Biogenic Synthesis of Graphitic Carbon Nitride for Photocatalytic Degradation of Organic Dyes

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**ABSTRACT:** A simple approach of template growth of graphitic-carbon nitride (g-CN), a polymeric unit consisting of C, N, O, and H elements derived from extracts of green plant Aloe vera, which are rich in several chemical constituents, has been successfully experimented in this work. Comparing several other methods used for synthesizing g-CN involving a large amount of toxic components, here, we propose the simplest route economically and environmentally highly viable for near future. Green plants are highly rich in natural carbon and nitrogen compounds, such as acemannan, glucose, aloin, protein, etc. Way before g-CN research, many carbon-based materials have been synthesized for multifunctional properties, but g-CN has much benefit over them due to the presence of elements such as C, N, O, and H, thus making it electron-rich. Multifunctional properties of graphitic-carbon nitride interface bonding as a supercapacitor or as a metal-free catalyst thus help degrade dyes. Violet-blue broad band emission was even noticed when excited at 240 nm via C−C bonding (π−π* transition) in the absorption band with an extinction coefficient of ∼10^4 M^-1 cm^-1. With our research, we want to pave new ways of synthesizing such materials present in our nature in a biological form, which can protect our environment, thus causing less harm to mankind.

1. INTRODUCTION

An insatiable demand for energy by humans has to be soon satisfied by replacing it with other ways of harvesting energy. Problems related to the shortage of energy and environmental decay are paving way for considering strategies to utilize solar energy resources efficiently and effectively. In the last few decades, several inorganic materials have been catalytic material for dye degradation and hydrogen production from water under light irradiation have been synthesized using various techniques. Such materials are metal species used for energy conversion produced chemically. Like TiO₂-based materials for photocatalysts, which have been modified by incorporating several other materials such as gold and carbon nitride, which increase the surface area, leading to an increase in adsorption due to enhanced active sites on the surface of the TiO₂. For devising metal-free materials with such applications, attention was made toward graphitic carbon nitride, a new catalyst that is metal-free with a suitable band gap for the wide optical regime, having unique optical, electronic, photocatalytic, and other properties. Graphitic carbon nitride is a polymeric semiconductor mainly composed of C, O, and N, which is generally environmentally friendly and, due to covalent C−N bonds, is highly stable both thermally (up to 600 °C) and chemically. Several investigations have been done from nonporous to mesoporous and 2D- to 1D-type graphitic carbon nitride that can help increase and modulate the photocatalytic properties. Unfortunately, as-prepared graphitic carbon nitride has low photocatalytic efficiency due to a low surface area and low e^−−h^+ carrier generation when light is irradiated upon it. To overcome this issue, several methods were developed to design the nanoarchitecture of bare graphitic carbon nitride with soft and hard template approaches, functionalizing them at an atomic level and modifying them electronically at energy levels. One way to overcome these issues is novel biosynthetic routes that are explored using green plant extracts that are even environmentally friendly. In Table 1, we have compared the bioroute (using Aloe vera gel)-synthesized graphitic carbon nitride with the literature (research done in the last 2–3 years). These methods help in controlling the growth of crystal and its morphology. Aloe vera is a widely used plant for its medicinal value consisting of phytochemicals such as acemanan, aloin, protein, glucose, etc. Aloe vera and such other green plants have low cost and are easily available as a substitution to hazardous (toxic) chemicals.

Owing to the recent demands of 2D (two-dimensional) nanosheets due to its special optical, electrical, catalytic, and sensing properties, it has become an emerging field. Graphene is one of the well-known carbon sheets that have good chemical and thermal stability and good electronic properties and provide a larger surface area. It usually consists of an atomic-layer-thick planar sheet consisting of a sp²-bonded carbon layer. Analogous to graphene is graphene oxide having C−O moieties obtained by chemical treatment of graphite, either dissolving in water or other organic/inorganic solvents. The attachment of oxygen to carbon is via functional groups that are exhibited at the edge or basal planes of the...
These functional groups help in the interaction of other materials with graphene sheet by charge transfer-tuning its electronic, catalytic, and optical properties. In recent years, the study of graphene oxide-based nanomaterials has become popular, particularly in the field of electrochemical applications. Reducing graphitic carbon nitride to graphene oxide by simply washing it using organic solvents such as acetone was even demonstrated in our research. Here, we propose a facile method of biogenic synthesis by simply burning the Aloe vera extract using camphor (green fuel agent) in a vacuum condition. Thus, the obtained pristine powder was annealed at 600 °C in a vacuum furnace to remove excess amorphous carbon. This method is promisingly more effective in a large-scale for next-generation nanotechnology and materials revolution. Further, the powders were analyzed using XRD, FTIR, Raman, SEM, and TEM and then employed to study various properties.
2. RESULTS AND DISCUSSION

