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Harmonizing the photocatalytic activity of g-C₃N₄ nanosheets by ZrO₂ stuffing: from fabrication to experimental study for the wastewater treatment

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Abstract

ZrO₂@g-C₃N₄ photocomposite has been prepared from ZrO₂ nanoparticles and g-C₃N₄ nanosheet using methanol via the ultrasonic method. The prepared photocomposite was characterized using XRD, TEM, EDX, DRS, FTIR, and XPS techniques and compared with pure ZrO₂ and g-C₃N₄. A comparative study between the photocatalytic performance of the nanocomposite prepared material with ZrO₂ and g-C₃N₄ used to degrade indigo carmine (IC) dye in an aqueous suspension has been developed. The experimental photodegradation data were asserted to conform to the Lagergren kinetics model, and the fabricated nanocomposite registers a higher rate constant and lower half-life time than pure g-C₃N₄. The findings showed that ZrO₂ nanomaterials were adequately predisposed on the g-C₃N₄ surface, resulting in an expanded surface area and lowering band-gap energy. Furthermore, ZrO₂@g-C₃N₄ heterojunctions fabricated was hindered the recombination of superoxide radicals, electrons, and holes and resulted in the magnified photodegradation of IC dye.

Keywords: ZrO₂@g-C₃N₄ photocomposite; XPS; IC dye photodegradation; pH efficacy

1- Introduction

Lately, researchers have concentrated on two-dimensional (2D) nanomaterials because of their large specific surface area, the high amount of existing active sites, and unique optical and electrical characteristics [1, 2]. Amongst them, g-C₃N₄ (graphite-carbon nitride) has attracted expanding interest in the photocatalysis domain in an environment due to its 2D graphene-like construction along with its features of non-poisonous, stable, plentiful [3, 4] and lowering band-gap width near ≈ 2.75 eV [5-7]. Notwithstanding, the g-C₃N₄ received using the conventional thermal decomposition process regularly manifests bulk structure; the low specific surface areas and quick recombination of photo-generated charge carriers considerably restrict its more usage [8-10].

These different important characteristics of g-C₃N₄ encourage its application for visible illuminated photocatalytic purposes employing solar energy. Besides, g-C₃N₄ is abundant and simplistic fabricated through one-stage polymerization of affordable feedstocks similar to urea [11, 12], dicyandiamide [13], thiourea [14], melamine [15], and cyanamide [16, 17]. Although, purely g-C₃N₄ suffers from deficiencies such as accelerated recombination of photo-created electron-hole pairs, a low specific surface area, and a lowering visible light application performance [13, 15, 18, 19]. Then, investigate easy and reliable approaches to manufacturing the g-C₃N₄ nanomaterials based on application as photocatalysts with enhanced physicochemical features and great photocatalytic performance.

Newly, various efforts and strategies have been manipulated to magnify the visible light photocatalytic activity of g-C₃N₄, for instance, the development of heterojunction employing such as TiO₂@g-C₃N₄ [20], ZnO@g-C₃N₄ [21], Bi₂WO₃@g-C₃N₄ [22], CdS@g-C₃N₄ [23], which can comprehensively grow the utilization of the g-C₃N₄ as nanocomposites. Furthermore,

limited nanomaterials can couple with g-C₃N₄ to form a heterojunction composition. The critical requirement to develop an adequate visible-light-induced g-C₃N₄ based nanocomposite is that the nanocomposites should have a suitable band construction that is profitable to generate a coupling hybridization structurally.

Depending on the advantages mentioned earlier, the ZrO₂@g-C₃N₄ photocomposite was prepared from its precursors via ultrasonic irradiation. The features of the prepared nanocomposite were investigated, and its possible utilization as a ZrO₂@g-C₃N₄ was examined. A study on the photocatalytic degradation capability of the IC dye using ZrO₂@g-C₃N₄ nanocomposite at various pH conditions was monitored.

2- Experimental part

2.1. g-C₃N₄ nanosheets fabrication

2.2. ZrO₂@g-C₃N₄ photocatalyst preparation

ZrO₂@g-C₃N₄ photocatalyst was manufactured via a simplistic step ultra-sonication procedure. At first, 920 mg of g-C₃N₄ nanosheet was weighted and sonicated in 0.150 L of methanol solvent for 15min. A 400 mg of ZrO₂ nanomaterials were combined with the methanolic blend, and the resulting mixture was subjected to sonication for 15 min. The yellow collected suspension was subjected to sonication for an extra 45 min and drained in an oven at 363 K for 1440 min. At last, the obtained materials were milled and annealed in a programmed furnace at 453 K for 120 min.

2.3. Characterization

The morphology construction of the specimens was examined through X-ray diffraction (XRD), Bruker AXS, Ger-man, by CuK α radiation source (1.5406 Å) at a scan rate of 0.02.s⁻¹. A stimulating voltage and selection current of about 40 kV and 20 mA, respectively, were employed. The TEM photographs of pure ZrO₂, g-C₃N₄, and ZrO₂@g-C₃N₄ were performed

using a transmission electron microscope, with accelerating voltage 200 kV, via a Tecnai G20 (USA) device. The absorbance in the diffuse reflection method, utilizing barium sulphate as reference, was measured employing a UV-2550 spectrophotometer (Japan). A Nicolet 5700 FT-IR spectrophotometer has served to report the FT-IR spectra of the fabricated specimens on a wavenumber interval ranging from 400 to 4000 cm^{-1} . In order to investigate the chemical bonding and the interaction features of $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ catalyst with an Al Ka X-ray source (1486.68 eV, VG ESCALAB 220i-XL, UK), XPS (X-ray photoelectron spectroscopy) was operated. The nanocomposites' surface areas and average pore size distributions were studied using the Brunauer-Emmett-Teller (BET) method using a Micromeritics ASAP 2020 apparatus, where samples are outgassed for 120 min, at 150 $^{\circ}\text{C}$, then weighed and analyzed. The photoluminescence (PL) spectra were measured on the $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ nanocomposites samples using a fluorescence spectrophotometer (Perkin Elmer LS55) equipped with a xenon lamp, and the selected excitation wavelength is $\lambda = 340$ nm.

2.4. Photocatalytic degradation experiment details

Indigo carmine (IC) dye has been chosen as a pollutant organic compound to assess the photocatalytic capability for the fabricated $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ photocomposite. In the conventional photocatalytic trial, 0.050 g of the specimens were suspended separately in 0.100 L IC liquid dye with a fixed concentration of 30 ppm. The degradation of the IC dye was studied in the visible light region at ambient requirements. Before the photocatalytic activity trial, specimen suspension was put in darkness for 30 min and continuously agitated till achieving the equilibrium between the nanomaterials and the IC dye. After adsorption dye equilibrium, 0.05 L of the mixture solution was taken as an original IC concentration (C_0). The remaining mixture was then subjected to visible-light radiation (OSRAM lamp 58 IM/W). Then with fixed time

intervals, 0.05 L from the suspension was taken and centrifuged for 10 min in order to separate IC dye and estimate its photodegradation. The effectiveness of the photodegradation treatment was evaluated by measuring the difference in the dye concentration via the absorbance measurement at $\lambda_{\text{max}} = 610 \text{ nm}$ using SHIMADZU-UV-1650 PC spectrophotometer.

