

Research Article

Synthesis of ZnO nanorods on TiO₂ and ZnO inverse opal structures prepared via thermal-atomic layer deposition and hydrothermal growth for photocatalytic applications

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ABSTRACT

Industrial pollutants, including synthetic dyes and organic compounds, pose serious environmental risks, making efficient remediation methods crucial. In this study, opal templates were fabricated using the Evaporation Induced Confined Area Assembly (EICAA) method, where polystyrene nanospheres (300 nm) were precisely assembled on silicon wafers. Subsequently, ZnO and TiO₂ layers were deposited onto the templates using thermal ALD. The polystyrene templates were then removed via calcination at 500 °C. Hydrothermal synthesis was employed to grow ZnO nanorods on the prepared structures. Comprehensive characterization was conducted using TG/DTA/DTG, SEM-EDX, XRD, Raman spectroscopy, UV–Vis spectrophotometry, and photoluminescence analysis. The results showed that the samples exhibited a well-ordered, crystalline inverse opal structure with vertically aligned nanorods on their surface. The photocatalytic performance of the samples was evaluated through the degradation of methylene blue and 4-nitrophenol under UV and visible light irradiation.

Photocatalytic tests revealed that ZnO inverse opals exhibited higher photocatalytic activity than TiO₂ inverse opals. The growth of ZnO nanorods on TiO₂ inverse opals significantly improved their activity, owing to the formation of a micro p–n junction between TiO₂ and ZnO, which enhanced electron–hole separation and reduced recombination rates. ZnO nanorods on ZnO inverse opals demonstrated overall higher activity, benefiting from their increased surface area and charge transport properties. These findings highlight ZnO-based photocatalysts as promising for the degradation of various pollutants, demonstrating potential for environmental remediation applications.

1. Introduction

Rapid industrial and urban development has led to the discharge of

numerous chemical pollutants, including dyes, pharmaceuticals, organic and inorganic contaminants, and heavy metals, into natural water bodies without proper treatment, resulting in severe environmental and

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public health hazards [1]. Developing sustainable and eco-friendly techniques to cleanse contaminated water is essential, given that many of these pollutants are carcinogenic and mutagenic [2]. Semiconductor photocatalysis technology has gained significant attention for its promising applications in wastewater treatment, air purification, and surface cleaning [3]. Materials such as metal oxides (CeO_2 , WO_3 , ZrO_2 , V_2O_5 , TiO_2 , ZnO) and sulfides (CdS , ZnS) are commonly used in this technology [4]. While photocatalysis has proven highly effective in real-world applications such as surface coatings and air purification, extending its efficacy to water treatment remains a significant challenge.

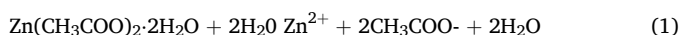
Among semiconductor metal oxides, TiO_2 and ZnO have gained prominence as effective photocatalysts due to their excellent electronic properties, chemical durability, natural abundance, and non-toxic nature [5]. Research comparing the photocatalytic (PC) activity of TiO_2 and ZnO has consistently shown that ZnO exhibits higher PC activity, attributed to its high electron mobility, which ranges from 200 to 300 cm^2/Vs , compared to TiO_2 , which has a range of 0.1–4.0 cm^2/Vs and this results in a higher quantum efficiency for ZnO [6–8]. However, the wide band gap characteristics of both ZnO (3.3 eV) [9] and TiO_2 (3.2 eV) [10] photocatalysts limit their efficiency in utilizing sunlight. Their poor absorption in the visible region and inefficient separation and transfer of photogenerated carriers further restrict their overall photocatalytic performance [11].

Enhancing the photocatalytic (PC) performance of ZnO and TiO_2 has been a primary focus of recent research, with approaches that include dye sensitization, doping with non-metals or metals, and forming composites [12]. A novel approach involves the use of inverse opal photonic crystals. The photonic crystals are materials with periodic structure that affects the propagation of photons, creating photonic bandgaps that control and manipulate light in specific ways [13]. The unique architecture of inverse opal structures allows for precise absorption engineering, particularly in the visible spectrum, as their periodicity can be tailored to reflect and trap light effectively. This design not only increases light-matter interactions but also enhances light absorption efficiency, making these photonic crystal structures particularly advantageous for improving the PC activity of TiO_2 and ZnO under light irradiation [14].

Building on these advancements, recent studies have increasingly focused on the development of ZnO nanostructures on inverse opals to further enhance photocatalytic performance. ZnO nanostructures, including nanotubes, nanorods, microrods, nanowires, nanoflowers, nanobelt, and nanoballs [15], have garnered significant interest because of their non-toxic nature, affordability, effective sunlight utilization, and enhanced PC performance [16].

In this study, ZnO and TiO_2 inverse opals were fabricated by depositing 30 nm thick layers of ZnO and TiO_2 onto polystyrene (PS) templates using thermal atomic layer deposition (T-ALD). Following deposition, the PS templates were eliminated by heating the samples in a furnace at 500 °C. ZnO nanorods (NRs) were then grown on the inverse opals using a hydrothermal synthesis technique. This procedure involved immersing the samples in a 50 mL aqueous solution with equal concentrations (2.5 mM each) of zinc acetate dihydrate and hexamethylenetetramine, maintained at 90 °C under autogenous pressure. The chemical equations involved in this hydrothermal process are as described by V. Gerbreder et al., [17].

1. Dissociation of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in water:



2. Hydrolysis of $\text{C}_6\text{H}_{12}\text{N}_4$:



3. Formation of hydroxide ions:



4. Formation of $\text{Zn}(\text{OH})_2$:



5. Decomposition of $\text{Zn}(\text{OH})_2$ to form ZnO



These reactions result in the nucleation and growth of ZnO nanorods.

This technique was chosen over alternatives such as electrochemical deposition, sol-gel synthesis, physical and chemical vapor deposition, solvothermal synthesis, and nanosphere lithography [18], due to its ability to offer precise control over the nanorod morphology, including length, diameter, and aspect ratio, by simply modifying the growth parameters such as temperature, time, and precursor concentration [19].

This study aimed to conduct a comparative analysis of the PC activity of ZnO nanorods grown on TiO_2 inverse opal, ZnO inverse opal, and silicon wafers. It focuses on the photodegradation of methylene blue and 4-nitrophenol under both ultraviolet and visible light. The goal is to address existing gaps in understanding the relative efficiency of these configurations, offering insights that could greatly influence the development of more effective PC systems.

2. Methodology

2.1. Preparation of opals: Evaporation Induced Confined Area Assembly (EICA)

Polystyrene (PS) nanospheres, with a diameter of 300 nm (purchased from Sigma Aldrich), were supplied as a 10 % (w/w) aqueous suspension. To prepare the working solution, 10 μL of this suspension was mixed with 440 μL of deionized water and subjected to ultrasonication for 2 h at 35 °C. Concurrently, Si wafers were cut into 1.5 × 1.5 cm pieces and subjected to sequential cleaning using soap, ethanol, and deionized water. This was followed by treatment with a "piranha" solution (a 3:1 ratio of concentrated H_2SO_4 and 30 % H_2O_2) for 1 h to enhance hydrophilicity and eliminate organic residues. A rubber ring with a 1 cm diameter was placed on each substrate and held in place with clips. Using a micropipette (Thermo Scientific EH50476 4500), 200 μL of the polystyrene suspension was added within the ringed area. The prepared substrates were then heated in a furnace (Nabertherm L9/11/B410) following a specific temperature program: 50 °C for 14 h, followed by 80 °C for an additional 1.5 h.

2.2. Thermal atomic layer deposition (T-ALD)

T-ALD was performed with a Beneq TFS-200-186 ALD reactor. The specific deposition parameters are provided in Table 1 below.

Before proceeding with hydrothermal synthesis, the PS opal template was removed by heating in the furnace at 500 °C for 4 h, with an additional 2-h hold at this temperature.

2.3. Hydrothermal synthesis of ZnO nanorods

The hydrothermal synthesis was conducted in a stainless-steel autoclave (Vessel 4744, Parr Instrument Company) equipped with a

Table 1
Parameters for the T-ALD deposition of ZnO and TiO_2 .

