Photocatalysis

Copyrolysed C₃N₄-Ag/ZnO Ternary Heterostructure Systems for Enhanced Adsorption and Photocatalytic Degradation of Tetracycline


Abstract: The graphitic carbon nitride (g-C₃N₄) Ag/ZnO (CAZ) nanocomposite heterostructure was prepared by the copyrolysis of a precursor mixture containing melamine and nitrates of zinc and silver. This one-pot synthetic approach facilitated the incorporation of fine dispersions of Ag and ZnO on C₃N₄ sheets. The CAZ sample thus prepared exhibited higher adsorption capacity and enhanced sunlight-induced photocatalytic activity towards tetracycline degradation when compared with compositions of g-C₃N₄-Ag, g-C₃N₄-ZnO, ZnO-Ag, and g-C₃N₄. Incorporation of ZnO helped to utilize the UV component of sunlight, whereas ultrafine dispersions of Ag on the surface of the composite created intimate interfaces, facilitating the direct migration of photogenerated electrons to the Ag surface for an efficient separation of photogenerated electron-hole pairs. The present work exemplifies a simple and convenient synthetic protocol for processing the tricomponent heterostructured system of g-C₃N₄-Ag/ZnO for the effective degradation of pollutants such as tetracycline.

Introduction

The growing awareness of environmental protection and the need for energy conservation has stimulated researchers to undertake intensive studies on green technologies for hydrogen production from water splitting and photocatalytic degradation of organic pollutants.[1–3] Visible-light active semiconductor nanoparticles are one of the most important materials exploited to extend the efficient use of solar energy for environmental and energy applications. Graphitic carbon nitride, generally known as g-C₃N₄, has been widely studied as a new metal-free visible-light photocatalyst for potential applications in energy storage, purification of contaminated water, solar cells, sensors, and CO₂ capture.[4–7] It has a medium band gap of about 2.7 eV and suitable tuning of the degree of condensation with distinctive heptazine rings could turn them into a stable visible-light-active photocatalyst.[8,9] However, low levels of visible-light utilization efficiency and fast recombination of photogenerated electron-hole pairs in pure g-C₃N₄ hinder the widespread practical application of this material.[10,11] To address these issues, multiple strategies have been employed to enhance the photocatalytic performance of g-C₃N₄; such approaches include the construction of mesoporous structures, doping with metal or nonmetal species, surface modification, and sensitizing with organic dyes and quantum dots.[10,12–14] Of the diverse range of attempts at modification, heterostructure development with compatible semiconductors has led to unprecedented opportunities to favorably explore the photocatalytic activity of g-C₃N₄.[5,15–18]

Heterostructure formation with g-C₃N₄ can be achieved with low- and wide-bandgap photocatalysts that have compatible energy levels to reduce the recombination of photogenerated excitons. This has led to the development of g-C₃N₄ based binary composites that display enhanced visible-light activity.[19–21] However, this modification was not sufficient to avoid the rapid recombination of charge carriers, and ternary systems incorporating noble metallic nanoparticles such as Ag, Au, Pt, and Pd thus emerged into prominence.[14,22–25] Noble-metal-modified g-C₃N₄ has been shown to exhibit improved photocatalytic activity. The inclusion of noble metals on the semiconductor surface facilitates surface plasmon resonance (SPR).[26] The collective coherent oscillation of surface electrons make noble-metal nanoparticles (NPs) potential candidates for harvesting both UV and visible light.[27]

