



Full Length Article

Hierarchical TiO₂/ZnO inverse opal photonic structures: ALD synthesis and pharmaceutical remediation applicationsHamsasew Hankebo Lemago^{a,*}, Petra Pál^b, Csaba Cserhádi^b, Barbara Sárközi^b, Eszter Mónika Baradács^b, Zoltán Erdélyi^b, Imre Miklós Szilágyi^{a,*}^a Institute of Physical Metallurgy, Metal Forming and Nanotechnology, University of Miskolc, H-3515, Miskolc- Egyetemváros, Hungary^b Department of Solid-State Physics, Faculty of Sciences and Technology, University of Debrecen, P.O. Box 400, 4002 Debrecen, Hungary

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ABSTRACT

The persistence of pharmaceutical antibiotics in aquatic environments remains a critical challenge due to their poor removal by conventional treatment processes. Herein, hierarchical TiO₂/ZnO inverse opal (IO) photonic crystal heterostructures are fabricated via a double-templating method combined with atomic layer deposition (ALD), enabling precise control of surface architecture and heterointerfaces. The resulting materials exhibit highly ordered frameworks with pore structures and crystalline anatase TiO₂ and wurtzite ZnO phases, as confirmed by SEM, XRD, and Raman spectroscopy. UV–Vis spectroscopy showed two photonic band gap (PBG) regions at ~400 nm and ~590 nm, indicating enhanced light–matter interaction with strong slow-light effects for surface light harvesting, while the TiO₂/ZnO IO exhibited a red-shifted PBG at ~590 nm (~15 nm shift). Photocatalytic activity was assessed using Ciprofloxacin (CIP) and Rhodamine 6 G (Rh6G) under UV and visible-light irradiation. Under UV light, the hierarchical IO heterostructures achieved up to 70 % Rh6G degradation in 240 min and 60–65 % CIP degradation in 120 min, outperforming the single-component IOs. Under visible light, the TiO₂/ZnO and ZnO/TiO₂ IOs further improved performance, reaching 77–80 % Rh6G degradation and 74–75 % CIP degradation, respectively. This improvement resulted from the dual-templating strategy, which formed a highly ordered hierarchical photonic structure with a stronger slow-photon effect, enhanced light–matter interaction, more available adsorption sites, and more efficient charge separation across the TiO₂/ZnO heterojunctions.

1. Introduction

Global environmental pollution has become one of the most critical challenges of the 21st century, driven by rapid industrialization, urbanization, and population growth. Among various forms of pollution, water contamination by organic and pharmaceutical compounds has raised serious concerns due to their persistence, bioaccumulation, and potential toxicity to ecosystems and human health [1–3]. In particular, pharmaceutical residues such as antibiotics are frequently detected in aquatic environments, where they contribute to the emergence of antimicrobial resistance and are inadequately removed by conventional wastewater treatment technologies [4–6]. This challenge is further intensified by the global energy crisis and is closely linked to the broader water–energy nexus, where the growing demand for clean water and sustainable energy necessitates the development of efficient, low-energy, and environmentally friendly treatment strategies [7,8].

Inverse opal (IO) photonic crystals were synthesized using colloidal templating strategies based on sacrificial polymer spheres, producing highly ordered three-dimensional porous architectures with pore diameters typically ranging from ~150 to 800 nm [9–11]. Template size strongly influenced the photonic bandgap (PBG), thereby governing light–matter interactions, slow-photon effects, and enhanced photocatalytic performance [12–14]. Smaller templates provided a higher specific surface area and increased adsorption sites compared to larger-pore IO structures [15–19], leading to improved interfacial reactivity, more efficient charge separation, and transfer [20,21], and higher generation of reactive oxygen species [22]. Collectively, these structural and optical advantages contribute to defect-mediated bandgap engineering [23], improved structural stability [24,25], and significantly enhanced photocatalytic activity, durability, and reusability.

Recently, composite IO systems have been fabricated via infiltration

* Corresponding authors.

E-mail addresses: hamsasew.hankebo.lemago@uni-miskolc.hu (H.H. Lemago), imre.miklos.szilagyi@uni-miskolc.hu (I.M. Szilágyi).<https://doi.org/10.1016/j.apsadv.2026.101043>

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of metal oxides into the interstitial voids of single-template structures [10,17], representing a widely used route for functional integration. In addition, hierarchical IO architectures have been developed through sequential coating with multiple metal oxides, deposition of plasmonic metal layers [26,27], or sputtering techniques, further enhancing surface functionality and light-harvesting efficiency for photocatalytic applications. Beyond environmental remediation, these uniquely engineered IO materials have demonstrated superior performance in hydrogen evolution [28], CO₂ reduction [29], photoelectrochemical water splitting [30], energy storage [31], sensing [32], biological applications [33,34], and solar energy conversion [35], establishing IO photonic crystals as versatile platforms for sustainable energy and environmental technologies.

Building upon our previous ALD-derived IO studies [36–38] this work introduced a sequential double-templating methodology to fabricate hierarchical TiO₂/ZnO IO photonic structures. Unlike conventional single-template approaches, two sacrificial colloidal templates of different sizes were used to construct a multiscale IO architecture with interconnected macro- and mesoporous networks. This dual-periodic structure broadened and enhanced the PBG, extending slow-photon effects over a wider spectral range and strengthening light confinement and light-matter interactions. The resulting increase in optical path length, along with higher surface area and improved pore connectivity, promoted better reactant diffusion, adsorption, and photon utilization. In addition, atomic layer deposition (ALD) enabled conformal TiO₂/ZnO heterointerface formation throughout the framework, facilitating efficient charge separation, suppressing electron-hole recombination, and enhancing reactive oxygen species generation. The combined effect of double-templated architecture and ALD-engineered heterojunctions overcame the limitations of single-template and earlier IO systems, leading to significantly improved photocatalytic degradation efficiency. The structure-property-performance relationships were systematically analyzed using SEM, XRD, Raman spectroscopy, UV Vis spectroscopy, photoluminescence, and photocatalytic degradation measurements.

2. Experimental

2.1. Synthesis of colloidal opal templates by vertical layer deposition

A colloidal nanosphere template was fabricated using a 10 wt % suspension of 300 nm and 600 nm PS nanospheres (Sigma-Aldrich). Microscope glass slide substrates were cleaned with detergent, ethanol, and deionized water, followed by a 1 h piranha (1:3 volumetric ratio of H₂SO₄ to H₂O₂) treatment to remove organic residues and enhance

surface hydrophilicity. The slides were then dried at 40 °C. The colloidal suspension was prepared by diluting 0.15 mL of PS suspension with 4.85 mL of deionized water and stirring thoroughly, resulting in a 0.30 % solution. Glass substrates (2.5 × 3.5 cm) were vertically immersed in the suspension inside a sealed container to minimize evaporation. Vertical layer deposition (VLD) was performed in a furnace equipped with a water reservoir to control humidity. The temperature was increased to 50 °C and maintained for 14 h to promote self-assembly, followed by heating at 80 °C for 1.5 h to complete solvent evaporation and stabilize the colloidal crystal (See Fig. 1 below). This method reproducibly yielded well-ordered opal templates [37].

2.2. Atomic layer deposition

Before ALD, the Beneq TFS-200–186 reactor was operated in thermal mode and stabilized by preheating the chamber at 50 °C for 2 h. The prepared substrates, along with a reference Si (100) wafer, were subsequently loaded into the reactor. High-purity nitrogen (99.999 %) was employed as the carrier and purge gas, maintaining pressures of 6.8 mbar in the vacuum chamber and 1.4 mbar in the reactor. ALD was carried out at 70 °C using TiCl₄ and diethylzinc (DEZ) as precursors for TiO₂ and ZnO, respectively. The film thickness was controlled by the number of ALD cycles, yielding TiO₂ and ZnO layers with thicknesses of approximately 42 nm after 374 and 333 cycles, respectively. These values correspond to growth-per-cycle (GPC) rates of ~0.11 nm cycle⁻¹ for TiO₂ and ~0.12 nm cycle⁻¹ for ZnO. For the bilayer structures (TiO₂/ZnO and ZnO/TiO₂), 111 and 125 cycles were employed, respectively, to obtain layers approximately 21 nm thick, as confirmed by ellipsometry. The corresponding GPC values were 0.19 and 0.17 nm cycle⁻¹, respectively.

After ALD deposition, the samples were placed in alumina crucibles and thermally treated to remove the polymeric opal templates and form IO architectures. The calcination procedure involved heating from room temperature to 500 °C over 4 h, followed by a 2 h dwell at 500 °C. This process completely removed the template material, yielding IO structures of TiO₂, ZnO, and their bilayer composites (TiO₂/ZnO and ZnO/TiO₂).

2.3. Materials characterization

The samples were investigated using a ThermoFisher Scientific Scios 2 dual-beam microscope. The equipment is built with an acceleration tube, a unique in-lens Trinity detector system, and a retarding-field option. Taking advantage of this setup, the low-voltage scanning

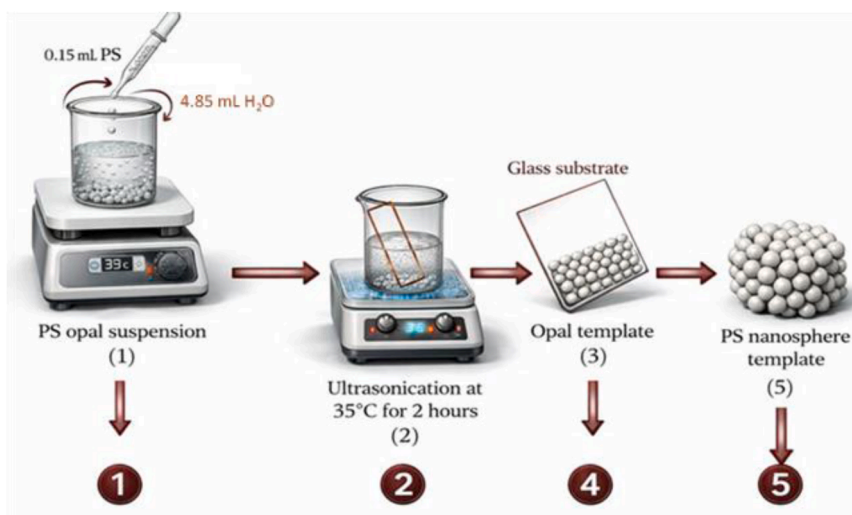


Fig. 1. Synthesis of PS template using VLD method.

electron microscopy (LVSEM) technique was applied to make high-resolution images of the samples. 2 kV acceleration voltage 20 V reverse bias was applied for the investigations. The horizontal field of view was set to 2.54 μm .