Sample	Temp (°C)	No. of ALD cycles	Purge time (seconds) for 1 cycle	Planned thickness (nm)	Pressure (mbar)	
					Chamber	Reactor
ZnO	50.6	305	3 s DEZ - 3sec H_2O	30	6.94	1.49
TiO_2	52.9	290	3sec TiCl_4 - 3 s H_2O	30	7.09	1.49

50 mL Teflon inlet. To prepare the growth solution, 2.5 mmol of Zn ($(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ and $\text{C}_6\text{H}_{12}\text{N}_4$ (all from Sigma Aldrich) were dissolved in 50 mL of deionized water and then transferred into the Teflon inlet. ZnO IO, TiO_2 IO, and Si wafer were secured with a rubber ring, ensuring their orientation towards the bottom of the inlet. The reaction was conducted in a furnace at 90°C for 3 h. After completion of the reaction, the samples were rinsed with deionized water and left to air-dry for 24 h before further analysis.

2.4. Photocatalytic (PC) activity

The PC degradation of MB and 4-NP by the prepared samples was examined under both UV and visible light for 3 h. Initially, the degradation of MB was tested using all synthesized samples. Each sample was immersed in a glass vessel containing 5 mL of a 1.0×10^{-8} M MB solution. For visible light exposure, six fluorescent lamps (T8-18W-40S RoHS) were arranged in two rows of three, spaced 10 cm apart, with the sample positioned 5 cm in front of the midpoint between the lamp rows. A similar configuration was used for UV testing, with six Phillips TL-D 18W UV lamps.

The photocatalytic process was monitored using an Avantes AvaSpec-2048 fiber optic spectrometer with an Ava Light-DHS light source, and data was analyzed using AvaSoft software. Every 30 min, a 3 mL aliquot was obtained from the solution, and its absorbance measured using a quartz cuvette, and then returned to the glass vessel to maintain the reaction volume. The degradation of MB was assessed by tracking the reduction in absorbance (A/A_0) at its main absorption peak (≈ 665 nm).

Following the results from MB degradation tests, only the ZnO nanorods on TiO_2 inverse opal (TiO_2 IO + ZnO NRs) and ZnO inverse opal (ZnO IO + ZnO NRs) samples, were selected for further testing against 4-NP. A 5 mL solution of 4-NP (2.7×10^{-4} M, $\text{pKa} = 7.15$) was prepared and exposed to the same light setup as described for MB. Absorbance measurements were taken every 30 min, focusing on the primary absorption peak (≈ 400 nm), to evaluate the extent of 4-NP degradation.

2.5. Sample characterization

The samples were analyzed using several analytical techniques. For thermal analysis, the PS template was scrubbed off from the silicon wafer and analyzed with a TG/DTA/DTG system (TA Instruments SDT2960). This analysis covered temperatures from room temperature to 600°C , with a heating rate of $10^\circ\text{C}/\text{min}$ and an air flowrate of $130 \text{ cm}^3/\text{min}$.

Infrared (IR) spectrum of the PS was measured using a PerkinElmer Spectrum 400 FTIR/FT-NIR spectrometer, with a spectral range from 4000 to 400 cm^{-1} .

The surface morphology and composition of the samples were analyzed using SCIOS™ 2 DualBeam™ FIB-SEM (Thermo Fisher Scientific) equipped with an in lens secondary electron detector and field emission gun source which featured unique electron optical components, including the annular in column detector system. The analysis occurred within a low voltage system ($V = 1 \text{ kV}$, and $I = 10 \text{ pA}$). To counteract the charging effect on uncoated samples, a reverse bias of 20V was applied to the specimen holder. EDX spectroscopy was conducted with a JEOL JSM-5500LV SEM at 20 kV, with three measurements per sample and averaged atomic percentages reported.

Crystallinity was assessed using a PANalytical X'Pert Pro MPD X-ray diffractometer, employing Cu K- α radiation over a diffraction angle range of 0° – 70° .

The Raman spectra were acquired using a Jobin Yvon Labram spectrometer coupled with an Olympus BX41 microscope, utilizing a green 532 nm Nd-YAG laser and covering a spectral range from 100 to 1800 cm^{-1} .

UV-Vis spectra were obtained with an Avantes AvaSpec-2048

spectrophotometer, using Si wafer as a reference, across a wavelength range of 200–800 nm.

Photoluminescence (PL) spectra were measured using an Edinburgh Instruments FS5 spectrofluorometer using stationary fluorescence spectra, the excitation wavelength was 260 nm. Notch filters were placed in the emission beam, with nominal wavelengths of 280 nm.

3. Results and discussion

3.1. Thermal analysis of the opal template

The thermal degradation of the polystyrene (PS) template under air conditions is presented in [Supplementary Fig. S1](#). A slight mass reduction is observed between 100 and 297°C , with a 3.8 % mass loss, attributed to the evaporation of residual water used during the dissolution process. Subsequently, a more pronounced mass loss is observed between 297 and 397°C , constituting 90.5 % of the total mass. This significant loss is attributed to the decomposition of polystyrene. Following this, a slower decomposition occurs between 397 and 500°C , resulting in a 6.1 % mass loss. This stage is described as the point where the remaining polystyrene char is combusted.

The DTA curve provides further insight, indicating that the degradation process begins as an endothermic reaction between 28 and 320°C due to the decomposition of polystyrene. Beyond this point, as organic materials begin to combust, the reaction becomes exothermic. The thermal assessment of the PS opal template suggests that annealing at 500°C is an efficient method for removing the template. This conclusion is supported by the observed stages of degradation and the corresponding mass losses.

3.2. Infrared (IR) analysis of the polystyrene (PS) opal

The IR absorption spectrum of PS opal with an approximate particle size of 300 nm is presented in [Supplementary Fig. S2](#). Several absorption peaks are evident within the specified wavenumber range. The peak observed at 3026 cm^{-1} is attributed to aromatic C–H stretching, while the peak at 1602 cm^{-1} represents the vibrations from C=C bonds in vinyl groups. Stretching vibrations of CH_2 are indicated by peaks at 2923 cm^{-1} (asymmetric) and 2850 cm^{-1} (symmetric). The deformational vibrations of the benzene ring are identified by a peak at 1492 cm^{-1} , and the signal at 756 cm^{-1} is linked to the deformation of a substituted benzene compound. The peak at 698 cm^{-1} indicates C–H out-of-plane bending, suggesting a single substituent on the benzene ring. The absorption band at 3437 cm^{-1} indicates O–H vibration absorption, likely due to a hydroxyl group from the water used for dissolution. Similar results are reported by Fathi et al., [20].

3.3. Morphology of the samples

[Fig. 1a](#) shows top view surface morphology of polystyrene spheres on Silica substrate. It is notable that the PS spheres are orderly arranged corresponding to (111) plan of face-centered cubic opal [21]. A noticeable cavity at the center of the image reveals the internal structure, providing insight into the layer-by-layer assembly of the opal.

[Fig. 1b](#) and [c](#) shows the surface morphology of TiO_2 and ZnO inverse opals, respectively. The micrographs reveal TiO_2 and ZnO ALD layers uniformly coated outside of the colloidal spheres. After annealing the PS spheres have completely decomposed, leaving behind an interconnected network of spherical shells composed of TiO_2 and ZnO. This suggests that T-ALD process facilitated the consistent deposition of TiO_2 and ZnO films, not only on the top surface of the PS spheres but also throughout their entire structure. The resulting highly porous and ordered structure is beneficial for photocatalysis as it enhances light harvesting and charge separation by providing efficient pathways for charge carriers [22].