To our knowledge, there is only one report on the synthesis of Ag and ZnO nanoparticles incorporated into a g-C₃N₄ system.[28] Adhikari et al. synthesized a Ag-ZnO/g-C₃N₄ nanocomposite by utilizing hydrothermal synthesis of Ag and ZnO from...
an aqueous precursor mix of zinc and silver nitrates onto g-C₃N₄, utilizing commercially available g-C₃N₄ particles. Although g-C₃N₄ is a visibly active photocatalyst and incorporation of Ag nanoparticles is expected to enhance its visible light activity, the authors chose to evaluate the photocatalytic efficiency of the resulting composite by methylene blue degradation under UV light. Hence, to explore the beneficial effects of this system under sunlight irradiation and to circumvent any limitations imposed by the hydrothermal procedure, we propose herein a one-pot copyrolysis approach for the synthesis of this ternary composite g-C₃N₄-Ag/ZnO (CAZ) from melamine, silver nitrate, and zinc nitrate. The simultaneous decomposition of the precursors leading to the formation of ZnO, Ag, and C₃N₄ has been shown to result in a uniform distribution of ZnO and Ag nanoparticles on the g-C₃N₄ sheets in this work. The adsorption of tetracycline (TC) followed by its photocatalytic degradation has been evaluated and compared with combinations of g-C₃N₄-Ag, g-C₃N₄-ZnO, ZnO-Ag, and g-C₃N₄. The TC adsorption on the surface of CAZ has been further analyzed by using different kinetics and equilibrium adsorption isotherm models. The "as prepared" g-C₃N₄-Ag/ZnO (CAZ) sample exhibited higher adsorption capacity and enhanced sunlight activity compared with both the single and binary systems.

Results and Discussion

Structure and Morphology

The structural and morphological developments of the as-prepared samples were evaluated by using a range of characterization tools. The XRD patterns of the as-prepared g-C₃N₄-Ag/ZnO, g-C₃N₄-Ag, g-C₃N₄-ZnO, ZnO-Ag, and g-C₃N₄ samples are shown in Figure 1. The XRD patterns showed two distinct diffraction peaks of pure g-C₃N₄ at 27.4° and 13.1°.[1] These peaks could be assigned to (002) and (100) diffraction planes (JCPDS 87–1526), corresponding to interplanar stacking of aromatic systems and interlayer structural packing, respectively.[29] Compared with pure g-C₃N₄, the g-C₃N₄-Ag/ZnO, g-C₃N₄-Ag, and g-C₃N₄-ZnO samples exhibited additional peaks at 31.9°, 34.5°, 36.4°, 47.7°, 56.7°, 62.9°, 66.5°, and 69.2° corresponding to (100), (002), (101), (102), (110), (103), (200), (112), and (201) crystalline planes of ZnO (JCPDS 36–1451) and peaks at 37.8°, 44°, and 64° corresponding to (111), (200), and (220) plane of Ag metal (JCPDS 04–0783).

The TEM images of g-C₃N₄ and g-C₃N₄-Ag/ZnO (CAZ) nano-composite are shown in Figure 2; g-C₃N₄ exhibited a layered structure of thin sheets with irregular morphology (Figure 2, a).[30] Images of the CAZ composite revealed oval ZnO particles with average size of 20–50 nm, and spherical nanoparticles of Ag having sizes below 5 nm are well incorporated on the surface of g-C₃N₄ sheets forming a ternary composite (Figure 2, b and c). HRTEM images of CAZ composite (Figure 2, d) clearly revealed the lattice of ZnO and Ag. This is further substantiated by the selected area electron diffraction (SAED) pattern (Figure 2, e). The EDAX of the CAZ composite shown in Figure 2 (f) indicated the presence of all the elements supported by the SEM EDS mapping provided in Figure S1.

The optical properties of the prepared composite photocatalysts, measured by UV/Vis diffuse reflectance spectra (DRS), are presented in Figure 3. The main absorption edge of ZnO-Ag occurred at 390 nm and was confined to the UV region, whereas the absorption edge of pure g-C₃N₄ was seen at 450 nm, indicating visible-light absorption. After loading ZnO on g-C₃N₄ sheets, the absorption intensity was enhanced in the visible-light region. Similarly, Ag-loaded g-C₃N₄ and g-C₃N₄-Ag/ZnO (CAZ) composites showed enhanced visible-light absorption. The significant enhancements of optical absorption in the visible-light region can be attributed to the synergistic effect of ZnO with C₃N₄ and plasmonic resonance of Ag nanoparticles.[24,31] Given that the amount of silver in the ZnO-Ag binary composition is much less (below 0.5 wt.-%), the intensity of the SPR is not readily visible in the multi plot. The expanded image in the inset suggests a very limited SPR effect on ZnO-Ag.