2.1. Model Reactions and Growth of Formation of Small g-C2N Template. As shown in Scheme 1a, Aloe vera leaves have unique technological and biological properties since our history of usage in cosmetics; wound/burn healing promoters; anti-inflammatory, antiprotozoal, and ultraviolet radiation protectors; and several others.\(^\text{11}\) Aloe vera gel contains various constituents such as glucose, protein, acemannan, amino acid, aloin, etc. having C, O, N, and H elements. It mainly contains two parts, flesh and gel; the inner gel can be taken out by simply peeling the outer surface and etching the gel inside the green leaves, releasing nectar having a major product: a gel dispersed in an ample amount of water (≥98 wt %) of a light green liquid. The nectar was then cleaned free from any outer flesh as we had to use only the gel as a medium in a way it forms a biotemplate of pristine g-C2N, as follows. So, the obtained gel was dried in air and burnt with camphor (Scheme 1b), which itself is a biofuel, in a vacuum furnace for 10 min at 250 °C. The powder formed as the end product (Scheme 1c) contained a large amount of amorphous soot such as carbon that was removed by annealing the sample at 600 °C for 2 h in a vacuum furnace. As shown in Scheme 1c, the pristine g-C2N is brownish in color, which soon turned blackish upon annealing at 600 °C, as shown in Scheme 1d. Let us not confuse this g-C2N with g-C3N4 as, here, two atoms of carbon bond to one nitrogen atom. Scheme 1e,f shows the polycrystalline reactions occurring where monomers having two functional groups (OCN and OH groups) form a chain-like network by a chemical reaction via successive bonding (van der Waals force exists between the graphitic layer and carbon nitride). This is akin to g-C2N network bonding of C and N elements via O and H elements, thus forming the scaffold of the whole structure, as shown in Scheme 1g,h, forming a template-like growth of carbon nitride over graphic sheets of carbon. A usual triazine-based pattern of g-C2N is shown in Scheme 1i, where a chain of a monomeric unit forms a bonded polymer via C, N, and H elements. At room temperature, graphitic carbon nitride is a layered structure material where van der Waals force acts on to hold the stacked layers of covalent C–N bonds. Thus, each layer is composed of tri-s-triazine units that are connected with polymeric amino groups. This tri-s-triazine ring kind of structure provides the polymer unit chemical stability in both alkaline and acidic media and high thermal stability up to 600 °C temperature in air.\(^\text{14}\) Scheme 1j shows how the bonds (van der Waals force) present between graphic sheets and carbon nitride weaken at 600 °C and break completely when annealed above it in Scheme 1k.

