chemicals (and their degradation products) possess dreadful properties like carcinogenicity, mutagenicity, and teratogenicity. Their presence in water streams strikingly decrease the dissolved oxygen levels and eventually increase the chemical and biochemical oxygen demand. Indeed, they impact our natural ecosystems in all possible dimensions.⁴

Carbon-based soft semiconductor nanomaterials have been explored as catalysts for the removal of pollutants via photoinduced redox processes. In particular, the metal-free semiconductor material, graphitic carbon nitride (g-C₃N₄), has been investigated since it is able to photodegrade organic pollutants into CO₂, water, and harmless compounds using O₂ as the clean oxidant in an environmentally friendly manner.⁵ This unique property stems from the high reactivity and non-selectivity of, among other, the hydroxyl radicals (HO·) generated.⁶ An additional pollutant is not created, such as heavy metals/metal ions in the case of metal-based semiconductor materials, and it is therefore considered as a sustainable technology due to its capacity of driving its process at ambient conditions through the utilization of solar energy only.⁷ g-C₃N₄ absorbs in the UV and visible portion of the solar spectrum and is, simultaneously, stable in aqueous environments.

The application of g-C₃N₄ in a large-scale water effluent refinement is limited due to its higher density (1.71–2.39 g cm⁻³)⁸ than water; hence, g-C₃N₄ sinks immediately to the bottom of the water bodies when applied in real-life conditions. Consequently, the photodegradation efficiency rapidly decreases due to a lower oxygenation rate and a light attenuation effect in the liquid phase — only 1% of photons from the UV region and 20% from the visible region reaches a depth of 0.5 m.⁹ To tackle the above-mentioned problems, the photocatalyst should be located close to the air–water interface. Such positioning is achieved when the photocatalyst is embedded in a buoyant material.

To date, very few floating carriers have been suggested for g-C₃N₄ with perilone being the most explored.¹⁰ Most floating carriers have been developed for other photocatalysts, in
particular TiO$_2$.\textsuperscript{16} An optimal carrier should enable facile photocatalyst immobilization, possess adequate photocatalyst–carrier compatibility so that the photocatalyst remains with the carrier throughout its use, be stable, potentially transmit a large portion of the light, and possess long floatation times. Simultaneously, it should not release toxic pollutants, e.g., plastic pollution in the case of plastic carriers, be easily recovered, and preferably have additional properties, such as eco-friendly cellulose nano fibers (CNF)-based foams, present unique possibilities in this respect. Additionally, it was recently shown that environmental pollutants, such as poorly soluble drug molecules\textsuperscript{19–21} and dye molecules,\textsuperscript{22,23} adsorb and surface-precipitate onto native high uptake of dye molecules and high diffusivity of these in the material (when the photocatalyst is embedded in the interior of the carrier) to ensure rapid photodegradation of pollutants. Additionally, the preparation protocol should be facile. Designing a carrier that combines all of these aspects is, however, challenging.

Polysaccharide-based buoyant carriers are rare, even though some, such as eco-friendly cellulose nanofiber (CNF)-based buoyant foams, present unique possibilities in this respect. Neat CNF films are optically transparent; \( \sim \)80 to 90% of photons with wavelengths between ca.350 and 1000 nm are transmitted,\textsuperscript{1} and CNFs are known to facilitate the dispersion of carbon-based nanoparticles, e.g., carbon nanotubes.\textsuperscript{18} Additionally, it was recently shown that environmental pollutants, such as poorly soluble drug molecules\textsuperscript{19–21} and dye molecules,\textsuperscript{22,23} adsorb and surface-precipitate onto native or chemically modified CNFs, which can further aid in the removal of them. In particular, CNF-based foams can, very easily, be prepared by trapping air bubbles in a suspension of CNF/surfactant, i.e., by mechanically whipping the suspension.\textsuperscript{24,25} The air–water interface of the air bubbles are stabilized by CNFs/surfactants via a Pickering mechanism, which enhances thermal stability as a result of the steric hindrance against coalescence provided by the CNFs and the very high particle-desorption energies.\textsuperscript{26} The CNF-based cellular solids are obtained by casting the wet-stable foam suspension followed by water evaporation. The rewetted foams are stable and possess buoyancy properties. Additionally, the diffusivity of small molecules in the swollen CNF-based cell wall is expected to be fast, approximately one order of magnitude smaller than the small molecule diffusion in water.\textsuperscript{23}