The N₂ adsorption–desorption isotherms of the samples are shown in Figure 4. The adsorption isotherms are typical of Type IIb (BDDT Classification) behavior and indicated adsorpt-
The ZnO-Ag composite showed the lowest surface area value of <1 m²/g, whereas the surface area of pure g-C₃N₄ was approximately 8 m²/g. On incorporation of Ag and ZnO, the surface area of ternary C₃N₄-Ag-ZnO (CAZ) composite increased to twice that of the pure g-C₃N₄ sheets. The surface area analysis of the samples is summarized in Table 1. Incorporation of finer particulates during the synthesis can presumably impart exfoliation of bulk C₃N₄ sheets, leading to enhanced surface area and pore volume for the ternary composites.

Table 1. Surface area analysis of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET SA [m²/g]</th>
<th>Pore volume [cm³/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-C₃N₄-Ag/ZnO</td>
<td>18.5</td>
<td>0.1086</td>
</tr>
<tr>
<td>g-C₃N₄-ZnO</td>
<td>11.7</td>
<td>0.0738</td>
</tr>
<tr>
<td>g-C₃N₄-Ag</td>
<td>11.3</td>
<td>0.0804</td>
</tr>
<tr>
<td>ZnO-Ag</td>
<td>0.087</td>
<td>0.0003</td>
</tr>
<tr>
<td>g-C₃N₄</td>
<td>7.7</td>
<td>0.0123</td>
</tr>
</tbody>
</table>

The surface elemental composition of the composite CAZ was investigated by using XPS. The XPS survey spectrum of g-C₃N₄-Ag/ZnO presented in Figure 6 (a) indicated the presence of C, N, Zn, Ag, and O elements. The high-resolution C 1s spectrum of the g-C₃N₄-Ag/ZnO sample provided in Figure 6 (b) illustrated that the sample had four C 1s peaks sited at 284.3, 286.2, 288.1, and 289.5 eV. The peaks centered at 284.3 eV were ascribed to C=C coordination and the peaks at 286.2 eV were attributed to C=N sp² bonds. The peak at 288.1 eV was assigned to N–C=N species, whereas those at 289.5 eV were ascribed to the C–O bonds due to the oxygen absorbed in the surface.[34,35] The high-resolution spectrum of N 1s (Figure 6, c) showed three peaks at 398.3, 400.8, and 403.0 eV, corresponding, respectively, to the C–N sp³ bonds, C=N sp² bonds and to the interaction of g-C₃N₄ sheets with ZnO.[36,37] The high-resolution spectrum of O 1s (Figure 6, d) showed two distinct peaks at 531.6 and 533.4 eV. These peaks at 531.6 eV were assigned to O²⁻ ions in the Zn–O bonds, whereas the peak at 533.4 eV was ascribed to the chemisorbed oxygen due to hydroxyl radicals.[38] The high-resolution spectrum of Zn 2p (Figure 6, e) showed two distinct peaks at 1024.22 and 1047.72 eV, attributed to Zn 2pₓᵧ and Zn 2p₁/₂ of the CAZ composite. The conventional peaks of pure ZnO were observed at 1022.0 and 1045.0 eV, as reported. The shift in the peaks of Zn in the composite prepared could be attributed to the formation of N–Zn bonds.[37] The chemical shift observed is presumably due to the change in the g-C₃N₄ sheets after incorporation of ZnO.[38] In the ternary composite, the prepared amount of silver was very low (< 0.2 wt.-%) and, therefore, the high-resolution spectrum of Ag (Figure 6, f) contained no sharp peaks. The peaks at 368.3 and 374.2 eV were ascribed to Ag 3d₃/₂ and Ag 3d₅/₂, respectively.[39]
TC Adsorption of g-C₃N₄-Ag/ZnO Nanocomposite