XRD analysis was performed using a PANalytical XPert Pro MPD diffractometer with Cu K α radiation (2θ range 5–70°, step size 0.025°). The resulting patterns were compared to the International Centre for Diffraction Data (ICDD) database to identify crystalline phases. The mean size of the crystallites, D , was determined with the Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

Where K is the constant, λ is the wavelength of the radiation, β is the full width of diffraction peaks at half-maximum (FWHM), and θ is the angle at which the peak occurs (Bragg angle).

The crystallinity (%) of the thin films was estimated using OriginPro 2026 by comparing the crystalline peak area (A_c) to the total diffraction area (A_t) as:

$$\text{Crystallinity (\%)} = \frac{A_c \times 100}{A_t} \quad (2)$$

This estimation is crucial for thin films, as it provides insight into their structural quality, which directly affects optical, electronic, and mechanical properties.

Using the Tauc relation (Eq 3) and the Kubelka-Munk theory [39], optical band gap energies (E_g) of IOs TiO $_2$, ZnO, and their composites were calculated from absorption data (α) and photon energy ($h\nu$). For indirect E_g (TiO $_2$) and direct E_g (ZnO) and their composites, Tauc plots $(\alpha h\nu)^{1/2}$ vs. $h\nu$ and $(\alpha h\nu)^2$ vs. $h\nu$ were made (Fig. 7a–d). The optical band gap energy was obtained by extrapolating the linear portions of the plots to $(\alpha h\nu)^{1/n} = 0$.

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (3)$$

The optical properties of the samples were studied using UV Vis spectroscopy, recorded with an Avantes AvaSpec-2048 fiber optic spectrometer and an Ava Light DHS light source, utilizing Ava Soft software in both absorbance and reflectance modes.

Raman spectra were gathered using a Jobin Yvon Labram Raman spectrometer equipped with an Olympus BX41 microscope and a 532 nm Nd-YAG laser. Measurements were collected from 100 to 1800 cm^{-1} with a pixel resolution of 1.4–1.5 cm^{-1} and a spectral resolution of approximately 4 cm^{-1} . Three spectral accumulations were performed.

Spectroscopic ellipsometry (Semilab SE-2000) was used to determine the film thickness of the reference samples. For this, reference Si (100) wafers were also introduced as control samples into the ALD system together with the opal and IO samples.

Photoluminescence (PL) spectra were recorded using an Edinburgh Instruments FS5 spectrofluorometer with a stationary fluorescence setup, featuring an excitation wavelength of 280 nm at room temperature and the inclusion of a long pass glass filter in the emission beam set at a nominal wavelength of 320 nm.

The photocatalytic activity of IO samples was evaluated under UV and visible-light irradiation. Under UV light, rhodamine 6 G (Rh6G, 9.6 mg/L, $\lambda_{\text{max}} = 528$ nm) and ciprofloxacin (CIP, 17 mg/L, pH 11 $\pm$ 0.09, $\lambda_{\text{max}} = 271$ nm) were used as model pollutants. The pH of CIP solutions was adjusted using 6 M KOH and measured with a CLEAN PH500 pH meter. The samples were immobilized on the inner walls of a glass reactor, magnetically stirred, and pre-equilibrated in the dark for 30 min for Rh6G and 40 min for CIP until adsorption–desorption equilibrium was reached, respectively. UV photocatalysis was performed using an Osram 18 W Blacklight (three-lamp stacked configuration, 5 cm distance), with aliquots periodically collected and analyzed by UV Vis spectroscopy (AvaSpec-2048 with AvaLight-DHS) to monitor degradation over 4 h (Rh6G) and 2 h (CIP). For visible-light photocatalysis,

(Rh6G, 9.6 mg/L, $\lambda_{\text{max}} = 528$ nm) and ciprofloxacin (CIP, 17 mg/L, pH 11 $\pm$ 0.09, $\lambda_{\text{max}} = 271$ nm) were used under identical experimental conditions. The dark adsorption step was extended to 30 min for Rh6G and 40 min for CIP. Irradiation was performed using LED tube lamps (G13 T8, 1200 mm Ecofit) arranged in a three-lamp stacked configuration at 5 cm. Photocatalytic activity was evaluated over 240 min for Rh6G and 120 min for CIP.

The photocatalytic activity of the samples was assessed by monitoring the relative absorbance of Rh6G and CIP. The relative absorbance was calculated using:

$$A_0/A_t = 1 - (A_t/A_0) \quad (4)$$

where A_0 is the initial absorbance of the pollutant, and A_t is the absorbance at irradiation time t . The degradation kinetics were analyzed using a pseudo-first-order model:

$$k = \ln (C_0/C_t)/t \quad (5)$$

where k is the rate constant, C_0 is the initial pollutant concentration, and C_t is the concentration at time t . A linear regression of $\ln (C_0/C_t)$ versus time (t) was performed to evaluate the model fit, from which the slope (k), intercept (b), coefficient of determination (R^2), and residual percentage were determined.

The half-life ($t_{1/2}$) for first-order kinetics was calculated using:

$$t_{1/2} = \ln (2)/k \quad (6)$$

This parameter represents the time required for the pollutant concentration to decrease to half of its initial value.

3. Results and discussion

3.1. Double templating for hierarchical inverse opal synthesis

The synthesis of hierarchical TiO $_2$ /ZnO bilayer IO architectures was achieved through a sequential double-templating and ALD strategy in Fig. 2 below. In the first templating stage, a three-dimensional colloidal crystal scaffold was constructed using PS nanospheres with a diameter of 600 nm (PS-600). This template was then infiltrated with a conformal 42 nm layer of TiO $_2$ via thermal ALD. To generate the primary inverse-opal framework, the composite was subjected to an annealing process at 500 °C, which facilitated the thermal decomposition of the PS nanospheres and left behind a periodic, porous metal-oxide lattice. The second phase of fabrication involved the deposition of a smaller-scale template, consisting of 300 nm PS nanospheres (PS-300), directly onto the pre-existing TiO $_2$ IO scaffold. This secondary template was subsequently coated with a 21 nm layer of ZnO using a second ALD cycle. A final annealing step at 500 °C was performed to remove the remaining polymer template and promote the crystallization of the ZnO coating. This integrated two-step process yielded a highly ordered, bilayered TiO $_2$ /ZnO composite characterized by a hierarchical pore structure, precise thickness control, and high interconnectivity between the distinct oxide layers.

3.2. SEM result analysis

3.2.1. Polystyrene sacrificial templates of varying sizes

PS nanospheres self-assembled into highly ordered hexagonal close-packed (hcp) mono- and multilayer colloidal crystal films via VLD driven by capillary forces during solvent evaporation [40]. Fig. 3a–b shows LVSEM images confirming long-range hcp ordering with smooth, monodisperse nanospheres and well-defined triangular interstitial sites, indicative of high packing quality and low defect density. The template periodicity and sphere size, determined by PS sphere diameters of 300 and 600 nm, enabled precise tuning of PBG properties. The resulting interconnected void network and structural integrity made these PS templates ideal sacrificial scaffolds for fabricating IOPCs using

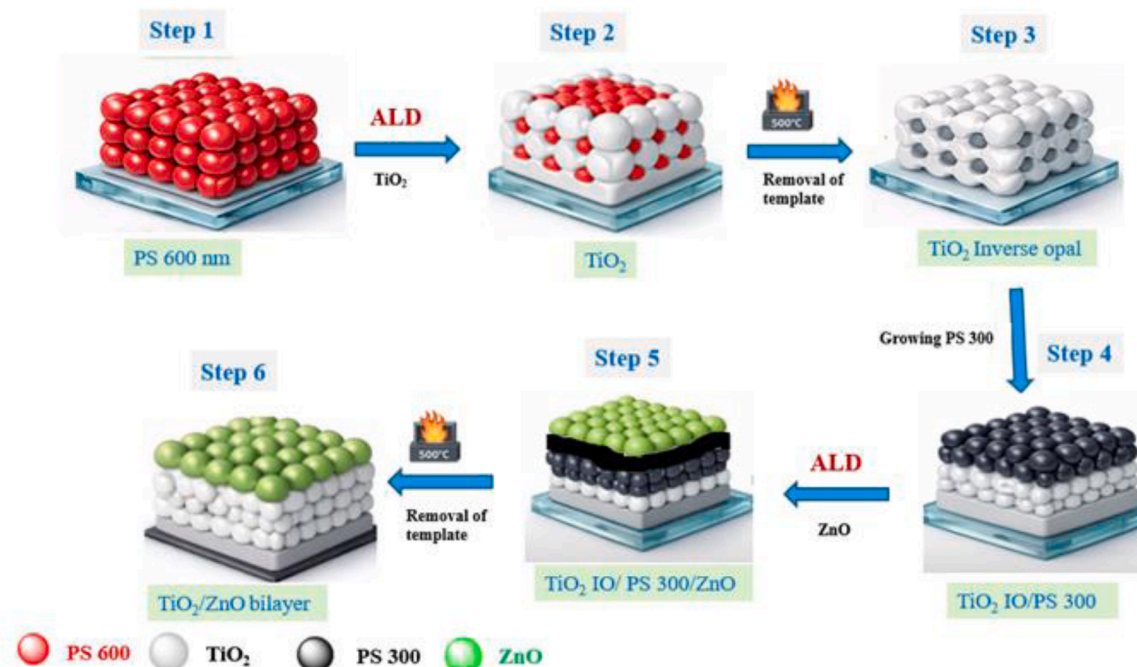


Fig. 2. Synthesis of hierarchical TiO_2/ZnO bilayer IO architectures via sequential colloidal templating and ALD.