In this work, we report a facile method for the incorporation of the semiconductor g-C$_3$N$_4$ photocatalyst in a CNF-based foam. The morphology, buoyancy, and photocatalytic properties of these g-C$_3$N$_4$–CNF nanocomposite foams are assessed. The photocatalytic activity under visible light irradiation for the buoyant g-C$_3$N$_4$–CNF nanocomposite foam is compared to the neat g-C$_3$N$_4$ photocatalyst powder at similar conditions for the refinement of aqueous dye solutions and their corresponding results are discussed.

2. RESULTS AND DISCUSSION

2.1. Synthesis of Polymeric g-C$_3$N$_4$. The thermal treatment of urea resulted in polymeric g-C$_3$N$_4$, which is the most stable allotrope of carbon nitride. A prolonged polymerization (3 h) of urea after the attainment of a high temperature (600 °C) was employed, similar to that previously reported in the literature, because it is known to facilitate in the formation of g-C$_3$N$_4$.\textsuperscript{27} The XRD diffractogram and FTIR spectrum of the carbon nitride powder confirmed the basic structure of g-C$_3$N$_4$.\textsuperscript{27} The XRD peak at 2\( \theta \) = 13.4° (100) crystal plane, reported values of 2\( \theta \) \( \approx \) 13°–13.6° in literature)\textsuperscript{27–29} was assigned to the in-plane repeating motif, and the peak at 28.0° (002) crystal plane, ca. 27.4°–27.7° in literature)\textsuperscript{27–29} was due to the stacking of the conjugated aromatic system, see Figure 1a. The second peak (002) was a bit higher than the previously reported values, implying a reduced stacking distance between the g-C$_3$N$_4$ sheets. Such shifts have previously been observed when the treatment stacking and/or time are increased.\textsuperscript{30,31} The bands in the FTIR spectrum (3400–2900 due to amino groups, \( -\text{NH}_x \) in g-C$_3$N$_4$, and \( -\text{OH} \) in residual water, and characteristic bands in 1650–1200 cm$^{-1}$ are due to, among other, stretching vibrations of the repeating heptazine rings) were similar to previously reported

![Figure 1. Analysis of synthesized g-C$_3$N$_4$: (a) X-ray diffractogram, (b) FTIR spectrum including the repeating heptazine unit in g-C$_3$N$_4$, and (c) X-ray photoelectron spectroscopy. (d) Representative TEM image of the g-C$_3$N$_4$ nanosheets is shown. Scale bar: 200 nm. (e) Absorbance spectrum calculated from the diffuse reflectance (R) spectrum and the Kubelka–Munk model, F(R). Inset: Tauc plot.](https://doi.org/10.1021/acsomega.0c02872)
FTIR spectra and confirmed the successful formation of g-C$_3$N$_4$, see Figure 1b. The surface chemistry and specific bonding of g-C$_3$N$_4$ is provided by the XPS results in Figure 1c. The observed C 1s, N 1s, and O 1s peaks and their corresponding deconvoluted fittings agree well with the previously reported data. The fitted C 1s spectra display peaks at 288.2 and 284.8 eV corresponding to the sp2-bonded carbon species from the C$\equiv$C bond, respectively. The fitted N 1s spectra had two well-defined high intensity peaks: 401.2 and 404.5 eV. The former peak corresponds to the C$\equiv$N bonding. Additionally, the very small intensity peaks observed in the N 1s spectra were 401.2 and 404.5 eV. The 401.2 eV peak corresponds to C$\equiv$N species. The 404.5 eV peak is either due to charging effects or $\pi$-excitations. The composition of resultant g-C$_3$N$_4$ through XPS analysis, was 63.01 wt % (N), 34.75 wt % (C), and 2.11 wt % (O), which is very close to the ideal composition of g-C$_3$N$_4$. Finally, the residual O 1s spectrum peak at 532.2 eV emanates from the oxygen contamination during the thermal polymerization, see Figure S3 in the Supporting Information. The representative TEM image in Figure 1d showed that the obtained g-C$_3$N$_4$ had a two-dimensional sheet-like morphology with a disordered appearance of silk sari. These nanosheets were of thin and transparent nature and pores were observed in random places of the nanosheets. In addition, the edges of the nanosheets were occasionally thicker, indicated by the white arrows in Figure 1d. On closer observation, a distinctive curvature of the nanosheets on the edges, very similar to the curling of a silk cloth, was seen; see Figure S2 in the Supporting Information. The structural twist/distortion is concordance with previous studies.