2.2. X-ray Diffraction and Phonons in Small g-C2N Template Nanostructures. g-C2N is preferentially grown in small template nanostructures of (131) facets exhibiting a modified XRD pattern of a well-known g-C3N cubic (c) crystal structure (Pu-3 space group\(^\text{28}\)). For example, a typical XRD pattern in Figure 1a,\(^\text{b}\) from as-burnt and annealed g-C2N at 600 °C for 2 h in vacuum has markedly tailored peak positions and intensities relative to those of bulk g-C2N prepared in a solid-state reaction.\(^\text{28}\) It contains a part of oxygen that bonds the graphitic layer to the carbon nitride nanostructure. A normalized value \(I_p = 100\) of a maximum peak intensity arises in the (131) peak at an interplanar spacing \(d_{131} = 0.3178 \text{ nm}\) instead of the (111) peak at 0.6224 nm in the bulk sample. Here, one prominent peak that is marked as (210) with an interplanar spacing \(d_{210} = 0.4244 \text{ nm}\) shows a cubic phase, which grows over amorphous graphite with a small increase in lattice parameters. A polymorphic (cubic to hexagonal phase) \(c \rightarrow h\) change occurs in a bared g-C2N on a surface layer upon release. In Table 2 are given \(d_{hkl}\) \(I_p\) and \((hkl)\) values in XRD peaks observed in the samples. The \(d_{hkl}\) values calculated by average lattice parameters \(a = 1.0205 \text{ nm}, b = 1.0514 \text{ nm}, \) and \(c = 1.1184 \text{ nm}\) reproduce the observed values within a deviation of ±0.0005 nm (under an error in the measured values) in the major peaks of the as-burnt sample. A template of graphitized C-sp² layer adapts its lattice parameters due to surface force exerted by the C–N functional groups so as it has a decreased lattice volume \(V' = 1.2501 \text{ nm}^3\) (density \(\rho' = 1.213 \text{ g-cm}^{-3}\)) for the annealed sample and lattice volume \(V = 1.1999 \text{ nm}^3\) (density \(\rho = 1.264 \text{ g-cm}^{-3}\)) for as-burnt g-C2N over a bulk value \(V_b = 1.2531 \text{ nm}^3\) (density \(\rho_b = 1.210 \text{ g-cm}^{-3}\)). Upon annealing, the as-burnt sample causes the graphitized layer to desorb off gradually, thus showing a decrease in the intensity of peaks (broadening occurs) due to surface C–N functional group reordering. Thus, a (220) peak in the as-burnt sample depresses upon heating the sample at 600 °C, as shown in Table 3.

The C–N moieties arrange itself via oxygen and hydrogen groups present at the surface of the graphitic carbon sheet. Some functional groups such as OH presented at \(3400 \text{ cm}^{-1}\) due to intermolecular H bonds could be easily removed by heating the samples at 100 °C before taking the IR spectra. In Figure 2a, the five phonon bands shown at ∼2360, 1715, 1615, 1438, and 1065 cm\(^{-1}\) have been assigned to C≡N stretching, C=O stretching, C≡C stretching, benzene ring, and C–N stretching vibrations.\(^\text{10,29,30}\) When g-C2N is annealed at 600 °C for 2 h, IR phonon bands in Figure 2b from 600–1800 cm\(^{-1}\) disappear while thinning g-C2N in a sample by removal of functional groups from the surface of template graphene. The band group assigned at 1428 cm\(^{-1}\) is a benzene-like carbon ring as it reproduces a 2D network over a graphitic carbon in a co-bonded surface layer. The IR bands of annealed samples can be well compared with those of carbon dots formed by washing the as-prepared sample, as shown in Figure 2c, which connotes the clear picture of assignments (functional groups) to each band present.

The phonons of wide group C≡C stretching are seen in Figure 3 in the Raman spectrum in the graphitic carbon nitride g-C2N where C-sp² is bonding coherently with a carbon nitride
group forming a template. As seen for a single D-band of 1329 cm$^{-1}$ known in graphene, two distinct overlapping bands are displaced one another at 1310 and 1415 cm$^{-1}$ in a group in the as-burnt g-C$_2$N sample (a bit shifted to 1350 and 1395 cm$^{-1}$ in the annealed sample), similarly in two major graphitized carbon bands assignments framed on C$_2$N facets (mostly likely (131) and (031), as seen in template growth of g-C$_2$N plates as in the HRTEM images. Similarly, Raman bands expand in the single-phonon band with a high-intensity G-band (of 1591 cm$^{-1}$ in graphene) with an average frequency of 1580 cm$^{-1}$ (a bit shifted to 1585 cm$^{-1}$ in the annealed sample) as a result of graphitized carbon template trying to oscillate coherently to the C–N functional groups bonded via oxygen. Further, the $I_D/I_G$ ratio has grown further from 0.80 for as-prepared g-C$_2$N to 0.85 in account of an induced local microstrain in the conjoint structure, as evident from a large $\gamma = 0.86\%$ value analyzed for the samples in terms of inhomogeneous broadening in the XRD peaks in Table 2. Even a core–shell nanostructure of C-Fe$_3$O$_4$ shows only a single G-band at $\sim$1590 cm$^{-1}$ when the shell thickness of the nanostructure is varied. The part of the graphitized template bonded to the carbon nitride functional group via oxygen tries to release and rebind upon annealing at 600°C, reducing the intensity of D and G phonon bands in a wide group with a shift to higher frequencies by smaller values. When the as-burnt g-C$_2$N is probed to measure at higher frequencies, the Raman phonon bands generated $D'$, 2D, and $G + D$ at 2387, 2616, and 2883 cm$^{-1}$, respectively.