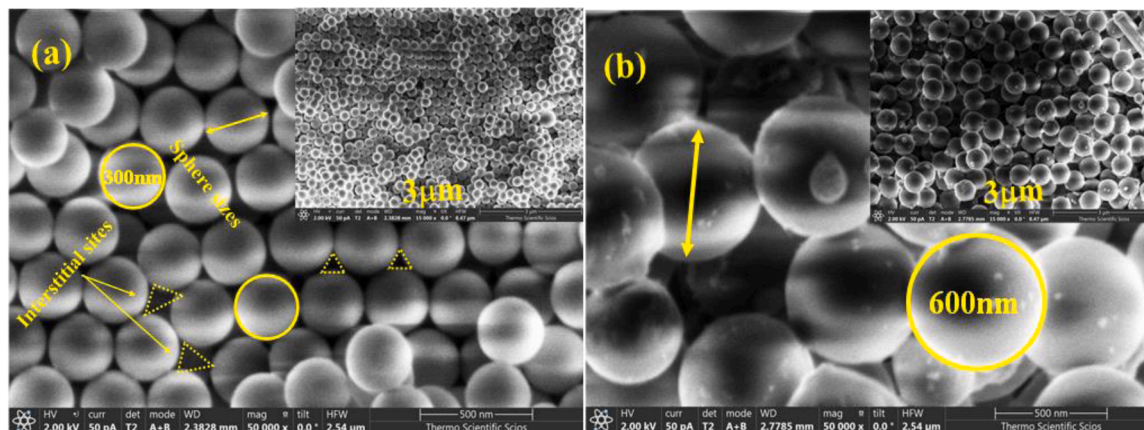


Fig. 3. LVSEM micrographs taken by SE in-lens detector (a) PS 300 nm template, and (b) PS 600 nm template, respectively.

conformal thin-film deposition techniques such as ALD, CVD, and related methods [41].

3.2.2. SEM analysis of the inverse opal materials

Morphological analysis in Fig. 4a and c showed that the IO structures (pure TiO_2 and pure ZnO) derived from the 600 nm PS templates exhibited more pronounced cracking than their templated counterparts. However, these IO materials demonstrated larger sphere sizes and interstitial voids, characteristics advantageous for applications involving photocatalysis and light-matter interactions [1,2]. In contrast, the IO structures fabricated using the 300 nm PS templates showed reduced cracking but also exhibited smaller sphere sizes and lower void areas, which limit their effectiveness in such applications [42]. For the composite IOs, the morphological evolution involved a secondary templating step. The final thermal annealing step not only crystallized the deposited materials but also removed the second layer of PS templates. The resulting TiO_2/ZnO and ZnO/TiO_2 composite IO architectures exhibited a combination of the larger 600 nm diameter from the first template and potentially smaller, more intricate features or surface

coatings derived from the 300 nm PS nanospheres. This intricate morphology, with varying sizes and material distribution, is critical for enhancing their photocatalytic performance by increasing surface area and facilitating light harvesting within the photonic crystal structure.

3.3. XRD analysis

Based on the XRD patterns, clear differences in crystallinity, preferred orientation, peak intensity, and phase composition were observed among the pure IOs and the bilayer composite structures, which arise from the layer-by-layer ALD growth and template-directed architecture. The pure TiO_2 IO exhibited sharp and distinct diffraction peaks at $2\theta = 25.6^\circ, 38.4^\circ, 44.5^\circ, 55.5^\circ$, and 62.5° , (Fig. 5) which are characteristic of the tetragonal anatase phase of TiO_2 (ICDD No 98-002-4276), reflecting the highly conformal TiO_2 coating produced by the first ALD cycle on the PS-600 template. The strong intensity of the (101) reflection at 25.6° indicated a preferred orientation along this plane, suggesting crystallographic ordering, which was promoted by the uniform pore geometry of the IO scaffold. With an FWHM of 0.3 rad and

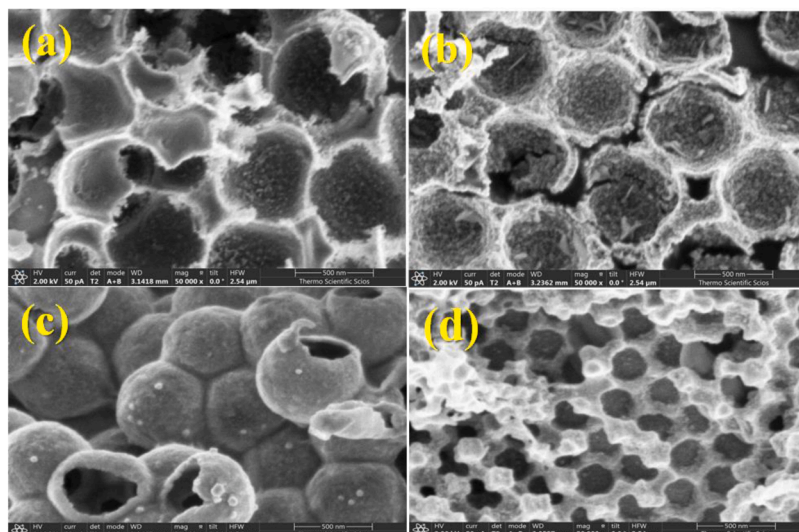


Fig. 4. LVSEM micrographs taken by SE in-lens detector micrographs of the ALD IO materials (a) pure TiO_2 IO, (b) TiO_2/ZnO , (c) pure ZnO IO, and (d) ZnO/TiO_2 , respectively.

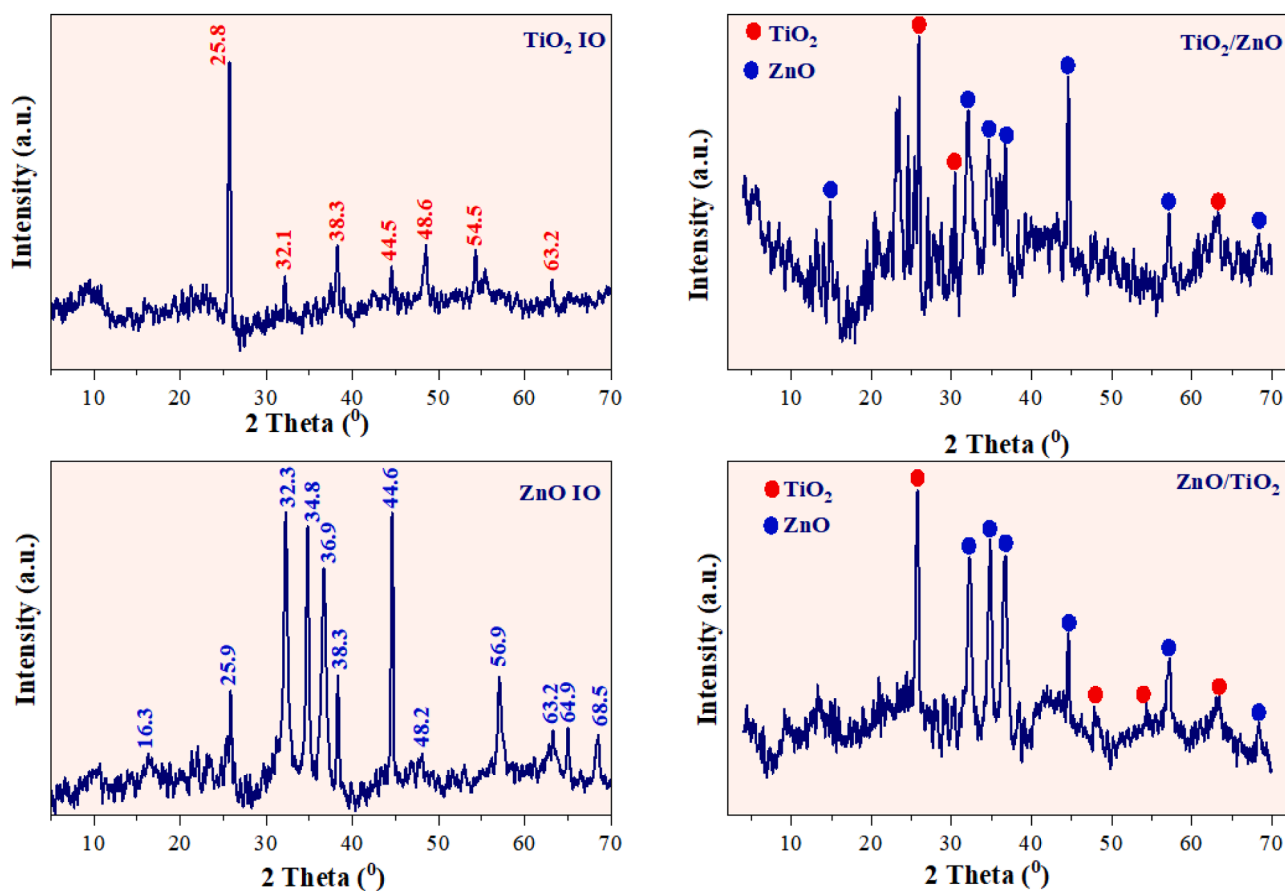


Fig. 5. XRD patterns of pure TiO_2 IO, TiO_2/ZnO , pure ZnO IO, and ZnO/TiO_2 samples. Pure TiO_2 and ZnO IOs show characteristic anatase and wurtzite peaks with good crystallinity. Bilayer composites display peaks of both phases, confirming successful heterostructure formation. Differences in peak intensity and broadening indicate that deposition sequence affects crystallite growth and structural ordering.

an average crystallite size of ~ 30.5 nm, the TiO_2 IO showed a relatively high crystallinity of 78 %, consistent with its sharp and intense peaks, indicating effective crystallization during the 500°C template-removal annealing step (see Table 1 below).

Following the deposition of the ~ 21 nm ZnO IO layer to form the

TiO_2/ZnO composite, a visible reduction in TiO_2 peak intensity was observed, reflecting partial attenuation of the TiO_2 signal by the over-grown ZnO layer and increased structural disorder, which is typical of sequential ALD coating on an already crystallized IO framework. Residual TiO_2 anatase peaks remained visible at 25.6° , 32.1° , and 63.2° ,

Table 1

Crystallite size (D), full width at half maximum (β), and crystallinity percentage (%) of pure IOs and bilayer composite IO structures determined from XRD patterns using the Scherrer equation, showing the effect of deposition sequence on crystal growth and structural ordering.