The adsorption capacity of CAZ nanocomposite was evaluated by estimating the amount of tetracycline adsorbed from solutions of various concentrations. The adsorption property of the composite was evaluated for 2 h, although the adsorption-desorption equilibrium was attained within 60 min. The plot of the same is provided in Figure S2. The data was utilized to calculate the amount of TC adsorbed on the surface at equilibrium per unit mass of adsorbent; i.e., \( q_e \) (mg g\(^{-1}\)). The variation in \( q_e \) as a function of different TC concentrations is presented in Figure 7. As the initial TC concentration was increased, the value of \( q_e \) also increased. The \( q_e \) reached a maximum value \([q_m \text{ (mg g}^{-1}])\) and then decreased with further increase in the concentration of TC. The decrease in the \( q_e \) value can be attributed to the saturation of adsorption sites on the surface of the adsorbent. The highest adsorption capacity obtained was 44 mg g\(^{-1}\), corresponding to 100 μM TC. The adsorption property of CAZ nanocomposite can be attributed to the strong π–π interaction between the aromatic rings of TC and the heptazine rings of CAZ.\(^{[40,41]}\) Moreover, higher surface area values and enhanced pore volume of the composite should also help to increase the adsorption of tetracycline.

The adsorption data thus obtained for 100 μM TC was analyzed by using different adsorption models. The adsorption of TC by CAZ followed the Freundlich isotherm model (Figure 8, a) in which the linear form of the Freundlich isotherm model can be represented as Equation (1).\(^{[42]}\)

\[
\ln q_e = (1/n) \ln C_e + \ln K_f
\]

where \( K_f \) (mg\(^{1-1/n}\) g\(^{-1}\) L\(^{1/n}\)) is the Freundlich constant related to the Gibb’s free energy of adsorption and \( n \) (g L\(^{-1}\)) is another Freundlich constant related to the adsorption intensity. The Freundlich isotherm plot presented in Figure 8 (a) provided the adsorption of TC on the surface of the g-C₃N₄-Ag/ZnO nanocomposite. The Freundlich isotherm describes the nonideal and reversible adsorption meant for nonuniform distribution of adsorption over the heterogeneous surface. The slope value is a measure of adsorption intensity or surface heterogeneity and a value closer to zero implies more heterogeneity.\(^{[43]}\)

The rate at which the TC is adsorbed from an aqueous solution on the surface of the g-C₃N₄-Ag/ZnO nanocomposite was
analyzed by using different kinetics. The TC adsorption on the surface of the g-C3N4-Ag/ZnO nanocomposite followed pseudo-second-order kinetics. The linear form of this kinetics model is expressed as Equation (2).[44]

\[
t/q_t = (1/q_e) \ t + 1/(K_2 \times q_e^2)
\]

Where \( K_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is the pseudo-second-order rate constant and \( q_t \) is the amount of TC adsorbed on the surface per unit mass of adsorbent (mg g\(^{-1}\)) at contact time \( t \).[34] Figure 8 (b) shows a typical pseudo-second-order kinetics plot for the adsorption of TC on the surface of the composite prepared at 100 μM. The regression correlation coefficient \(< R^2>\) value is closest to 1, and the estimated \( q_e \) value using this model is comparable with the experimentally determined value of \( q_e \). Thus, it is verified that the adsorption of TC on the surface of g-C3N4-Ag/ZnO follows pseudo-second-order kinetics. Tables 2 and 3 summarize the details of Freundlich isotherm and pseudo-second-order kinetics.

Table 2. Summary of the parameters related to Freundlich isotherm.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Isotherm</th>
<th>( R^2 )</th>
<th>( 1/n )</th>
<th>( K_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 μM</td>
<td>Freundlich isotherm</td>
<td>0.995</td>
<td>0.759</td>
<td>0.725</td>
</tr>
</tbody>
</table>

Table 3. Summary of the parameters related to pseudo-second-order kinetics.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Kinetics</th>
<th>( R^2 )</th>
<th>( K_2 )</th>
<th>( q_e ) (calculated)</th>
<th>( q_e ) (experimental)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 μM</td>
<td>Pseudo-second-order</td>
<td>0.995</td>
<td>0.04</td>
<td>50</td>
<td>44</td>
</tr>
</tbody>
</table>

Other isotherm models with their fitting lines are presented below (Figure 9, a and b).