The optical properties of the organic polymeric (g-C$_3$N$_4$) powder were studied using UV−vis diffuse reflection spectroscopy. The onset of the absorption edge was at 427 nm, see Figure 1e. The band gap of this soft semiconductor was 2.9 eV; the Tauc plot is included in the inset of Figure 1e. Previously reported values for the band gap are in the range from 2.7 to 3 eV. The large band gap (0.2 eV greater than the conventional bulk band gap of g-C$_3$N$_4$, 2.7 eV) observed here can be attributed to the quantum confinement behavior exhibited by the as-obtained ultrathin g-C$_3$N$_4$ nanosheets. Thus, resulting in the repositioning of the conduction and valence band edges. Through the XPS VB characterization, the valence band maxima of our g-C$_3$N$_4$ was disclosed at +1.9 eV, see Figure S3 in Supporting Information, and the corresponding conduction band minimum (−1 eV) was calculated with the help of the band gap value. The VB and CB edge values were in agreement with the previously studied g-C$_3$N$_4$ samples.

The reason for obtaining such quantum confined g-C$_3$N$_4$ was due to the attainment of ultrathin silk-like layered g-C$_3$N$_4$ by the high temperature (600 °C) and prolonged polymerization (3 h) of the urea precursor. Such synthetic conditions resulted in the generation of ultrathin nanosheets.