Sample IOs	β (radian)	D (nm)	Crystallinity (%)
TiO ₂	0.3	30.5	78
TiO ₂ /ZnO	0.2	39.0	62
ZnO	0.3	30.0	85
ZnO/TiO ₂	0.3	30.0	79

(Fig. 5) while new diffraction peaks at 16.3°, 32.3°, 34.8°, 44.6°, and 56.9° (Fig. 5) corresponded to the hexagonal wurtzite ZnO phase, confirming successful phase integration from the second PS-300 templated ALD step. The narrower FWHM (0.2 rad) and larger crystallite size (~39.1 nm) indicated grain growth during ALD ZnO deposition; however, the overall crystallinity decreased to 62 % (Table 1), implying increased interfacial strain and phase mixing within the composite, caused by lattice mismatch and constrained growth at the TiO₂/ZnO interface formed during bilayer fabrication. This discrepancy indicated that crystallite growth occurred together with increased structural distortion at the heterointerface. The reduced crystallinity resulted from lattice mismatch between anatase TiO₂ and wurtzite ZnO, which generated interfacial strain, lattice distortion, and defects during sequential crystal growth. This strain-induced disorder reduced the fraction of well-ordered crystalline domains without preventing grain growth [43,44].

The pure ZnO IO exhibited sharp and intense diffraction peaks, consistent with the hexagonal wurtzite structure (ICDD No 98-003-1052), demonstrating that ALD on the PS-300 template produced highly crystalline ZnO after annealing. The dominant (101) and (002) reflections suggested preferential orientation along the c-axis, which is typical for ALD-grown ZnO thin shells on ordered templates. With a narrow FWHM of 0.3 rad, a crystallite size around 30.0 nm, and the highest crystallinity (85 %) among the samples, the ZnO IO demonstrated excellent crystalline quality (See also Table 1). In the ZnO/TiO₂ composite, the diffraction peaks became broader and less intense, reflecting reduced long-range order, due to interfacial strain introduced during the sequential bilayer deposition process. The presence of TiO₂ anatase peaks confirmed the coexistence of both phases. Table 1 below presents that the crystallite size (~30 nm) and slightly lower crystallinity (79 %) suggested that TiO₂ incorporation introduced minor disruption to ZnO crystallinity while maintaining a mixed-phase heterostructure. Therefore, the XRD analysis indicated successful formation of TiO₂/ZnO IO composites with tunable crystallinity, orientation, and phase composition influenced by deposition sequence and interfacial interactions, directly governed by the double-templating and ALD-based synthesis strategy. Compared with TiO₂/ZnO, the smaller decrease in crystallinity shows that the deposition sequence affects interfacial stress and crystal ordering. Since ZnO has higher initial crystallinity, it provides a more stable template for TiO₂ growth, causing less lattice distortion. These results show that structural ordering strongly depends on deposition order and interfacial growth during ALD. Therefore, the XRD results demonstrated that the double-templating strategy and sequential ALD controlled the phase composition, preferred orientation, and crystallinity through interfacial strain and phase interactions. The observed changes in peak intensity, crystallinity, and crystallite size were attributed to grain growth during annealing and strain-induced lattice distortion at the TiO₂/ZnO interfaces, consistent with previous reports on oxide heterojunctions [45–47].

3.4. Raman analysis

The Raman spectra confirmed the expected crystal phases and defect

chemistry of all four IO thin films, showing well-resolved phonon modes and strong thickness-dependent intensities. The pure TiO₂ IO exhibited the characteristic anatase phase modes at 144 cm⁻¹ (E_g), 192 cm⁻¹ (E_g), 396 cm⁻¹ (B_{1g}), 512 cm⁻¹ (A_{1g}), and 637 cm⁻¹ (E_g) (See Fig. 6). The very intense 144 cm⁻¹ peak indicated high crystallinity and long phonon coherence length, while its slight broadening suggested phonon confinement caused by the nanocrystalline IO framework [48]. The weak red shift and asymmetric broadening of this mode, together with the enhanced background, served as fingerprints of oxygen vacancies and Ti³⁺ defect states. These features were further intensified in the TiO₂/ZnO heterostructure, where additional ZnO-related bands appeared at approximately 297, 435, 487, and 625 cm⁻¹ (See Fig. 6), and the TiO₂ anatase modes were partially suppressed and broadened, reflecting interfacial strain and charge transfer from ZnO to TiO₂ that stabilized Ti³⁺ centers.

In contrast, pure ZnO IO in the wurtzite crystal phase exhibited ZnO modes at ~297 cm⁻¹ (E₂-high-related defect mode), 435 cm⁻¹ (E₂-high), 487 cm⁻¹ (A₁(longitudinal optical mode (LO))), 625 cm⁻¹ (defect-induced LO), and strong multi-phonon features at 1004 and 1153 cm⁻¹ (See also Fig. 6). Their high intensities indicated good crystalline order, whereas the enhanced LO modes confirmed a high density of oxygen vacancies (V_o). When capped by anatase-phase TiO₂ in ZnO/TiO₂, both ZnO and TiO₂ phonons were observed but with reduced and broadened intensities, which evidenced phonon confinement and interfacial disorder, while the relative enhancement of LO modes again signified an increased defect density caused by heterojunction formation [49,50].

Furthermore, the Raman results matched the XRD patterns, confirming anatase TiO₂ and wurtzite ZnO crystal phases. Both Raman and XRD showed reduced intensities and peak broadening in bilayer heterostructures, indicating smaller crystalline domains, phonon confinement, and interfacial strain. These structural and defect features correlated with UV-Vis absorption, where bilayers exhibited enhanced visible-light absorption and red-shifted band edges due to oxygen vacancies (V_o) and Ti³⁺ states.

3.5. UV visible spectroscopy

As shown in Figs. 7 and 8, the pure TiO₂ IO exhibited a lower absorption intensity compared with the composite samples, consistent with its optical band gap (E_g) of ~3.2 eV. The spectrum showed a broad absorption band in the UV region, centered at approximately 345 nm, with an absorption edge around 380 nm, characteristic of intrinsic anatase-phase TiO₂ [51]. In addition, a broad PBG feature was observed near 390 nm, attributed to the periodic structure originating from the spherical artificial opal template with an average diameter of ~600 nm. Upon coating a 300 nm PS opal template followed by deposition of a ~21 nm ZnO layer via ALD, the resulting TiO₂/ZnO composite (E_g = ~3.4 eV) (See Fig. 8) exhibited a pronounced enhancement in optical absorption relative to pure TiO₂ IO. The main absorption band appeared near 300 nm with a slight blue shift, indicating modified electronic transitions due to ZnO incorporation. Moreover, the composite exhibited a PBG at ~390 nm and a broader, more intense band at ~590 nm, indicating double-templating-induced redshift and improved spectral response (Fig. 7b). In comparison, the pure ZnO IO (band gap ~3.1 eV) (See also Fig. 8) displayed significantly enhanced UV absorption with a sharper and higher-intensity band centered around ~300–320 nm, characteristic of the intrinsic wide-bandgap ZnO excitonic transition, while its absorption edge remained in the near-UV region (~370–380 nm) [52]. At the same time, the PBG became more clearly defined and red-shifted to ~590 nm (Fig. 7b) due to the periodicity imposed by the 300 nm PS artificial opal template.

After conformal deposition of ~21 nm ZnO by ALD onto the TiO₂ IO framework to form the ZnO/TiO₂ composite (band gap ~3.4 eV), (Fig. 8), the UV absorption was further intensified and broadened compared with both individual IOs. This behavior indicates improved

