

Unveiling the exceptional photocatalytic activity of SmO/g-C₃N₄ nanocomposites for dye industries wastewater treatment

Sachin Shoran^a, Sweety Dahiya^a, Sudesh Chaudhary^{a,*}, S.P. Nehra^{a,*}, Anshu Sharma^{b,*}

^a Centre of Excellence for Energy and Environmental Studies, Deenbandhu Chhotu Ram University of Science and Technology, Murthal 131039, India

^b Department of Applied Sciences and Humanities, School of Engineering & Technology, Central University of Haryana, Mahendergarh 123031, India

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ABSTRACT

On a global scale, wastewater dye pollution has become a major environmental issue. Photocatalysis is a well-known and promising technology for removing organic pollutants, such as dyes, from wastewater. In this work, SmO/g-C₃N₄ nanocomposites were fabricated and used as a photocatalyst for the degradation of anionic dyes, cationic dyes, and mix dyes due to their high specific surface area and outstanding photocatalytic capabilities. Characterization of the synthesized nanocomposites included Fourier-transform infrared (FTIR), Scanning electron microscopy (SEM), Ultraviolet-visible diffuse reflectance spectroscopy (UV-DRS), X-ray Diffraction (XRD), Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The photocatalytic activity of SmO/g-C₃N₄ nanocomposites was studied against anionic dyes (Rose bengal (RB) and Xylenol Orange (XO)), cationic dyes (Auramine O (AO) and Crystal Violet (CV)) and their mixture (Mix Dyes). The results indicated that SmO/g-C₃N₄ nanocomposite (SmG-1.5) exhibited superior photocatalytic activity compared to its precursors, degrading dyes at rates of Rose bengal-84.7 %, Xylenol Orange-75.3 %, Auramine O-82.2 %, Crystal Violet-72.3 %, and Mix dyes-80 %. Thus, SmO/g-C₃N₄ nanocomposites demonstrate significant potential as an efficient photocatalyst for degrading dyes in wastewater.

1. Introduction

Wastewater pollution due to dyes is a significant environmental issue globally [1,2]. Dealing dye-containing wastewater into water bodies can harm aquatic life, human health, and the environment [3]. Dyes are synthetic and natural organic compounds that can cause severe damage to the ecosystem by decreasing the amount of sunlight penetration [4,5], reducing dissolved oxygen levels, and altering water pH [6]. Additionally, some dyes contain toxic heavy metals and carcinogenic substances that can threaten human health [7]. Therefore, the treatment of dye-containing wastewater is necessary to prevent contamination and ensure the environment's sustainability [8]. Photocatalysis has been identified as a sustainable and efficient technique for degrading wastewater's organic pollutants [9,10], including dyes [11]. Using photocatalysis is a promising approach to treating wastewater, especially for breaking down organic pollutants like dyes [12]. Compared to conventional techniques, photocatalysis utilizes a photocatalyst and light energy to initiate the degradation mechanism [13,14], resulting in more rapid and efficient treatment [15]. Another advantage of photocatalysis is that it is environmentally safe and sustainable, as it does not require

harmful substances or produce toxic byproducts [16].

Many semiconductor photocatalysts, especially those incorporating metal elements, face challenges related to high material costs and limited sustainability [17]. Unlike metal oxide photocatalysts, graphitic carbon nitride (g-C₃N₄) is a metal-free semiconductor composed solely of carbon and nitrogen. This makes g-C₃N₄ an attractive, low-cost, and sustainable photocatalyst with broad potential applications [18]. Because of a small bandgap of 2.7 eV [19], which allows it to absorb visible light, g-C₃N₄ is an excellent choice for photocatalysis [20]. However, g-C₃N₄'s inability to separate photo-generated electron-hole pairs limits its photocatalytic activity, which can result in electron-hole recombination and decreased efficiency [21,22]. The problem can be solved by increasing g-C₃N₄'s photocatalytic activity by doping it with metals or metal oxides [20,23,24].

In this context, incorporating metal oxides like Samarium into g-C₃N₄ offers a strategic approach to overcome these limitations. Orthovanadates, such as Samariumvanadate (SmVO₄), has demonstrated significant potential in photocatalysis, particularly for acetone degradation under visible light [25]. This highlights the motivation for using Samarium-based compounds for enhanced photocatalytic performance.

* Corresponding authors.

E-mail addresses: sudesh.energy@dcrustm.org (S. Chaudhary), nehraasp@gmail.com (S.P. Nehra), anshushsharda@gmail.com (A. Sharma).

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Fig. 1. Synthesis route of SmO/g-C₃N₄ nanocomposites.

Samarium, a rare earth element, is desirable in photocatalysis due to its remarkable electrical properties [26]. Because of its narrow bandgap energy [27], Samarium (Sm) is chosen as the doping element, which can improve the photocatalytic activity by increasing its light absorption [28]. Samarium also has superb catalytic qualities that increase the chemical stability of the nanocomposites [29]. Increased surface area and pore volume, improved charge separation efficiency, better light absorption, and increased reusability are all benefits of using samarium-doped g-C₃N₄ for photocatalysis [30]. As a result, samarium-doped g-C₃N₄ offers a practical and affordable method for reducing organic pollutants in wastewater [31,32].

To the best of the author's knowledge, there are limited studies exploring the combination of Samarium and g-C₃N₄ nanocomposites, highlighting an opportunity to harness the synergistic effects of these materials [28,33,34]. Addressing this research gap, the present study introduces a novel approach by synthesizing SmO/g-C₃N₄ nanocomposites for the first time. The innovative heterojunction structure formed between SmO and g-C₃N₄ effectively reduces electron-hole recombination, improves charge carrier dynamics, and broadens light absorption into the visible range. These SmO/g-C₃N₄ nanocomposites demonstrate enhanced photocatalytic performance for degrading various organic dyes, including Rose Bengal, Xylenol Orange, Auramine O, Crystal Violet, and mixed dyes, under visible light irradiation, making this material a promising candidate for efficient and sustainable wastewater treatment applications.

2. Experimental section

2.1. Synthesis of g-C₃N₄

Urea is used as a precursor in a hydrothermal process to synthesize g-C₃N₄ (Fig. 1a). 10 g of urea is first heated in a crucible at 550 °C at a ramp rate of 5 °C in a furnace for 3 h. Using an agate mortar and pestle, the finished product of the synthesis is ground into a fine powder. This synthesis method produces g-C₃N₄, which has a high surface area and exceptional photocatalytic activity thanks to its highly porous and layered structure [35].

2.2. Synthesis of SmO nanoparticles

SmO nanoparticles were synthesized via the co-precipitation method (Fig. 1b). First, 20 mL of distilled water was used to dissolve 1 g of Sm₂O₃ powder. Next, 4 g of NaOH was added, which caused the Sm₂O₃ to undergo hydrolysis and create Sm(OH)₃. The mixture was stirred until the Sm(OH)₃ was evenly distributed and the NaOH was completely dissolved. The Sm(OH)₃ underwent dehydration and formed SmO nanoparticles after 20 mL of ethanol was gradually added to the mixture while stirring continuously. For the SmO nanoparticles to ultimately precipitate, the solution was left to sit for a few hours or overnight. After being separated by centrifugation, the SmO nanoparticles underwent a series of ethanol washes to separate any remaining impurities. The sample was then dried in hot air oven to obtain SmO nanocomposites.

2.3. Synthesis of SmO/g-C₃N₄ nanocomposites

In (Fig. 1c), SmO/g-C₃N₄ nanocomposites were created efficiently by doping different molar ratios of SmO in g-C₃N₄ nanoparticles at a fixed ratio 1:x (where x = 1, 1.5, and 2). The resulting mixture was then sonicated at room temperature for 2 h to ensure uniform dispersion of the SmO nanoparticles in the g-C₃N₄ matrix. The mixture was sonicated, dried at 60 °C for 24 h, and then calcined at 500 °C for 2 h to form the SmO/g-C₃N₄ nanocomposite. This method enabled the controlled growth of SmO nanoparticles on the surface of g-C₃N₄, yielding a well-dispersed SmO/g-C₃N₄ nanocomposite. The nanocomposites were abbreviated as SmG-1, SmG-1.5, and SmG-2.

2.4. Characterisation-

The SmO/g-C₃N₄ composite was characterized by several analytical techniques to investigate its structural, morphological, and optical properties. On a Bruker D8 diffractometer, X-ray diffraction (XRD) analysis was carried out using Cu-K radiation at 40 kV and 40 mA. The data were collected in the 2θ range of 10°–80° with a scanning rate of 0.02 s⁻¹. Fourier transforms infrared (FTIR) spectroscopy was performed on a Perkin Elmer Spectrometer instrument in the 4000–400 cm⁻¹ using the KBr pellet technique. Transmission electron microscopy

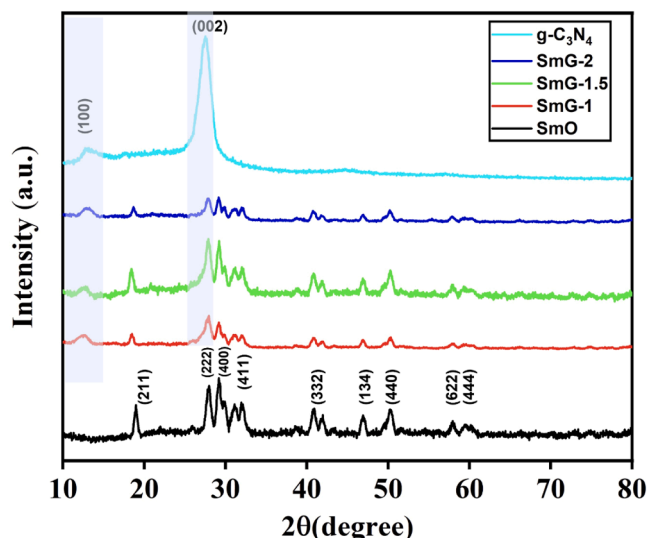


Fig. 2. XRD pattern of g-C₃N₄, SmO and SmO/g-C₃N₄ nanocomposites.

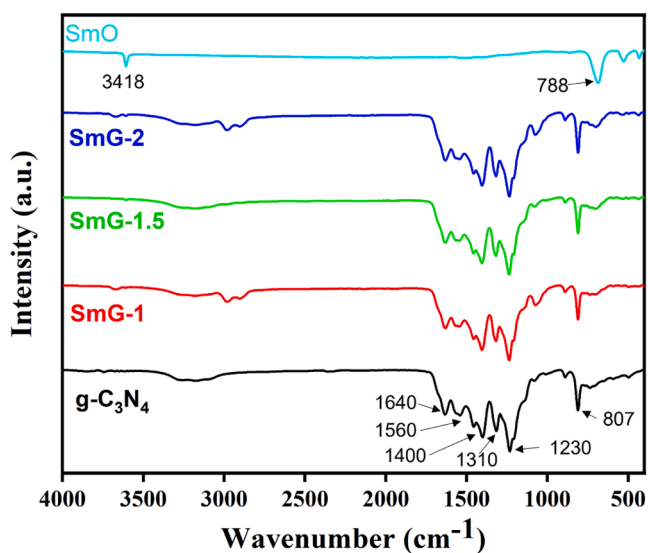


Fig. 3. FTIR Spectrum of SmO nanocomposites.