2.2. Neat CNF and g-C$_3$N$_4$−CNF Cellular Solids. Gas bubbles that are stabilized with particles, a so-called Pickering stabilization, will be thermodynamically stable because the adsorbed particles present a steric hindrance against coalescence. The particles can be considered as irreversibly adsorbed at the gas bubble−water interface. Small molecule surfactants, on the other hand, will be in dynamic equilibrium with the surfactants in the bulk. In this work, we use the Pickering concept to first create suspensions that contained CNF surfactant-stabilized air bubbles. These suspensions were then loaded with g-C$_3$N$_4$ nanosheets by simply mixing them with a g-C$_3$N$_4$ dispersion in MilliQ water. By drying the g-C$_3$N$_4$-loaded suspension, a cellular solid with photocatalytic properties was attained. The resultant cellular solid (pure CNF foam) and g-C$_3$N$_4$−CNF nanocomposite foam possessed a very low density of 19 ± 4 and 40 ± 3 kg m$^{-3}$, respectively. To achieve the wet-stable foam, we used cellulose nanofibers in combination with a nontoxic surfactant (LA). The g-C$_3$N$_4$ nanosheets themselves have also been proposed to possess...
amphiphilic properties, but this was not exploited in the present study. A schematic illustration of the different processing steps is found in Figure 2a–c. The role of the surfactants is to change the surface energy of the CNFs, in order to facilitate their accumulation at the air bubble−water interface. To realize this, it is important to use the precise amount of surfactant. In Figure 2d–f, representative images of the final dry foams and a close-up of the foam structure, both with and without g-C3N4, are shown. The images illustrate the cellular structure of the final materials. The g-C3N4–CNF nanocomposite contained 78 wt % CNF and 22 wt % g-C3N4 (calculated dry weight composition). The XRD and FTIR analyses (see Figure S4 in the Supporting Information) of the above nanocomposite foam confirmed the presence of the g-C3N4 photocatalyst within the foam structure. The internal structure of the pure CNF and g-C3N4–CNF nanocomposite foams were studied using SEM; see micrographs in Figure 3a–d. These SEM images clearly portray that the as-obtained pure CNF foams contained enclosed air-pockets, which provided the buoyancy properties of the material (see next section). Note that the cross-sections in Figures 3a–c were created by first freezing the foam with liquid nitrogen followed by cutting the foam in its brittle state. Apart from the cut, this most likely induced additional cracks in the cell wall. On closer observation of the cell structure within the pure CNF foam, it is very obvious that the cell wall is composed of cellulose nanofibers, which were arranged into laminar sheet-like structures, see Figure 3b. The thickness of the cell wall seen here was ca. 1 μm (Figure 3b). In the case of the nanocomposite g-C3N4–CNF foam, the positioning of the g-C3N4 nanosheets within the predominantly closed cell structure was clearly seen; see black arrows in Figure 3c,d that point to g-C3N4 aggregates. Hence, the 2D platelet-like g-C3N4 nanosheets were successfully immobilized and embedded within layers of CNFs in the cell wall of the foam. The advantageous as it may enhance the utilization of the irradiation. The transmittance of light also increased slightly (to ca. 63%) as the CNF foams were wetted with water (Figure 4a).

The solid cellular g-C3N4–CNF nanocomposite foam displayed an onset of high absorption at around 460 nm, corresponding to a band gap of 2.70 eV (Figure 4b). The slight redshift in the absorption spectrum of the nanocomposite foam and reduced band gap compared to the pristine g-C3N4 used for the fabrication of such foam can be attributed to the agglomeration of the g-C3N4 nanosheets within the cell wall of the foam, resulting in the immobilization of bulk g-C3N4 materials within the cell wall and not the ultrathin g-C3N4 nanosheets. Another reason could be the passivation of surface states of g-C3N4 by the CNFs and surfactant.
2.3. Photocatalytic Activity. The photocatalytic activity of the as-obtained novel nanocomposite g-C\textsubscript{3}N\textsubscript{4}−CNF foam was evaluated through the decomposition of Rhodamine B (RhB) dye in aqueous solution, and its activity was compared with that of g-C\textsubscript{3}N\textsubscript{4} powder. RhB is a chemically stable molecule and previous studies employing this dye have reported no photolysis, which also fits well with our observations (results in Figure S5 in the Supporting Information).\textsuperscript{39}

The performance of the photocatalyst and the degradation rate of RhB, depend on the access to photons, and in this work, low energy LED lamps were used to illustrate that high photocatalytic activity can be achieved even under such distinctive limiting conditions. Also, in the present analysis, no magnetic stirring was employed in order to limit the oxygenation of the solution. This condition was decided in order to mimic a natural-like environment case where negligible agitation is present. The results of the observed photocatalytic activity are systematically depicted in Figure 5a,b. Here, \( C_0 \) corresponds to the initial dye concentration and \( C \) is the concentration of the dye in the solution at a particular time, \( t \). The dye solution with the photocatalyst/foam was first kept for 1 h in the dark to establish a material which was nearly saturated with the dye. Light was then turned on. To demonstrate the profound effect of stirring on the performance of the g-C\textsubscript{3}N\textsubscript{4} powder, one experiment with magnetic stirring was also performed, and the result is included in Figure S6 in the Supporting Information.