![Langmuir and DKR adsorption isotherms](image)

Figure 9. (a) Langmuir and (b) DKR adsorption isotherms.

The Langmuir isotherm model is given by Equation (3).[45]

\[
C_e/q_m = 1/q_m \times C_e + 1/q_m \times K_l
\]

Where \( q_m \) is the adsorption intensity and \( K_l \) is Langmuir constant.

The DKR model is given by Equation (4).[45]

\[
\ln q_e = \ln q_m - \beta \varepsilon^2
\]

\( \beta \) [mol\(^2\) J\(^{-2}\)] is constant related to adsorption energy and \( \varepsilon \) is Polanyi potential, given by Equation (5).

\[
\varepsilon = RT \ln [1 + 1/C_e]
\]

Where \( R \) (J mol\(^{-1}\) K\(^{-1}\)) is the gas constant and \( T \) (K) is the absolute temperature.

Thus, g-C3N4-Ag/ZnO (0.5 g L\(^{-1}\)) nanocomposite exhibited adsorption capacity \((q_m)\) of 44 mg g\(^{-1}\) at 100 μM TC following the pseudo-second-order kinetics and fitted the Freundlich isotherm model well.

**Adsorption in Dark and Photodegradation of TC**

To demonstrate the potential applicability of the prepared CAZ composites, adsorption and photocatalytic experiments were carried out under dark and sunlight irradiation, respectively. Figure 10 presents the adsorption cum photocatalytic activities of the as-prepared g-C3N4-Ag/ZnO, g-C3N4-Ag, g-C3N4-ZnO, ZnO-Ag, and g-C3N4 under sunlight irradiation.

![Adsorption cum photocatalytic activities of g-C3N4-Ag/ZnO, g-C3N4-Ag, g-C3N4-ZnO, ZnO-Ag, and g-C3N4 under sunlight irradiation](image)

Figure 10. Adsorption cum photocatalytic activities of 100 μM TC by using the as-prepared g-C3N4-Ag/ZnO, g-C3N4-Ag, g-C3N4-ZnO, ZnO-Ag, and g-C3N4 under sunlight irradiation.

The plot shows that for the adsorption process in the dark, the g-C3N4-Ag/ZnO composite exhibited the highest adsorption capacity of about 47 % for TC and, on 60 min of sunlight irradiation, the g-C3N4-Ag/ZnO composite degraded 80 % of TC. The other binary composites showed a close contention to the photocatalytic activity. ZnO-Ag, g-C3N4-Ag, and g-C3N4-ZnO degraded almost 60 % within 120 min of irradiation. The enhanced activity of the prepared composite can be ascribed to the synergistic effect of ZnO and SPR effect of Ag NPs. The incorporation of ZnO in the composite also helped to utilize the UV component of sunlight. The Ag NPs on the surface of the composite created intimate interfaces, which facilitated the direct migration of photoinduced electrons onto the Ag surface for an efficient separation of photogenerated electron-hole pairs. Thus, the prepared nanocomposite behaved as a bi-functional material with appreciable adsorption and sunlight-induced photocatalytic activity.
Recyclability tests were performed to ascertain the utility of the catalyst for practical applications. In the present study, four cyclic tests were performed using the CAZ photocatalyst; the data are presented in Figure 11.

The g-C3N4-Ag/ZnO (CAZ) photocatalyst showed very little loss (5%) of activity after four cycles, suggesting excellent stability of the photocatalyst. The XRD and FTIR patterns of samples recorded after the cyclic studies, presented in parts (a) and (b) of Figure 12, indicated no changes in phase and functional groups, respectively.