3. Results and discussions

3.1. XRD confirmation

g-C₃N₄, ZrO₂, and ZrO₂@g-C₃N₄ accumulated XRD models are reported in figure 1. For real g-C₃N₄, characteristic diffraction peaks are located at $2\theta = 13.0^\circ$ and 27.58° with interlayer stacking plane (002) of the hexagonal crystal for JCPDS 87-1526 and the in-plane structural sorting motif (100) [24]. The powder x-ray diffraction design of pure ZrO₂ nanomaterials is manifested in Fig. 1. The peaks located at two theta angles of 24.00 (110), 28.22 (-111), 31.35 (111), 34.07 (200), 35.27 (002), 40.64 (120), 44.80 (211), 49.24 (220), and 50.09 (022) were matched to monoclinic crystals of ZrO₂ phase for JCPDS No.00-37- 1484 [25, 26]. Besides, the ZrO₂@g-C₃N₄ bands' pattern shows both g-C₃N₄ and ZrO₂ peaks, establishing the precursors rapprochement of in the nanocomposite crystalline composition. The confirmation of the nanocomposite pureness was based on the nonappearance of other crystalline state. Although, the ZrO₂ principal intensity height has changed towards fewer 2θ values from 28.1924 to 28.0514° ; meanwhile the FWHM also increased from $\beta = 0.3731^\circ$ to 0.6128° . These findings may be attributed to the reduction of the crystallite size (D) which was assessed using the Scherrer formula [27]:

$$D = \frac{0.9 \cdot \lambda}{\beta \cdot \cos\theta}$$

Where:

θ corresponds to the diffraction angle,

β corresponds to the line expanding at half the maximum intensity (FWHM),

λ corresponds to the wavelength of the Cu K α radiation,

0.9 corresponds to the dimensionless configuration factor.

Selecting the most intense reflection (-111), the ZrO₂@g-C₃N₄ crystallite was found to be 13.95 nm, while the pure ZrO₂ has D = 23.03nm and absolute g-C₃N₄ equal 7.94 nm.

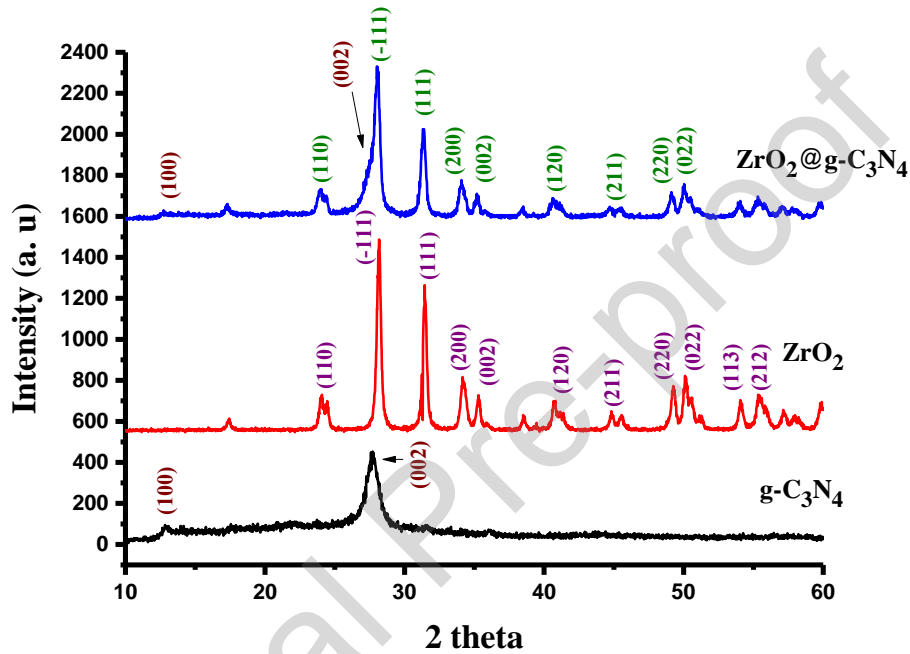


Fig. 1. XRD outlines of g-C₃N₄, ZrO₂, and ZrO₂@g-C₃N₄ photocomposite

3.2. Morphological study

The TEM photographs of the real g-C₃N₄ nanosheets, ZrO₂ nanoparticles, and ZrO₂@g-C₃N₄ hybrid nanostructures are depicted in Figs. 2a, c, and e. The primary g-C₃N₄ TEM picture exhibits soft surface sheets' layers as a common graphitic nanostructure one [28]. On the other hand, the ZrO₂ TEM image (Fig. 2c) presents like-spherical shape nanoparticles with regular size, agreeing with the XRD findings. Furthermore, the TEM photograph (Fig. 2e) of the ZrO₂@g-C₃N₄ photocomposite manifests ZrO₂ nanoparticles separated over the g-C₃N₄ nanomaterials. Therefore, an interface and efficient solid interplay that attaches g-C₃N₄ to ZrO₂

is performed to facilitate the photo-excited charge carriers' detachment for lowering the energy band-gap and improving the photodegradation process. The elemental composition results from the EDS spectrum (Fig. 2b) confirm only C and N for the crumpled layered nanosheet of pure g-C₃N₄. Besides Fig. 2d, the elemental composition of ZrO₂ consists of only Zr and O elements. However, the ZrO₂@g-C₃N₄ reveals the presence of Zr, O, C, and N elements. These results successfully proved the coupling of the ZrO₂ with the g-C₃N₄ nanosheets to develop the photocomposite, as noted in (Fig. 2f).

3.3. Optical properties and DRS calculations

The UV-vis and DRS results of pure g-C₃N₄, ZrO₂, and ZrO₂@g-C₃N₄ photocomposite are presented in Fig. 3. The optical specimen characteristics' findings revealed that the highest absorption wavelength of pure g-C₃N₄ for radiation is 420 nm and for ZrO₂ is about 390.8 nm. Besides, the maximum absorption line edge of ZrO₂@g-C₃N₄ photocomposite is 451.7 nm, and the absorption of visible light is notably improved. Furthermore, these obtained results designate that combining ZrO₂ develops the visible radiation absorption appearance of pure g-C₃N₄. The energy gap estimation was computed employing the Kubelka–Munk equation [29, 30]:

$$\alpha hv = A (hv - E_g)^{n/2}$$

Where:

h corresponds to the Plank's constant,

v corresponds to the light frequency,

α corresponds to the absorption coefficient

E_g is the band-gap and A is a constant,

n is a constituent based on the semiconductor optical transition features (i.e., for direct n = 1 transition, for indirect transition n = 4).