The degradation of RhB dye under promoted agitation was fast, 95% of the dye was degraded within 6 h of illumination (rate constant, \( k = 8.1 \times 10^{-3} \text{ min}^{-1} \); pseudo first-order kinetics). On the other hand, when the predominant part of the g-C\textsubscript{3}N\textsubscript{4} powder was sedimented on the bottom of the ca. 2 cm-high water pillar in the reaction container, as in the case when no stirring was employed, the degradation rate was significantly lowered (\( k = 4.8 \times 10^{-4} \text{ min}^{-1} \)), and only 16 ± 4% of RhB was removed after 6 h of illumination (Figure 5a). This low photocatalytic efficiency is due to the low light utilization and simultaneous low oxygenation of the water.

The foams were wetted very quickly in the RhB solution and small air bubbles were observed in the wet foam structure. The pure CNF foam sorbed 14 ± 4% of RhB in the dark, which is higher than the powder g-C\textsubscript{3}N\textsubscript{4} (4 ± 1.3% sorption in the dark), which could be attributed to a higher dye affinity to the CNFs, see Figure 5a. The pure foam was measured after 6 h when the dye sorption had reached a steady state (>3 h). Pieces of g-C\textsubscript{3}N\textsubscript{4}−CNF foam floating on top of MilliQ water at (d) \( t = 0 \) and (e) after 4 weeks of continuous light exposure.
CNF foam and g-C₃N₄ immobilized within the foam. The subsequent light illumination degraded the dye molecule and 47 ± 2% of the dye was removed after 6 h. This can be compared to the g-C₃N₄ powder that resided on the bottom of the reaction vessel, where 16 ± 4% of RhB was removed after the same amount of time. The higher degradation rate for the nanocomposite g-C₃N₄–CNF foam is due to its appropriate position in the photoreactor system at the air/surface–water interface due to floatation, where it is highly exposed to light and oxygen, resulting in the enhanced photocatalytic activity. The difference in performance between the floating and sunken/sedimented photocatalyst is expected to become even greater as the height of the water pillar increases. The experimental degradation time was also prolonged for the nanocomposite g-C₃N₄–CNF foam (results in Figure 5b), and after 16 h, 90% of RhB had been removed. A second important observation is that the maximum absorption peak of the dye solution shifted from 553 to 535 nm, see Figure 5b, indicating that there is an exhaustive degradation of RhB. The pattern of the shift was such that up to 74% dye removal, a subtle shift, occurred from 553 to 549 nm, indicating that the fragmentation of the conjugated chromophore dye molecule was dominating the photocatalytic process. Beyond 74% dye removal, the shift was more pronounced, with a shift from 549 to 535 nm. The last shift is attributed to the N-de-ethylation of the RhB molecule by the oxidizing species generated from the photoinduced process. Overall, the observed pattern of shift of maximum absorption of RhB dye agrees well with previously reported photocatalytic studies.⁴⁰,⁴¹ In the inset in Figure 5b, the clear color difference of the RhB solution prior to and after 14 h of degradation (with the floating nanocomposite photocatalyst) are shown. It should be noted that, as a consequence of the current experimental setup, some water evaporation (see results in Figure S5 in the Supporting Information) occurred; hence, the reported values in Figure 5a,b are most likely overestimates and the true RhB concentrations (C) are expected to be lower at the different time points (t > 0).

The colors of the different foam pieces used in the experiments were also investigated. The absorbance spectra for the wet CNF and wet nanocomposite foam prior to the dye experiments and after specific periods of time are included in Figure 5c. In the case of the pure CNF foam, where the dye was only sorbed, the foam’s color was pinkish, observed as a shifted (maximum absorption peak at 524 nm) RhB spectrum in Figure 5c. The shift is due to that the RhB was sorbed in the CNF foam, compare with the absorbance spectrum for the RhB present in solution (prior to degradation, Figure 5b), which had a maximum absorption at 553 nm. Such a shift in the dye spectrum is typically observed when a change in the surrounding dye environment has occurred, in this case the interaction of dye molecules with the surface of CNFs and surfactant.² For the nanocomposite foam, however, the color after 14 h of experiment was analogous to that of prior to the photocatalytic study which means that very little sorbed RhB was left and below the detection limit of the instrument (see results in Figure 5c).