[Fig. 1d](#) and [e](#) shows SEM micrographs of ZnO nanorods synthesized via the hydrothermal method on TiO_2 and ZnO inverse opals,

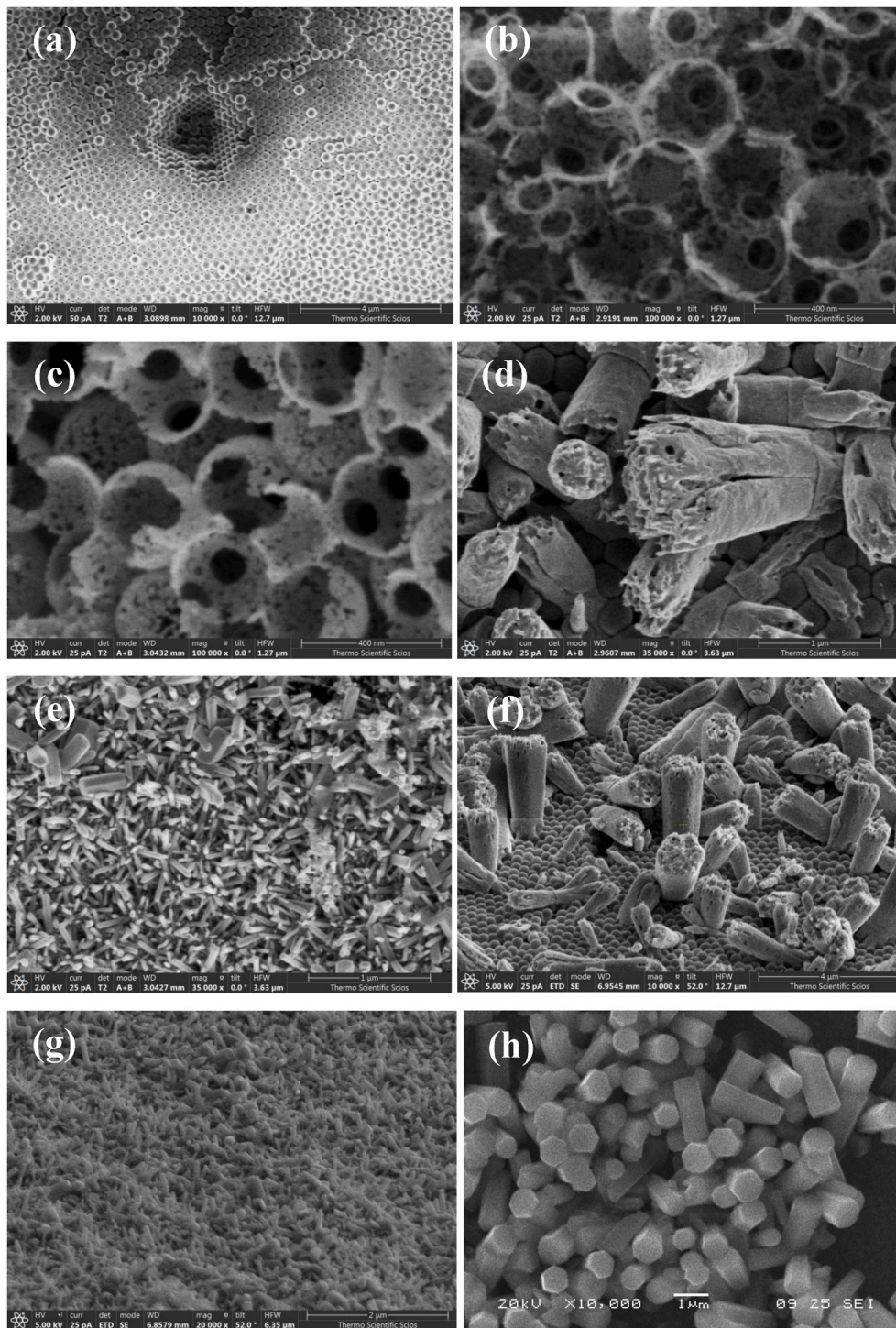


Fig. 1. SEM micrographs of (a) Polystyrene opal, (b) TiO_2 IO, (c) ZnO IO, (d) TiO_2 IO + ZnO NRs, (e) ZnO IO + ZnO NRs, cross sectional view of (f) TiO_2 IO + ZnO NRs and (g) ZnO IO + ZnO NRs, (h) Si + ZnO NRs.

respectively. As seen in the micrographs the density of ZnO nanorods is higher on ZnO IO than on TiO_2 IO. ZnO provides a highly compatible surface for nucleation due to similar crystal structures and minimal lattice mismatch which results in numerous nucleation sites, leading to high-density growth of ZnO nanorods [23]. Each nanorod might be smaller in diameter due to the competition for resources among the many nucleation sites. The increased density of ZnO NRs enhanced photocatalytic performance by providing a larger active surface area for reaction sites and reducing charge recombination through effective charge transport along the nanorods [24].

The conformal nature of this growth on ZnO IO is further confirmed by the cross-sectional SEM image in Fig. 1g, where the ZnO nanorods are seen to densely blanket the underlying inverse opal structure, effectively obscuring the spherical shell framework. This compact and continuous coverage indicates strong interfacial compatibility and promotes directional growth along the c-axis, likely resulting in better-defined nanorod morphology.

In contrast, TiO_2 , while still promoting growth, offer fewer nucleation sites compared to ZnO due to lattice mismatch and different surface energies. This result in lower nucleation density, but potentially

larger individual nanorods as fewer compete for growth resources [25]. These observations are corroborated by the cross-sectional SEM image in Fig. 1f, where the characteristic interconnected spherical shells of the TiO₂ inverse opal remain clearly visible beneath the ZnO nanorods. This indicates partial surface coverage and a lower degree of nanorod penetration into the IO matrix. Furthermore, the nanorods grown on TiO₂ exhibit less-defined edges, lacking the typical hexagonal cross-sectional morphology commonly observed in well-crystallized ZnO nanorods. This deviation from the expected faceting may reflect a lower degree of crystalline order, possibly due to suboptimal nucleation conditions and interfacial strain at the ZnO–TiO₂ interface.

Fig. 1h shows ZnO NRs grown on Si wafer. The surface coverage of ZnO NRs on Si wafer is uneven, with clusters of NRs in some regions and bare substrate in others. Without a seed layer to guide the growth, the NRs tend to grow in random directions due to absence of nucleation sites on ultra-smooth single crystal surface of Si wafer [26]. They are not uniformly aligned and point in various angles relative to the substrate as seen in the micrograph. The lack of ordered growth and poor interfacial contact between ZnO and Si explains the observed photocatalytic activity, as it leads to increased charge recombination and a reduction in the overall active surface area.

3.4. EDX analysis

Table 2 summarizes the EDX results of the prepared samples, while the corresponding EDX spectra are provided in the supplementary data Fig. S3. From the table only Ti, Zn, O, and Si were present. This suggests that the polymer template was completely burnt-out during annealing as no carbon content was detected.

ZnO nanorods on ZnO inverse opal (IO) have a relatively higher zinc content as compared to IO, showing effective deposition of ZnO NRs on the ZnO IO structure. The silicon content is relatively low, suggesting minimal influence from the underlying layer.

For ZnO NRs grown on a TiO₂ IO, the zinc content was measured at 18.7 %, confirming the successful growth of the ZnO nanorods. The higher silicon content in this sample, compared to ZnO IO with ZnO NRs, is attributed to the lower density of ZnO nanorods, which allows more signals from the silicon substrate to be detected. Although the EDX results show a lower concentration of Ti, the actual concentration of Ti remains unchanged during the growth process since TiO₂ substrate is neither consumed nor transformed during the ZnO nanorod growth process. However, the difference might be due to the presence of ZnO nanorods on its surface that partially block the X-ray signals originating from the TiO₂ substrate during the EDX analysis [27].

The ZnO nanorods on the silicon wafer show a low zinc and oxygen content, with silicon being the dominant element. The incomplete coverage of Si wafer with ZnO nanorods means that a large portion of the EDX signal comes from the exposed silicon substrate rather than the ZnO nanorods.

3.5. XRD analysis

Fig. 2 presents XRD patterns for (A) Si substrate, (B) ZnO inverse opal (IO), (C) TiO₂ IO, and ZnO nanorods grown on (D) Si, (E) ZnO IO, and (F) TiO₂ IO. Fig. 2A which corresponds to the Si substrate, shows peaks at

Table 2
Sample composition analysis.