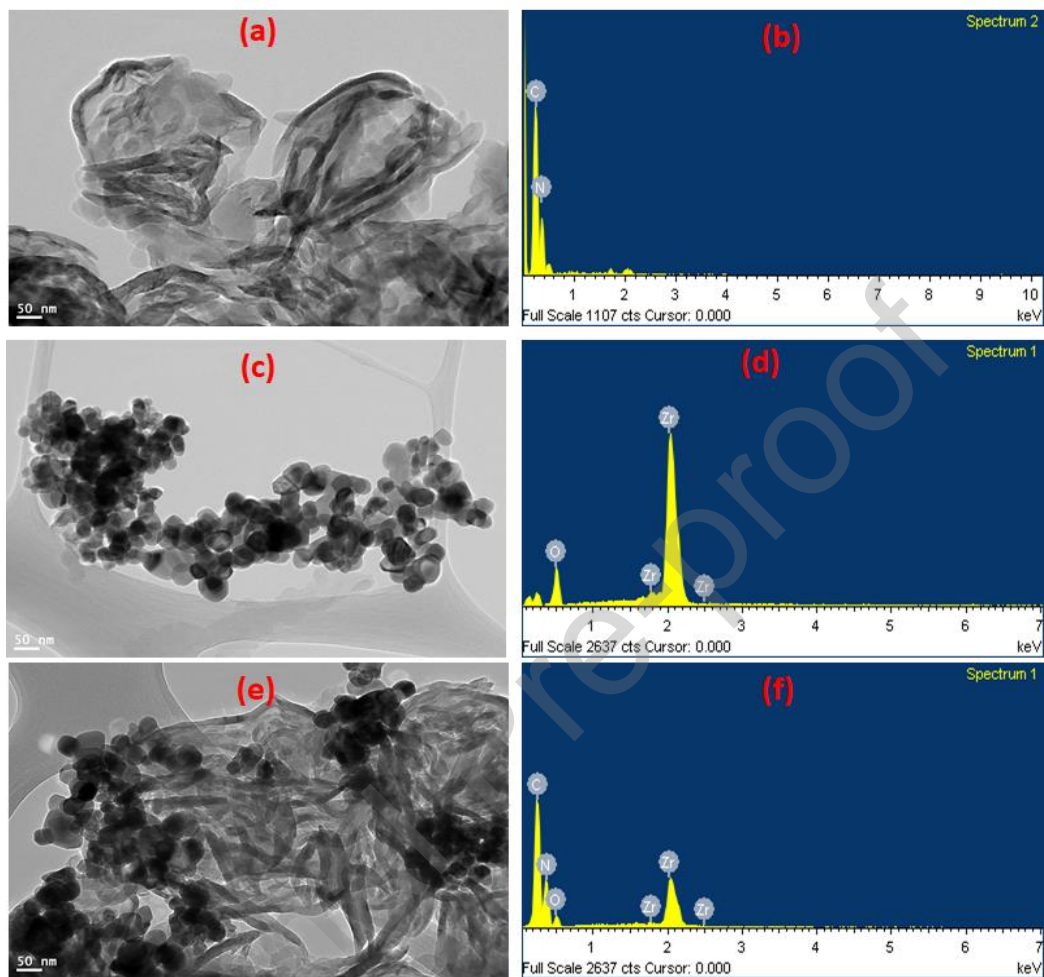


Fig. 2. TEM pictures and EDX (a, b), (c, d), and (e, f) for $g\text{-C}_3\text{N}_4$, ZrO_2 and $\text{ZrO}_2@g\text{-C}_3\text{N}_4$

The energy band gaps of ZrO_2 nanoparticles, $g\text{-C}_3\text{N}_4$ nanosheets, and $\text{ZrO}_2@g\text{-C}_3\text{N}_4$ were counted as 3.64, 2.89 and 2.86 eV, severally. These obtained results were confined to the similar distinguished values in earlier statements [31, 32]. The enhancement of the optical characteristics of photocomposite than purely $g\text{-C}_3\text{N}_4$ nanosheets may be owing to the interaction of ZrO_2 nanoparticles with graphitic carbon nitride. In addition to the formation of chemical bonds within the ZrO_2 and $g\text{-C}_3\text{N}_4$ also increased visible absorption characteristics.

3.4. FTIR and functional groups determination

The large absorption lines in the FTIR spectrum of purely $g\text{-C}_3\text{N}_4$, in the wavenumber range ($3500\text{-}3000\text{ cm}^{-1}$) may be attributed to N–H's stretching vibration [33].

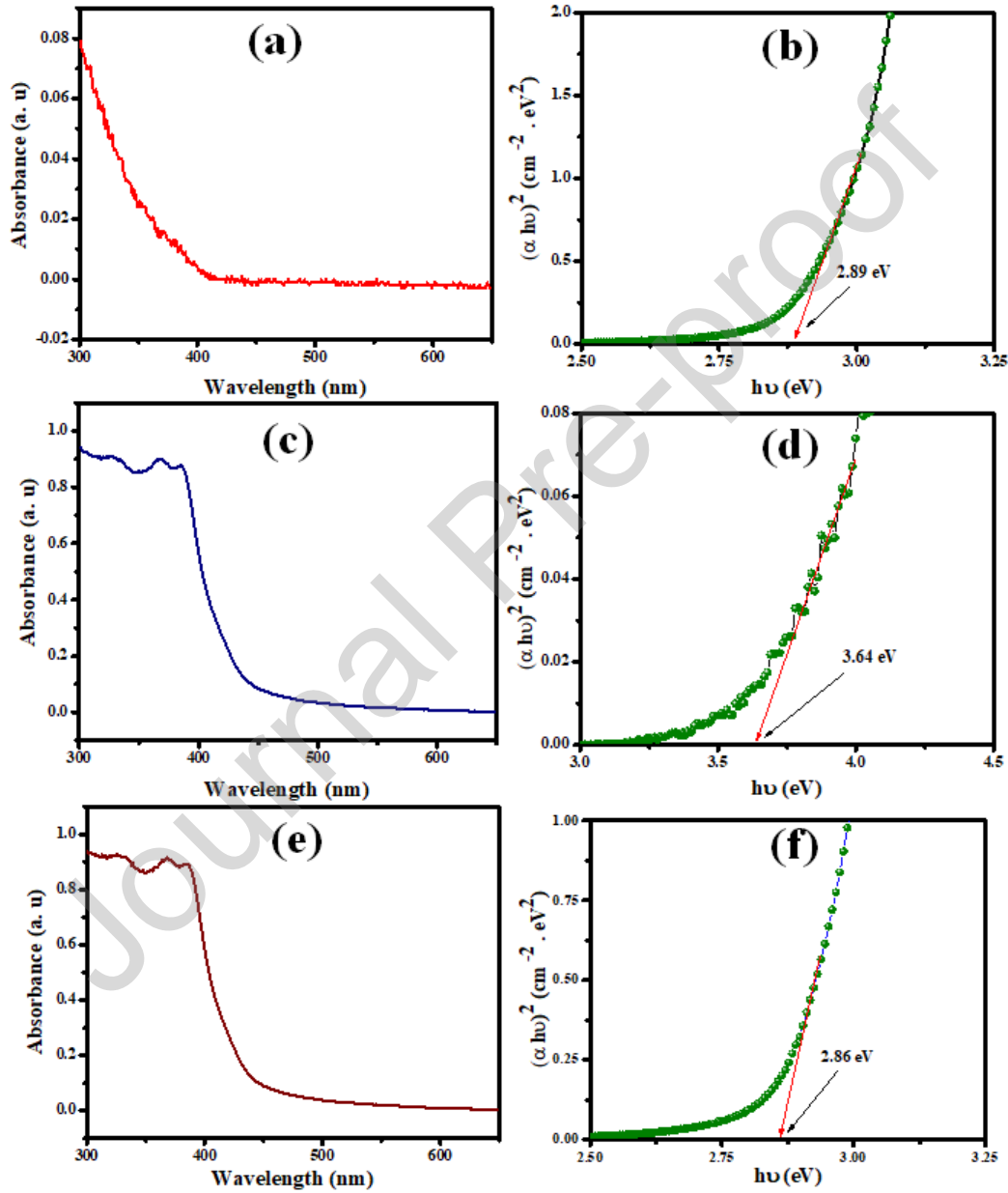


Fig. 3. (a, c, and e) UV-Visible spectra, and (b, d, and f) band-gaps of $g\text{-C}_3\text{N}_4$, ZrO_2 , and $\text{ZrO}_2@g\text{-C}_3\text{N}_4$ photocomposite, correspondingly.

