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Ablation-Order-Directed Core-Shell and Decorated WO₃/g-C₃N₄ Nanohybrids by Sequential Pulsed Laser Ablation in Liquid

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ABSTRACT

Sequential pulsed laser ablation in liquid (PLAL) controlled the interfacial architecture of WO₃/g-C₃N₄ nanohybrids through two pre-optimized reciprocal routes. R1 formed WO₃@g-C₃N₄ by ablating g-C₃N₄ at 20 J cm⁻² in a preformed WO₃ colloid, whereas R2 formed g-C₃N₄@WO₃ by ablating WO₃ at 70 J cm⁻² in a preformed g-C₃N₄ colloid. These target-specific second-step fluences were established through prior work and preliminary optimization. X-ray diffraction (XRD) confirmed retention of monoclinic WO₃ in both hybrids. Relative to pristine WO₃, R1 reflections shifted 0.29–0.31° toward higher 2θ, compared with 0.14–0.15° for R2, while both retained a mean coherent-domain length of approximately 47 nm. Electron microscopy revealed WO₃ cores surrounded by carbon-nitride-rich shells in R1 and discrete WO₃-rich domains distributed over g-C₃N₄ sheets in R2. Their zeta potentials were –46.3 and –41.7 mV, respectively. Atomic force microscope (AFM) mean particle sizes were 74.1 and 82.5 nm, respectively. Direct-transition Tauc analysis resolved energies of 1.80 and 3.04 eV for R1 and 1.80 and 2.95 eV for R2. R2 exhibited lower transmittance, whereas R1 delivered stronger photocatalysis. Under xenon-lamp irradiation, R1 achieved 83% methylene-blue degradation after 180 min with k_{app} = 1.00 × 10⁻² min⁻¹, exceeding R2 at 71% and 7.03 × 10⁻³ min⁻¹. R1's superior performance results from its continuous core-shell interface, carbon-nitride-rich adsorption surface, rougher topography, and stronger electrostatic attraction toward cationic dye molecules. These findings establish ablation order and target-specific fluence as coupled controls of nanohybrid morphology, optical response, and photocatalytic performance.

Keywords: pulsed laser ablation in liquid; WO₃/g-C₃N₄; ablation order; core-shell nanohybrid; decorated heterostructure; photocatalysis

1. INTRODUCTION

The performance of a semiconductor heterojunction is determined by its interfacial architecture. Junction area governs the probability of carrier transfer between phases, domain dimensions set the transport distance to the interface, and external phase exposure controls adsorption and surface redox reactions. Graphitic carbon nitride (g-C₃N₄) provides a visible-light-active, metal-free framework with a conjugated electronic structure, but interlayer restacking and rapid electron-hole recombination reduce the number of accessible reactive sites [1,2]. Monoclinic WO₃ features the merits of strong visible-light absorption, chemical stability, and an oxidizing valence band, while its photoresponse is restricted by charge recombination and limited reduction capacity. Coupling WO₃ with g-C₃N₄ creates an interfacial pathway that integrates the optical and redox functions of both semiconductors and improves the utilization of photogenerated charge carriers [3–5].

WO₃/g-C₃N₄ photocatalysts have been prepared as nanoparticle-decorated sheets, 2D/2D assemblies, mixed aggregates, and core-shell structures [3–8]. These architectures are not equivalent. A continuous g-C₃N₄ shell around a WO₃ core maximizes radial contact and produces an outer carbon-nitride-rich adsorption surface, whereas discrete WO₃ domains on g-C₃N₄ sheets preserve simultaneous exposure of both phases and create a high density of local junction perimeters. Self-assembly has produced WO₃@g-C₃N₄ core-shell photocatalysts [6], and electrostatic or hydrothermal routes have produced face-to-face and particle-on-sheet structures [7,8]. These studies reveal the importance of intimate interfacial contact, however their morphologies are dictated by precursor chemistry, surfactants, thermal treatment and post-synthesis assembly. They do not show how the order of physical generation of nanoparticles influences the transition between shell growth and surface decoration.

Pulsed laser ablation in liquid provides a direct route to ligand-free nanostructures through rapid target vaporization, plasma-plume confinement, supersaturation, nucleation, and cavitation-bubble collapse [9–12]. Sequential PLAL adds a decisive architectural variable: the first material forms the receiving colloidal surface, and the second material is generated directly inside that colloid. Species created during the second ablation either nucleate independently, attach to the suspended first-phase surface, or wrap around pre-existing particles during bubble expansion and collapse. Sequential laser routes have generated core-shell and decorated structures in metallic, oxide, ceria-based, and carbon-supported systems [13–15]. Recent studies further demonstrate laser-

directed architecture control: laser ablation in liquid has been used to decorate multi-walled carbon nanotubes with In_2O_3 nanoparticles, with surface coverage governed by pulse number [16], while pulse-number-dependent formation and morphological evolution have also been reported for $\text{Au@Nb}_2\text{O}_5$ core-shell nanoparticles [17]. PLAL has also produced ternary $\text{TiO}_2/\text{WO}_3/\text{g-C}_3\text{N}_4$ and $\text{WO}_3/\text{BP}/\text{g-C}_3\text{N}_4$ photocatalysts [18,19]. The literature contains no reciprocal binary PLAL study that reverses the WO_3 and $\text{g-C}_3\text{N}_4$ ablation order and connects the resulting core-shell or decorated morphology directly with optical and photocatalytic behavior.