Sample	% w/w Zn	% w/w Ti	% w/w O	% w/w Si
TiO ₂	–	16.2	45.7	38.0
ZnO	35.4	–	40.7	23.8
ZnO IO + ZnO NRs	46.5	–	43.7	9.8
TiO ₂ IO + ZnO NRs	18.7	10.5	44.6	26.3
Si wafer + ZnO NRs	3.5	–	29.2	67.4

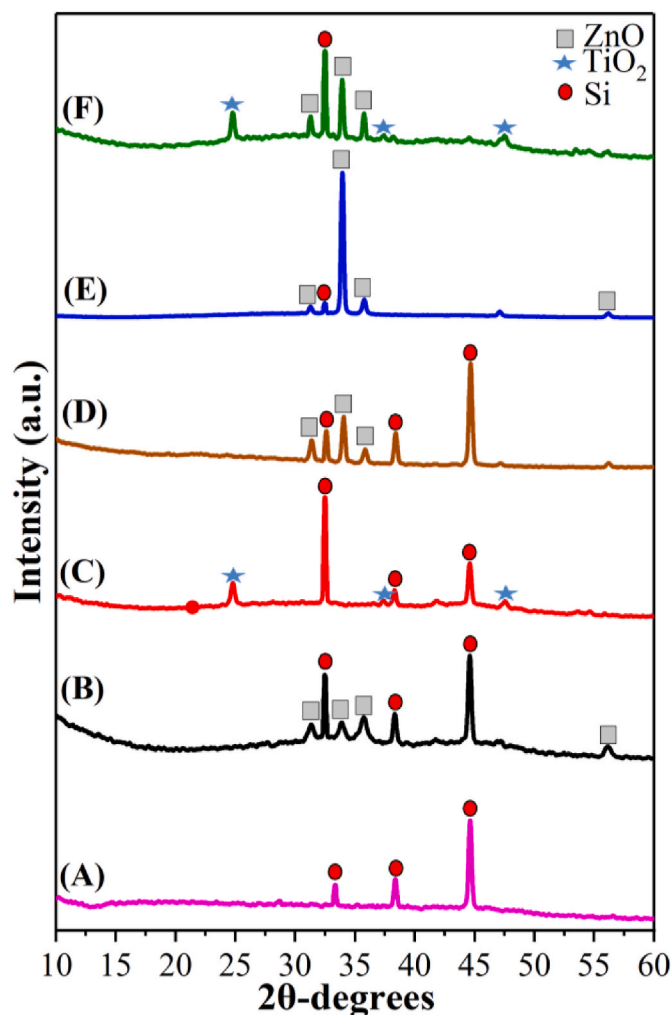


Fig. 2. X-Ray diffractogram of (A) Si substrate, (B) ZnO IO, (C) TiO₂ IO, (D) Si + ZnO NRs, (E) ZnO IO + ZnO NRs, and (F) TiO₂ IO + ZnO NRs.

around 33.3°, 38.3°, and 44.6° corresponding to 111, 200, and 220 planes of crystalline Si phase [28].

ZnO inverse opal (Fig. 2B) shows peaks at 2-theta of 31.3°, 33.9°, 35.7°, and 56.3° corresponding to 100, 002, 101, and 110 respectively. The sample is identified with the JCPDS 36–1451 card and with previous results by Yang & Li, 2019 [29]. These peaks confirm a hexagonal wurtzite crystalline structure which is known for its superior charge transport properties in photocatalysis [30]. The well-defined diffraction peaks indicate a high level of crystallinity, suggesting minimal defects that could otherwise act as charge recombination centers [31].

TiO₂ inverse opal (Fig. 2C) shows peaks at around 24.8°, 37.4°, and 47.5° which are attributed to 101, 103, and 200 planes of anatase TiO₂ respectively. These results correlate with file number JCPDS 21–1272 [32]. The exclusive presence of the anatase phase is particularly significant, as it has been widely reported to possess the highest photocatalytic efficiency among TiO₂ polymorphs due to its favorable band alignment and slower electron-hole recombination rates [33].

ZnO nanorods on Si substrate (Fig. 2D) show peaks at 31.4° (100), 34.0° (002), and 35.9° (101) which shows that ZnO nanorods have good crystallinity. However, compared to ZnO NRs on ZnO and TiO₂ IOs, the lower intensity of the (002) peak suggests less preferential growth along the C-axis, which may negatively impact charge transport efficiency in photocatalysis.

ZnO nanorods on ZnO inverse opal (Fig. 2E) show a very strong peak at 33.9° (5307 a.u.) confirming a highly oriented growth of the ZnO NRs

along the preferred (002) C-axis orientation. This preferred orientation is critical for enhancing photocatalytic performance, as it facilitates efficient charge carrier transport along the nanorods, thereby reducing recombination losses and improving overall efficiency [34]. The presence of additional peaks at 31.3° , 35.7° , and 56.3° further confirms the ZnO wurtzite structure.

ZnO nanorods on TiO_2 inverse opal (Fig. 2F), show peaks corresponding to both ZnO and TiO_2 . Three peaks identified at 2-theta of 31.3° , 33.9° , and 35.7° are indexed to ZnO. Peaks at 24.8° , 37.4° , and 47.5° are attributed to TiO_2 . The coexistence of these phases indicates a heterojunction formation between ZnO and TiO_2 , which is highly beneficial for photocatalysis [35]. Such heterostructures create favorable band alignments, facilitating efficient charge separation and reducing recombination losses, which directly contribute to enhanced photocatalytic activity [36].

3.6. Raman analysis

Fig. 3A shows the Raman spectra of Si wafer before and after the growth of ZnO nanorods on its surface. The characteristic peaks of the Si wafer appears at 301 cm^{-1} and 521 cm^{-1} [37]. After hydrothermal process, a peak at 437 cm^{-1} is seen and corresponds to ZnO. This peak indicates the successful synthesis of ZnO nanorods on the silicon substrate.

Fig. 3B, illustrates Raman spectra of ZnO inverse opal and ZnO IO + ZnO NRs. A single peak at 437 cm^{-1} correspond to the E_2 vibrational mode, a signature of the wurtzite phase of ZnO. Comparable findings have also been reported by Paul et al., [38]. After hydrothermal deposition of ZnO NRs on ZnO IO, the Raman spectrum remains largely unchanged, showing the continued presence of wurtzite-phase ZnO. The similarity in Raman spectra suggests that ZnO NRs have grown epitaxially on the ZnO IO surface, maintaining structural continuity.

In Fig. 3C, five peaks appear at around 142 , 195 , 394 , 520 , 637 cm^{-1} , and are assigned to vibration modes E_g , E_g , B_{1g} , (B_{1g}/A_{1g}) , and E_g , respectively [39]. Absence of peaks around 450 cm^{-1} and 610 cm^{-1}

indicates that the prepared TiO_2 IO is pure anatase, a conclusion supported by findings reported in a study by Rajendran et al., [40].

After hydrothermal growth of ZnO nanorods on TiO_2 IO, a distinct peak at 437 cm^{-1} is evident and is assigned to ZnO. The peak is specifically attributed to the E_2 (high) mode, a characteristic of the wurtzite crystal structure of ZnO [41]. This Raman scattering result agrees with XRD analysis Fig. 2 above.

3.7. Ultraviolet-visible absorption analysis

Fig. 4A illustrate the optical properties of TiO_2 IO structures and TiO_2 IO + ZnO NRs. The absorption edge for TiO_2 IO is observed at 417 nm , corresponding to an optical band gap of approximately 3.15 eV . This slightly lower band gap compared to commercial TiO_2 nanoparticles ($E_g \approx 3.2\text{ eV}$) suggests that the periodic porous structure of TiO_2 IO enhances light absorption, potentially due to improved light scattering and localized optical effects within the photonic crystal structure [42].