(TEM) and scanning electron microscopy (SEM) were used to analyze the morphological characteristics of the samples. JSM 7900-F was used to acquire SEM images instrument at 1 m, 2 m resolution, and 10,000 magnification. TEM images (100-nm resolution) were taken on a (TEM Talos F200X instrument operating at 200 kV. On a Thermo Scientific K-Alpha XPS instrument, X-ray photoelectron spectroscopy (XPS) was performed with monochromatic Al-K α X-rays (1486.6 eV). On a Shimadzu UV-2600 I spectrophotometer, ultraviolet-visible diffuse reflectance spectroscopy (UV-DRS) measurements were made in the 200–800 nm range. The optical bandgap of the composite was calculated using the Taucs Equation.

2.5. Photocatalytic activity

The photocatalytic activity of the synthesized SmO/g-C₃N₄ nanocomposites was evaluated using five different dyes, including anionic dyes (such as Rose Bengal and Xylenol Orange), cationic dye (including Auramine O and Crystal Violet) and Mix dyes. The degradation experiments were performed by adding 10 mg of the nanocomposites to a 100 mL aqueous dye solution with an initial ten mg/L concentration. The

suspension was irradiated under a 400 W Xe lamp for 120 min, with a constant stirring rate of 600 rpm. The following equation was used to calculate the degradation efficiency:

$$\text{Degradation efficiency (\%)} = [(C_0 - C_t) / C_0] \times 100 \quad (1)$$

Where the dye's initial and final concentrations are denoted by the letters C_0 and C_t , respectively. The absorption spectra of the dyes were recorded at regular intervals using a UV-Vis spectrophotometer to monitor the degradation process. The experimental setup was carefully designed to ensure the irradiation was uniform throughout the solution. Reaction conditions were optimized to maximize the dye degradation rate for each dye.

3. Results and discussion

3.1. XRD

The XRD pattern of g-C₃N₄ (Fig. 2) displays distinct peaks at 13.2° and 27.4°, which correspond to the (100) and (111) planes (002). These peaks demonstrate that g-C₃N₄ has a multilayer hexagonal structure with a preferred orientation along the x-axis, perpendicular to the carbon and nitrogen atom layers. The XRD peaks of SmO nanoparticles observed at 20°, 28°, 30°, 32°, 41°, 46°, 51°, 58°, and 60° for SmO nanocomposites correspond to the (211), (222), (400), (411), (332), (134), (440), (622), and (444) planes, respectively. These peaks confirm the crystalline nature of the nanoparticles and suggest the presence of a cubic structure. These results confirm the presence of both precursors in the nanocomposite. The XRD analysis of SmO/g-C₃N₄ nanocomposite indicates successful nanocomposite synthesis by showing the characteristic peaks of both precursors g-C₃N₄ and SmO.

3.2. FTIR

FTIR (Fourier transform infrared) spectra of SmO nanoparticles and g-C₃N₄ (graphitic carbon nitride) were analyzed to study the SmO/g-C₃N₄ nanocomposites. In the FTIR spectrum (Fig 3) of the SmO nanoparticle, a sharp absorption band was observed at 3418 cm⁻¹, corresponding to the tensile vibration of the O–H group. The peak observed at 788 cm⁻¹ confirms the existence of an Sm–O bond in the crystal [36]. The FTIR spectrum of g-C₃N₄ showed characteristic peaks at 1640 cm⁻¹, attributed to the stretching vibration of C = N bonds [37]. The peaks observed at 1560, 1400, and 1310 cm⁻¹ are associated with the stretching vibrations of aromatic C = C bonds [38]. The peaks observed at 1230 and 807 cm⁻¹ correspond to the bending vibrations of C–N bonds and the out-of-plane deformation of C–H bonds, respectively [39]. The SmG nanocomposites showed characteristic peaks of both precursors, confirming their successful synthesis. The FTIR analysis revealed the Sm–O bond and crystalline water in the SmO nanoparticle. At the same time, g-C₃N₄ showed characteristic peaks associated with the stretching vibrations of C = N and C = C bonds.

3.3. SEM analysis

Scanning electron microscopy (SEM) is useful for studying material surface morphology. The SEM analysis of pure g-C₃N₄ in Fig. 4a revealed a lamellar structure aggregation at 10,000x magnification due to the rapid breakdown of nitrates during heating.

SEM analysis of SmO nanoparticles in Fig. 4b revealed only a minor amount of agglomeration, indicating the co-precipitation method's efficiency in synthesizing well-dispersed nanoparticles. The SmG-0.5 nanocomposite in Fig. 4c had a one-of-a-kind structure with small, irregularly shaped SmO particles distributed on the surface of the g-C₃N₄ nanoparticle.

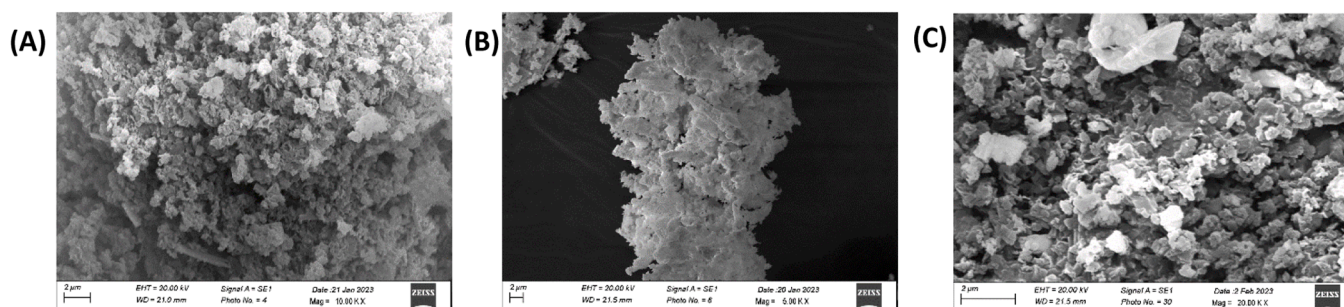


Fig. 4. SEM morphology of two nanomaterials (a) $\text{g-C}_3\text{N}_4$, (b) SmO , (c) SmG-1.5 nanocomposite.

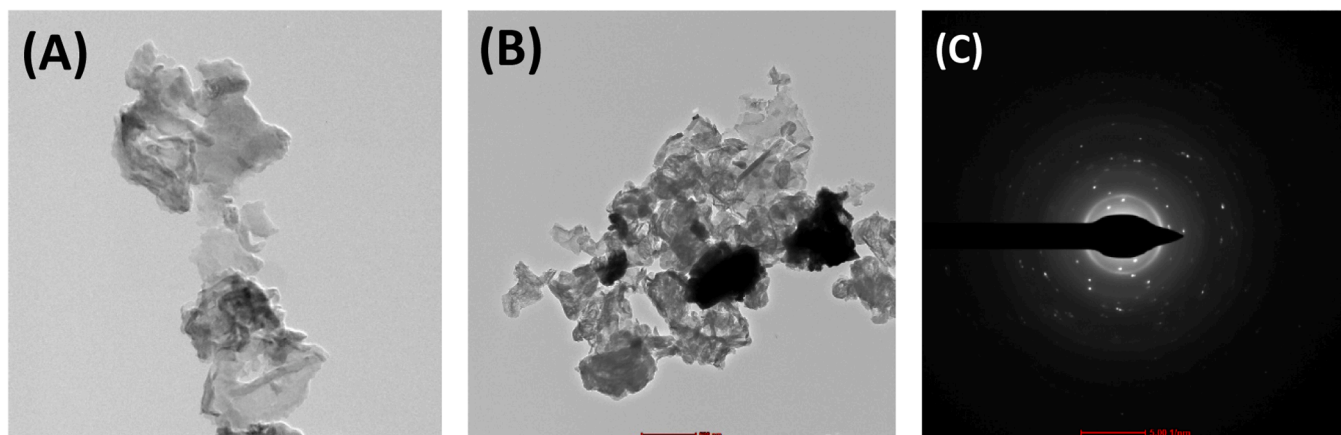


Fig. 5. TEM images of (a) $\text{g-C}_3\text{N}_4$, (b) SmG-1.5 nanocomposite, (c) SAED pattern of SmG-1.5 nanocomposite.

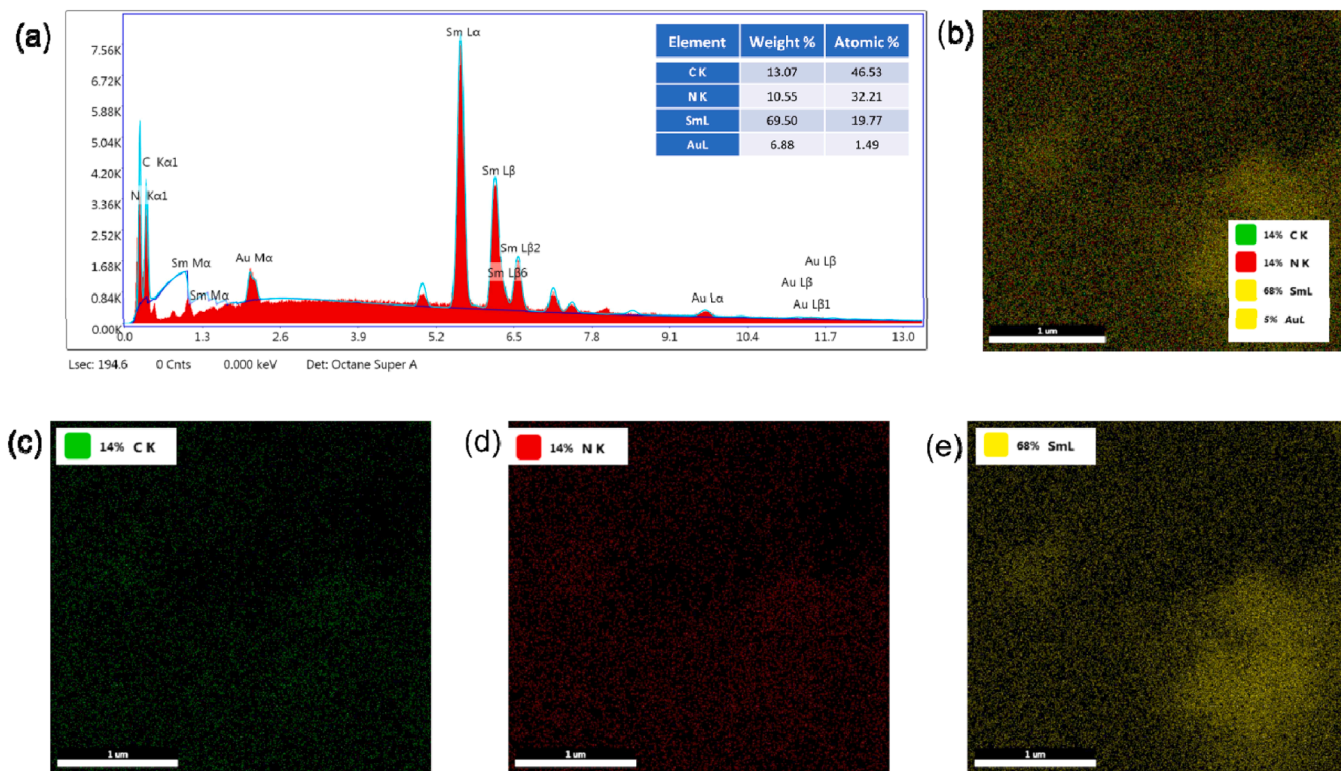


Fig. 6. (a) EDX pattern of SmG-1.5 nanocomposite; (b-e) Elemental mapping of SmG-1.5 nanocomposite.