In the interval ranging from 1600 to 1200 cm^{-1} , the detected set of bands could be accredited to the common C–N bonds stretching [34]. The presence of a peak located at 810 cm^{-1} is appropriate for the bending vibration of the s-triazine ring, suggesting the existence of hexazine structure in the chemical formation of the as-fabricated g- C_3N_4 nanosheets materials consequently [35].

As shown in (Fig. 4), peaks detected at 1232 cm^{-1} and 1444 cm^{-1} in the FTIR spectra of the ZrO_2 nanopowders are consecutively related to the twisting oscillation of an absorbed water (H_2O) compound and a surface hydroxyl group (OH), [36] A wide vibration band is detected in the wavenumber variety 3330 – 3456 cm^{-1} due to surface hydroxyl group and the absorbed water molecule [37]. The band recognized at 412 cm^{-1} designates the appearance of pure ZrO_2 nanoparticles [38]. The results of pure g- C_3N_4 are similar with FT-IR spectra of ZrO_2 @g- C_3N_4 , as presented in Fig 4. Notwithstanding, the variation in the peaks at 493.7 to 434.7 cm^{-1} after adding of ZrO_2 clearly confirms the occurrence of the ZrO_2 phase structure. Therefore, these received results reveal the formation of ZrO_2 @g- C_3N_4 photocomposite

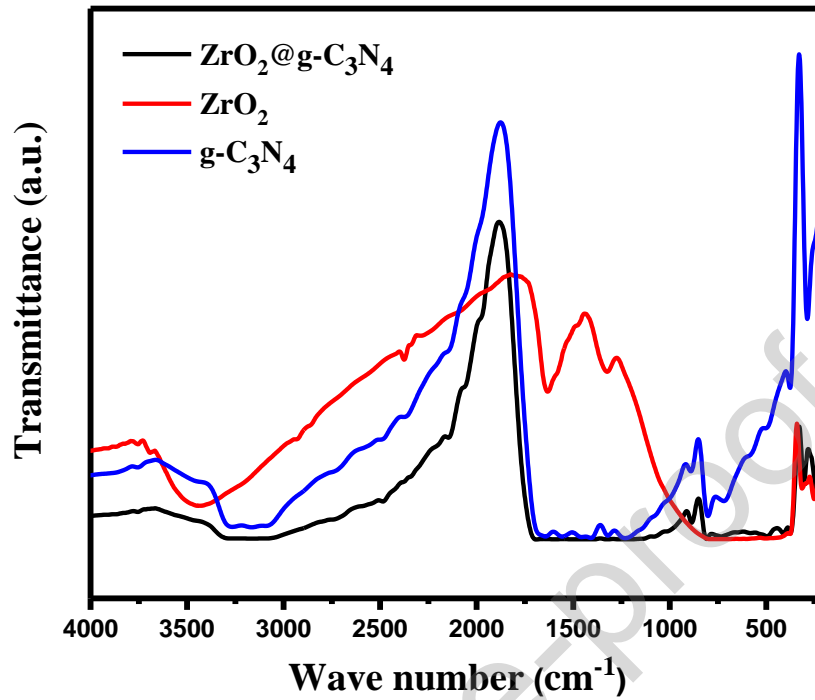


Fig. 4. FTIR spectra results for g-C₃N₄, ZrO₂, and ZrO₂@g-C₃N₄ nanomaterials

3.5. XPS analysis

The chemical bonding and configuration of the ZrO₂@g-C₃N₄ surface were observed using the XPS technique, as displayed in Fig. 5(a-d). The XPS chemical outline spectra of the ZrO₂@g-C₃N₄ photocomposite catalyst exhibition just Zr, O, C, and N components revealed the creation amid zirconium oxides (ZrO₂) and graphitic carbon nitride (g-C₃N₄) as in Fig. 5(a-d).

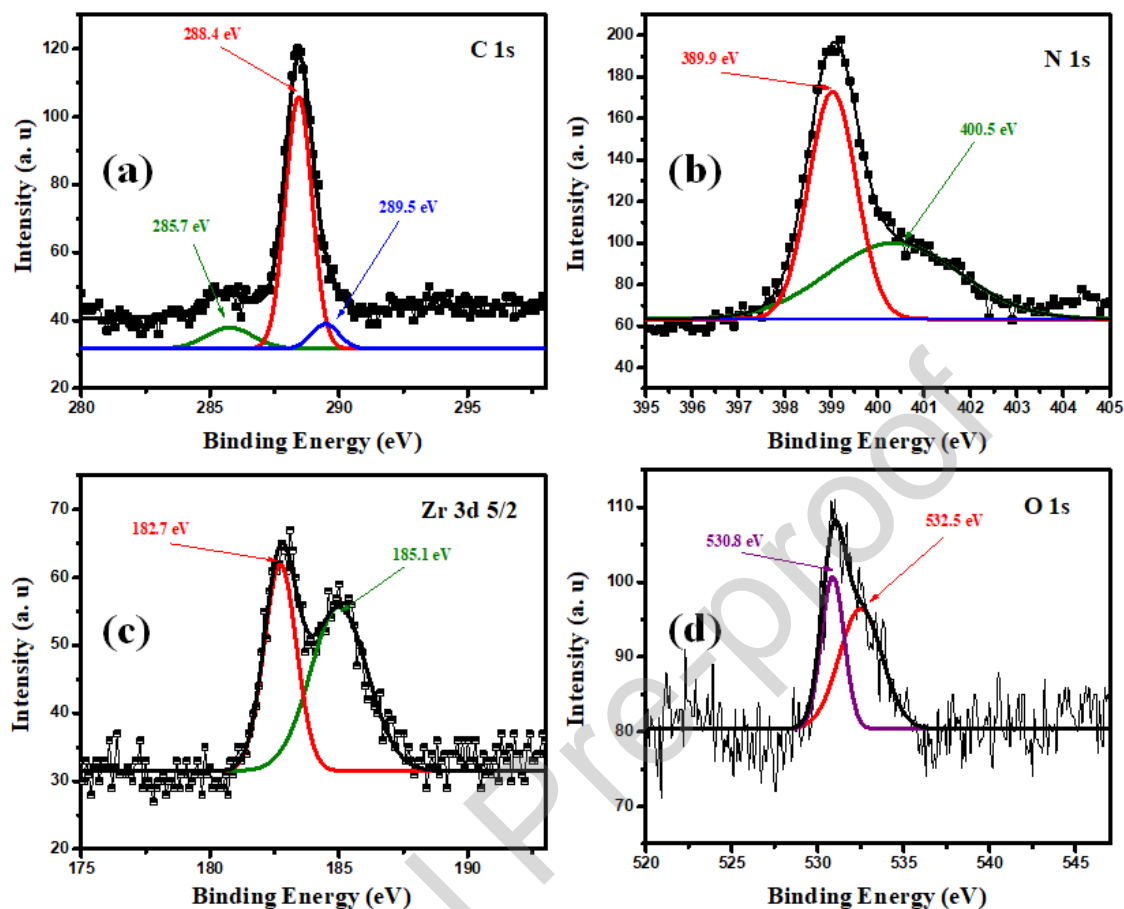


Fig. 5. XPS spectra, (a) C 1s, (b) N 1s, (c) Zr, and (d) O 1s for $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ photocomposites.