Active Species Trapping

The trapping experiments for the determination of active species formed during the photocatalytic reaction of g-C3N4-Ag/ZnO (CAZ) are presented in Figure 13. Different scavengers were employed to detect the ROS species. The addition of 10 mM isopropanol (IPA) as a quencher of hydroxyl radicals (OH·), 6 mM AgNO3 as a quencher of an electron, 6 mM benzoquinone (BQ) as a quencher of superoxide anions (O2·−), or 10 mM triethanolamine (TEA) as a quencher of holes, to the photocatalytic system and irradiation under sunlight[2] was investigated. The photocatalytic degradation of TC was not affected by the addition of IPA, whereas the degradation was quenched by the presence of BQ, TEA, and AgNO3. Therefore, it can be concluded that photogenerated holes, superoxide anions (O2·−), and electrons are the main active species of CAZ, for TC degradation under sunlight irradiation.

The mass-normalized PL spectra of g-C3N4, g-C3N4-Ag, g-C3N4-ZnO, and g-C3N4-Ag/ZnO (CAZ) composite are presented in Figure 14. Electron-hole recombination is analyzed in photoluminescence measurements and a lower PL intensity is an indication of the lower recombination of electron-hole pairs.[46] The main emission peak of g-C3N4 and g-C3N4-Ag/ZnO appeared at 454 nm and the fluorescence intensity of the latter was considerably lower compared with that of g-C3N4. This indicated a lower rate of recombination of photogenerated charge carriers in the prepared composite, contributing to the enhancement of photocatalytic efficiency (Figure 14).
Figure 14. PL spectra of g-C3N4, g-C3N4-Ag, g-C3N4-ZnO, and g-C3N4-Ag/ZnO samples.

Photocatalytic Mechanism

Based on the results of active species trapping experiments, a possible mechanism (Figure 15), illustrating the degradation pathway of TC using g-C3N4-Ag/ZnO (CAZ) was elucidated. As observed from the UV/Vis spectra presented in Figure 3, a significant enhancement of optical absorption in the visible region of g-C3N4-ZnO, g-C3N4-Ag, and g-C3N4-Ag/ZnO was observed. As reported by Zhang et al., combining the surface plasmon resonance effect of Ag with the excited semiconductors under irradiation could lead to a synergistic effect in plasmon-related photocatalytic processes.[47] However, on sunlight irradiation, the SPR excitation of Ag NPs will create electron-hole pairs that may transiently occupy the empty states of the Ag conduction band. On the other hand, sunlight irradiation will excite the electrons in the conduction bands of g-C3N4 and ZnO with simultaneous generation of holes in their VBs. These electrons on the CB of g-C3N4 (–1.09 eV) will migrate easily to the CB of ZnO (–0.31 eV), whereas Ag in the ternary composite acts as an electron bridge.[39,48] Moreover, a Schottky barrier formed at the interface of the ZnO and Ag NPs, could facilitate the movement of electrons from g-C3N4 to Ag NPs, which may act as an electron acceptor due to the larger electron capacity.[49] This electron-transfer pathway could improve the photogenerated charge carrier separation and accelerate the transportation process.

The photogenerated electrons that are transferred to ZnO and Ag react with O2 in the system and could reduce it into superoxide radical (O2·−) anion. This O2·− anion could then react with the TC molecule to produce nontoxic by-products. The holes that emerge from the VB of ZnO (3 eV) can directly engage with the TC molecules or can migrate to the VB of g-C3N4 (+1.57 eV). At the same time, the holes in the VB of g-C3N4 could react with the TC molecules directly, because the standard redox potential of OH*/H2O (+2.68 eV vs. SHE) and OH*/OH− (1.99 eV vs. SHE) is higher than the standard potential of holes.[39,50,51]

Conclusions

In this study, we have synthesized g-C3N4-Ag/ZnO heterostructure nanocomposites by a one-pot copyrolysis technique. ZnO and Ag were found to be well dispersed on the surface of g-C3N4 sheets. The ternary g-C3N4-Ag/ZnO system exhibited higher adsorption capacity and enhanced sunlight activity to TC removal compared with the combinations of g-C3N4-Ag, g-C3N4-ZnO, ZnO-Ag, and g-C3N4. Ultrafine dispersions of Ag nanoparticles on the surface of the composite created close interfaces between g-C3N4 and ZnO, facilitating the direct migration of photoinduced electrons on the Ag surface and efficiently promoting the separation of photogenerated electron-hole pairs. In summary, a novel, efficient, bifunctional, and regenerative photocatalyst has been developed by a facile one-pot copyrolysis technique that has enormous potential for the removal of organic pollutants that exist in the environment.