To find out the chemical state of g-C$_2$N, we probed in to comprehend the details of XPS by analyzing the spectrum in

![Figure 2](https://example.com/figure2.png)

**Figure 2.** FTIR spectra of the (a) as-prepared and (b) annealed g-C$_2$N from Aloe vera gel at 600 °C for 2 h in air and (c) the spectra after washing (a) in acetone (inset).

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Raman spectra of the (a) as-prepared and (b) annealed g-C$_2$N using an Aloe vera gel.

Table 2. Interplanar Spacings ($d_{hkl}$) and Relative Intensities ($I_p$) in XRD Peaks Observed for As-Burnt and Annealed g-C$_2$N at 600 °C for 2 h in Air from an Aloe vera Gel

|          | $d_{hkl}$ (nm) | $I_p$ | $h$ | $k$ | $l$ | $d_{hkl}$ (nm) | $I_p$ | $h$ | $k$ | $l$ |
|----------|---------------|-------|-----|-----|-----|---------------|-------|-----|-----|-----|
| observed |               |       |     |     |     | observed      |       |     |     |     |
| 0.4249   | 0.4244        | 22    | 2   | 0   | 0   | 0.3944        | 40    | 2   | 2   | 0   |
| 0.3340   | 0.3344        | 49    | 0   | 3   | 1   | 0.3474        | 3471  | 4   | 0   | 1   |
| 0.3178   | 0.3178        | 100   | 1   | 3   | 1   | 0.3228        | 3228  | 100 | 1   | 3   |
| 0.3063   | 0.3063        | 39    | 2   | 2   | 2   | 0.3109        | 3109  | 88  | 2   | 2   |
| 0.2849   | 0.2851        | 13    | 1   | 3   | 2   | 0.2875        | 2870  | 13  | 3   | 1   |
| 0.2695   | 0.2696        | 9     | 1   | 0   | 4   | 0.2758        | 2753  | 9   | 0   | 4   |
| 0.2509   | 0.2513        | 5     | 3   | 0   | 3   | 0.2544        | 2549  | 12  | 3   | 0   |
| 0.2314   | 0.2317        | 10    | 1   | 4   | 2   | 0.2331        | 2335  | 18  | 4   | 1   |
| 0.2237   | 0.2237        | 44    | 3   | 3   | 2   | 0.2285        | 2285  | 72  | 3   | 3   |
| 0.2112   | 0.2116        | 22    | 3   | 1   | 4   | 0.2128        | 2130  | 21  | 3   | 1   |
| 0.2019   | 0.2018        | 5     | 1   | 2   | 5   | 0.1942        | 1944  | 23  | 5   | 2   |
| 0.1909   | 0.1909        | 11    | 2   | 2   | 5   | 0.1900        | 1901  | 22  | 2   | 2   |
| 0.1819   | 0.1816        | 4     | 3   | 4   | 3   | 0.1841        | 1842  | 28  | 4   | 3   |

The $d_{hkl}$ values are calculated according to the average lattice parameters given in Table 3. The $I_p$ values are normalized over a maximum value of 100.

Table 3. Lattice Parameters for g-C$_2$N of Small Crystallites

| g-C$_2$N | $a$ (nm) | $b$ (nm) | $c$ (nm) | $D$ (nm) | $V$ (nm$^3$) | $\rho$ (g·cm$^{-3}$) | $\varepsilon$ (%) |
|----------|----------|----------|----------|----------|-------------|----------------------|-----------------|
| as-prepared | 1.0205  | 1.0514  | 1.1184  | 12.5     | 1.1999      | 1.264                | 0.864           |
| 600 °C    | 1.0629  | 1.0682  | 1.1010  | 14.0     | 1.2501      | 1.213                | 0.447           |
| bulk      | 1.0781  | 1.0781  | 1.0781  | 15.8     | 1.2531      | 1.210                |                 |

The values are reported from JCPDS file 01-075-1341 in ref 28.
Figure 4. XPS spectra of the (a) as-prepared g-C$_2$N for (b) carbon, (c) oxygen, and (d) nitrogen elements.