Upon growing ZnO NRs on the TiO_2 IO surface the absorption edge is red shifted to 425 nm , indicating a reduction in the band gap energy to 3.07 eV . This shift can be attributed to the formation of a TiO_2 -ZnO heterojunction and the introduction of structural defects at the interface, both of which play a crucial role in modifying the optical properties. The heterojunction formed between TiO_2 and ZnO alters the electronic band structure by influencing charge transfer and carrier dynamics at the interface. Since ZnO has a slightly lower conduction band edge than TiO_2 , electron redistribution occurs, modifying the optical transitions and contributing to the observed band gap shift [43]. Additionally, the heterojunction introduces localized states that allow sub-band-gap transitions, further enhancing light absorption in the visible region [36]. Beyond heterojunction effects, structural defects particularly oxygen vacancies and Ti^{3+} states also contribute to the band gap reduction. Oxygen vacancies in ZnO can create mid-gap states, enabling photon absorption at lower energies, while Ti^{3+} centers in TiO_2 lead to additional electronic states near the conduction band. The interaction between ZnO and TiO_2 further induces lattice distortions, which hybridize

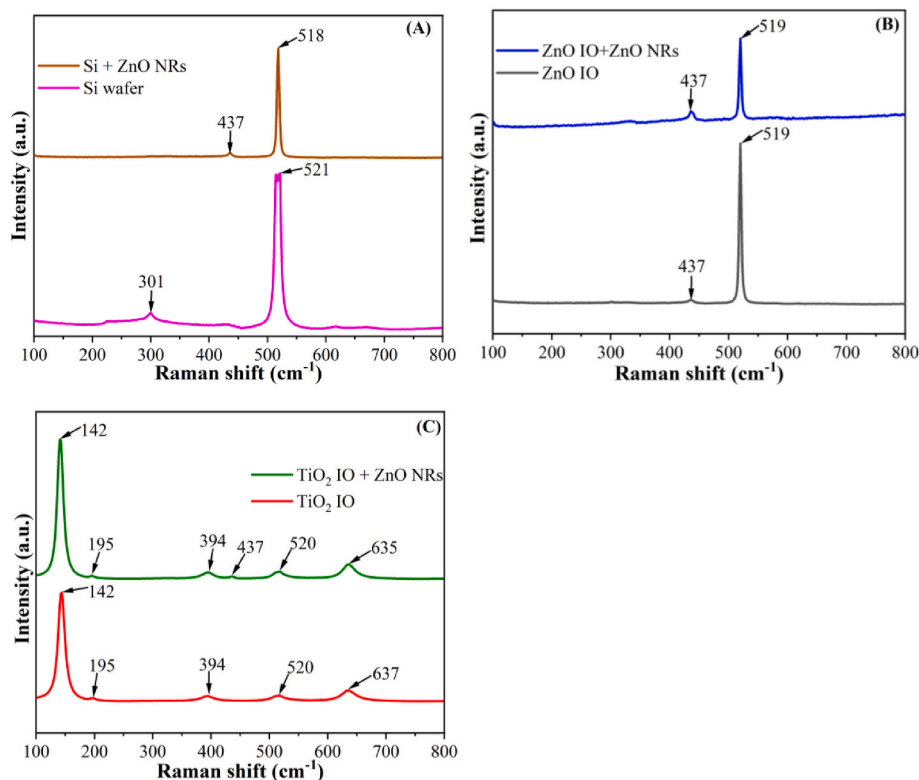


Fig. 3. Raman spectra of Si wafer and Si + ZnO NRs (A), ZnO IO and ZnO IO + ZnO NRs (B), TiO_2 IO and TiO_2 IO + ZnO NRs (C).

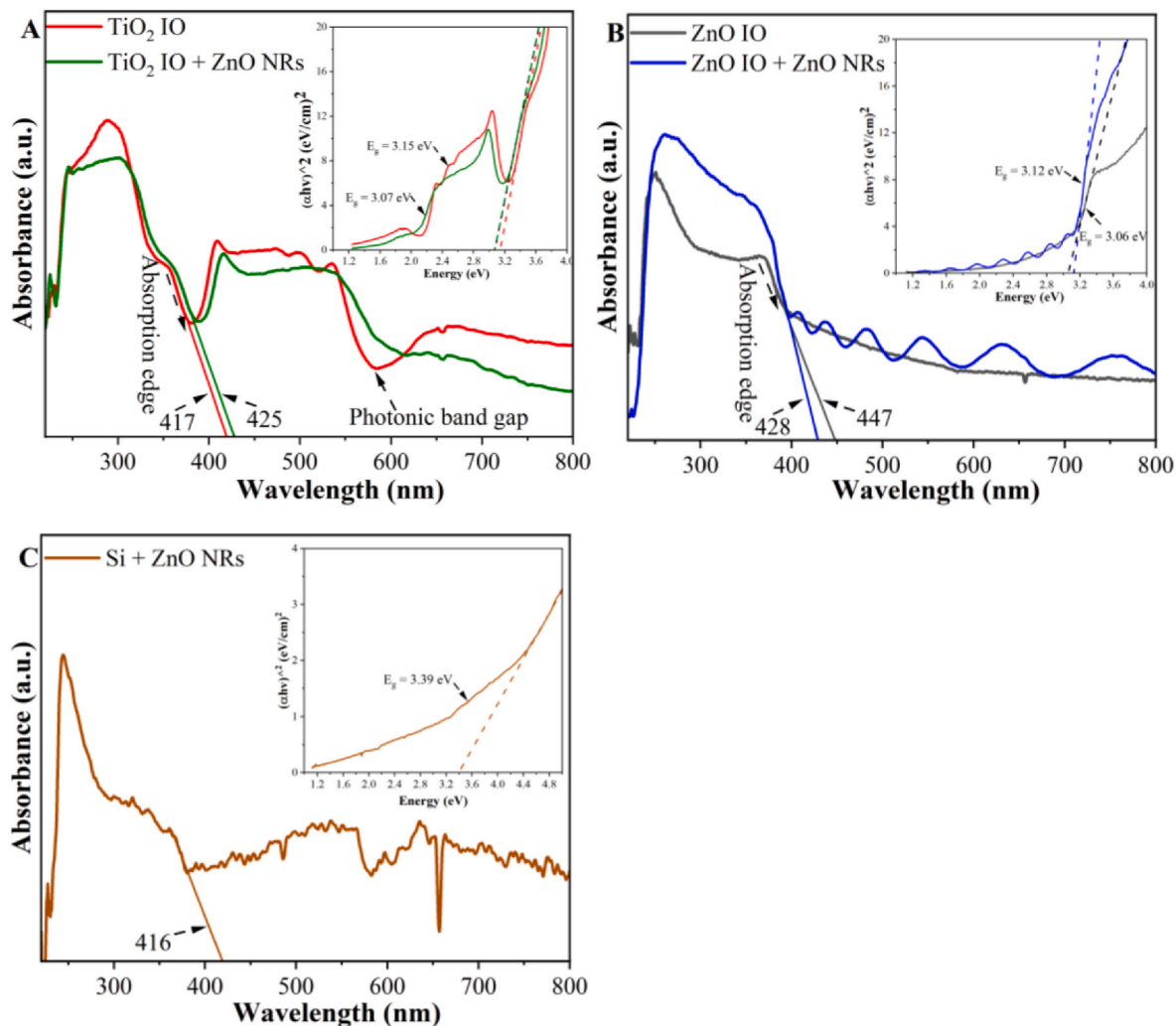


Fig. 4. UV-Vis spectra of (A) TiO₂ IO and TiO₂ IO + ZnO NRs, (B) ZnO IO and ZnO IO + ZnO NRs, and (C) Si + ZnO NRs.

electronic states at the interface, reducing the effective band gap [44].

Fig. 4B illustrates the optical properties of ZnO IO and ZnO IO + ZnO NRs. ZnO IO structure exhibits an absorption edge at approximately 447 nm, corresponding to an optical band gap of 3.06 eV. Upon the growth of ZnO NRs, a noticeable blue shift in the absorption edge is observed, shifting to 428 nm, which corresponds to an increased band gap of 3.12 eV. This shift is attributed to Burstein-Moss effect, which arises from an increase in free carrier concentration due to defect states introduced during nanorod growth [45]. In ZnO-based systems, intrinsic defects such as oxygen vacancies and zinc interstitials can lead to an upward shift in the Fermi level, effectively occupying the lower-energy states in the conduction band. As a result, the onset of optical absorption is shifted to higher energy, leading to an apparent increase in the band gap [46]. Another contributing factor is the quantum confinement effect [47]. The ZnO NRs, having smaller diameters, confine charge carriers within restricted dimensions, thereby modifying their electronic states. As the diameter of the nanorods approaches the exciton Bohr radius of ZnO (~2.34 nm), the discretization of energy levels results in an increase in the band gap [48]. This behavior is consistent with previous studies on ZnO nanostructures, where a reduction in size leads to a widening of the band gap due to the increased energy required for electronic transitions [49].

Fig. 4C presents the optical properties of ZnO NRs grown on a Si wafer. The ZnO NRs exhibit an absorption edge at approximately 416 nm, a characteristic feature of ZnO. The inset Tauc plot reveals a band gap of 3.39 eV, which is consistent with the expected values for ZnO

nanostructures.