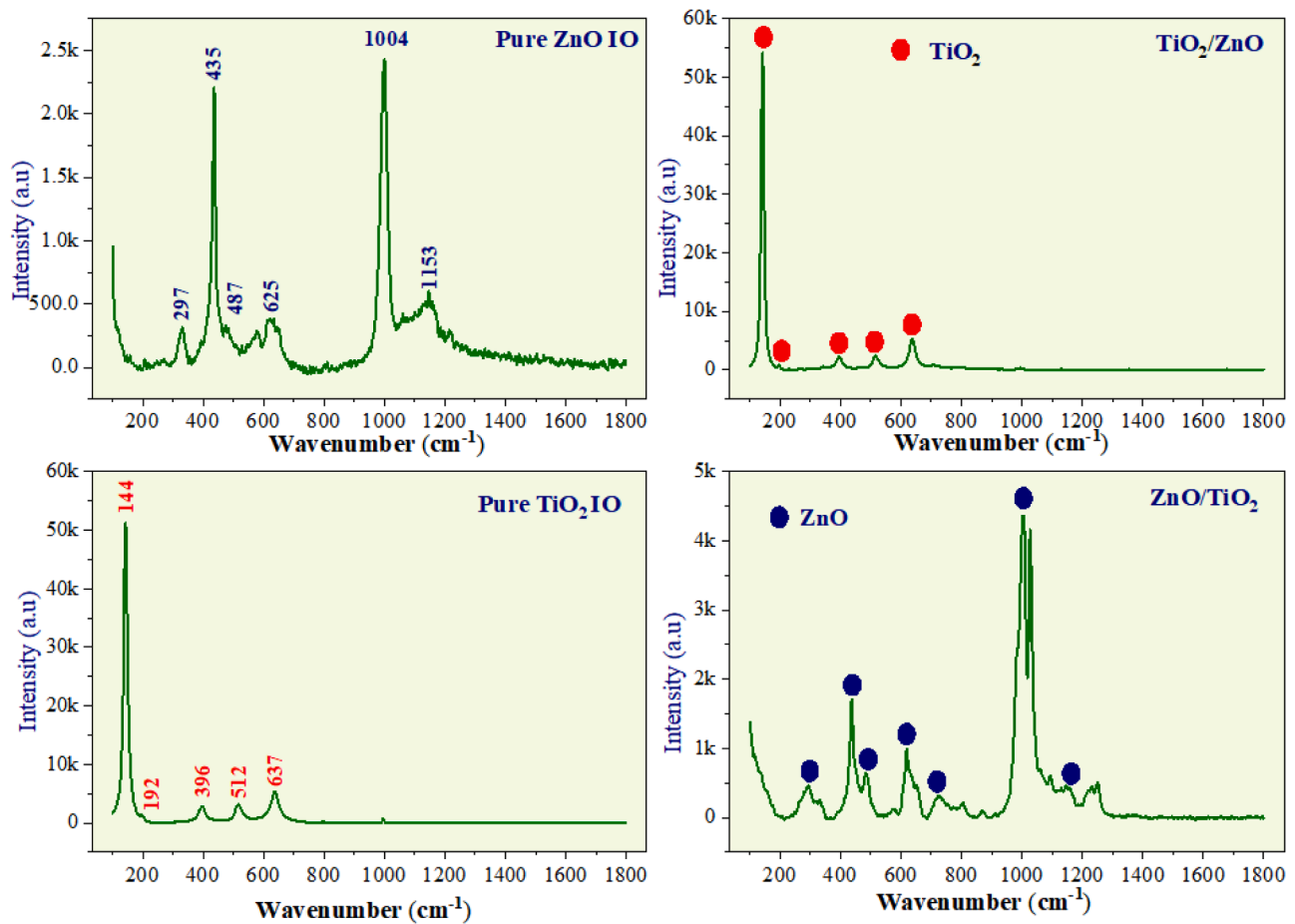


Fig. 6. Raman spectra of TiO_2 IO, ZnO IO, and their bilayer composites. Pure IO TiO_2 shows anatase E_g (144 cm^{-1}), ZnO shows wurtzite/LO modes with oxygen vacancies, while bilayers exhibit both phases with broadened, weakened peaks due to strain, phonon confinement, and defects, consistent with XRD-confirmed heterostructures.

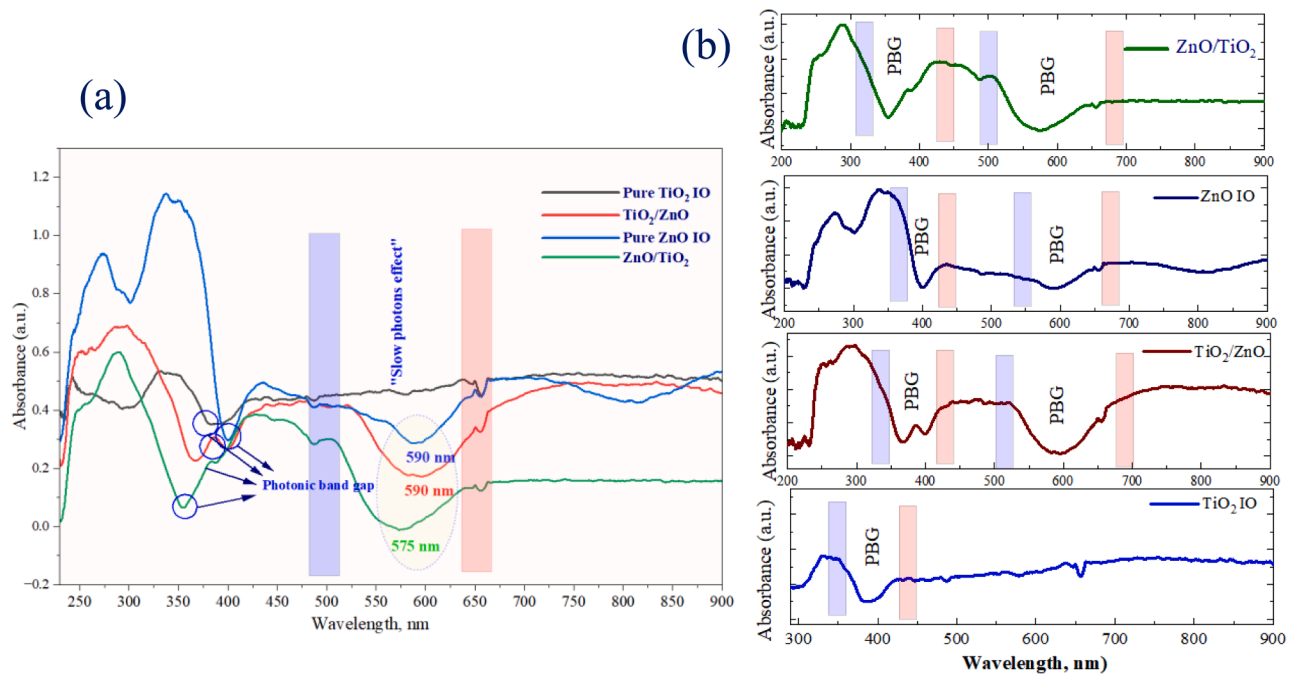


Fig. 7. (a) UV Visible spectra of TiO_2 IO, ZnO IO, and composites. TiO_2 shows weak UV absorption ($\sim 380 \text{ nm}$ edge), while ZnO shows stronger absorption ($\sim 300\text{--}320 \text{ nm}$). Composites exhibit enhanced, broadened absorption with a slight blue shift ($\sim 300 \text{ nm}$) due to heterojunction formation and improved light harvesting, and (b) PBG analysis: pure IOs of TiO_2 , ZnO , and composites show broadened/modified PBG, confirming preserved photonic structure and optical tuning.

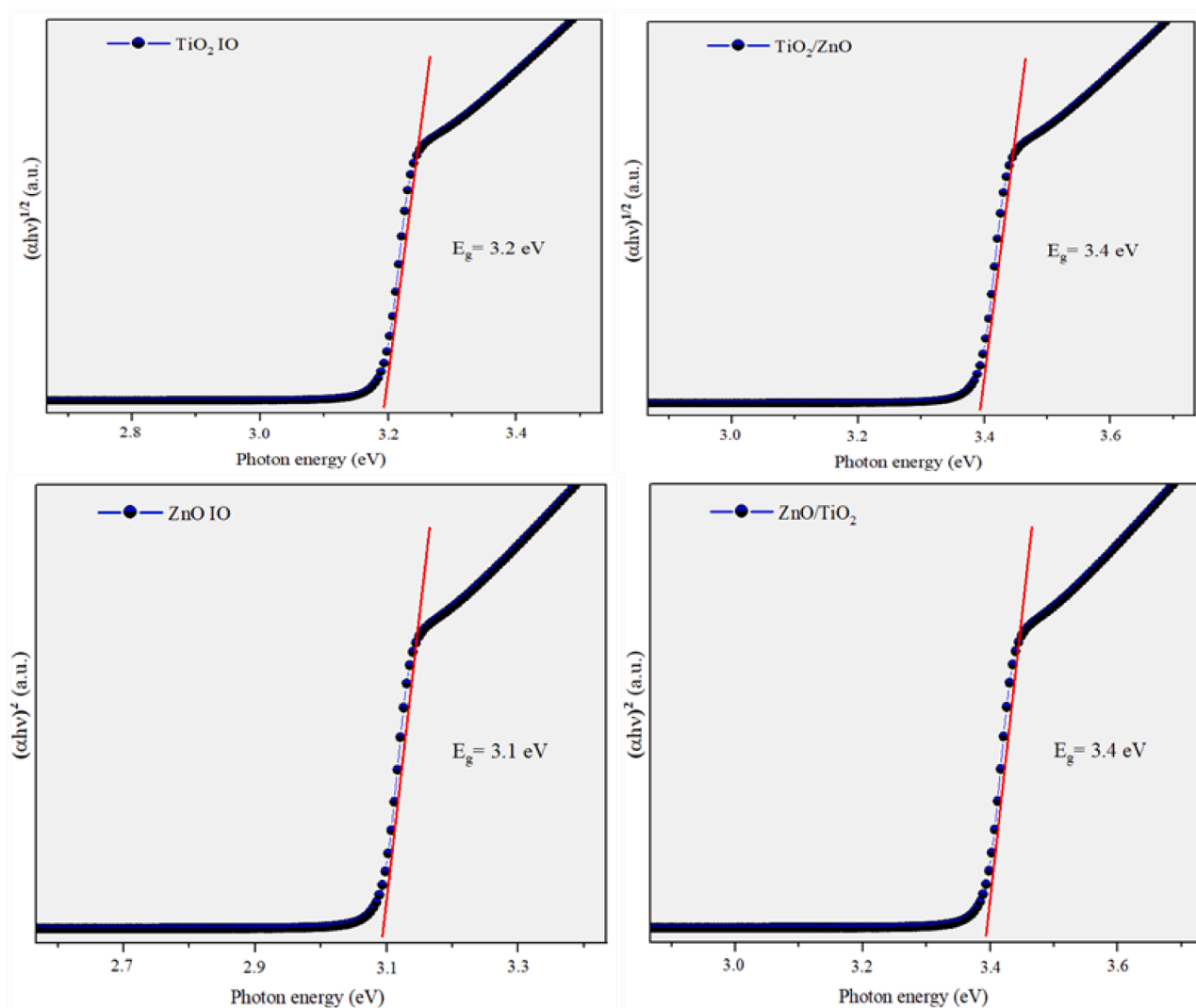


Fig. 8. Tauc plot from UV–Vis absorption analysis of ALD samples used to determine the indirect band gaps of TiO_2 IO and TiO_2/ZnO , and the direct band gaps of ZnO IO and ZnO/TiO_2 , at the X-axis intercepts.

light harvesting arising from heterojunction formation and enhanced multiple scattering within the photonic crystal. The main absorption maximum remained near ~ 300 nm with a slight blue shift relative to TiO_2 , while the composite exhibited a pronounced and broader PBG around 360 nm and 575 nm. These results confirm that the ordered macroporous architecture was preserved and that the coupled ZnO/TiO_2 photonic–electronic structure provides improved UV light trapping and absorption.