The developed nanocomposite foams were able to float for a long period of time (throughout the experiment) without disintegrating, which we hypothesize is a consequence of the Pickering stabilization of the air bubbles and the physicochemical stability of the cell wall materials. In Figure 5d,e, pieces of nanocomposite foams floating on the surface of MilliQ water are shown prior to (Figure 5d) and after 4 weeks (Figure 5e) of continuous light exposure. These g-C₃N₄–CNF foams did not disintegrate during this time period and clearly showed both excellent stability and floatability. Hence, the carrier fabricated from CNFs has the propensity to provide prolonged contact between the photocatalyst and pollutants.

3. CONCLUSIONS

Through this work, we have demonstrated a general production protocol for the immobilization of photocatalysts; here, a soft semiconductor (g-C₃N₄) photocatalyst, within the cell walls of buoyant CNF-based foams. The materials were produced via a facile mixing and drying protocol. The derived CNF-based nanocomposite foams were floating throughout the whole 4 weeks of irradiation experiment without disintegrating, which is hypothesized to be a consequence of the cell wall materials and the Pickering stabilization provided by the CNF surfactants at the interface of the encapsulated air bubbles. Additionally, since it was possible to make a very thin foamed CNF-based carrier (<1 mm in thickness), both good sorption/uptake properties of the model pollutant (Rhodamine B) and suitable combinations of transmission and scattering of light in the wet state (63% for the pure CNF foam, 300–800 nm) were achieved. When tested in the absence of agitation and under mild illumination conditions (low power LEDs), the g-C₃N₄–CNF nanocomposite foams removed almost three times more dye after 6 h of illumination than pure g-C₃N₄ powder, which was a consequence of the buoyancy and physicochemical properties of the CNF-based carrier material. The pure g-C₃N₄ powder, on the other hand, remained on the bottom of the reaction vessel (with a ~2 cm-high water pillar on top), due to its higher density than water.

The facile and general production protocol reported herein, potentially enables further tailoring possibilities of the photocatalytic performance, which could be achieved by e.g., modifications to the outer foam dimensions and optimized dispersion and localization of the photocatalyst within the foam structure.

4. MATERIALS AND METHODS

4.1. Materials. Urea, nitric acid, lauric acid sodium salt (LA), ethanol (EtOH, 97 vol %), and sodium hydroxide were all purchased from Merck, Sweden. The cationic quaternary ammonium grafted CNFs in MilliQ water (1 wt %) were prepared using cellulose-rich dissolving-grade acid-sulfated pulp (a gift from Domjö Fabriker AB, Ornsköldsvik, Sweden) cooked from a softwood mixture (60% Norway spruce and 40% Scots pine). The pulp contained about 4% hemicellulose and <0.3% lignin. The CNFs were prepared as described in detail in a previous study and consisted briefly of a chemical reaction step with glycidyltrimethylammonium chloride followed by a homogenization step.¹⁹ The resulting CNFs had a net surface charge density of 531 μeqiv g⁻¹ fiber, determined by streaming potential titration (Stabino particle charge titrator, Particle Metrix GmbH, Meerbusch, Germany) as described previously.¹⁹ The CNFs were 2.7 ± 0.9 mm in width and had a length in the micrometer range (measured by atomic force microscopy).¹⁹

4.2. Synthesis of Graphitic Carbon Nitride (g-C₃N₄). An amount of 20 g of urea was dried in a glass petri dish at 100 °C. The dry powder was transferred to a 30 mL porcelain crucible, which was closed with a lid and wrapped...
with aluminum foil. The crucible was heated in a muffle furnace (Micropyretics Heater International) at 600 °C in an air-filled environment. The polymerization temperature (600 °C) was reached within 20 min (from 19 °C) and maintained at 600 °C for 3 h. Afterward, the heater was turned off and the crucible was cooled back to room temperature. Approximately 0.792 g of g-C_{3}N_{4} was produced. This amount was suspended in 100 mL of 0.1 M of nitric acid in a beaker and stirred for 1 h. The suspension was centrifuged at 10 k rpm for 10 min; the supernatant was discarded and the remaining powder was redispersed in fresh MilliQ water. This centrifugation step was repeated three times. The final powder was dispersed in fresh MilliQ water and kept for further usage.