The bandgap of the material was determined using Tauc's formula (Equation (6)):

$$(\alpha h\nu)^{\frac{1}{y}} = B(h\nu - E_g) \quad (6)$$

where α is the absorption coefficient, E_g is the band gap energy, h represents the Planck constant, ν denotes the photon frequency, and B is a constant. The factor y varies based on the type of electron transition, taking a value of $1/2$ for direct band gap transitions and 2 for indirect transitions [50]. In the current study Tauc plot was calculated by $y = 2$. The plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$), enable the determination of the bandgap energy (E_g) by extending the linear portion to meet the X-axis (energy axis).

3.8. Photoluminescence analysis

Fig. 5A illustrates the photoluminescence spectra (PL) of TiO₂ IO and TiO₂ IO + ZnO NRs. The TiO₂ IO spectrum exhibits a prominent peak at 422 nm, which corresponds to the near-band-edge (NBE) emission associated with the recombination of free excitons or electron hole pairs near the conduction band edge [51]. After the hydrothermal growth of ZnO NRs on TiO₂ IO, this peak undergoes a notable blue shift to 398 nm. The PL blue shift can be attributed to changes in charge carrier recombination dynamics at the TiO₂-ZnO heterojunction. Upon ZnO NR growth, electron transfer from ZnO to TiO₂ modifies the recombination

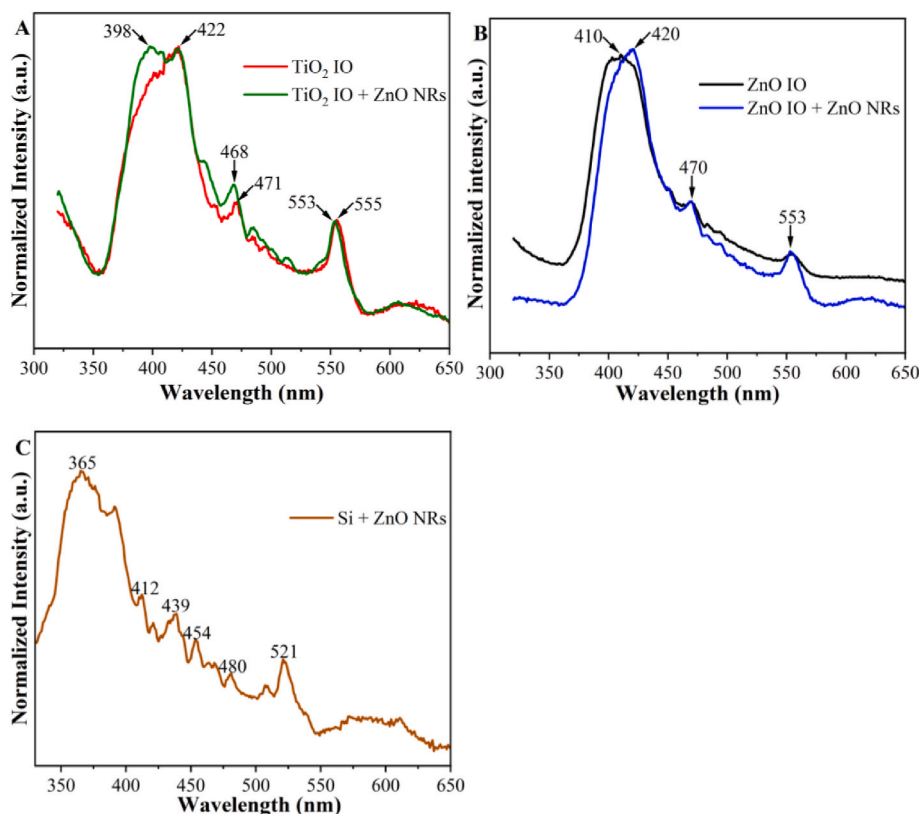


Fig. 5. Photoluminescence spectra of (A) TiO_2 IO and TiO_2 IO + ZnO NRs, (B) ZnO IO and ZnO IO + ZnO NRs, and (C) Si + ZnO NRs.

pathways, effectively shifting radiative transitions to higher energy states [52]. Additionally, interface defects introduced during nanorod growth may contribute to localized charge trapping, altering the emission characteristics.

Both spectra exhibit deep-level emission peaks at approximately 471 nm and 555 nm, which correspond to defect-related transitions. The 471 nm peak is associated with the recombination of electrons trapped at oxygen vacancies or titanium interstitials, while the 555 nm emission is linked to defect states such as interstitial oxygen or surface defects [53]. The presence of these peaks in both spectra indicates that despite the structural modifications introduced by ZnO NRs, defect states remain prominent. However, the intensity variations suggest a slight modification in defect concentration and charge carrier recombination dynamics upon the incorporation of ZnO nanorods.

Fig. 5B presents the PL spectra of ZnO IO and ZnO IO + ZnO NRs. Both samples exhibit distinct emission features, with ZnO IO showing a strong near-band-edge (NBE) emission at 410 nm, along with defect-related emissions at 470 nm and 553 nm. After the hydrothermal growth of ZnO NRs, the NBE peak undergoes a redshift from 410 nm to 420 nm, while the intensity of the defect related emissions at 470 nm and 553 nm increases.

From UV–Vis absorption measurements (Fig. 4B), it was observed that the bandgap increased from 3.06 eV to 3.12 eV, which was attributed to the Burstein-Moss effect and quantum confinement. This initially suggests that a blue shift in PL would be expected, yet a redshift is observed instead, indicating that other effects are dominating the PL behavior. The process of growing nanorods can create additional defect states, such as oxygen vacancies and zinc interstitials, which introduce localized energy levels within the bandgap. These defects act as carrier trapping centers, leading to an increase in defect-related PL emissions at 470 nm and 553 nm [54].

The PL spectrum of ZnO NRs on a Si wafer (Fig. 5C) shows a large peak at 365 nm and smaller peaks at 412 nm, 439 nm, 454 nm, 480 nm, and 521 nm. The presence of these peaks indicates a significant

concentration of intrinsic and extrinsic defects within the ZnO NRs, influenced by the growth conditions and the Si wafer. Si wafer can introduce strain and affect the defect landscape in the ZnO nanorods, contributing to the observed PL characteristics [55,56].

3.9. Photodegradation activity

3.9.1. Photodegradation of methylene blue

The PC activity of all prepared samples was initially evaluated through the photodegradation of MB solution under both UV and visible light irradiation. The photodegradation activity of ZnO nanorods on TiO_2 and ZnO inverse opals was further evaluated against 4-Nitrophenol.

The degradation was calculated using the following equation:

$$\text{Degradation} = A/A_0 \quad (7)$$

Where A_0 is the initial absorbance of the solution and A is the absorbance at time t .

The degradation kinetics of MB and 4-NP (Fig. 8) were analyzed by applying a pseudo-first-order kinetic model, described by equation (8):

$$\ln\left(\frac{C_0}{C_t}\right) = Kt \quad (8)$$

Here, C_0 represent the initial concentration, C_t is the concentration at time t , and K is the rate constant [57].

Photodegradation under UV light irradiation (Fig. 6A): ZnO inverse opal (IO) shows considerably higher PC efficiency than TiO_2 IO. Previous studies [6,7,58] on the photodegradation of MB has indicated that ZnO exhibits higher efficiency compared to TiO_2 . This performance of ZnO can be explained by its effective generation, mobility, and separation of photoexcited electrons-holes pairs when compared to TiO_2 [59]. Nonetheless, a study by Boyadjiev et al., [60] reported TiO_2 fibers to have higher PC activity as compared to ZnO fibers; thus, the

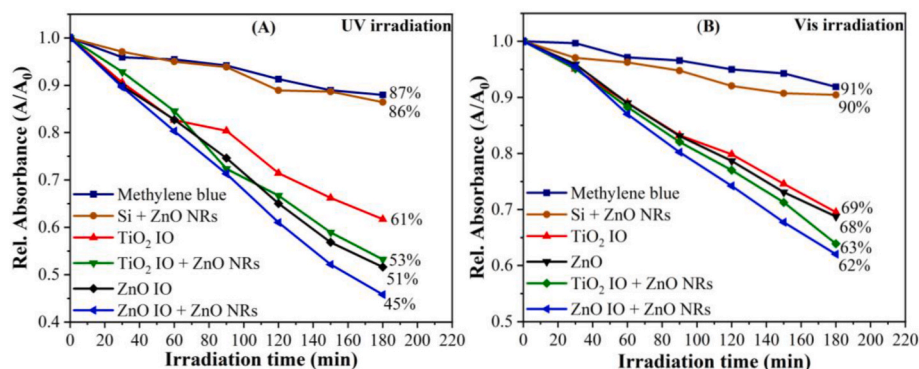


Fig. 6. Photodegradation of methylene blue solution under ultraviolet (A) and visible light (B) irradiation. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

preparation route and the obtained morphology have an influence on the final PC activity.