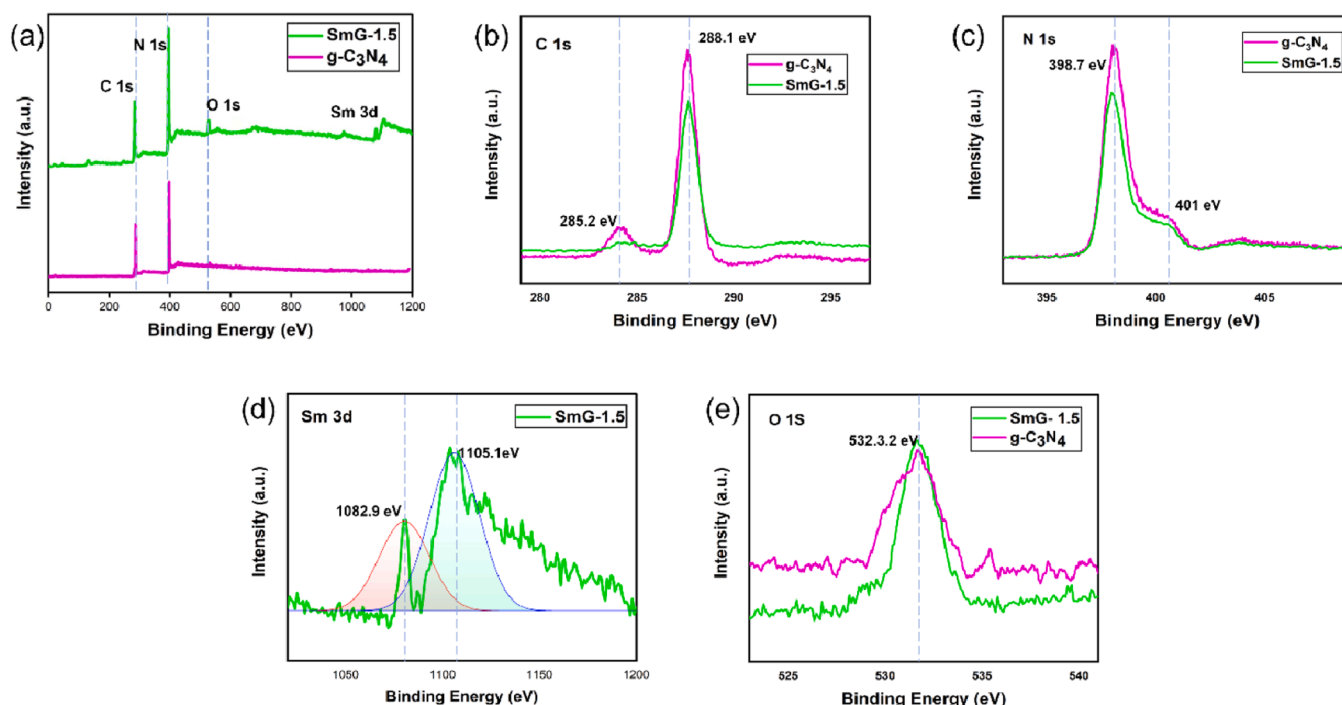


Fig. 7. (a) wide XPS spectra of SmG-1.5 composite and g-C₃N₄; XPS spectra of (b) C 1s (c) N 1s and (e) O 1s.

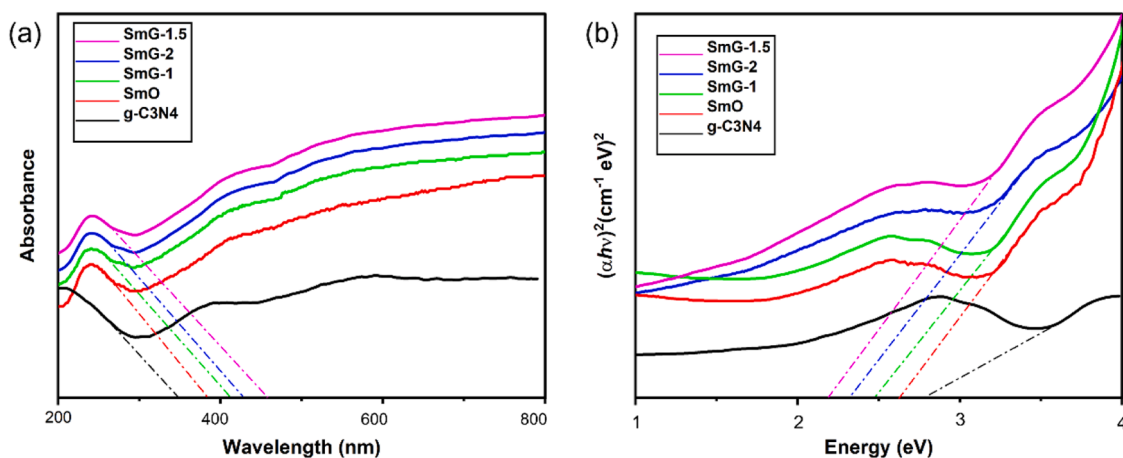


Fig. 8. (a) UV DRS of g-C₃N₄, SmO, and SmG nanocomposites. (b) Tauc plot for a bandgap of g-C₃N₄, SmO, and SmG nanocomposites.

3.4. TEM analysis

In Fig. 5a, TEM analysis of pure g-C₃N₄ revealed a layering structure with many stacking layers, typically of 2D layered material. The TEM images of SmG-1.5 nanocomposite in Fig. 5b revealed a rough texture, which should improve its catalytic activity. The SmG-1.5 composite also had small, irregularly shaped SmO nanoparticles wrapped around the surface of the g-C₃N₄ layer giving it a distinct morphology. The selected area electron diffraction (SAED) pattern of the SmG-1.5 composites revealed bright rings of spots in Fig. 5c, indicating the crystalline nature and reduced size of SmO nanoparticles. Due to the g-C₃N₄ matrix, isolated dots were also observed in the pattern. The image suggests that SmO nanoparticles were successfully dispersed on the surface of g-C₃N₄, which could lead to increased photocatalytic activity. Because of this morphology, it can provide more active sites for dye adsorption and degradation, making it an efficient photocatalyst [40].

3.5. EDX analysis

The elemental composition of SmO/g-C₃N₄ nanocomposites was determined using energy-dispersive X-ray spectroscopy (EDX) analysis (Fig. 6). The weight percentage and atomic percentage of carbon (13.07 % and 46.53 %), nitrogen (10.55 % and 32.21 %), and Sm (69.50 % and 19.77 %) was determined. The EDX data confirm the presence of carbon, nitrogen, and Samarium in the SmO/g-C₃N₄ nanocomposite. The high percentage of Samarium indicates that the SmO nanoparticles are well dispersed in the g-C₃N₄ matrix. The atomic percentages of carbon and nitrogen indicate that g-C₃N₄ is present in the composite. X-ray diffraction (XRD) analysis also confirmed the presence of these elements. Elemental mapping was also carried out to investigate the spatial distribution of the elements in the nanocomposite. The results showed that carbon and nitrogen were uniformly distributed throughout the composite. At the same time, Samarium was mainly concentrated in specific regions, indicating that the SmO nanoparticles were dispersed in the g-C₃N₄ matrix with some aggregation.

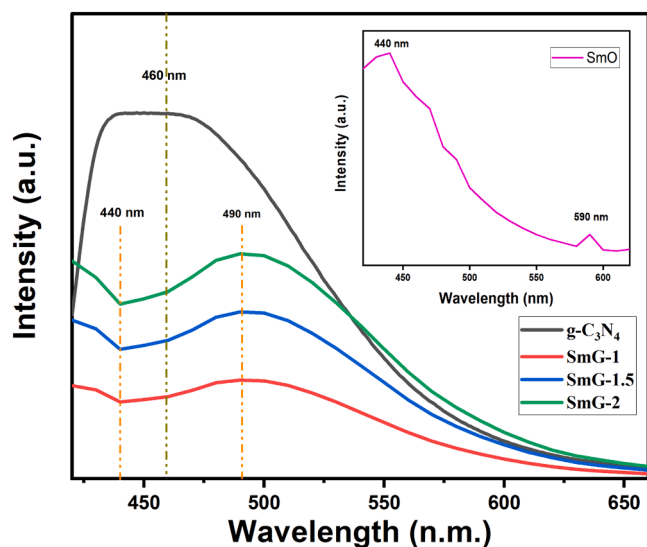
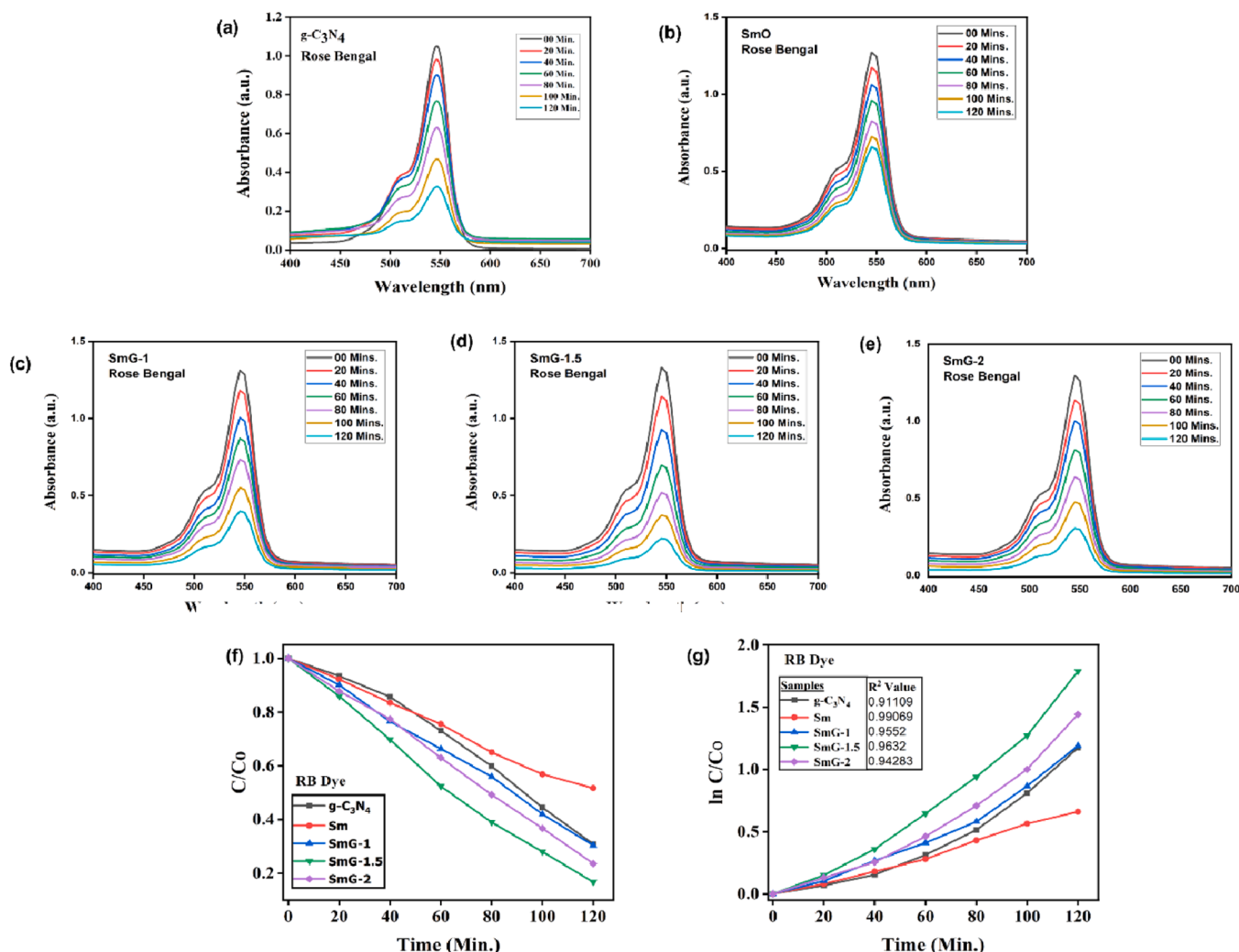