The band is located at 285.7, 288.4, and 289.5 eV for C 1s (Fig. 5(a)), which matches the covalent bond of sp^2 hybridized graphic carbon, sp^2 carbon chemical bonded to N (N-C=N), and dependency features owing to $\pi - \pi^*$ excitation, sequentially. [39, 40]. Fig. 5(b) shows the distinct high-resolution peaks for N 1s in $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ at 389.9 eV, and 404.4 eV can be associated with sp^2 hybridized aromatic N incorporated in the triazine structure (C=N-C) and π excitation [41]. The high-resolution peaks at 182.7 and 185.1 eV for Zr 3d could be correlated individually with Zr 3d_{5/2} and Zr 3d_{3/2} [42]. The O 1s spectra of $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ exhibit two bands at 530.8 eV, and 532.5 eV, accredited to the oxygen (O) crystal structure in zirconium oxide and materially adsorbed oxygen, severally as exhibited in Fig. 5(d) [11, 43]. As apparent

from the XPS information, the components existing in the $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ photocomposite are Zr, O, N, and C, managing the incorporation of any impurities. Certain decisions comply with earlier data reported for the $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ construction [32, 44].

3.6. PL analysis

Photoluminescence spectra were used to examine the effectiveness of photogenerated. Fig. 6 displays the photoluminescence spectra of graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) and the $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ photocomposite at a 360 nm excitation wavelength. As illustrated in Fig. 6, the PL spectra of pure $\text{g-C}_3\text{N}_4$ and the $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ photocomposite exhibit a prominent main emission peak centered at approximately 440 nm, which may be due to electron-hole recombination in $\text{g-C}_3\text{N}_4$ [45]. Additionally, the PL intensity of the $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ photocomposite is lower than that of pure $\text{g-C}_3\text{N}_4$, implying that the $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ photocomposite has a reduced electron-hole recombination rate of electrons and holes when exposed to visible light [46].

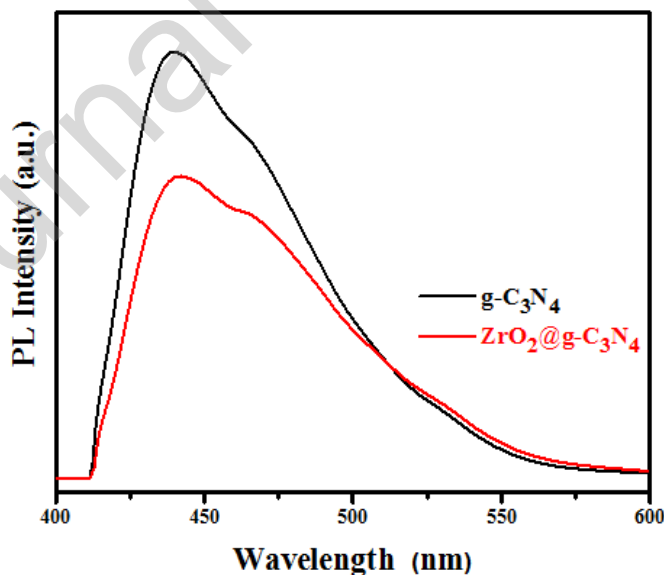


Fig. 6. PL spectra of pure $\text{g-C}_3\text{N}_4$, and $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ photocomposite

3.7. Nanomaterials surface area Assessment

The nitrogen adsorption-desorption isotherms of pure g-C₃N₄ and ZrO₂@g-C₃N₄ nanocomposite are shown in Fig. 7a and b. The isotherms of the ZrO₂@g-C₃N₄ nanostructures are type IV, indicating the presence of mesopores during sample formation due to the weak hysteresis loop generation. Pure g-C₃N₄ specimen display also type IV behavior, explained by the weak hysteresis loop generation [47, 48]. The specific surface area of ZrO₂@g-C₃N₄ nanostructures was 95.685 m²/g, characterized by a pore volume of 0.216 cm³/g, which is less than the specific surface area of pure g-C₃N₄ (154.055 m²/g and pore volume of 0.912 cm³/g). Thus, while the large specific surface area of pure and nanocomposite is shown to boost the photocatalytic activity for IC dye degradation, the surface area is not the only factor contributing to the nanocomposite's activity. The charge separation between the two semiconductors is the determining factor in composite production.

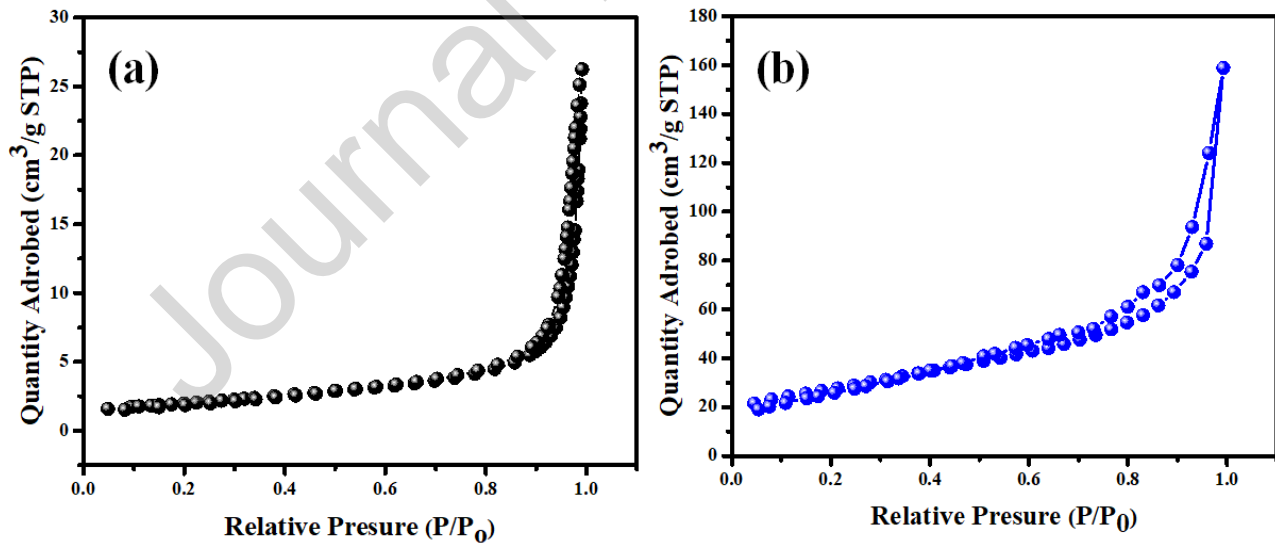


Fig 7: Surface area isotherms characteristics of pure g-C₃N₄ (a), and ZrO₂@g-C₃N₄ photocatalyst

(b).

3.7. Photodegradation analysis

3.7.1. The IC dye photodegradation test

The photocatalytic activities of fabricated specimens were observed by decomposing IC dye under visible irradiation. The photodegradation results of IC dye over pure ZrO_2 nanoparticles, pure $\text{g-C}_3\text{N}_4$ nanosheets and $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ photocatalyst under visible light are presented in Fig. 8 (a and b). Before exposition to light, the adsorption equilibrium of IC dye over the nanomaterials was examined in dark conditions, and adsorption balances were reached after 30 min for each specimen. Fig. 8a illustrates the dye photodegradation rates, where C_t and C_0 are the concentration of the IC dye at time t and time zero, measured at λ_{max} equal 610 nm.