ZnO nanorods grown on ZnO IO and TiO₂ IO exhibited enhanced PC activity for the degradation of MB surpassing inverse opals. As discussed in Section 3.7, this increased photocatalytic activity is attributed to the formation of a heterojunction between TiO₂ and ZnO, which induces a band gap shift to shorter wavelengths, thereby enhancing light absorption. This improved light-harvesting capability promotes the generation of charge carriers, ultimately leading to higher photocatalytic efficiency [61].

The increased PC activity of ZnO IO + ZnO NRs compared to bare ZnO IO is likely due to synergistic effect between the nanorods and the underlying IO structure. The IO structure provides a high surface area and effective light management capabilities, while the nanorods contribute efficient charge transport and additional active surface sites for photodegradation of MB [24]. Si + ZnO NRs showed considerable low rate of photodegradation, and this can be explained by low density of the NRs on the surface.

Photodegradation under visible light irradiation (Fig. 6B): Under Vis light irradiation the PC activity of the materials displayed a different trend. Although ZnO IO continued to show higher activity than TiO₂ IO, the addition of ZnO NRs to TiO₂ IO (forming TiO₂ IO + ZnO NRs) resulted in enhanced photodegradation efficiency, surpassing that of ZnO IO alone. This suggests that under visible light, the TiO₂ IO + ZnO NRs structure benefits from synergistic effects that boost electron-hole separation and utilize visible light more effectively than ZnO IO alone [62]. Nevertheless, ZnO IO + ZnO NRs still achieved the highest activity under visible light, mirroring its superior performance under UV light.

The partial degradation of MB observed under both UV and visible light can be attributed to its capacity to absorb light in the 500–700 nm range. This absorption enables MB to undergo electronic transitions and intersystem crossing, leading to the formation of singlet and triplet excited states, which in turn can cause self-decomposition [63].

3.9.2. Photodegradation of 4-nitrophenol

Based on the findings on photodegradation of MB, ZnO IO + ZnO NRs and TiO₂ IO + ZnO NRs were selected for further investigation using 4-NP under both UV and visible light irradiation.

Photodegradation under UV light irradiation (Fig. 7A): ZnO IO + ZnO NRs demonstrated superior photocatalytic activity compared to TiO₂ IO + ZnO NRs, consistent with the trends observed for MB degradation. However, the overall degradation rate of 4-NP was lower than that of MB, indicating differences in photocatalytic reactivity between the two pollutants.

Photodegradation under visible light irradiation (Fig. 7B): The degradation trend remained similar to that observed under UV irradiation, indicating that the presence of micro p-n junctions in TiO₂ IO + ZnO NRs enhances charge separation, thereby boosting photocatalytic efficiency [61].

The performance difference between ZnO IO + ZnO NRs and TiO₂ IO + ZnO NRs was smaller under UV irradiation (5 %) but widened significantly under visible light irradiation (9 %) during the photodegradation of 4-NP. This trend differs from the MB degradation tests, where the performance gap was larger under UV light (8 %) and reduced to only 1 % under visible light. These observations suggest that the PC activity is affected by both the type of pollutant and the specific light conditions.

3.9.3. Photodegradation rate of methylene blue and 4-nitrophenol

Table 3 presents a comparison of the apparent rate constants (K_{app} min⁻¹) for the photodegradation of 4-NP and MB under UV and visible light irradiation. In all prepared samples, the degradation rate is higher under UV light than under visible light, which can be attributed to higher photon energy of UV light as compared to visible light, enabling more efficient electron excitation from valence band to the conduction band [64]. Table 3 further highlights that samples with higher PC activity exhibited correspondingly higher K_{app} min⁻¹, indicating a direct

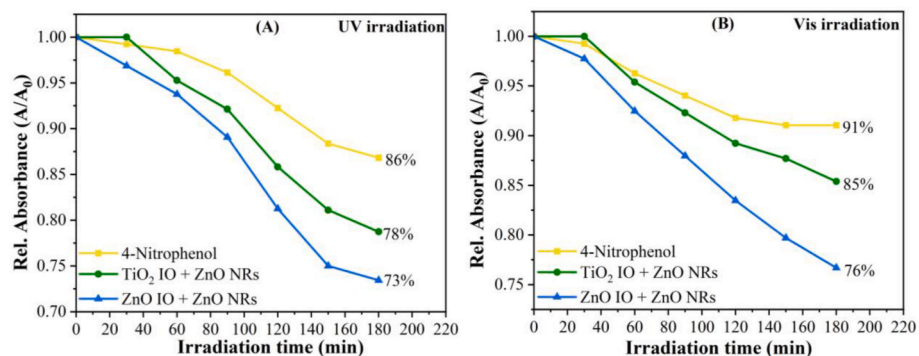


Fig. 7. Photodegradation of 4-nitrophenol solution under ultraviolet (A) and visible light (B) irradiation.

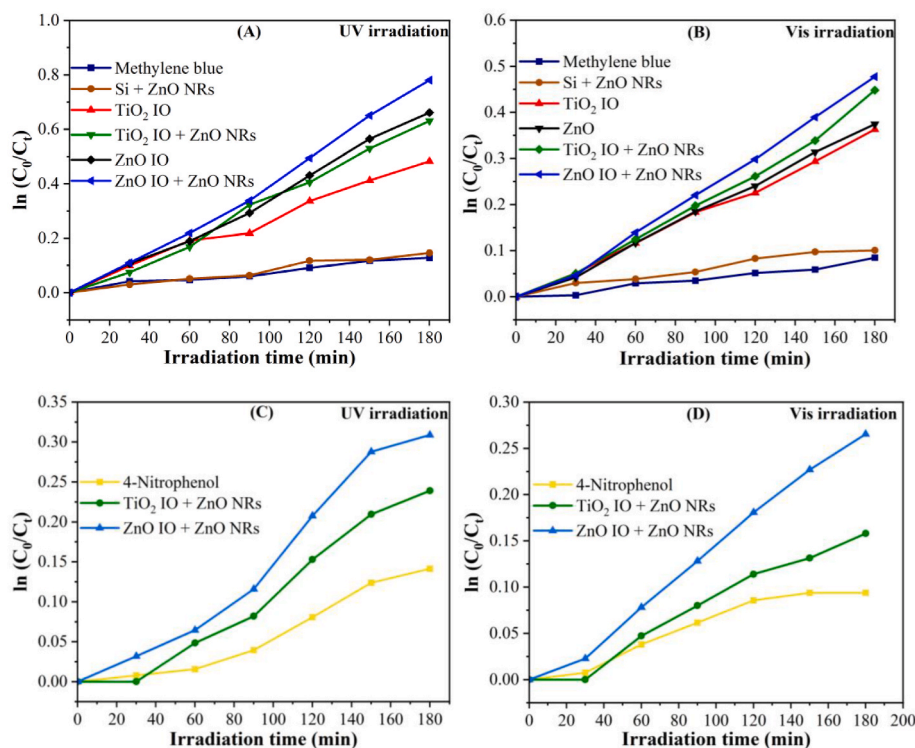


Fig. 8. Pseudo-first-order kinetic plots for the photodegradation of methylene blue (MB) and 4-nitrophenol (4-NP) under UV and visible light irradiation. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 3

Reaction rate constant K_{app} (min^{-1}) and r^2 values for the photodegradation of methylene blue and 4-nitrophenol under ultra-violet and Visible light.