Fig. 9. PL spectra of prepared nanocomposites.

3.6. XPS analysis

A robust method for examining the elemental makeup and chemical bonds of various materials is X-ray photoelectron spectroscopy (XPS). The C1 s, N1 s, and O1 s spectra of g-C₃N₄ and SmO composites were analyzed using XPS. In Fig. 7b, the C1 s spectrum of g-C₃N₄ displayed two chemical states of the carbon element. The peaks at 288.1 eV are attributed to sp² hybrid C-C (N), and 285.2 eV peaks are due to C-(N)₃, respectively. In Fig. 7c, the N1 s spectrum of g-C₃N₄ could be fitted to two peaks, 401.0 eV and 398.7 eV. The peak at 401.0 eV was assigned to the amino functional group (N-H), mainly derived from the incomplete polymerization of urea. The peaks at 398.7 eV were identified as sp² hybridization of N, corresponding to N of the N = C bond. In Fig. 7d, the O1 s spectrum of g-C₃N₄ displayed one prominent peak at 532.3 eV, which is attributed to the oxygen atoms bonded to carbon or nitrogen atoms in the lattice structure of the material. The C1 s, N1 s, and O1 s spectra of the SmO composites showed similar peaks to those observed in g-C₃N₄. As shown in Fig. 7d, the interaction of spin orbits caused the Sm 3d high-resolution spectrum to split into two peaks at 1082.9 eV (Sm 3d 5/2) and 1105.1 eV (Sm 3d 3/2). The two dipole peaks belong to Sm³⁺ ions in Sm₂O₃, indicating no other valence state of Sm in the sample, and the doped Sm exists in the Sm (III) state. Comparing the broad spectrum of SmO and g-C₃N₄ composites (Fig. 7a), SmO showed additional peaks corresponding to Sm3d and O1s. At the same time, g-C₃N₄ displayed additional peaks in the C1 s and N1 s regions. These

Fig. 10. (a-e): UV-Vis absorbance spectra for RB dye, (f) Photocatalytic activity comparison (g) $\ln(C_0/C_t)$ degradation kinetics.

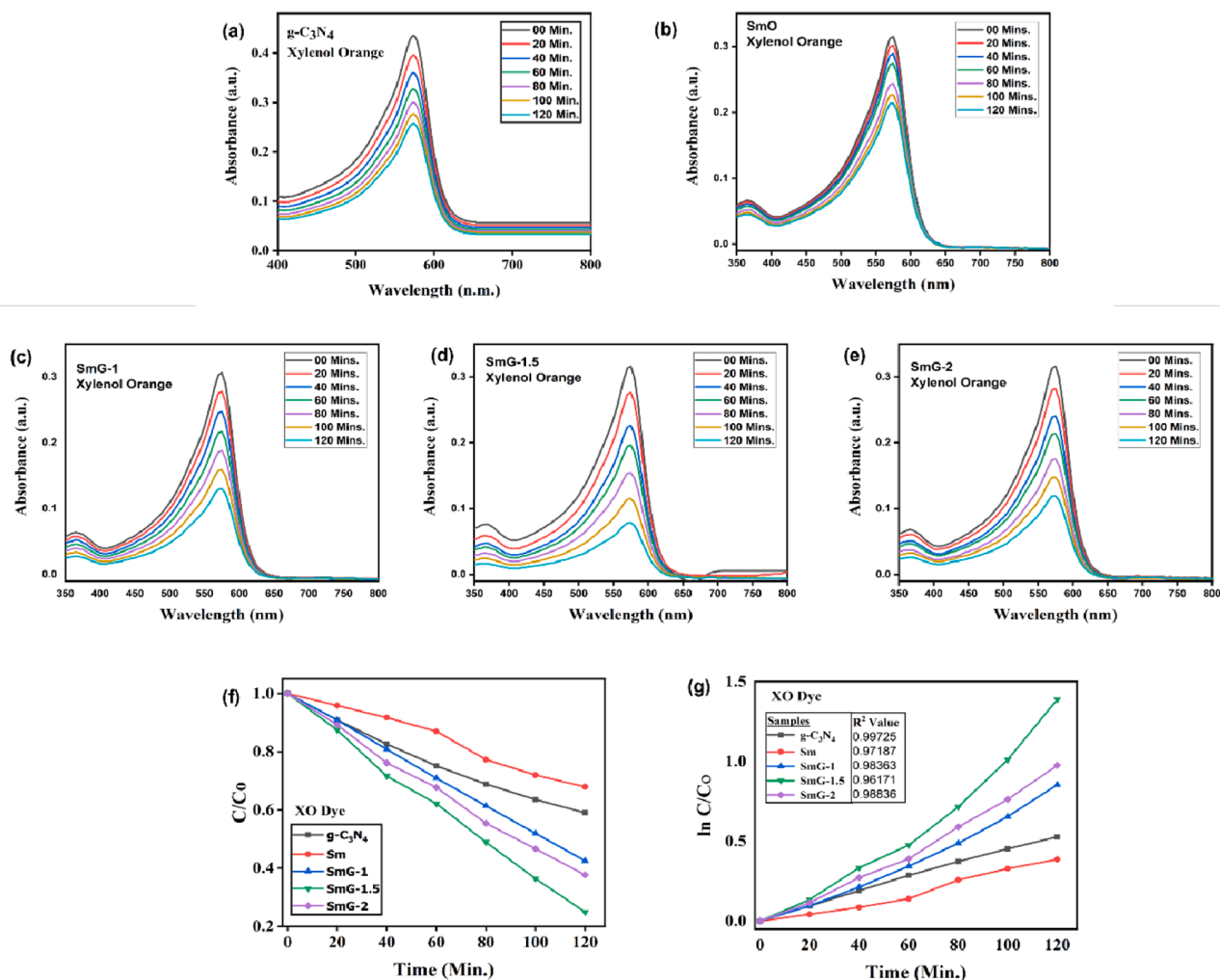


Fig. 11. (a-e): UV-Vis absorbance spectra of nanocomposites for XO dye, (f) Photocatalytic activity comparison (g) $\ln(C_0/C_t)$ degradation kinetics.

results indicate that SmO nanoparticles have been successfully dispersed on the surface of g-C₃N₄, and the composites are formed through chemical bonding between the two materials. XPS analysis confirms strong electronic interactions between SmO and g-C₃N₄, evidenced by shifts in the C1 s, N1 s, and O1 s binding energies. The presence of Sm³⁺ ions indicate successful integration, facilitating efficient charge transfer at the SmO/g-C₃N₄ interface.

3.7. UV-DRS

The UV-Vis DRS spectra of SmO/g-C₃N₄ nanocomposites were analyzed to investigate their optical properties. The absorption peaks observed at various wavelengths in these Spectra indicated the presence of distinct energy levels within the materials (Fig. 8). The energy bandgap is a crucial parameter for investigating the electrical properties of a material that can be determined using the Tauc relation

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

Equation two describes the relationship between the absorption coefficient (α), the photon energy ($h\nu$), the optical band gap (E_g), and a constant value (A). The specific value of the index (n) depends on the form of transition, with the values of $\frac{1}{2}$, $\frac{3}{2}$, 2.0 , and 3.0 corresponding to directly permitted, indirectly permitted, and end prohibited transition, respectively. Fig. 8b depicts the relationship between absorbance and photon energy for the manufactured composites, with the suitable match observed at $n=2$, indicating the existence of a direct allowed band

gap. [41]. g-C₃N₄ has an absorption edge at 343 nm and 2.79 eV At 380 nm, SmO exhibited an absorption peak with a 2.63 eV energy. As the quantity of SmO added to g-C₃N₄ increased, the absorption shifted to longer wavelengths, resulting in a decrease in energy. SmG-1 exhibited an absorption maximum at 410 nm with a 2.48 eV energy. SmG-1.5 exhibited an absorption peak with an energy of 2.18 eV at 456 nm. SmG-2 had a maximum energy of 2.33 eV at 426 nm. The UV-Vis DRS results show a shift toward longer wavelengths in the absorption edge of the SmO/g-C₃N₄ composites, indicating bandgap narrowing. This shift suggests the formation of a heterojunction, improving visible light absorption and charge separation. The decrease in energy levels as SmO concentration increases suggests that SmO/g-C₃N₄ nanocomposites have a narrower bandgap, which could improve their photocatalytic activity. The lower wavelength and bandgap observed in SmG-1.5 compared to SmG-2, despite a higher molar concentration of SmO, can be attributed to various factors, including enhanced interaction and integration of SmO within the g-C₃N₄ matrix, potential modifications in the electronic structure and energy levels, and the size and distribution of SmO nanoparticles. The increased absorption region observed in SmG-1.5 indicates higher production of electron-hole (e^-h^+) pairs, contributing to enhanced photocatalytic activity. This improvement is widely attributed to the efficient separation of these electron-hole pairs within the composite. Therefore, the charge transfer at the heterojunction interface between SmO and g-C₃N₄ plays a crucial role in preventing recombination, significantly boosting the overall photocatalytic performance.