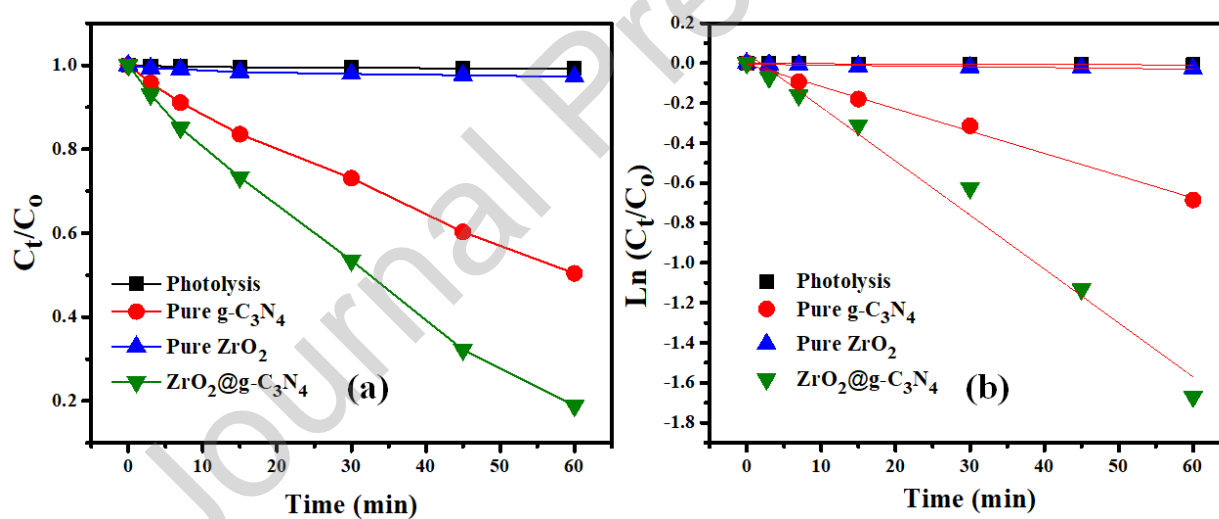


Fig. 8. (a) nanomaterials for IC dye degradation against time, and (b) Lagergren kinetics model.

The photodegradation kinetics of the IC dye obeys the Lagergren kinetics model (Fig. 8b) as designated using the linear correlation of $\ln(C_0/C_t)$ incremented by the time [49], which is established through the acceptable regression coefficient as shown in Table 1. The developed photocatalytic performance of the $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ photococomposite is indicated through the high

degradation rate constant (k) and lower half-life time values recorded in Table 1. The degradation impact of the photocomposite fabricated is five folds of pure g-C₃N₄ nanosheets, proving that the hetero-structured junction within ZrO₂ and g-C₃N₄ is essential for accomplishing enhanced action ZrO₂@g-C₃N₄ photocomposite [32].

Table 1: photocatalysis parameters of IC dye decomposition

Samples	k (min ⁻¹)	$t_{1/2}$ (min)	R^2	RSS
Pure g-C ₃ N ₄	0.00512	135.4	0.99	0.00100
Pure ZrO ₂	0.00041	1690	0.89	0.00006
ZrO ₂ @g-C ₃ N ₄	0.02790	24.84	0.98	0.03500

3.7.2. pH impact on The IC dye degradation

The organic dye degradation takes place on the surface of nanomaterials, so the dye adsorption phenomena are an essential step in the photocatalytic rule. Earlier attempts stated that organic dye compounds with significant adsorption capability decompose quickly [50, 51]. Also, a greater pH value can provide a larger hydroxyl ions (OH⁻) concentration to respond with holes and generate hydroxyl radicals ([•]OH), magnifying the dye photodegradation rate. Besides at below pH value, the before-mentioned IC dye will deliver a higher photodegradation appearance owing to the convenience of holes that will respond with water to create [•]OH. Therefore, the amount of adsorbed dye on the nanomaterial's surface and [•]OH concentration will define the quantity of photodegradation [52]. The pH of the dye solution is a disturbing parameter in photodegradation experiments due to its influence on the ionization state, the surface phase

catalyst, and the IC dye structure [53, 54]. Fig 9(a and b) represents the pH variation of IC dye photodegradation as a function of time and photocatalytic rate % in the pH range from 2 to 11.

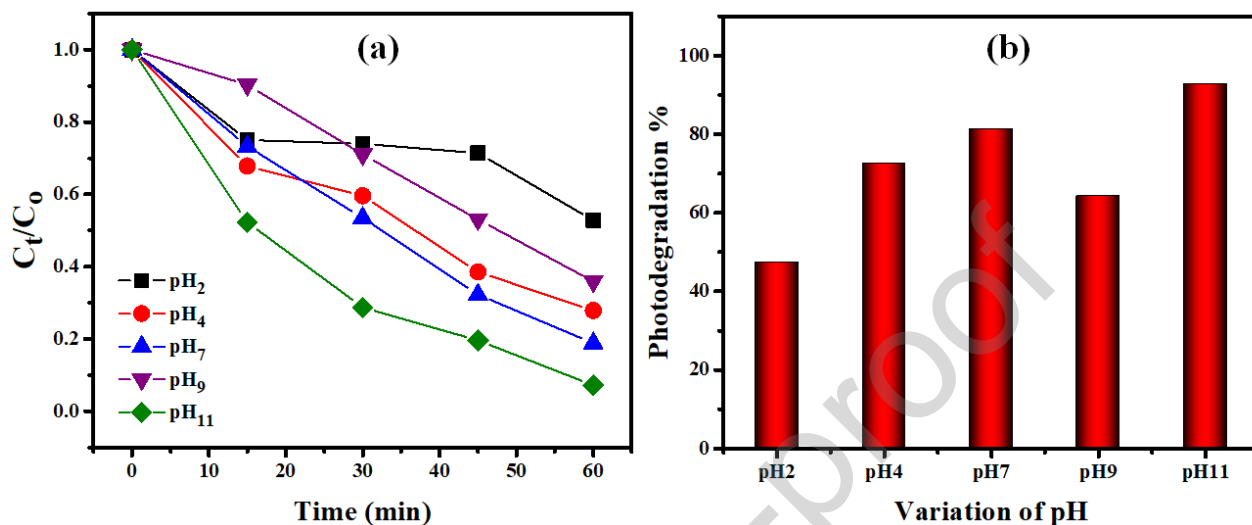


Fig 9: influence of pH variations on IC dye (a) photodegradation time and (b) photodegradation percentage

The results of photocomposite exhibit extremely weak capability at pH in the acidic range. This behavior is because, at low pH, ZrO_2 present with $ZrO_2@g-C_3N_4$ nanostructures responds to the free H^+ in the water and is thoroughly destroyed in the solution. Besides, the H^+ complex with the negatively charged IC dye diminishes the electrostatic interactions force with active sites $ZrO_2@g-C_3N_4$ nanostructures [55]. Accordingly, the maximum pH necessary to destroy IC dye molecules is the neutral conditions when the best competence occurs (i.e., at pH 7).