Figure 4a. The quality and composition of samples are well shown through XPS spectra. The oxidation states of carbon, nitrogen, and oxygen elements in g-C$_2$N were obtained in Figure 4b–d. These XPS spectra were calibrated using the C1s peak at 284.6 eV. The existence of the carbon peak was attributed to the adsorption of the residue of organics present in the Aloe vera gel during the synthesis process. The carbon element in the g-C$_2$N sample gives two broad peaks at $\sim$287.6 (285.3), and 283.7 eV for C=O (2p$_{1/2}$), and C−C (marked with 2p$_{3/2}$). The asymmetric XPS of O1s shows that several oxygen moieties are present on the surface region; lattice oxygen centered at 529 and 530 eV is assigned for the OH$^-$ group, 532 eV for the O$_2^-$ group, and 533 eV for H$_2$O. The nitrogen N1s element present in g-C$_2$N shows one band assigned to C−N−C group centered at 398 eV and another at 400 eV assigned to the N−H group.$^7,20$

The local g-C$_2$N microstructure is refined, thereby releasing the template graphitized carbon with embedded carbon nitride nanodots bonded via functional groups. In Figure 5a,b, FESEM images show how tiny nanodots as small as 10−50 nm embed the surface of the graphitized carbon layer, forming a template. Thus, embedding as a "second-level hierarchical structure" as a composite template with a thickness of 15−20 nm. Figure 5c displays the plate-like sheets uniformly separated when seen in a microscale range of FESEM. When this image was magnified as in Figure 5d, it clearly shows the embedded nanodots on the surface layer bonding via functional groups to the graphitized carbon sheets. As soon this graphitized carbon layer is heated or washed with organic solvents (acetone), it etches out, leaving nanodots of the carbon with templates as rectangular prisms/plates (w = 20−40 nm width and $\theta$ = 10−20 nm depth), which contain a pure carbon layer that is displayed as a bright outline with a thickness of 10−20 nm, as seen in the FESEM images in Figure 5d. The stage of template growth of pure g-C$_2$N nanostructures has a better stability in a rigid C-sp$^2$ template layer bonded via C−N−O bonds in a regular two-dimensional network. Such g-C$_2$N cross-link through C−N−O bonds as a second-level hierarchical structure in a small nanotemplate structure, as seen in FESEM images in Figure 5. Similarly, HRTEM images in Figure 6a–d show a close view of template plates of graphitized carbon bonded to surface carbon
nitride nanodots via functional groups of C−O entities, with a magnified region in inset of Figure 6a. Figure 6b,c displays the carbon plate-embedding nanodots of g-C\textsubscript{2}N\textsubscript{0} of 20−55 nm in the dispersed microstructure. Exfoliated graphitized plates in the form of films (150−250 nm wide and 300−600 nm long) are seen in the lattice image of HRTEM as in Figure 6a,b, which looks transparent with a few nanometer thickness. Figure 6a shows the layers of graphite sheets more in region A (darker) and less in region B (brighter) similarly in Figure 6b, which exhibits thin sheets of graphite-like carbon grafted with small carbon nitride crystallites marked as A and B on carbon sheet C, which has a \(d\)-spacing of 0.3344 nm for the (343) crystallographic plane (fringe formed due to interference of light refracted from carbon nitride lattice and graphite layers). Thus, from the literature, O\textsuperscript{2−} inclusion as in a graphitized C−O network markedly gets stretched to over a \(d\)-spacing of 0.3356 nm for the (002) plane in the pure graphite.\textsuperscript{33,34} A C−sp\textsuperscript{2} graphitic network thus expands via co-bonding with N\textsuperscript{2−} and O\textsuperscript{2−} on carbon plates, which adapts concurrently as foresaid using Raman and FTIR bands in softer phonons. Figure 6c shows the carbon nitride crystallites of sizes 20−50 nm bonding to the graphite layered sheets of carbon. Figure 6d shows the lattice image of g-CN where a boundary separates the amorphous graphite sheet with carbon nitride crystallites with a \(d\)-spacing of 0.1816 nm of the (343) crystallographic plane. Some larger lattice entities found in FESEM images become opaque, which are not easy to be seen in HRTEM images. Figure 6e,f shows the SAED pattern of graphitic carbon nitride (small g-C\textsubscript{2}N plates/prisms (\(w = 10−20\) nm)) having concentric rings, indicating that the carbon nitride particles are well dispersed and bonded in a polycrystalline form. It clearly exhibits from the pattern of (332) and (343) arrays with spacing values of \(d\textsubscript{332} = 0.2240\) nm and \(d\textsubscript{343} = 0.1816\) nm, stacking \(\perp\) to a [131] zone axis, as studied using an e− beam incident facing its (303) facet.