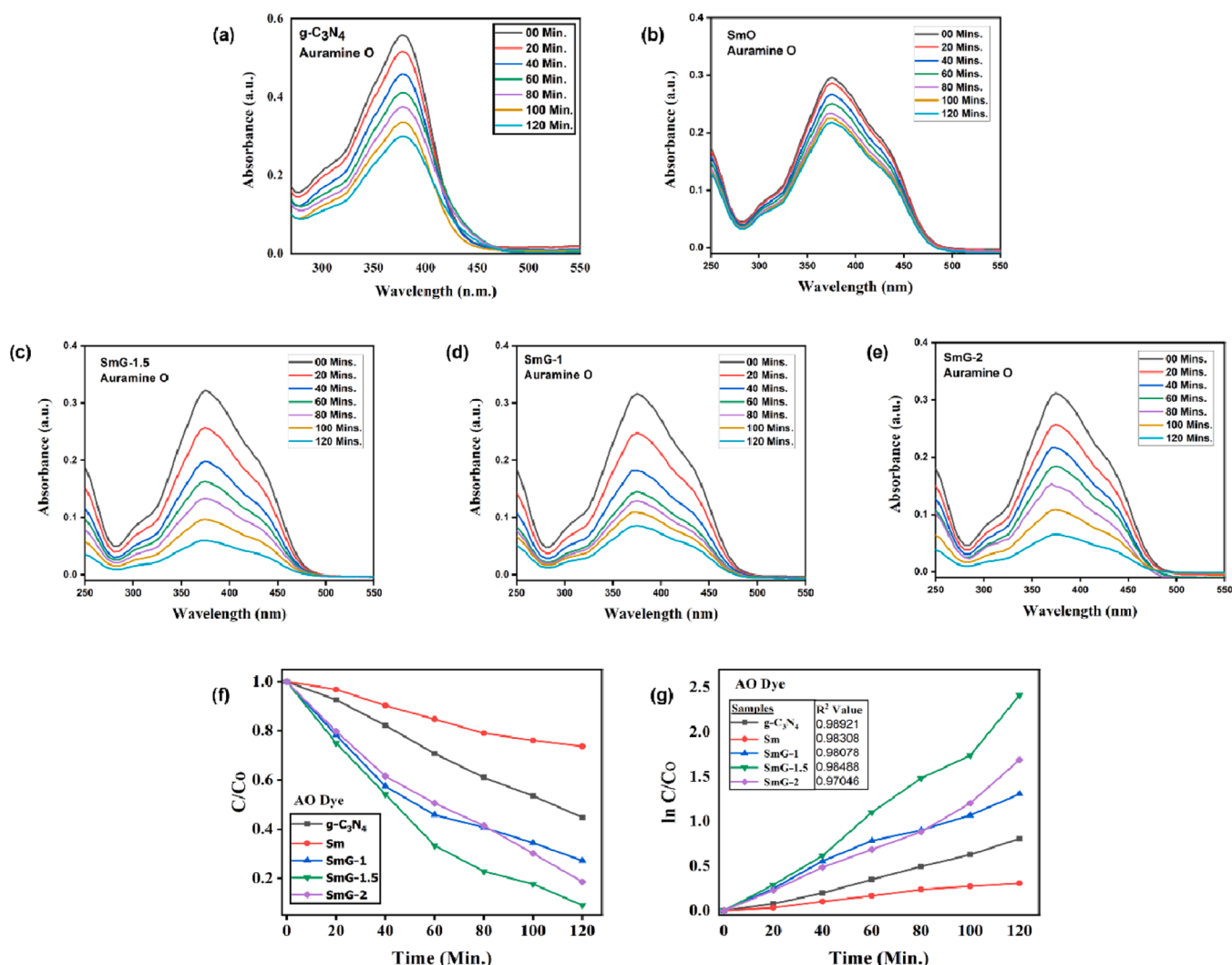


Fig. 12. (a-e): UV-Vis absorbance spectra of nanocomposites for AO dye, (f) Photocatalytic activity comparison (g) $\ln(C_0/C_t)$ degradation kinetics.

3.8. Photoluminescence

Photoluminescence (PL) is the phenomenon in which material emits light after absorbing light of a different wavelength. Considering that the PL emission results from the free charge carrier recombination, the lower peak indicates that the composite has a lower electrons and hole recombination rate under visible-light irradiation, which is mainly due to the fact that the electrons and holes are separated by the charge transfer at the heterojunction interfaces of SmO and g-C₃N₄. In the case of g-C₃N₄, the main peak in the PL spectrum is around 460 nm (Fig. 9). This peak corresponds to the radiative recombination of electron-hole pairs that are created when g-C₃N₄ absorbs light in the visible region of the spectrum [42]. The PL spectrum of SmO nanoparticles typically shows two main peaks one at 440 nm, and another at 490 nm. The peak at 440 nm is attributed to the radiative recombination of electron-hole pairs that are created in the SmO lattice. The peak at 490 nm is caused by the transition between defective states in the SmO lattice. These emission peaks confirm the presence of Sm³⁺ ions in the SmO composite and their contribution to photoluminescence behavior [43]. The suitable SmO concentration causes its good dispersion in the composite, which favors the formation of heterojunction structures between the g-C₃N₄ and SmO particles. Therefore, high separation of the charge carriers and photocatalytic activity are obtained on the SmO/g-C₃N₄ nanocomposites. The decrease in peak intensity of SmO/g-C₃N₄ nanocomposites in the order SmG-2, SmG-1.5, and SmG-1 can be attributed

to the increased surface area to volume ratio of nanocomposites. The result in Fig. 9 indicates that the composite has the lowest electrons-hole recombination rate, consistent with the PL and photocatalytic testing results. Therefore, the high photocatalytic activity of the SmO/g-C₃N₄ nanocomposite can be attributed to the g-C₃N₄ and SmO heterostructure, which enhances the photogenerated electron-hole pair separation.

3.9. Photocatalytic activity

The photocatalytic activity of SmO/g-C₃N₄ nanocomposites was evaluated by testing their efficiency in visible light irradiation for 120 min and determining the degradation of anionic, cationic dyes, and Mix dyes. Rose Bengal is an anionic dye used in the textile industry and as a biological stain. The order of photocatalytic degradation of Rose Bengal dye was found to be SMG-1.5 (84.7 %) > SMG-2 (76.5 %) > SMG-1 (70.2 %) > g-C₃N₄ (65 %) > SmO (48.8 %). The results indicate that SmO/g-C₃N₄ composites are highly efficient photocatalysts for degrading Rose Bengal dye (Fig. 10a-e). SMG-1.5 exhibited the highest degradation efficiency, which can be attributed to the synergistic effect of SmO and g-C₃N₄. SmO nanoparticles acted as electron acceptors, and g-C₃N₄ acted as an electron donor, which led to efficient charge separation and enhanced photocatalytic activity.

Xylenol Orange is an anionic dye commonly used in analytical chemistry as an indicator for detecting transition metals. The order of

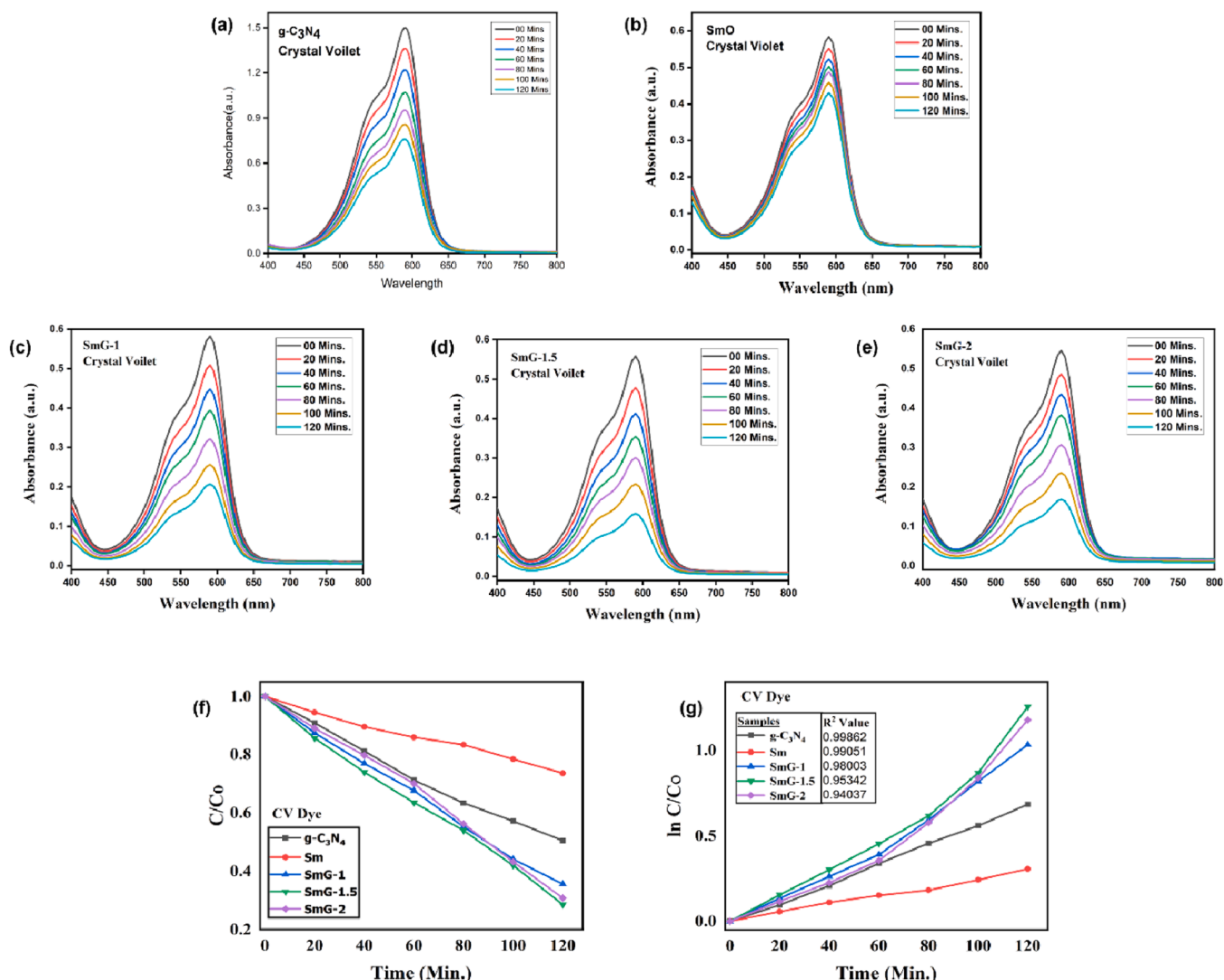


Fig. 13. (a-e): UV-Vis absorbance spectra of nanocomposites for CV dye, (f) Photocatalytic activity comparison (g) $\ln(C_0/C_t)$ degradation kinetics.

photocatalytic degradation of Xylenol Orange dye was found to be SMG-1.5 (75.3 %) > SMG-2 (62.2 %) > SMG-1 (57.3 %) > g-C₃N₄ (41.6 %) > SmO (2.4 %). It can be observed that the SmO/g-C₃N₄ composites showed much better photocatalytic activity than their respective precursors (Fig. 11a-e). Among the composites, SMG-1.5 showed the highest degradation efficiency of Xylenol Orange dye. This can be attributed to the smaller size of the SmO nanoparticles and increased interfacial contact with g-C₃N₄, leading to higher surface area and more active sites for photocatalytic activity.