3.7.3. Radical Scavengers Assessment

The radical trapping factors were examined to determine the effectiveness of radicals that contribute to dye degradation. Fig. 10 illustrates the IC dye photodegradation percentage rate *versus* t using a different scavenger. The results demonstrated that dye degradation yields are 82, 39, 90, 20, and 93%, which quenched with the interest of $AgNO_3$ (e^-) [54], EDTA (h^+) [56], IPA ($\bullet OH$) [57], ASC ($\bullet O_2^-$) [57], and free scavenger. The findings show a large reduction in the

rate percentage IC dye photodegradation utilizing ASC, implying a vital purpose of $\bullet\text{O}_2^-$ [58] in the degradation method.

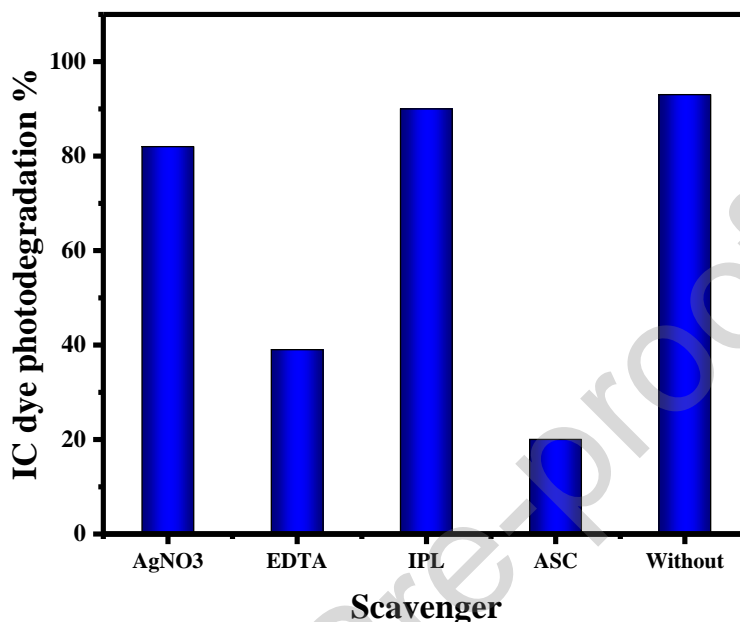


Fig 10: the reactive varieties trapping test of IC dye photodegradation via $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ nanostructures

A significant position of holes (h^+) in the destruction activity is displayed by the strong influence of the EDTA on the IC dye photodegradation [59]. Alternatively, a second part is performed during the $\bullet\text{OH}$ radicals [60] as designated by the weaker influence of its scavenger, the IPL, whereas there is no impact of nitric acid on the IC dye decolorization rule intimates no direct relationship electrons in the IC dye degradation [12]. This impact of scavenger results demonstrated that $\bullet\text{O}_2^-$ and h^+ are playing principal reactive species in the IC dye catalytic degradation by $\text{ZrO}_2@\text{gC}_3\text{N}_4$ photocomposite.

3.7.4. The IC dye photodegradation Mechanism

Determined CB and VB values of $\text{ZrO}_2@\text{gC}_3\text{N}_4$ are obtained using the expressions [61]:

$$E_{\text{CB}} = X - E_{\text{C}} - 0.5 E_{\text{g}}$$

$$E_{VB} = E_{CB} + E_g$$

where X corresponds to the semiconductor's absolute electronegativity (X for g-C₃N₄ and Zr O₂ are 4.72 and 5.91 respectively) [29, 62, 63], E_C corresponds to the free electron energy on the hydrogen scale (≈ 4.5 eV) and E_g is the band-gap energy of the semiconductor. The conduction and valence band potentials respectively presented as E_{CB} and VB . The CB and VB band-gap locations for g-C₃N₄ and ZrO₂ are therefore -1.170 and 1.700 eV, and -0.465 and 3.285 eV, respectively.

The boosted photodegradation performance of binal composite may be attributed to the simulated photocatalytic Z-scheme model playing a vital role in the photogenerated charge carriers' spatial separation [64]. Conferring to the scavengers' findings, it was proven that $\bullet O_2^-$ and e^- primarily contributed to the photodegradation procedure. As visible light illumination strikes the g-C₃N₄ surface, it absorbs the light photons. Subsequently, the excited electrons acquire energy to get exalted from the VB to the CB, leaving behind the holes (h^+) [65]. Because of the direct contact among the composite semiconductors, the photo-excited electrons get conveyed from the g-C₃N₄ CB to the ZrO₂ CB; therefore, the 3D separation of electrons and holes occurs [66]. The electrons can then act the adsorbed oxygen on the composite surface and generate the reactive $\bullet O_2^-$ ($O_2/\bullet O_2^- = -0.33$ eV vs. NHE) [67]. However, the edges potential of VB for g-C₃N₄ (1.70 eV vs. NHE) is less favourable compared to the oxidation potential of $OH^-/\bullet OH$ (2.40 V vs. NHE). Accordingly, the holes on the g-C₃N₄'s VB cannot react with hydroxide ions to form the $\bullet OH$ [49], as the radicals scavengers assessment proved. So, the photocatalytic dye elimination was accomplished by direct oxidation with the generated holes (h^+) on the g-C₃N₄ VB and the $\bullet O_2^-$ inducted from photo-excited e^- s. This process is possibly improved by the affinity of H₂SO₄ anionic groups of the dye to the VB-holes, which motivates

their sorption on the nanocomposite surface to perform the oxidation [68]. The significant difference between the migration rate of the photogenerated e^- and h^+ may rationalize the $\bullet O_2^-$ production. The following reaction with the dye molecules would be more expeditious than its direct oxidation by holes [28].

Consequently, this mechanism concurs adequately with the scavengers' processes imply that $\bullet O_2^-$ and h^+ are the effective species for the dye photodegradation utilizing the $ZrO_2@g-C_3N_4$ nanocomposite. This mechanism is in agreement with a similar study that investigated the generation of $\bullet OH$ on the TiO_2/C_3N_4 surface through $C_6H_4(CO_2H)_2$ (TA) where no $\bullet OH$ was identified. This phenomenon was attributed to the lower edges potential VB of $g-C_3N_4$ compared to that of $OH/\bullet OH$ couple potentials [49]. Therefore, the proposed photodegradation Z-scheme mechanism's model advocates the formation of excess $\bullet O_2^-$ along with additional powerful oxidizing agents' h^+ than in the 'type II-heterojunction' one. This assumption is consistent with the experiments of scavenger to support the presumed Z-scheme mechanism path in the photodegradation of the tested dye [69]. Fig. 11 exemplifies the plausible mechanism of the dye molecule degradation process.