3.6. Photoluminescence (PL) spectroscopy

PL spectroscopy was used to investigate the optical emission behaviour of IO architectures based on pure TiO_2 , pure ZnO , and their bilayer composites (TiO_2/ZnO and ZnO/TiO_2). Fig. 9 shows that pure ZnO IO exhibited a dominant near-band-edge emission at ~ 421 nm together with multiple blue–green defect-related emissions at 451, 468, 483, and 492 nm, as well as a broad green band centered at ~ 552 nm, which were attributed to oxygen vacancies, zinc interstitials, and surface-related states in the ALD-grown shells [53,54]. Fig. 9 also shows that pure TiO_2 IO also showed intense visible emission features associated with Ti^{3+} centers and oxygen vacancies generated during the high-temperature (500°C) template removal and crystallization process. In the bilayer structures, these characteristic emissions were still

present but exhibited changes in intensity distribution, indicating modified recombination behaviour due to interfacial interactions within the heterojunction [19,55].

Hence, the variation in PL intensity between single and bilayer IOs reflected changes in carrier relaxation pathways and recombination probability within the hierarchical framework. The reduced radiative emission in the composites, in conjunction with the enhanced and broadened UV Vis absorption and the red-shifted photonic band gap (~ 590 – 600 nm), suggested that photogenerated charge carriers were more effectively harvested and spatially redistributed within the coupled photonic–semiconductor system [56,57]. This behaviour implied that the IO periodicity increased photon residence time and excitation density, while the TiO_2 – ZnO heterojunction facilitated directional charge separation, thereby reducing the likelihood of electron–hole recombination [58]. Furthermore, XRD confirmed the preservation of crystallinity after the double-templated ALD process, indicating that the improved charge dynamics originated primarily from interfacial electronic coupling rather than structural degradation. SEM analysis supported the maintenance of the hierarchical macroporous architecture, which further contributed to multiple scattering and carrier generation. Collectively, the synergy between photonic band structure modulation and heterojunction-driven charge transfer effectively extended carrier lifetime and availability for surface redox

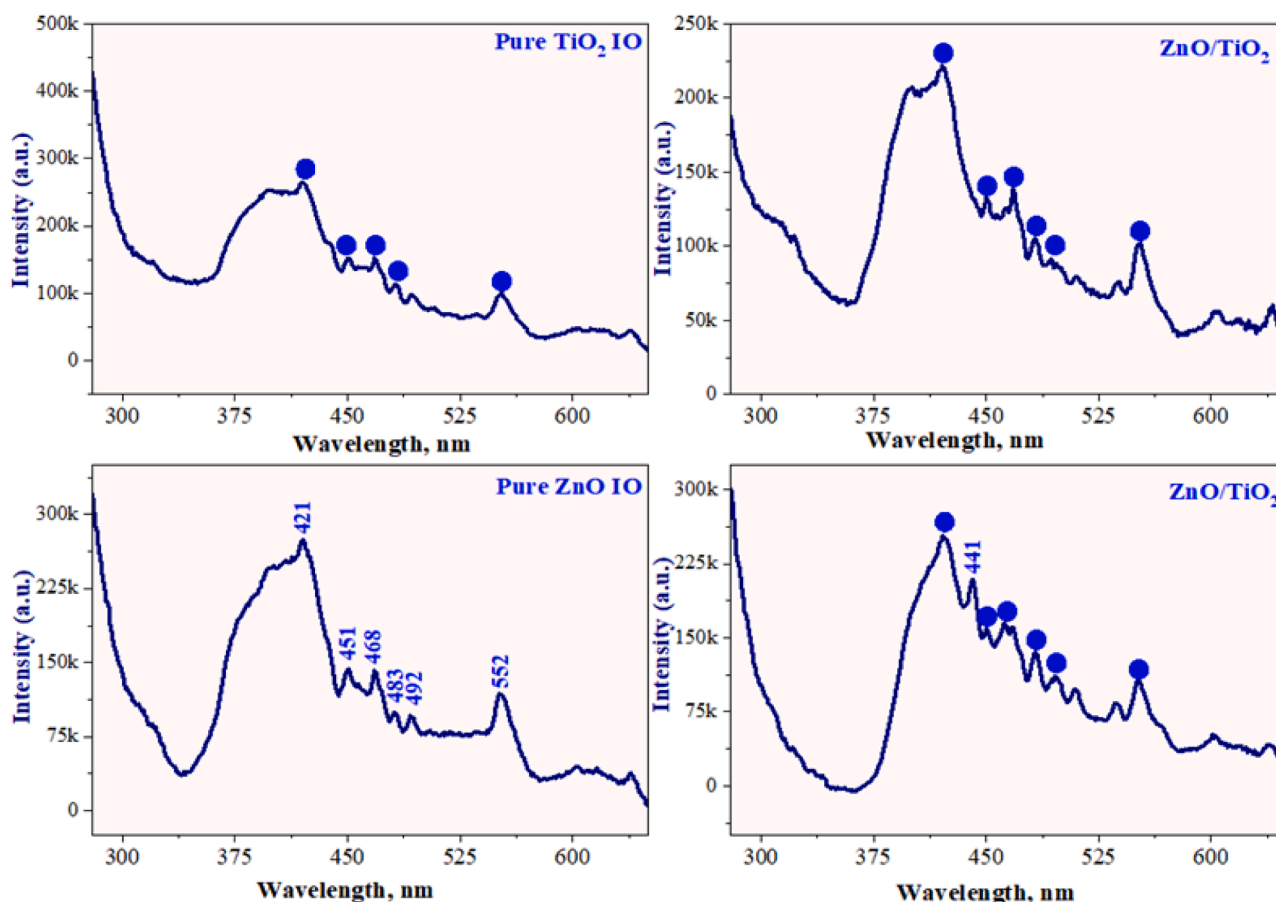


Fig. 9. PL spectra of TiO_2 IO, ZnO IO, and composite bilayers. The pure ZnO IO shows strong near-band-edge emission (~ 421 nm) with multiple defect emissions (451–552 nm), while pure TiO_2 IO exhibits strong defect-related visible PL. Composite bilayers retain emission bands with modified intensity due to interfacial charge transfer and defect changes.

reactions, which rationalized the enhanced photocatalytic activity of the bilayer IO systems [59–62].

3.7. Photocatalysis

Comparison between CIP and Rh6G in photocatalytic remediation: CIP is a fluoroquinolone antibiotic (~ 331 g/mol) with a quinolone core (Fig. 10a), fluorine atom, and piperazine ring, showing moderate pH-dependent solubility and strong UV absorption (~ 271 nm). Its photocatalytic degradation mainly occurs through hydroxyl radical attack, defluorination, and cleavage of the piperazine ring, and it is regarded as a persistent pharmaceutical pollutant [63,64]. Rh6G, a xanthene-based cationic pollutant (~ 479 g/mol), possesses a highly conjugated chromophore, high aqueous solubility, and strong visible-light absorption (~ 528 nm), with degradation proceeding via chromophore cleavage, N-deethylation, and ring opening (See also Fig. 10b) [65,66].

Under **UV irradiation**, both Rh6G and CIP were efficiently degraded by the IO photocatalysts, with the double-templated bilayer heterostructures consistently outperforming the single-component IOs

(Fig. 11a, c; Tables 2, 4). For Rh6G, the TiO_2/ZnO and ZnO/TiO_2 IOs showed the highest degradation efficiency (70 % after 240 min), compared with 62 % for ZnO IO and 61 % for TiO_2 IO, while direct photolysis resulted in only 10 % degradation. For the more persistent pharmaceutical pollutant CIP, comparable degradation efficiencies (60–65 %) were achieved within a shorter reaction time (120 min), with ZnO/TiO_2 IO exhibiting the highest activity (65 %, $k = 8.4 \times 10^{-1} \text{ min}^{-1}$), followed by TiO_2/ZnO IO (64 %, $k = 7.7 \times 10^{-3} \text{ min}^{-1}$). The negligible degradation observed in the absence of a photocatalyst (10 % for Rh6G after 240 min and CIP after 120 min under UV irradiation) confirmed that direct photolysis contributed minimally to pollutant removal, highlighting that the enhanced degradation achieved by the IO photocatalysts originated from their rationally double templated architecture rather than UV exposure alone. In particular, the hierarchical TiO_2/ZnO and ZnO/TiO_2 bilayer IOs consistently exhibited the highest photocatalytic efficiencies for both Rh6G (70 %) and CIP (64–65 %), demonstrating the beneficial synergy between the ordered macroporous framework and heterojunction-mediated charge separation.

Under **visible-light** irradiation, both Rh6G and CIP exhibited

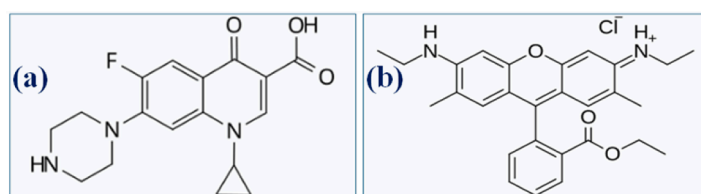


Fig. 10. Structure of (a) Ciprofloxacin and (b) Rhodamine 6 G pollutants, respectively.