Samples	$K_{app}(\text{min}^{-1})$ UV, MB	$K_{app}(\text{min}^{-1})$ Vis, MB	r^2 (UV, MB)	r^2 (Vis, MB)	$K_{app}(\text{min}^{-1})$ UV, 4-NP	$K_{app}(\text{min}^{-1})$ Vis, 4-NP	r^2 UV, 4-NP	r^2 Vis, 4-NP
Bare Methylene blue	0.0004	0.0006	97.1	96.6				
Si wafer + ZnO NRs	0.0005	0.0008	96.6	97.1				
TiO ₂ IO	0.0026	0.0020	98.3	99.6				
TiO ₂ IO + ZnO NRs	0.0036	0.0024	99.0	99.7	0.0015	0.001	96.8	97.3
ZnO IO	0.0037	0.0021	99.5	99.6				
ZnO IO + ZnO NRs	0.0044	0.0027	99.7	99.6	0.0019	0.0016	97.4	99.3
4-Nitrophenol (bare)					0.0009	0.0006	94.2	93.8

relationship between reaction kinetics and photocatalytic efficiency.

The differences in degradation rates between MB and 4-NP reflect variations in their molecular structure, adsorption behavior, and reaction mechanisms. The cationic nature of MB facilitates strong adsorption onto the photocatalyst surface, while its conjugated system enhances interaction with photogenerated charge carriers, accelerating degradation. In contrast, 4-NP, a phenolic compound, undergoes a multi-step oxidation process, requiring successive hydroxylation and ring cleavage reactions before complete mineralization, resulting in a lower degradation rate despite the same photocatalyst being used [65].

3.9.4. Mechanism for the photodegradation

When light is incident, electrons in the valence band (VB) of ZnO absorb photons with energy $\geq$ ZnO's bandgap (bandgap ~ 3.06 eV). These electrons are excited to the conduction band (CB), leaving behind holes in the VB [66]:



Electrons remain in the CB of ZnO, while holes are retained in the VB. The aligned ZnO nanorods provide fast pathways for charge transport, reducing the recombination rate of electron-hole pairs. They also add a

high surface area for photocatalytic reactions, exposing more active sites for radical generation [24].

In the case of ZnO nanorods on TiO₂ inverse opal, TiO₂ absorbs light photons (bandgap ~ 3.15 eV).



The photogenerated electrons in the CB of TiO₂ are transferred to the CB of ZnO nanorods, where they have a higher reduction potential. Similarly, the holes in the VB of TiO₂ are transferred to the VB of ZnO nanorods, which have a lower oxidation potential (illustrated in Fig. 9).

In both cases, CB electrons react with adsorbed O₂ molecules, forming superoxide radicals:



VB holes oxidize surface OH⁻ ions or H₂O molecules, generating hydroxyl radicals [67]:



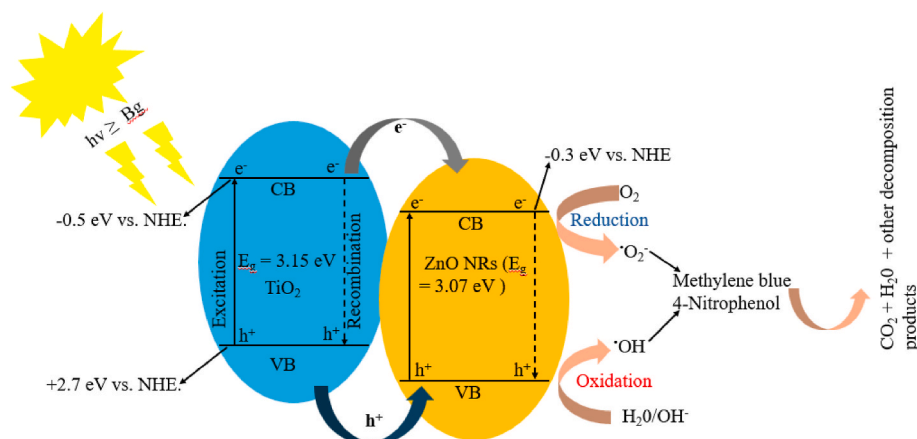


Fig. 9. Mechanism of the photodegradation of methylene blue and 4-nitrophenol by ZnO nanorods on TiO₂ inverse opals. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

- OH and $\bullet\text{O}_2^-$ radicals break the chromophore structure of MB, leading to color loss and mineralization into CO₂, H₂O, and smaller inorganic ions [68]. In the case of 4-NP, the radicals attack the nitro (-NO₂) group and aromatic ring, converting them to intermediates like hydroquinone and eventually mineralizing them into CO₂ and H₂O [67].

4. Conclusion

In this study, polystyrene (PS) opals with a diameter of 300 nm were fabricated on silicon wafers using EICAA method. ZnO and TiO₂ layers were subsequently deposited onto the opal template via thermal ALD. The PS opal template was removed at 500 °C in an oven before conducting hydrothermal synthesis to grow ZnO nanorods. These nanorods were successfully grown on TiO₂ inverse opal (IO), ZnO IO, and Si wafers using the hydrothermal synthesis.

The photocatalytic (PC) efficiency of the prepared samples was evaluated against a 1.0×10^{-8} M methylene blue (MB) solution and 2.7×10^{-4} M 4-nitrophenol. TG/DTA/DTG analysis revealed the degradation profile of PS opal template. FT-IR analysis provided clear identification of the characteristic functional groups of the PS opal template.

SEM images demonstrated the orderly arrangement of PS spheres corresponding to the (111) plane of the face-centered cubic opal. The SEM images of TiO₂ and ZnO IOs revealed the complete decomposition of PS spheres, leaving behind an interconnected network of spherical TiO₂ and ZnO shells. The grown nanorods were vertically aligned, with the density of the nanorods being higher on ZnO IO as compared to TiO₂ IO. ZnO NRs on Si wafer grew in random directions due to the absence of nucleation sites.

EDX analysis detected Ti, Zn, O, and Si without any carbon, suggesting the complete removal of the PS opal template. XRD and Raman spectra confirmed that the synthesized ZnO exhibited the wurtzite phase while the TiO₂ displayed the anatase phase. UV-Vis spectroscopy and photoluminescence provides insights into electronic and optical properties of the prepared samples. UV-Vis absorption spectra show band gap shifts attributed to the Burstein-Moss effect and quantum confinement in ZnO NRs on ZnO IO, while shifts in ZnO NRs on TiO₂ IO are linked to structural defects (oxygen vacancies, Ti^{3+}) and heterojunction formation. Photoluminescence analysis supports these findings, with emission peak shifts reflecting the influence of quantum confinement, strain, and defect states.

The PC tests showed that ZnO IO structures consistently exhibited higher efficiency compared to TiO₂ IO structures under both UV and visible light irradiation, validating previous findings on the superior charge separation properties of ZnO. The combination of ZnO NRs and the IO structures further enhanced the PC activity, with ZnO IO + ZnO

NRs showing the highest efficiency due to increased surface area, effective charge separation, and improved light utilization. The formation of a micro p-n junction in TiO₂ IO + ZnO NRs contributes to enhanced electron-hole separation, although the performance was still marginally lower than that of ZnO IO + ZnO NRs. In the case of 4-NP, ZnO IO + ZnO NRs consistently outperformed TiO₂ IO + ZnO NRs under both UV and visible light, highlighting the enhanced charge transport and surface properties provided by the ZnO nanorods. Overall, the study confirms that the photocatalytic efficiency of these hierarchical nanostructures is influenced by material composition, morphology, the type of pollutant, and illumination conditions, emphasizing the potential of ZnO-based composites for effective degradation of pollutants.

CRediT authorship contribution statement

Lucy Nyambura Karanja: Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation. **Dániel Karajz:** Methodology. **Dóra Hessz:** Methodology, Formal analysis. **Tamás Igricz:** Methodology, Formal analysis. **Baradács Eszter Mónika:** Methodology. **Pál Petra:** Methodology. **Zoltán Erdélyi:** Methodology. **Csaba Cserhádi:** Formal analysis. **Barbara Sárközi:** Formal analysis. **Imre Miklós Szilágyi:** Supervision.

Declaration of competing interest

The authors affirm that there are no conflicts of interest related to this manuscript. They have no financial ties, sponsorships, or affiliations with organizations or entities that could influence the research, findings, or interpretation presented in this article. Additionally, the authors hold no patents, trademarks, or copyrights that could be impacted by the publication of this work. The authors have no personal relationships with any individuals whose interests could be affected by the publication of this article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.optmat.2025.116989>.

Data availability

Data will be made available on request.

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