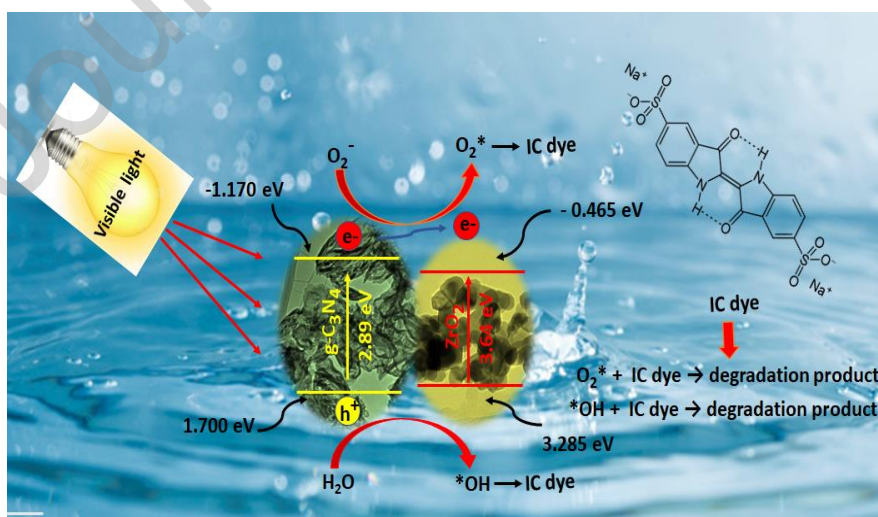


Fig 11: Scheme of IC dye photodegradation mechanism using $ZrO_2@g-C_3N_4$ nanocomposite

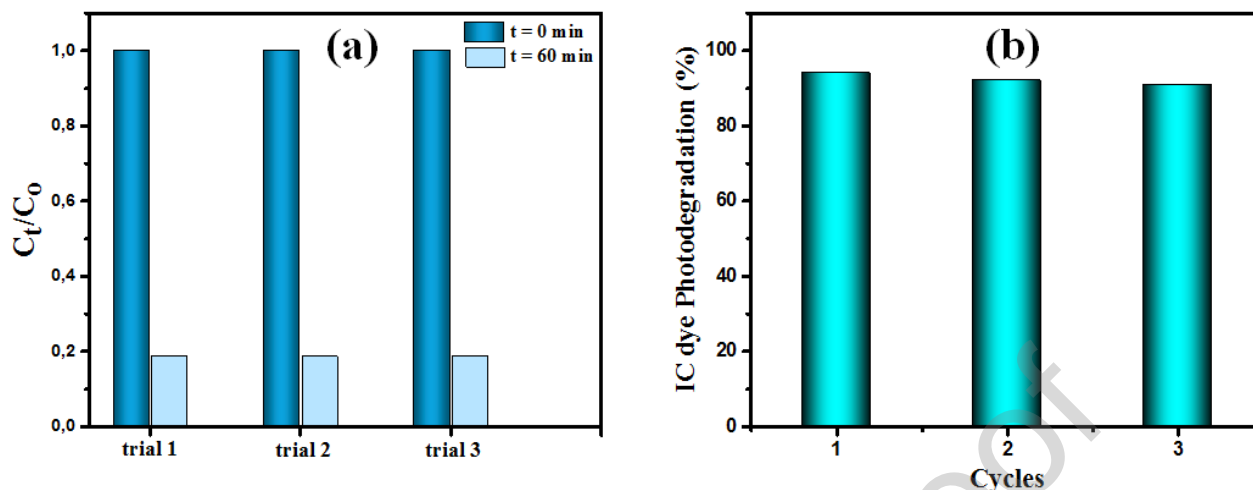
Table 2: A comparison of the $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ photodegradation efficiency with other composites from literature.

Photocatalyst	IC Photodegradation time	k (min^{-1})	Ref.
Cobalt doped ZrO_2	90 min	0.0024	[70]
$\text{ZnO}/\text{CuO}/\text{Si}$ nanocomposite	85 min	0.0220	[71]
Mg doping ZnO nanoparticles	90 min	0.0087	[72]
TiO_2 quantum dots	120 min	0.0230	[73]
Mg/ZnO nanomaterials	90 min	0.0180	[72]
Multi-element doped ZrO_2	150 min	0.0100	[74]
$(\text{CuO} + \text{NiO})/\text{AMSNC}$	60 min	0.0148	[75]
CaO nanomaterials	70 min	0.0149	[76]
alkali-activated magnesium	60 min	0.0124	[75]
$\text{ZrO}_2@\text{g-C}_3\text{N}_4$ photocomposite	60 min	0.0279	This work

A comparison of IC dye photocatalytic degradation with several nanomaterials' catalysts found in the literature is displayed in Table 2. The findings demonstrate the type of nanomaterials, rate of photodegradation, and IC Photodegradation time for various photocatalysts. The existing activity of $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ photocomposite utilizes visible radiation for photodegradation of IC dye associated with additional activities related. The contemporary $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ nanomaterial has the better photocatalytic ability for IC dye destruction.

3.7.5. Repeatability and reusability studies

The photocatalyst must be reusable and exhibit high repeatability to be effective in photocatalytic application. The photodegradation process was done three times under the same conditions to determine the repeatability of the IC dye degradation on the $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ photocomposite. As illustrated in Fig. 12 a, the photodegradation rates of IC dyes stay nearly constant throughout the degradation processes, indicating high repeatability in photodegradation measurement. The reusability of the utilized photocatalyst is critical for meeting financial requirements. For this reason, the photodegradation and regeneration processes must be repeated to validate the photocatalyst application. The utilized $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ photocomposite was regenerated by calcining for one hour at 776 K under the same optimized experimental conditions. The suspension was filtered after each experiment, and the photocatalyst was washed several times with distilled water, calcined at 776 K, and reused. Fig. 12 b illustrates the regeneration process. The photodegradation percentage of IC is found to be near 90% after three cycles, indicating that the $\text{ZrO}_2@\text{g-C}_3\text{N}_4$ photocomposite has the potential to be used efficiently for IC photodegradation.



Figs. 12: Photocatalytic repeatability (a) irradiated and reusability (b) for IC degradation

4- Conclusion

ZrO₂@g-C₃N₄ photocatalyst was developed through ultrasonication in the existence of methanol solvent, and the obtained nanomaterials were annealed at 183 °C for 120 mins. The characterization of fabricated nanomaterials using various analytical devices proved the fabrication of ZrO₂@g-C₃N₄ nanocomposite with a higher surface area and lowering energy band-gap of 2.86 eV. Photocatalytic properties of ZrO₂ nanoparticles, g-C₃N₄ nanosheets, and ZrO₂@g-C₃N₄ nanocomposite were described via decomposed IC dye under visible irradiation. The ZrO₂@g-C₃N₄ nanocomposite provided great photodegradation production compared with the ZrO₂ and pure g-C₃N₄ nanosheets. The photodegradation experimental data were affirmed to obey the Lagergren kinetics model. Moreover, the ZrO₂@g-C₃N₄ photocomposite has a greater degradation rate constant (68 times) and lower half-life time values (0.25 times) than using pure g-C₃N₄. The impact of pH variation and the photocatalytic degradation mechanism of IC dye using ZrO₂@g-C₃N₄ nanocomposite were also investigated. The proposed photodegradation Z-scheme mechanism's model advocates the formation of excess $\bullet\text{O}_2^-$ along with additional powerful oxidizing agents' h^+ than in the 'type II-heterojunction' one. From the obtained

findings, it can be concluded that the ZrO₂@g-C₃N₄ photocomposite, fabricated through a simplistic step ultra-sonication procedure, can be used as an effective catalyst to eliminate organic compounds from wastewater.

5-Acknowledgements

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Author contribution statement

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Conflict of interest statement

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

Highlights

- $\text{ZrO}_2@g\text{-C}_3\text{N}_4$ nanocomposite was ultrasonically fabricated using the precursors ZrO_2 and $g\text{-C}_3\text{N}_4$.
- The anchoring of ZrO_2 and $g\text{-C}_3\text{N}_4$ was verified by XPS, XRD, and EDX techniques.
- The nanocomposite has proficiently degraded the indigo carmine dye during a visible-light-driven process.
- A Z-scheme model was suggested for the enhancement as confirmed through the $\cdot\text{O}_2^-$ and h^+ involvement.

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