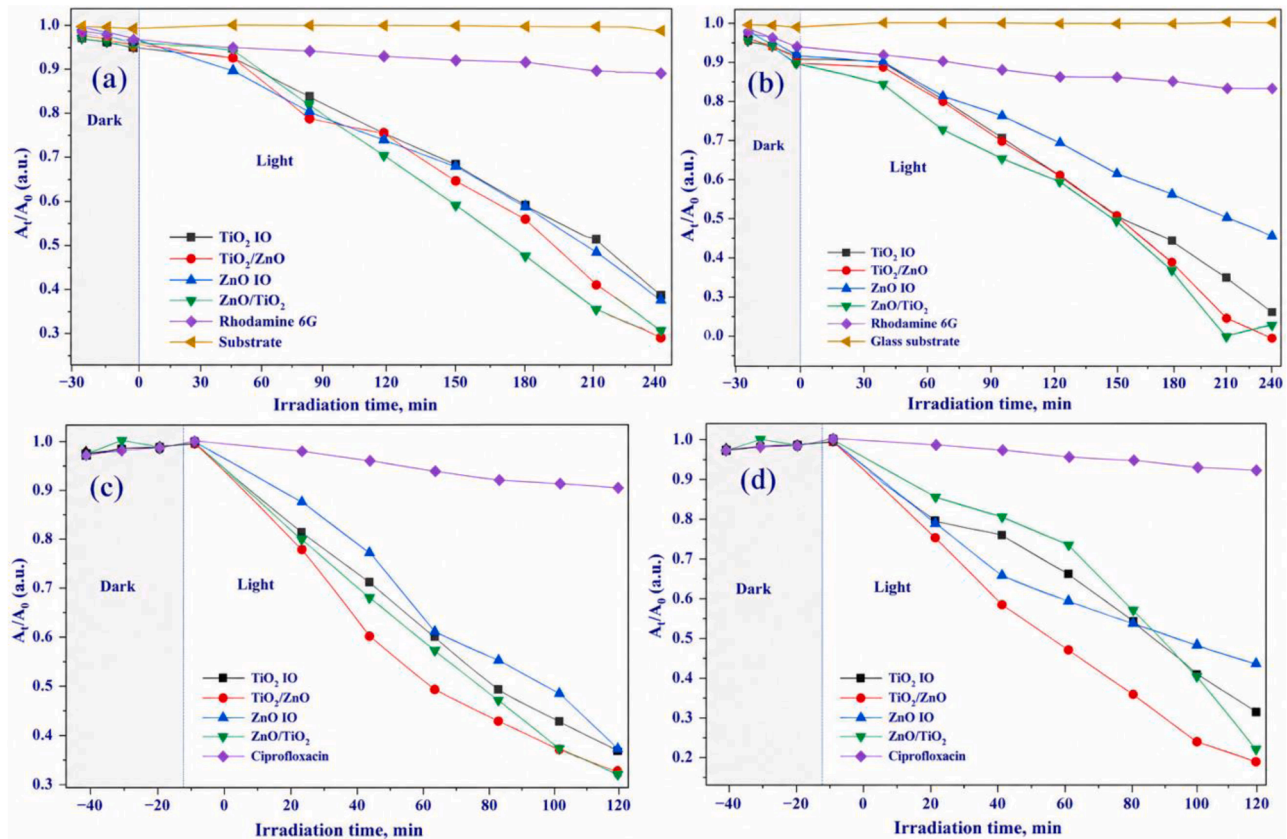


Fig. 11. Relative absorbance (A_t/A_0) profiles of ALD-fabricated photocatalysts during the degradation of Rhodamine 6 G under UV (a) and visible-light (b) irradiation over 240 min, and ciprofloxacin under UV (c) and visible-light (d) irradiation over 120 min.

Table 2

Kinetic analysis of rhodamine 6 G photodegradation under UV light irradiation at 240 min.

System	k (min^{-1})	R^2	$t_{1/2}$ (min)	Degradation (%)	Residual at (%)
TiO ₂ IO	4.6×10^{-3}	0.99	149	61	39
TiO ₂ /ZnO	5.4×10^{-3}	0.99	128	70	30
ZnO IO	4.2×10^{-3}	0.98	168	62	38
ZnO/TiO ₂	5.7×10^{-3}	0.99	122	70	30
Rhodamine 6G	0.03×10^{-3}	0.95	2567	10	90
Glass substrate	0.05×10^{-3}	0.90	13,860	1.0	99

significantly enhanced photocatalytic degradation over the hierarchical double templated IO heterostructures compared with the single-component IOs and blank controls (see Fig. 11b, d, and Table 3, 5. For Rh6G, negligible photolysis was observed in the absence of a catalyst ($\sim 16\%$ and $\sim 1\%$ on glass substrate), confirming that direct light-driven degradation was minimal. In contrast, TiO₂ IO and ZnO IO achieved moderate degradation efficiencies of 73 % and 54 %, respectively, while the heterostructured TiO₂/ZnO and ZnO/TiO₂ IOs further increased the removal efficiency to 80 % and 77 %. A similar trend was observed for CIP, where blank photolysis was limited to $\sim 7\%$, whereas TiO₂ IO and ZnO IO reached 66 % and 47 % degradation, respectively. TiO₂/ZnO and ZnO/TiO₂ IOs achieved 74 % and 75 % CIP removal. The hierarchical structure with dual pore sizes improved light harvesting through multiple PBGs and slow photon effects. Heterojunction

Table 3

Kinetic analysis of rhodamine 6 G photodegradation under visible light irradiation at 240 min.

Sample	k (min^{-1})	R^2	$t_{1/2}$ (min)	Degradation (%)	Residual (%)
TiO ₂ IO	5.2×10^{-3}	0.98	133	73	27
TiO ₂ /ZnO	7.3×10^{-3}	0.99	96	80	20
ZnO IO	3.4×10^{-3}	0.98	202	54	46
ZnO/TiO ₂	5.9×10^{-3}	0.99	116	77	23
Rhodamine 6G	0.4×10^{-3}	0.94	1650	16	84
Glass substrate	0.02×10^{-3}	0.89	34,650	1.0	99

formation reduced electron–hole recombination and increased charge separation, while the porous network provided more adsorption sites.

Hierarchical IO templating consistently demonstrated enhanced photocatalytic performance over single-layer, non-inverse opal, and conventional composite systems. This improvement was strongly associated with the use of hierarchical different template sizes, such as dual pore structures of 600 and 300 nm or bilayer IOs such as 310/220 nm, which generated multiple photonic stop bands and slow-photon regions, thereby maximizing light harvesting and increasing the probability of photon absorption. In addition, the hierarchical architecture promoted more efficient interfacial charge separation and suppressed electron–hole recombination, while the interconnected porous network provided more accessible active sites and improved reactant diffusion. Previous studies have shown that bilayer IOs achieved 97 % RhB degradation, far exceeding monolayer IO-310 (65 %) and IO-220 (56 %) and clearly demonstrating the advantage of hierarchical templating over single-template systems [67]. Similarly, our group has demonstrated the

effectiveness of TiO₂/ZnO composite IOs fabricated by ALD and PEALD, achieving Rh6G degradation efficiencies of 45–63 % under UV and visible irradiation after 3 h [37,68], with TiO₂ IO/ZnO nanorod heterostructures exhibiting the highest visible-light activity [69], further highlighting the benefits of hierarchical inverse opal heterostructures for enhanced photocatalysis. Similarly, Ag-decorated TiO₂ [70], Ag/ZnO/CeO₂ [71], and ZnO/ZnS [72] hierarchical IOs also exhibited markedly enhanced photocatalytic activity due to the combined effects of light trapping, plasmonic or heterojunction-assisted charge transfer, and improved mass transport.

In contrast, numerous non-IO composite photocatalysts, including ZnO [73], ZnO–TiO₂/rGO [74], Cu-doped ZnO [75], CuO@TiO₂ [76], and Fe-doped TiO₂/ZnO [77], have reported high degradation efficiencies (79–100 %) toward model organic pollutants under UV or simulated solar irradiation. However, these systems generally rely on different morphologies, irradiation conditions, and target contaminants, making direct performance comparisons difficult. Unlike these conventional composites, the present hierarchically templated ALD-grown bilayer IO heterostructures combine a highly ordered three-dimensional photonic architecture with efficient heterojunction charge separation, enabling enhanced light harvesting, slow-photon effects, and improved reactant accessibility without requiring noble metals or carbon-based sensitizers. These structural advantages establish hierarchical IO photocatalysts as a robust and versatile platform for the efficient degradation of both dye pollutants and more recalcitrant pharmaceutical contaminants (See Table 6: Comparison of CIP and other pollutant degradation efficiencies under UV and visible light irradiation).

3.7.1. Photocatalytic kinetics and proposed mechanistic interpretation of pollutant degradation

The photocatalytic degradation of Rh6G and CIP over TiO₂, ZnO, and TiO₂/ZnO IO photocatalysts followed pseudo-first-order kinetics under both UV and visible-light irradiation ($R^2 \approx 0.89$ – 0.99) (See Table 2–5). Under UV irradiation, Rh6G degradation proceeded with moderate rate constants ($k = 4.2$ – $5.7 \times 10^{-3} \text{ min}^{-1}$), corresponding to half-lives of 122–168 min, whereas CIP exhibited faster degradation kinetics ($k = 7.3$ – $8.4 \times 10^{-3} \text{ min}^{-1}$; $t_{1/2} = 83$ – 96 min), with the ZnO/TiO₂ IO showing the highest activity. Direct photolysis was negligible for both pollutants. Under visible-light irradiation, the heterostructured IOs demonstrated markedly enhanced performance, particularly for CIP, reaching rate constants up to $12.1 \times 10^{-3} \text{ min}^{-1}$ and degradation efficiencies of ~74–75 %, significantly outperforming the single oxides. Rh6G degradation was also enhanced under visible light, with TiO₂/ZnO and ZnO/TiO₂ IOs achieving k values of 5.9 – $7.3 \times 10^{-3} \text{ min}^{-1}$ and ~77–80 % removal.

The double-templated macroporous structure enhances light harvesting through multiple scattering, and prolonged photon residence times (i.e., slow photon effects), while the anatase–wurtzite TiO₂/ZnO heterojunction promotes efficient charge separation and suppresses

Table 4
Kinetic analysis of Ciprofloxacin photodegradation under UV light irradiation at 120 min.

Sample	$k \text{ (min}^{-1}\text{)}$	R^2	$t_{1/2} \text{ (min)}$	Degradation (%)	Residual (%)
TiO ₂ IO	7.3×10^{-3}	0.99	96	60	40
TiO ₂ /ZnO	7.7×10^{-3}	0.97	90	64	36
ZnO IO	7.4×10^{-3}	0.98	92	60	40
ZnO/TiO ₂	8.4×10^{-3}	0.99	83	65	35
Ciprofloxacin	0.7×10^{-3}	0.94	946	10	90

Table 5

Kinetic analysis of Ciprofloxacin photodegradation under visible light irradiation for 120 min.