### 2.3. Optical Properties of Small g-C\textsubscript{2}N Template Nanostructures

Figure 7. Electronic absorption spectra and Tauc plots for (a) as-prepared and (b) annealed g-C\textsubscript{2}N at 600 °C.

...plots of the as-prepared and annealed g-C\textsubscript{2}N at 600 °C, respectively, to manifest the band gap \(E_g\). Here, \(\alpha h\nu\) versus energy \(h\nu\) in eV was plotted, where \(\alpha\) is the normalized value of \(S\), \(h\) is Planck’s constant \((6.626 \times 10^{-34}\) J\(\cdot\)s), and \(\nu\) is the frequency of light. The following values of the exponent \(r\) denote the nature of the transition:\textsuperscript{35−37} \(r = 1/2\) for direct allowed transitions; \(r = 3/2\) for direct forbidden transitions; \(r = 2\) for indirect allowed transitions; \(r = 3\) for indirect forbidden transitions. The outcome plot of the analysis shows a distinct linear region that specifies the onset of absorption. Thus, we need to extrapolate the linear regime to the abscissa \(h\nu\) by reproducing the energy of the optical band gap of the g-C\textsubscript{2}N nanostructures for all its samples. The band gap of as-prepared g-C\textsubscript{2}N comes to be \(\approx 3.9\) eV, which increases to 4.12 eV upon annealing at 600 °C, thus showing a quantum confinement and blue-shift. The value \(\varepsilon\) varies in relation to absorbance, while the C value controls the solute−solvent and solvent−solvent interactions. The size and morphology of structures in the solute along with the solvent determine the interactions to the C value. For example, in the extinction coefficient of the sample (as-prepared g-C\textsubscript{2}N (molecular weight = 38), the concentration C is 0.1 mg in 10 mL, \(l\) (optical length of quartz cell) is 10 mm =...
1 cm, and absorbance $A = 1.31$ at 263 nm is calculated below, which comes to be $\sim 5 \times 10^3 \text{M}^{-1} \text{L cm}^{-1}$, while this extinction coefficient for g-C$_2$N annealed at 600 °C decreases to lower values of spin-allowed transitions of $\sim 6.9 \times 10^2 \text{M}^{-1} \text{L cm}^{-1}$ with a hike in the band gap.

$$
\varepsilon = A/Cl
$$

$$
= 1.31/((0.1/10)*1) \text{ (g/L)*cm)
$$

$$
= 1.31/((0.01/38)*1) \text{ (mol/L)*cm)
$$

$$
= 5 \times 10^3 \text{M}^{-1} \text{L cm}^{-1}
$$

It is interesting to learn that the synthesized as-prepared and annealed (at 600 °C) g-C$_2$N samples extend the strong emission in ultraviolet as well as along the visible regions. Unusually, the bands were not observed with significant intensity in the absorption spectra. For example, Figure 8a,b compares light excitation and emission spectra measured for the as-prepared, annealed, and washed samples of g-C$_2$N using a pulse xenon lamp as a light source. The present emission spectra were measured by exciting the samples at 240 nm from a xenon lamp for g-C$_2$N before (black and blue lines) and after (red line) burning out a residual carbon.