Auramine O is a cationic dye widely used as a textile dye in the pharmaceutical business. The order of photocatalytic degradation of Auramine O dye was found to be SMG-1.5 (82.2 %) > SMG-2 (76.6 %) > SMG-1 (72.7 %) > g-C₃N₄ (46.4 %) > SmO (27.3 %). The findings demonstrated that compared to their respective precursors, SmO/g-C₃N₄ composites had much higher photocatalytic activity (Fig. 12a-e). SMG-1.5, among the composites, demonstrated the most incredible Auramine O dye degradation efficiency. The synergistic impact of SmO and g-C₃N₄, which resulted in effective charge separation and increased photocatalytic activity, is responsible for the high efficiency of SMG-1.5.

A cationic dye called Crystal Violet is employed in the textile sector and as a histology stain. According to research, the Crystal Violet dye degrades photocatalytically in the following order: SMG-1.5 (72.3 %) > SMG-2 (69.7 %) > SMG-1 (64.8 %) > g-C₃N₄ (41.6 %) > SmO (27.1 %). The findings demonstrate that the photocatalytic activity of SmO/g-

C₃N₄ nanocomposites was superior to that of their respective precursors (Fig. 13a-e). SMG-1.5 showed the best efficiency for Crystal Violet dye degradation among the composites. SMG-1.5 has a more significant surface area and more active sites for photocatalytic activity as a result of the tiny size of the SmO nanoparticles and improved interfacial contact with g-C₃N₄.

The mix dye is a mixture of one ratio one mixture of anionic and cationic dyes. According to the research, the degradation of mixed dyes is in the following order: SMG-1.5 (80 %) > SMG-2 (73.3 %) > SMG-1 (68.7 %) > g-C₃N₄ (53.3 %) > SmO (33.1 %). These results highlight the synergistic effect of SmO and g-C₃N₄ in enhancing the photocatalytic activity, with SmG-1.5 demonstrating the highest degradation efficiency (Fig. 14a-e).

Table 1 shows the degradation efficiency of all nanocomposites. Overall, the findings indicate that the SmO/g-C₃N₄ composites exceed their precursors in photocatalytic activity for all five dyes examined. This might be explained by the composites' enhanced charge transfer effectiveness and greater surface area, which enhance charge carrier production and separation. Among the several SmO/g-C₃N₄ composites, SMG-1.5 had the maximum photocatalytic degradation efficiency for all five dyes. The SmG-2 composite showed decreased photocatalytic activity despite having a higher molar concentration of SmO than SMG-1.5. This might be caused by the agglomeration of SmO particles under heavier loading, which reduces surface area and prevents efficient

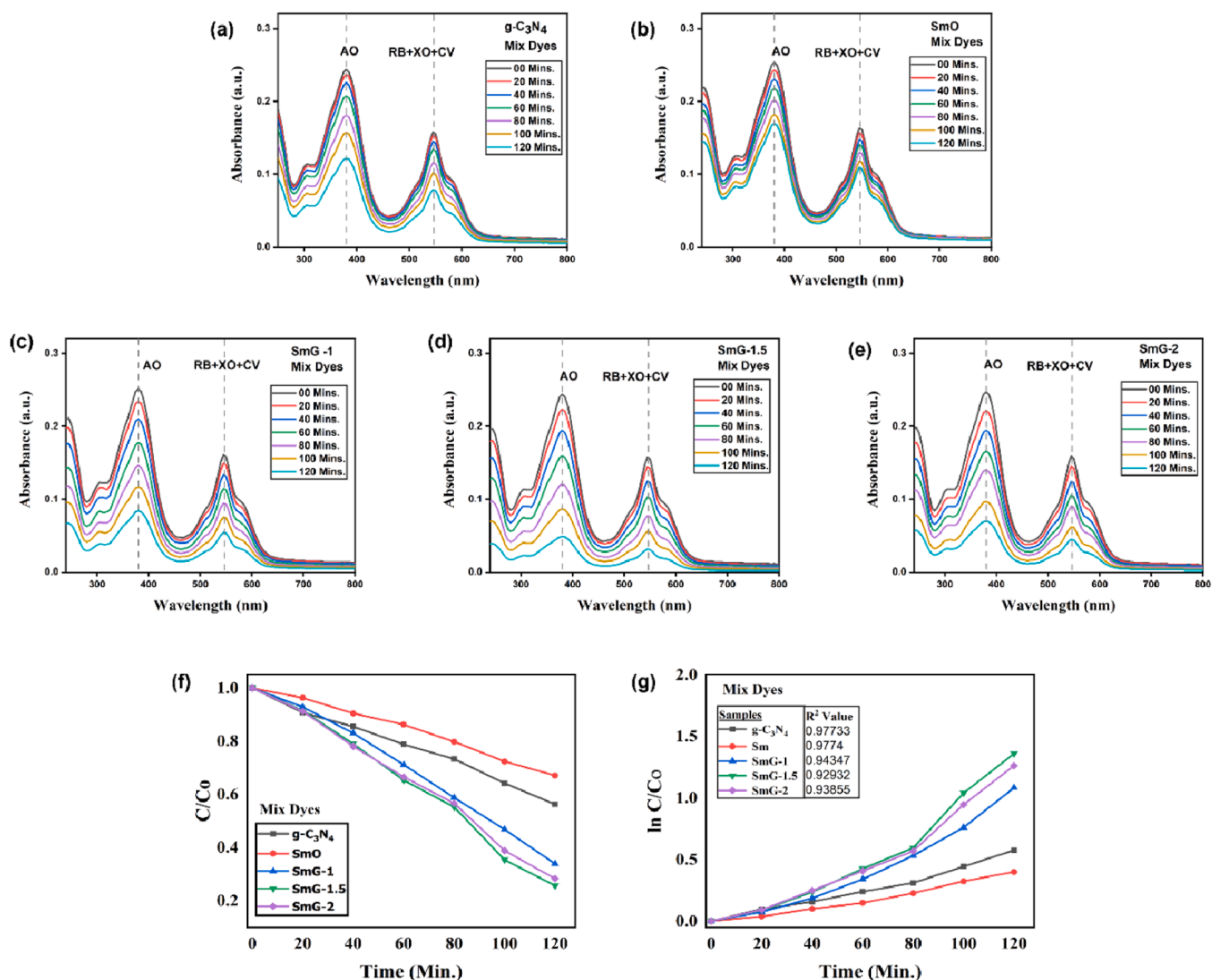


Fig. 14. -(a-e): UV-Vis absorbance spectra of nanocomposites for Mix dyes, (f) Photocatalytic activity comparison (g) $\ln(C_0/C_t)$ degradation kinetics.

Table 1

Degradation efficiency of precursors and nanocomposites.

S. No.	Sample	Rose Bengal Dye	Xylenol Orange Dye	Auramine O Dye	Crystal Violet Dye	Mix Dyes
1	g-C ₃ N ₄	69.2	41.6	46.4	48.6	53.3
2	SmO	48.8	32.4	27.3	27.1	33.1
3	SmG-1	70.2	57.3	72.7	64.8	68.7
4	SmG-1.5	84.7	75.3	82.2	72.3	80
5	SmG-2	76.5	62.2	76.2	69.7	73.3

charge transfer. As a result, an ideal SmO loading is necessary to achieve the most excellent photocatalytic activity in SmO/g-C₃N₄ composites. Table 2 compares the degradation efficiency of SmO/g-C₃N₄ composites with previously published work.

3.10. Kinetics analysis

The apparent rate constant (ARC) is an important parameter used to evaluate the photocatalytic efficiency of nanocomposites. Langmuir-Hinshelwood's pseudo-first-order kinetic Equation can model the photocatalytic degradation of dyes,

$$\ln(C_0/C_t) = K_{app}t \quad (3)$$

where the rate constant (K_{app}) is determined by the initial concentration of the dye (C_0) and its concentration at a specific time (C_t). The ARC values for different nanocomposites were measured for five dyes: auramine O, crystal violet, rose bengal, xylenol orange, and Mix dyes, as shown in Fig. 10(f-g), 11(f-g), 12(f-g), 13(f-g), 14(f-g) and presented in Table 3.

For auramine O dye, the highest ARC value was observed in the following order SmG-1.5 ($0.01963 \text{ K min}^{-1}$) > SmG-2 ($0.01323 \text{ K min}^{-1}$) > SmG-1 ($0.01054 \text{ K min}^{-1}$) > SmO ($0.00274 \text{ K min}^{-1}$) > g-C₃N₄ ($0.0068 \text{ K min}^{-1}$). These results suggest that the SmO/g-C₃N₄ nanocomposites have higher photocatalytic activity than the individual SmO or g-C₃N₄ precursors, with the SmG-1.5 nanocomposite being the most efficient. For crystal violet dye, the highest ARC value was observed in the following order SmG-1.5 ($0.00983 \text{ K min}^{-1}$) > SmG-2 ($0.00951 \text{ K min}^{-1}$) > SmG-1 ($0.00856 \text{ K min}^{-1}$) > SmO ($0.00243 \text{ K min}^{-1}$) > g-C₃N₄ ($0.00575 \text{ K min}^{-1}$). These results suggest that the SmO/g-C₃N₄ nanocomposites have higher photocatalytic activity than the individual SmO or g-C₃N₄ precursors, with the SmG-1.5 nanocomposite being the most efficient. The ARC for rose bengal dye for the nanocomposite was observed in the order: SmG-1.5 (0.01462) > SmG-2 ($0.01165 \text{ K min}^{-1}$) > SmG-1 ($0.00966 \text{ K min}^{-1}$) > g-C₃N₄ ($0.00959 \text{ K min}^{-1}$) > SmO (0.00571

Table 2

Comparative analysis of previously published dye degradation studies.

Dye	Catalyst	Light Source	Degradation Efficiency	Time (Min)	Reference
Auramine O	CeO ₂	50 W Halogen lamp	35 %	90 min.	[44]
	SiO ₂ /g-C ₃ N ₄	400 W Xe Lamp	70 %	120 min.	[39]
	SmO/g-C ₃ N ₄	Xe Lamp (400 W)	82.2 %	120 min.	This Work
Xylenol orange	g-C ₃ N ₄	200 W Tungsten Lamb	15 %	120 min.	[45]
	TiO ₂	7 W UV lamp	70 %	175 min.	[46]
	SmO/g-C ₃ N ₄	400 W Xe Lamp	75.3 %	120 min.	This Work
Rose Bengal	Ag/CeO ₂	Sunlight	96 %	180 min.	[47]
	CeO ₂ /GCN	400 W Xe Lamp	79.2 %	90 min.	[35]
	SmO/g-C ₃ N ₄	400 W Xe Lamp	84.7 %	120 min.	This Work
Crystal violet	g-C ₃ N ₄	200 W XE lamp	51 %	120 min.	[45]
	SmO/g-C ₃ N ₄	400 W Xe Lamp	72.3 %	120 min.	This Work

Table 3Apparent rate constant (K min⁻¹) for synthesized nanocomposites.