4.3. Synthesis of Pure CNF and g-C_{3}N_{4}-CNF Cellular Solids. A 0.28 wt % CNF suspension was attained by diluting a 36 g stock suspension of cationic CNF (1 wt %) with MilliQ water followed by magnetic stirring (750 rpm) for 4–8 h. The surfactant was dissolved in EtOH by mixing 9.3 mg of LA, 600 μL of EtOH, and 60 μL of 1 M of NaOH in an Eppendorf tube. To dissolve LA, the solution was sonicated in a water bath for 10–15 min. This surfactant solution was added to 65 g of the 0.28 wt % CNF suspension and wet-stable foams were obtained using probe sonication with a Sonics Sonifier equipment with a 1/8” inch tip at 70% amplitude (pulse mode 9.9 s sonication and 9.9 s pause) for 2 min. The resultant wet-stable foams were cast in a plastic petri dish (with a 8.6 cm inner diameter) to generate pure CNF foams, or 10 mL of MilliQ water containing 50 mg of g-C_{3}N_{4} was added to generate g-C_{3}N_{4}-CNF foams. The 10 mL suspension of g-C_{3}N_{4} in MilliQ water was sonicated in a water bath for 1 h prior to the addition. This mixture containing g-C_{3}N_{4} was gently swirled to avoid bigger air-bubble formation and subsequently casted in the same Petri dish. An amount of ~33 g was poured in each petri-dish. The cast wet-stable foams were dried at ambient conditions (19–22 °C and 20–30% relative humidity (RH)).

4.4. Photocatalytic Study. Rhodamine B (RhB) was studied as a model contaminant. The photocatalytic degradation was followed (at λ = 553 nm) with a UV–vis spectrophotometer (Shimadzu UV-2550). The reaction was performed in a top-open cylindrical glass container (6.4 cm in height and 11.3 cm in diameter, borosilicate). The photocatalyst setup consisted of 84 individual LEDs (CentloT, India); an image of the setup is included in Figure 5a. Information and a detailed elucidation regarding the fabrication of the illuminating device of the photocatalyst is provided in the Supporting Information (SI), see Figure S1 in the Supporting Information. The irradiation was in the range of λ = 280–400 nm with a total luminous flux of 660 lm, and the photon source was positioned at a height of 7 cm from the water surface in the cylindrical container. An amount of 200 mL of 5 mg L^{-1} of RhB dye solution was used and either neat CNF foam (182 mg), nano composite foam material (182 mg of CNFs +50 mg g-C_{3}N_{4}), or 50 mg of g-C_{3}N_{4} powder was used in each experiment. First, the suspensions were left unperturbed in the dark for 60 min to reach a near saturation of dye uptake in the materials studied. Then, the LED lamps were switched on and the photo reactive system was maintained at a constant temperature by constant purge of air on its sides. At predetermined times, an amount of 5 mL was drawn from the top part of the reaction vessel, centrifugated (10 k rpm) and the supernatant was analyzed with the UV–vis spectrophotometer, and the dye concentration was calculated from the linear calibration curve. Afterward, the (whole) analyzed sample was directly added back to the reaction vessel to maintain a constant ratio between the pollutant and the photocatalyst employed. The experiments were performed at an ambient temperature (19–21 °C) and, unless specified, no magnetic stirring was employed.