![Figure 8](image)

**Figure 8.** (a) Excitation spectra corresponding to $\lambda_{em} = 512 \text{ nm}$ and (b) emission spectra recorded after exciting the samples at 240 nm from a xenon lamp for g-C$_2$N before (black and blue lines) and after (red line) burning out a residual carbon.

A methylene blue dye with a concentration of $2.6 \times 10^{-6} \text{ M}$ was well mixed with g-C$_2$N photocatalysts of $\sim 1.6 \text{ mg}$ with a final concentration of $\sim 5 \times 10^{-5} \text{ M}$. This material acts as a sensitizer for the light irradiated to stimulate the whole mechanism due to its electronic structure that is formed by a completely/partially filled valence band (VB) and a vacant conduction band (CB). One of the best methods that can be used for applications such as degradation of hazardous pollutants of waste produced from industries, production of hydrogen gas, purification of air, and antibacterial activity is the photocatalytic mechanism. When light is irradiated (photons) on the surface-graphitized g-C$_2$N hybrid catalyst, if this energy is equivalent to or more than band gap energy, then valence band electrons are excited to the conduction band, causing hole formation in the valence band. These holes could oxidize donor molecules and react with water molecules to form hydroxyl ions. The electrons present in the conduction band could actively react with dissolved oxygen ions to form superoxide ions, leading to redox reactions. Now, the electrons and holes present in CB and VB can go under the oxidation and reduction process with any species absorbed on the surface of the catalyst. The degradation of methylene blue dye without a catalyst in the presence of UV and visible light shows a marked degradation of $\sim 12$–$13\%$, as shown in Figure 9a. Then, the performance of the photocatalytic degradation of g-C$_2$N powders (as-prepared and annealed at 600 °C) was studied by considering methylene blue (MB) as the target dye. Photocatalytic studies were done under UV (24 W; intensity, 400 lux; $\lambda < 400 \text{ nm}$) and visible light bulb irradiation at the sample surface under stirring condition. In Figure 9b, as the UV and visible light irradiating time $t$ reaches 60 min, the methylene blue dye in the as-prepared sample decays rapidly until a minimum $C/C_0 \cong 100\%$. A nearly two times larger dye lasts in the annealed sample under both UV and visible light irradiation, decaying much slowly at $\sim 60\%$. The graphitic surface layer in the as-prepared sample greatly favors its catalytic feature, which breaks down at $600 °C$ (van der Waals force weakens between the graphitic layer and carbon nitride groups), causing slow degradation of dye. A reasonably larger degradation rate constant $k = 0.015 \text{ min}^{-1}$ (against 0.003 min$^{-1}$ in the annealed graphitic carbon nitride) thus prolongs in a pseudo-first-order reaction in a nonlinear regression of $\ln(C/C_0) = -kt$ over $t$ in Figure 9c in this example. Other
samples involve much lower $k$-values as determined, assuming the linear plots in Figure 9c.

3. CONCLUSIONS

A biogenic template of graphitized carbon species bonded to surface carbon nitride via functional groups dispersed uniformly in a green Aloe vera gel has been explored to synthesize stable g-C$_2$N template hybrid nanostructure reactions in its small tissues at moderate temperature, a facile biogenic synthesis. An Aloe vera-obtained green gel was dried in air, then finely dispersed and pulverized in camphor, and burnt in a vacuum furnace at 250 °C for 10 min. The rate of production was obtained around 0.33%. Finally, the so-obtained 20 mg powder was pulverized using mortar and pestle to uniformly finely divide the powder. A hybrid-phase g-C$_2$N emerged after the organics had been burnt out in a self-propagating spontaneous combustion in camphor (a fuel). It was heated at 600 °C in a vacuum furnace for 2 h to remove impurities of carbon (soot) obtained while burning with camphor. We even derived graphene oxide by simply washing as-prepared g-C$_2$N in acetone, which certainly etches out the outer surface of g-C$_2$N; the only ones remaining were graphene-layered sheets with functional groups on it, which are also called as C–O moieties.