Experimental Section

Materials: Melamine (C3H6N6, 99.0 %, Sigma–Aldrich, India), silver nitrate (AgNO3, ≥ 99.0 %, Merck, India) and zinc nitrate hexahydrate [Zn(NO3)2·6H2O, Merck, India] were used as precursors for the composite preparation. Tetracycline (TC) was purchased commercially. All reagents for synthesis and analysis were used without further purification. Deionized water was used throughout this work.

Preparation of Photocatalyst: g-C3N4-Ag/ZnO nanocomposite was processed by a one-pot copyrolysis technique from melamine (C3H6N6), silver nitrate (AgNO3), and zinc nitrate hexahydrate [Zn(NO3)2·6H2O, Merck, India] were used as precursors for the composite preparation. Tetracycline (TC) was purchased commercially. All reagents for synthesis and analysis were used without further purification. Deionized water was used throughout this work.

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Characterization of Materials: The crystal structure and phase purity of the prepared samples were assessed by X-ray diffraction (XRD) with a Philips XPert Pro diffractometer in the 2θ range of 5–70° using Cu-Kα radiation. X-ray photoelectron spectra (XPS) were obtained with an ESCA + Omicron nanotechnology (Oxford instrument, Germany) spectrometer that was equipped with a Mg-Kα, X-
Adsorption Measurements: Adsorption equilibrium data was analyzed by dispersing 0.5 g L⁻¹ of adsorbent in various concentration of TC ranging from 25 to 400 μM. The resulting suspensions were stirred continuously in the dark for 60 min. Aliquots were taken every 10 min to measure the adsorbed concentration with a UV/Vis spectrophotometer. The concentration of surface adsorbed TC was calculated by using Equation (6).

\[
\% \text{TC Adsorbed} = \frac{[C_0 - C_t]}{C_0} \times 100
\]  

(6)

where \( C_0 \) (mg L⁻¹) and \( C_t \) (mg L⁻¹) correspond to the TC concentration at the start and after contact time \( t \) [min]. The adsorption capacity, \( q_e \) (mg g⁻¹) of TC solution retained per gram of adsorbent equilibrium concentration \( C_e \) was calculated by using Equation (7).

\[
q_e = \frac{[C_0 - C_e]}{m} \times V
\]  

(7)

\( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of TC in aqueous solution, \( V \) (L) is the solution volume and \( m \) (g) is the amount of adsorbent added.

Photocatalytic Degradation

Adsorption Cum Photocatalytic Activity: The synthesized composites were evaluated for their adsorption and photocatalytic activity by employing Tetracycline as the model pollutant (TC). In a typical experiment, 0.04 g photocatalyst was dispersed in 80 mL aqueous solution of TC (10⁻⁴ M). Prior to sunlight exposure, the suspension was magnetically stirred for 60 min in the dark to attain adsorption-desorption equilibrium. The suspension is then exposed to sunlight irradiation (31/03/2016, Trivandrum, India, between 11 am and 1 pm) and Aliquots were taken at 30 min interval to measure the concentration of TC with a UV/Vis spectrophotometer. For comparison, the photocatalytic experiments of g-CN₄Ag, g-CN₄ZnO, ZnO-Ag, and g-CN₄N₃ were also carried out under identical conditions. The degradation ratio was calculated by using Equation (8).

\[
\% \text{TC degradation} = \frac{[C_0 - C_t]}{C_0} \times 100
\]  

(8)

where \( C_0 \) (mg L⁻¹) and \( C_t \) (mg L⁻¹) correspond to the TC concentration at the start and after contact time \( t \) [min].

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