S. No.	Sample	Rose Bengal Dye	Xylenol Orange Dye	Auramine O Dye	Crystal Violet Dye	Mix Dyes
1	g-C ₃ N ₄	0.00959	0.00443	0.0068	0.00575	0.00459
2	SmO	0.00571	0.0034	0.00274	0.00243	0.00338
3	SmG-1	0.00966	0.00706	0.01054	0.00856	0.00886
4	SmG-1.5	0.01462	0.01125	0.01963	0.00983	0.01132
5	SmG-2	0.01165	0.00811	0.01323	0.00951	0.01039

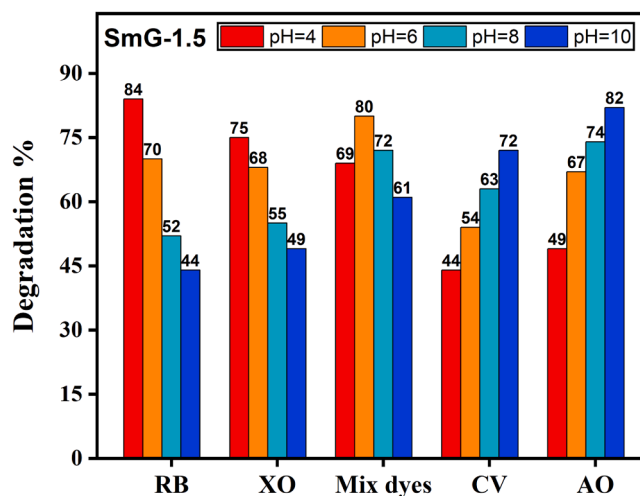
Table 4R² Value for prepared nanocomposites.

S. No.	Sample	Rose Bengal Dye	Xylenol Orange Dye	Auramine O Dye	Crystal Violet Dye	Mix Dyes
1	g-C ₃ N ₄	0.91109	0.99725	0.98921	0.99862	0.97733
2	SmO	0.99069	0.97187	0.98308	0.99051	0.9774
3	SmG-1	0.9552	0.98363	0.98078	0.98003	0.94347
4	SmG-1.5	0.9632	0.96171	0.98488	0.95342	0.92932
5	SmG-2	0.94283	0.98836	0.97046	0.94037	0.93855

K min⁻¹).

According to these findings, SmO/g-C₃N₄ nanocomposites, notably the SmG-1.5 nanocomposite, show better photocatalytic activity than SmO or g-C₃N₄ precursors alone. For the xylenol orange dye, the highest ARC value was observed in the following order SmG-1.5 (0.01125 K min⁻¹) > SmG-2 (0.00811 K min⁻¹) > SmG-1 (0.00706 K min⁻¹) > SmO (0.0034 K min⁻¹), g-C₃N₄ (0.00443 K min⁻¹). These results show that SmO/g-C₃N₄ nanocomposites (SmG-1.5) have higher photocatalytic activity than individual SmO or g-C₃N₄ precursors.

For Mix dyes, the highest ARC value was observed in the following order SmG-1.5 (0.01132 K min⁻¹) > SmG-2 (0.01039 K min⁻¹) > SmG-1 (0.00886 K min⁻¹) > g-C₃N₄ (0.00459 K min⁻¹) > SmO (0.00338 K min⁻¹). According to these findings, SmO/g-C₃N₄ nanocomposites show better photocatalytic activity than individual SmO or g-C₃N₄ precursors, with the SmG-1.5 nanocomposite being the most efficient.

**Fig. 15.** Effect of pH on Anionic, Cationic, and Mix dyes.**Table 5**

Photocatalytic Degradation efficiency of SmG-1.5 composite at various pH conditions.

S. NO.	pH Value	Rose Bengal dye	Xylenol Orange dye	Auramine O dye	Crystal Violet dye	Mix Dyes
1.	pH =4	84.7	75.3	44	49.6	69.7
2.	pH =6	70	66	54.2	67	80.2
3.	pH =8	52	54.1	63	74	72
4.	pH =10	44.1	48	72.3	82.2	61.9

Table 6

Degradation efficiency of photocatalysts at different concentrations.

S. No.	Catalyst Concentration (g / 100 mL)	Rose Bengal (pH =4)	Xylenol Orange (pH =4)	Auramine O (pH =10)	Crystal Violet (pH =10)	Mix Dyes (pH =6)
1.	0.01	84.7	75.3	82.2	72.3	80
2.	0.03	90.6	83.2	87.1	82.2	86.2
3.	0.05	96.5	90.2	93.4	88.9	93.6
4.	0.07	92.2	87.6	91.9	86.1	89.1

SmO/ g-C₃N₄ nanocomposites displayed stronger photocatalytic activity than individual SmO or g-C₃N₄ precursors for all five dyes evaluated. The SmG-1.5 Nanocomposite exhibited the greatest ARC value for all five dyes, indicating that it is the most efficient nanocomposite for photocatalytic degradation of these dyes.

3.11. Statistical analysis

In general, a high R² Means that the experimental data and the theoretical model fit well together and that the model is a good fit for the data. The high values of R² obtained from the first-order kinetic model (as presented in Table 4) demonstrate the efficacy of the SmO/ g-C₃N₄ nanocomposites as photocatalysts in degrading dyes (Fig. 10 g, 11 g, 12 g, 13g, 14g). The R² Value analysis of different nanocomposites for five dyes showed that the R2 value for SmO-1.5 nanocomposite was not the highest for all dyes, but it still showed a good correlation between the data points, suggesting a good fit. Because SmO/g-C₃N₄ nanocomposite has a high R2 value for these dyes, it may be a good option for photocatalytic applications that degrade these dyes. Thus, the SmG-1.5 nanocomposite Showed an excellent fit for all dyes studied, indicating

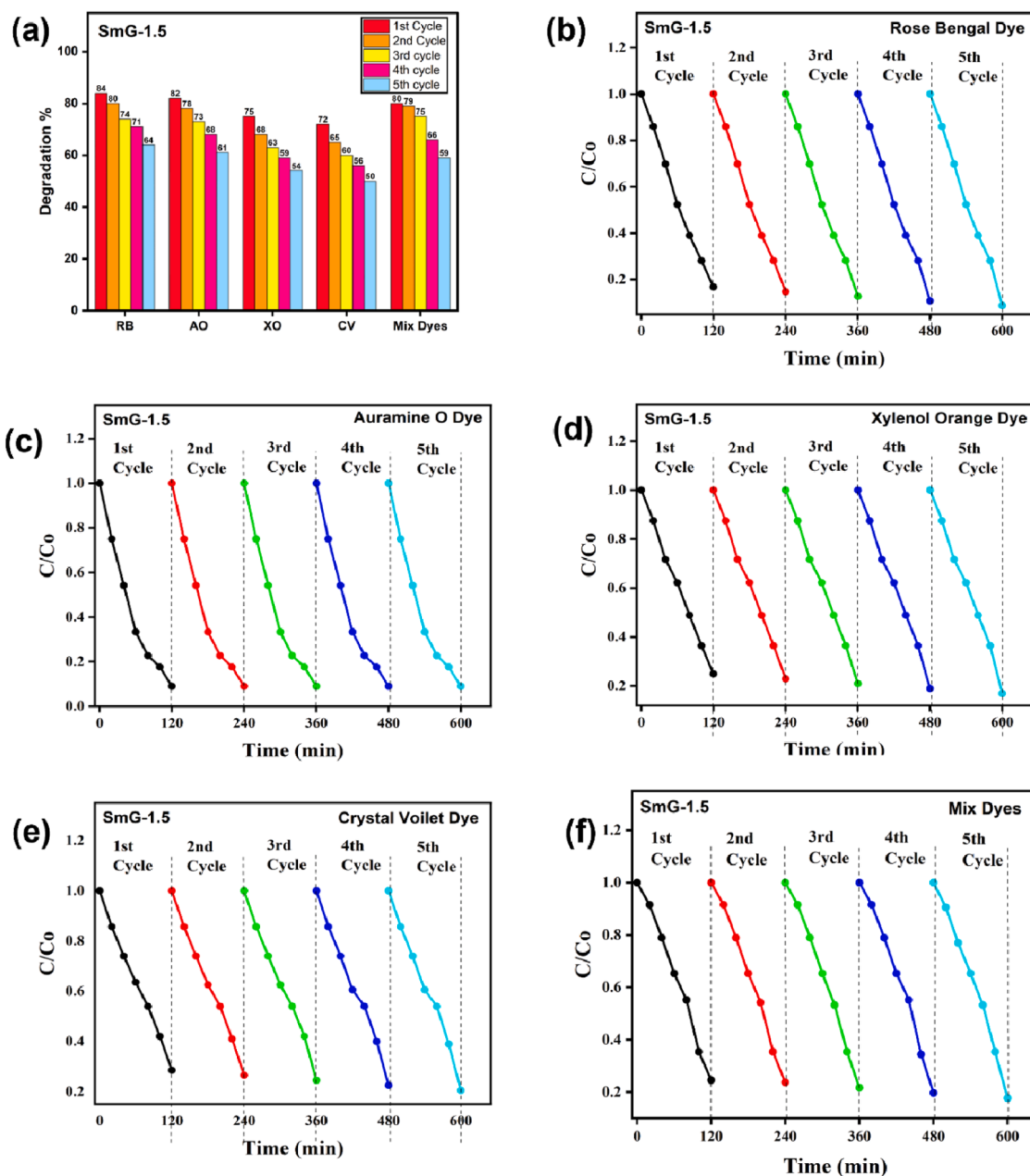


Fig. 16. (a) Investigation of dye photocatalytic degradation of dyes using SmG-1.5 nanocomposite in recycling experiments, (b-f) comparative analysis of photocatalytic degradation over 5 cycles using SmG-1.5 nanocomposite.

its potential for various photocatalytic applications.

3.12. Effect of pH-

SmG-1.5 nanocomposite was used to study the degradation of anionic, cationic, and mixed dyes at various pH levels (Fig. 1). The results show that SmG-1.5 nanocomposite degrades anionic dyes like rose Bengal and xylenol orange faster at lower pH levels. Rose Bengal and xylenol orange were degraded the fastest at pH 4, with 84.7 % and 75.3 % degradation rates, respectively. Cationic dyes, such as crystal Violet and auramine O, degraded faster at basic pH levels. At pH 10 the highest degradation rates for crystal Violet and auramine O were observed, at 72.3 % and 82.2 %, respectively. Mix dyes showed maximum degradation at pH 6 with an 80 % degradation rate. Because of the high H^+ concentration, cationic dyes bind strongly to the nanocomposite at lower pH values. Anionic dyes, on the other hand, have weaker

interactions due to H^+ ion shielding. Because of the presence of OH^- ions, anionic dyes have stronger interactions with the nanocomposite at higher pH values, whereas cationic dyes have weaker interactions due to OH^- ion shielding.