4.5. Characterization. Scanning electron microscopy (SEM) images were obtained using a Hitachi SEM S-4800 at an accelerating voltage of 1 or 3 kV. A small dry foam piece was frozen in liquid nitrogen (10 min), and the frozen sample was cut using a scalpel. This cross-sectionally dissected fresh samples were sputter coated using a Cressington 208HR sputter coater equipment with a Pt/Pd (60/40) coating (2 nm) prior to SEM imaging.

The density of the foams in the dry state was determined by measuring the outer dimensions of the foam pieces and its corresponding weight. The thickness of the foam pieces was obtained using the Hitachi TM-1000 Tabletop scanning electron microscope.

Transmission electron microscopy (TEM) images were obtained using a Hitachi HT7700 at an accelerating voltage of 100 kV. Formvar/carbon-coated 200 mesh copper grids (Ted Pella Inc.) were used to obtain the image depicted in Figure 1d, and for the images in Figure S2 in the Supporting Information, holey carbon grids (Ted Pella Inc.) were used. An amount of 15 μL of a g-C_{3}N_{4} suspension (50 mg of g-C_{3}N_{4} in 10 mL of MilliQ water) were dropped on the respective grids and dried in ambient lab conditions for 1 h prior to imaging. The g-C_{3}N_{4} suspension was sonicated for 1 h in a water bath prior to casting.

Fourier Transform Infrared (FTIR) spectra, using an attenuated total reflectance (ATR) module, were acquired using the equipment Perkin–Elmer belonging to the model of Spectrum 100 FTIR + Spotlight 400. The spectra were acquired in the absorbance or transmittance mode in the range of 600–4000 cm^{-1} (16 scans, with a resolution of 4 cm^{-1}). The dried foam-based samples and g-C_{3}N_{4} powder (obtained after drying the g-C_{3}N_{4} dispersion in MilliQ water for 8 h at 80 °C) were used directly for FTIR measurements.

X-ray diffraction (XRD) was performed using the ARL X’tra X-ray diffractometer operating at 40 kV and 45 mA, with Cu Kα radiation. The XRD patterns were recorded using a radiation wavelength of 1.54 Å at a scan rate of 0.065° 2θ/s in the 2θ range of 10–80°. As in the case of FTIR analysis, dried samples (both foam and g-C_{3}N_{4} powder) were used directly for this characterization.

X-ray photoelectron spectroscopy (XPS) was carried out using a PHI 5000 versa probe III scanning XPS microprobe. The survey scan on the g-C_{3}N_{4} powder, to evaluate the overall composition, was carried out in the range of 0–1250 eV with a step size of 1 eV. The chemical state of each element within the compound was analyzed through a selected region narrow scan with a step size of 0.1 eV, and the valence band (VB) characterization was done at a 0.025 eV step size.

The UV–vis diffuse reflectance spectra of powder g-C_{3}N_{4} or nanocomposite g-C_{3}N_{4}−CNF foam were measured using a UV–vis spectrophotometer (Shimadzu UV 2550) arrayed with an integrating sphere, ISR-2000, assembly. Here, BaSO_{4} was used as a standard reference. For determining the optical properties of powder g-C_{3}N_{4}, it was dry-pressed into a disc shape prior to measurement. In case of nanocomposite foams, the resultant foam was cut into a disc shape prior to UV–vis
diffuse reflectance measurement. The absorbance ($A(R)$) was calculated from the diffuse reflectance ($R$), using the Kubelka–Munk model.

The total transmission spectrum of the CNF-based foams in the wet and dry states was measured using the same UV–vis spectrophotometer assembly with the integrating sphere module. The wet foams were prepared by wetting the dry CNF foams with MilliQ water and then measuring the transmission spectra.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02872.

Photograph of the illumination device; TEM micrographs; XPS, XRD, and FTIR results of the photocatalyst and foams; the photolytic study of RbB, and the photodegradation of the dye over g-C$_3$N$_4$ powder under magnetic agitation (PDF)

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**Notes**

The authors declare no competing financial interest.

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