4. EXPERIMENTAL SECTION

4.1. Synthesis of Biogenic g-CN and C–O Moieties Template Growth. Regarding the biogenic template growth of graphitic carbon nitride using the self-combustion route of small tissues in a green Aloe vera gel, here, carbon nitride bonded to surface-layered graphitic sheets was synthesized as follows. A fresh gel of around 6 g was extracted from the inner parts of green leaves of an Aloe vera plant (from a garden at IIT-Kharagpur), and any immiscible fleshes were washed away by using a specific filter (made of steel) with 50–100 μm pores. It was then dried and burnt in a vacuum furnace using camphor as a fuel agent at 250 °C for 10 min. The rate of production was obtained around 0.33%. Finally, the so-obtained 20 mg powder was pulverized using mortar and pestle to uniformly finely divide the powder. A hybrid-phase g-C$_2$N emerged after the organics had been burnt out in a self-propagating spontaneous combustion in camphor (a fuel). It was heated at 600 °C in a vacuum furnace for 2 h to remove impurities of carbon (soot) obtained while burning with camphor. We even derived graphene oxide by simply washing as-prepared g-C$_2$N in acetone, which certainly etches out the outer surface of g-C$_2$N; the only ones remaining were graphene-layered sheets with functional groups on it, which are also called as C–O moieties.

4.2. Measurements of the g-C$_2$N Structure and Properties. The XRD patterns were scanned over 20° to 80° of diffraction angle 2θ by using an X-ray diffractometer (X’PertPro PANalytical), with an X-ray beam of Cu Kα of $\lambda = 0.15410$ nm in wavelength, which delineate a semi-crystalline g-C$_2$N of as-burnt and annealed powders. The data were collected slowly at small 2θ intervals under 0.01° in resolving the weak intensity peaks. Size, morphology, and surface topology in the g-C$_2$N samples were studied with field-emission scanning electron microscopy (FESEM) using a ZEISS EVO 60 FESEM at 5–20 kV acceleration voltages. High-resolution transmission electron microscopic (HRTEM) images, selected-area electron diffraction (SAED), and lattice images of the samples mounted on a carbon-coated copper mesh.
grid were studied using an analytical TEM of FEI Tecnai G2 20S-TWIN operating at 200 kV. The C-sp², as a breed of a 2D network (amorphous) on coherent g-C₃N₄ facets, exhibits multiple D- and G-bands in Raman spectra over 1200 to 1800 cm⁻¹ as studied by exciting the samples at 514.5 nm by an Ar⁺ ion laser. Binding energies (E_B) in the XPS bands were calibrated with the adventitious C₁s at 284.6 eV. The absorbance of particular λ values in such transitions. The Beer–Lambert relation describes A of a sample of a specific concentration through which a continuous beam of light is allowed to travel. In a logarithmic scale used in the absorption spectrophotometer, the realistic value l is the optical length that is 10 mm, and c is the concentration of the solution (0.1 mg of sample in 10 mL of distilled water) obtained from A = εC₁l, where ε is the extinction coefficient, also known as absorption coefficient with a unit M⁻¹ · L · cm⁻¹. Photocatalytic studies were done under UV (24 W; intensity, 400 lux; λ < 400 nm) and visible irradiation at the sample surface under stirring condition. Aqueous solutions of methylene blue with a concentration 5 × 10⁻⁵ M with a photocatalyst loading of 1 g/L were taken. The dispersions were equilibrated for dye adsorption on the photocatalyst surface for 30 min. During the degradation period, the dispersions were collected at regular intervals of 30 min in the case of UV light irradiation. To note down the extent of the degradation, the samples were centrifuged at 6000 rpm for 10 min to collect the so-far degraded dye solution. Using the PerkinElmer spectrophotometer, powder dispersed in distilled water (0.01 g L⁻¹) was used to measure its light absorption spectrum (200–850 nm) relative to distilled water as a reference, using an Edinburgh FL spectrometer by a xenon lamp 900.

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**ASSOCIATED CONTENT**

Supporting Information
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XRD pattern, extinction coefficient, and band gap analysis of carbon extracted from washing of as-prepared graphic carbon nitride and BET analysis of the g-C₃N₄ sample (PDF)

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**Author Contributions**
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**Notes**
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