Fig. 15, Table 5

3.13. Effect of catalyst loading

Table 6 below shows the result of an experiment to determine the effect of catalyst concentration on the photocatalytic activity of SmG-1.5 nanocomposite. The degradation percent of rose Bengal, xylenol orange, Auramine O, Crystal Violet, and mix dyes were measured at various catalyst concentrations and pH levels. The results show a significant relationship between catalyst concentration and degradation efficiency. The highest degradation percentages were observed up to a concentration of 0.005 gm/100 ml, indicating improved photocatalytic activity.

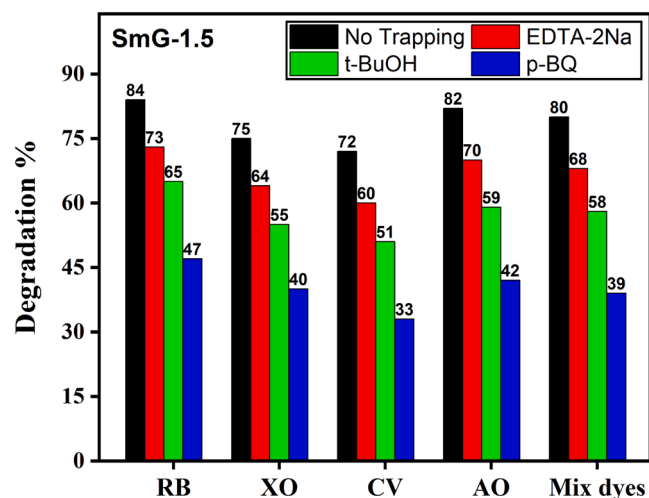


Fig. 17. The scavenger test of SmG-1.5 nanocomposite without radical trapping, EDTA-2Na, t-BuOH and p-BQ under visible irradiation.

Table 7

Photocatalytic degradation of dyes by SmG-1.5 nanocomposite under different scavenger conditions.

Dye	No Trapping (%)	EDTA-2Na (%)	t-BuOH (%)	p-BQ (%)
RB	84	73	65	47
XO	75	64	55	40
CV	72	60	51	33
AO	82	70	59	42
Mix Dyes	80	68	58	39

This improvement is due to more active sites on the catalyst surface, facilitating the photocatalytic process. However, the degradation percentage decreased slightly at the 0.007 gm/100 ml concentration. This decrease can be attributed to light scattering, caused by an excess of catalyst, which prevents light from efficiently interacting with dye molecules. As a result, exceeding the optimal catalyst concentration reduces photo activity degradation efficiency.

3.14. Reusability

The study also examined the recyclability and reusability of the SmO/g-C₃N₄ nanocomposite for the degradation of the five dyes (Fig. 16a). The results indicated that the nanocomposite could be used for up to five cycles while maintaining high photocatalytic activity. Specifically, for Rose bengal dye, the degradation efficiency of nanocomposite remained relatively stable over 5 cycles, with a slight decrease from 96.8 % to 88.4 %. Similarly, the nanocomposite showed stable degradation efficiency over 5 cycles for Xylenol Orange, slightly decreasing from 91.5 % to 85.2 %. Auramine O's degradation efficiency decreased from it is 86.6 % to 59.7 %

Moreover, the C/Co values for each dye were consistent with the previous studies, indicating that the nanocomposite maintained its high effectiveness in the long run (Fig. 16b-f). These results suggest that SmO/g-C₃N₄ nanocomposite is highly effective, recyclable, and reusable for the photocatalytic degradation of different types of dyes, making it a promising candidate for environmental remediation applications [48].

3.15. Scavenger test

Before proposing a potential mechanism for the SmG-1.5 nanocomposite, scavenger tests (illustrated in Fig. 17) were conducted to analyze its photocatalytic process. In these reactions, the primary active species are holes (h⁺), hydroxyl radicals (•OH), and superoxide radicals

(•O₂⁻). To identify the dominant species, various scavengers were used: EDTA-2Na for holes, tert-butanol (t-BuOH) for hydroxyl radicals, and p-benzoquinone (p-BQ) for superoxide radicals. The results (Table 7) showed a moderate decrease in degradation rates when EDTA-2Na and t-BuOH were used, indicating that holes and hydroxyl radicals play a limited role. In contrast, a significant reduction was observed with p-BQ, confirming that superoxide radicals (•O₂⁻) are the primary active species responsible for the photocatalytic performance of the SmG-1.5 nanocomposite.

3.16. Mechanism

The photocatalytic degradation mechanism of the SmO/g-C₃N₄ composite involves the excitation of the valence band (VB) electrons of g-C₃N₄ to the conduction band (CB) under UV light [49] (Fig. 18). This results in the generation of electron-hole pairs that migrate to the surface of the composite [17]. The SmO nanoparticles act as electron acceptors, which trap the electrons from the CB of g-C₃N₄, producing superoxide radicals (•O₂⁻) Eq.-5



The highly reactive superoxide radicals can directly react with the dye molecules, leading to their degradation [50]. Additionally, the holes generated in the VB of g-C₃N₄ can react with water molecules to produce hydroxyl radicals (•OH), which are also highly reactive and contribute to the degradation of the dyes Eq.-6.



Overall, the SmO/g-C₃N₄ composite's photocatalytic degradation mechanism involves the generation of superoxide and hydroxyl radicals, which react with dye molecules to degrade them. The high photocatalytic activity of the composite for various dyes makes it a promising candidate for environmental remediation applications.

4. Conclusion

The facile synthesis of SmO/g-C₃N₄ nanocomposites using the coprecipitation method has been demonstrated in this study. The characterization tests of the prepared nanocomposites, including XRD, SEM, TEM, and XPS, revealed their successful formation and proper morphology. The results of the photocatalytic degradation of five dyes, namely Auramine O, Xylenol Orange, Crystal Violet, Rose Bengal, and Mix dyes using SmG-1.5 nanocomposite as the photocatalyst, showed excellent degradation efficiency, with degradation rates ranging from 72.3 % to 84.7 % and ARC values ranging from 0.00706 to 0.01054 K min⁻¹. The highest degradation efficiency was observed for Rose Bengal, followed by Auramine O, Mix dyes, Xylenol Orange, and Crystal Violet. The superior photocatalytic activity of SmG-1.5 nanocomposite can be attributed to the efficient separation of photo-generated electron-hole pairs due to the formation of junctions between SmO and g-C₃N₄. The high Apparent rate constant values indicated that the nanocomposite could rapidly degrade the dyes when exposed to UV light. The pH-dependent degradation studies showed that the degradation efficiency of anionic dyes was higher at low pH values, while cationic dyes showed better degradation at high pH values. The recycling tests of the SmG-1.5 nanocomposite demonstrated its stability and reusability for up to 5 cycles.

In conclusion, the SmG-1.5 nanocomposite prepared via the coprecipitation method showed excellent photocatalytic activity for degrading dyes under UV irradiation. The superior photocatalytic performance of SmG-1.5 can be attributed to its morphology and the efficient separation of photo-generated electron-hole pairs. These results suggest that the SmO/g-C₃N₄ nanocomposite has excellent potential as a future photocatalyst for the degradation of various organic pollutants.

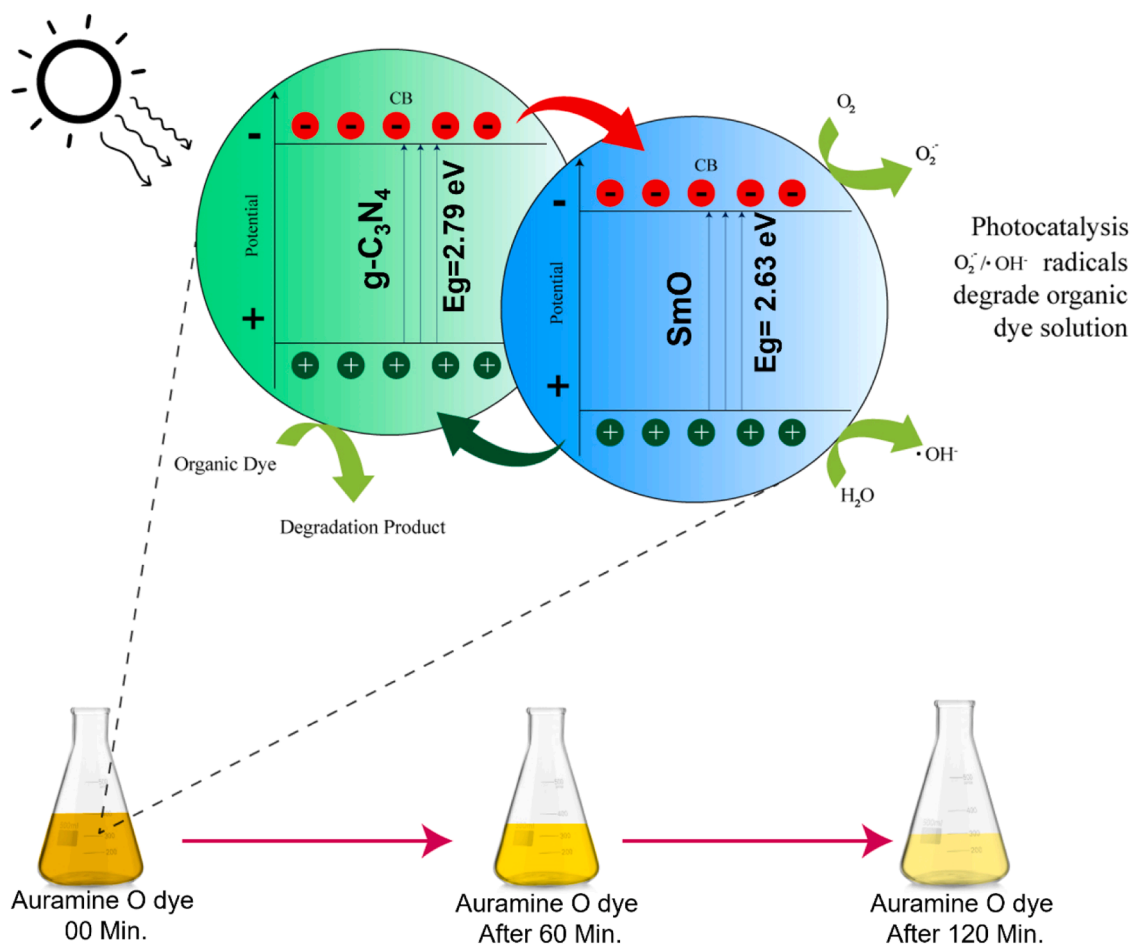


Fig. 18. Mechanism of dye degradation using prepared nanocomposites.

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Ethical approval

There is no need for formal consent for this sort of research.

Consent to participate

Not applicable.

Consent to Publish

Not applicable.

CRediT authorship contribution statement

Sachin Shoran: Writing – review & editing, Writing – original draft, Methodology, Validation, Formal analysis, Conceptualization, Investigation. **Sweetie Dahiya:** Data curation, Formal analysis, Investigation. **Sudesh Chaudhary:** Writing – review & editing, Supervision, Resources, Project administration, Conceptualization. **S.P. Nehra:** Resources, Funding acquisition, Conceptualization, Project administration, Writing – review & editing, Supervision. **Anshu Sharma:** Writing –

review & editing, Supervision, Resources, Project administration, Funding acquisition, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data are available on request.

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