Sample	$k \text{ (min}^{-1}\text{)}$	R^2	$t_{1/2} \text{ (min)}$	Degradation (%)	Residual (%)
TiO ₂ IO	8.3×10^{-3}	0.97	83	66	34
TiO ₂ /ZnO	10.9×10^{-3}	0.99	64	74	26
ZnO IO	5.1×10^{-3}	0.99	136	53	47
ZnO/TiO ₂	12.1×10^{-3}	0.98	58	75	25
Ciprofloxacin	0.6×10^{-3}	0.94	1146	7	93

electron–hole recombination [83,84]. Upon irradiation, photogenerated electrons and holes are spatially separated through interfacial band alignment, with electrons preferentially transferred from ZnO to TiO₂ and holes migrating in the opposite direction. These charge carriers subsequently generate reactive oxygen species (ROS), including $\cdot\text{O}_2$ and $\cdot\text{OH}$ radicals, through the reduction of dissolved oxygen and oxidation of surface hydroxyl groups or water. The ROS are expected to drive oxidative degradation of CIP and Rh6G via successive hydroxylation, bond cleavage, and ring-opening reactions, ultimately leading toward mineralization into CO₂, H₂O, and inorganic ions [85–89]. (See Fig. 12 below).

However, this degradation mechanism is proposed rather than experimentally confirmed, as it is not supported by scavenger tests or identification of degradation intermediates. The enhanced kinetics observed for the TiO₂/ZnO and ZnO/TiO₂ IOs under both irradiation regimes are nevertheless consistent with a heterojunction-mediated ROS pathway, further amplified by the photonic IO framework and, in the case of Rh6G under visible light, dye-sensitized charge injection.

Reactions [82,87,90,91]:

Photon excitation: $\text{TiO}_2/\text{ZnO} + h\nu \rightarrow e^-(\text{CB}) + h^+(\text{VB})$

Charge transfer: $e^-(\text{ZnO}) \rightarrow e^-(\text{TiO}_2)$ and $h^+(\text{TiO}_2) \rightarrow h^+(\text{ZnO})$

Reduction reactions:

$e^- + \text{O}_2 \rightarrow \cdot\text{O}_2$

$\cdot\text{O}_2 + \text{H}^+ \rightarrow \cdot\text{HO}_2$

$2\cdot\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$

$\text{H}_2\text{O}_2 + e^- \rightarrow \cdot\text{OH} + \text{OH}^-$

Oxidation reactions:

$h^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+$

$h^+ + \text{OH}^- \rightarrow \cdot\text{OH}$

CIP degradation and mineralization:

$\text{CIP} + \cdot\text{OH}/\cdot\text{O}_2^- \rightarrow \text{intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{NO}_3^- + \text{F}^-$

Overall reaction:

$\text{CIP} + \text{O}_2 + h\nu \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{NO}_3^- + \text{F}^-$

4. Conclusion

In this study, hierarchical IO photonic architectures based on TiO₂, ZnO, and their bilayered composites (TiO₂/ZnO and ZnO/TiO₂) were successfully fabricated through a sequential double-templating strategy combined with ALD. The use of 600 nm and 300 nm PS sacrificial templates enabled the formation of periodically ordered macroporous frameworks with multiscale porosity, while the precise thickness control offered by ALD ensured conformal coating and defined heterointerfaces. Subsequent annealing at 500 °C effectively removed the templates and induced crystallization, yielding anatase TiO₂ and wurtzite ZnO phases with tunable crystallinity and defect chemistry. Comprehensive structural, optical, and spectroscopic analyses confirmed pronounced photonic band-gap effects, enhanced light harvesting, and oxygen-vacancy-induced electronic modulation. The pure TiO₂ IO exhibited a PBG at ~390 nm; after 21 nm ALD ZnO coating, additional bands appeared at ~390 and 590 nm, indicating double-templating-induced redshift and spectral broadening. Whereas the pure ZnO IOs showed PBGs at ~400

Table 6

Comparative overview of CIP and other pollutant degradation efficiencies under UV, visible, and solar irradiation, summarizing previously reported photocatalytic systems alongside the present study.

Material	Pollutant	Conc. (mg/L)	Catalyst dose (g/L)	pH	Degradation (%)	Time (min)	Lamp type	Ref.
PS-TiO ₂	CIP	5	20	3	95	180	LED	[78]
TiO ₂ IO	RhB	5			> 95	2	UV	[79]
TiO ₂	CIP	20	0.12		75	480	UV LEDs	[80]
MoS ₂ -TiO ₂ IO	CIP	15 × 10 ⁻³	film	3	23	60	Visible	[81]
	Tetracycline	20 × 10 ⁻³		-	56			
TiO ₂ IO	RhB	20	2.6	-	~ 70	100	Visible	[55]
TiO ₂ IO	RhB	5		-	> 95	2	UV LED	[79]
ZnO-Al ₂ O ₃ IO	Rh6G	1.8	film	-	≤ 40	180	Visible	[38]
TiO ₂ -ZnO IO	Rh6G	1.8	film	-	31 & 27	240	UV	[37]
					55 & 45	240	Visible	
ZnO/GO	CIP	10	0.2	-	99	75	Natural light	[82]
	MB	10	0.2	-	98	65		
Hierarchical TiO ₂ -ZnO IO	Rh6G	9.6	film	-	70	240	UV	present study
					80	240	Visible	
					65	120	UV	
					75	120	Visible	

NB: RhB: Rhodamine B, LED: light-emitting diode, GO: graphene oxide.

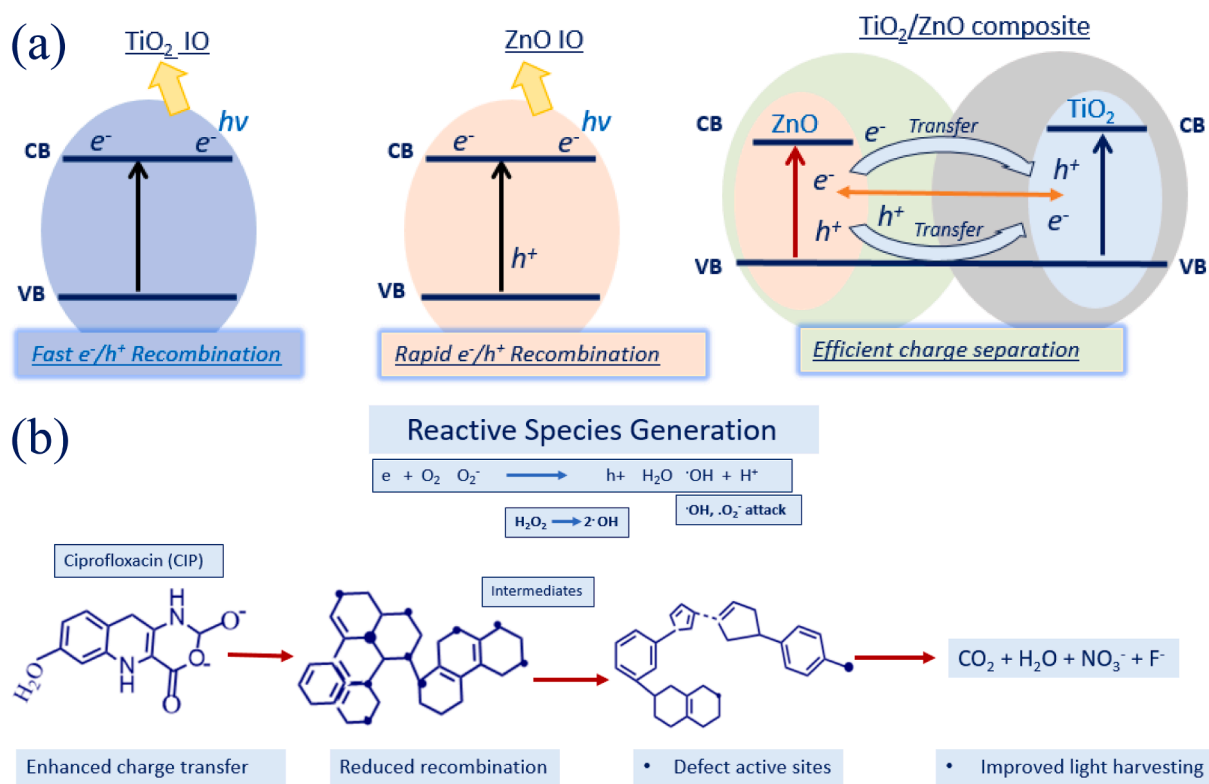


Fig. 12. (a, b) Schematic illustration of the photocatalytic degradation mechanism in an inverse opal structure for ciprofloxacin under UV illumination, showing light absorption, charge carrier generation, separation, and reactive species formation leading to pollutant degradation.

and 590 nm, while ZnO/TiO₂ composites displayed shifted bands at ~360 and 575 nm.

The synergistic coupling of photonic structuring and heterojunction engineering directly translated into higher photocatalytic performance toward both pharmaceutical CIP and Rh6G pollutants. Under UV irradiation, the hierarchical IO photocatalysts achieved up to 70 % degradation of Rh6G and 64–65 % removal of CIP, while under visible light, they further delivered enhanced efficiencies of ~74–75 % for CIP and up to ~80 % for Rh6G, outperforming their single-component IO counterparts. Significantly, these performances were achieved without noble metal cocatalysts or external sensitizers, underscoring the intrinsic advantage of the architected photonic–semiconductor system. In summary, this work presented a broadly applicable design strategy in which

sequential double-templated inverse opal assembly, together with ALD-engineered heterointerfaces, was integrated to construct multifunctional photocatalytic platforms. Moreover, the hierarchical architectures developed here played a central role in governing light transport, charge dynamics, and overall reaction performance, thereby establishing a framework for next-generation integrated photocatalysts aimed at sustainable water treatment and chemical production technologies.

CRedit authorship contribution statement

Hamsasew Hankebo Lemago: Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Petra Pál:** Software, Methodology, Investigation,

Formal analysis, Data curation. **Csaba Cserhádi**: Software, Resources, Methodology, Investigation, Formal analysis, Data curation. **Barbara Sárközi**: Software, Methodology, Investigation, Formal analysis. **Eszter Mónika Baradács**: Software, Resources, Methodology, Investigation, Formal analysis, Data curation. **Zoltán Erdélyi**: Writing – review & editing, Software, Resources, Methodology, Investigation, Funding acquisition, Conceptualization. **Imre Miklós Szilágyi**: Writing – review & editing, Supervision, Software, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

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Data availability

Data will be made available on request.

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