This study resolves that process-structure gap through two complete, pre-optimized sequential PLAL protocols. R1 begins with a WO_3 colloid and ablates $\text{g-C}_3\text{N}_4$ at 20 J cm^{-2} to form $\text{WO}_3@\text{g-C}_3\text{N}_4$, designated CN-on- WO_3 . R2 begins with a $\text{g-C}_3\text{N}_4$ colloid and ablates WO_3 at 70 J cm^{-2} to form $\text{g-C}_3\text{N}_4@\text{WO}_3$, designated WO_3 -on-CN. The two routes intentionally differ in both ablation order and second-step fluence because each second target is processed at its target-specific optimum established from prior work and preliminary screening. The comparison therefore evaluates two deliberately engineered synthesis protocols rather than a single-variable fluence series. XRD, FE-SEM, EDS, TEM, AFM, zeta potential, UV-Vis spectroscopy, and methylene-blue photocatalysis are integrated to establish how the receiving colloid and second-plume state direct interfacial contact, morphological evolution, and functional response.

2. MATERIALS AND METHODS

2.1. Materials, laser synthesis

Tungsten trioxide (WO_3 , 99.9% purity, Merck KGaA, Germany) and graphitic carbon nitride ($\text{g-C}_3\text{N}_4$, 99.5% purity, Merck KGaA, Germany) powders were used as the starting materials. Methylene blue (MB; Fluka Chemie AG, Switzerland) was used as the model dye for the photocatalytic experiments. Deionized water was used as the liquid medium throughout the pulsed laser ablation in liquid (PLAL) process. WO_3 and $\text{g-C}_3\text{N}_4$ powders were compacted into cylindrical targets. Each target was positioned approximately 5 mm below the surface of 8 mL of deionized water. A Q-switched Nd:YAG laser (SK EILY Photoelectric Technology Co., Ltd., China) operating at 532 nm delivered 9 ns pulses at a repetition rate of 3 Hz through a 100 mm focal-length lens. The focused spot diameter was approximately 1.1 mm. The reciprocal synthesis conditions are summarized in Table 1.

Table 1. Deliberately optimized reciprocal PLAL routes used to control $\text{WO}_3/\text{g-C}_3\text{N}_4$ architecture.

Route	Preformed colloid	Second target	Second-step fluence	Defined nanohybrid
R1	WO_3	$\text{g-C}_3\text{N}_4$	20 J cm^{-2}	R1 $\text{WO}_3@\text{g-C}_3\text{N}_4$
R2	$\text{g-C}_3\text{N}_4$	WO_3	70 J cm^{-2}	R2 $\text{g-C}_3\text{N}_4@\text{WO}_3$

R1 and R2 intentionally combine opposite synthesis order with different second-step laser fluences. In R1, the $\text{g-C}_3\text{N}_4$ target was ablated at 20 J cm^{-2} in a preformed WO_3 colloid, producing $\text{WO}_3@\text{g-C}_3\text{N}_4$ (CN-on- WO_3). In R2, the WO_3 target was ablated at 70 J cm^{-2} in a preformed $\text{g-C}_3\text{N}_4$ colloid, producing $\text{g-C}_3\text{N}_4@\text{WO}_3$ (WO_3 -on-CN). The 20 J cm^{-2} condition for $\text{g-C}_3\text{N}_4$ and the 70 J cm^{-2} condition for WO_3 were selected from prior work and preliminary route optimization. The lower $\text{g-C}_3\text{N}_4$ fluence preserves the fragment population required for capture and wrapping, while the higher WO_3 fluence supplies the nucleation density required for extensive decoration of the carbon-nitride surface. Each route is therefore a complete optimized protocol in which order defines the receiving interface and fluence defines the state of the second ablation plume. A schematic illustration of the reciprocal sequential PLAL synthesis routes is provided in Figure 1 to give a clear overview of the preparation steps and the formation pathway of the two $\text{WO}_3/\text{g-C}_3\text{N}_4$ nanohybrids.

2.2. Structural, morphological and colloidal characterization

X-ray diffraction (XRD) patterns of pristine $\text{g-C}_3\text{N}_4$, pristine WO_3 , and both nanohybrids were recorded using a Shimadzu XRD-6000 diffractometer (Shimadzu Corporation, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) over $2\theta = 10\text{--}60^\circ$ at 3° min^{-1} . WO_3 reflections were indexed against the monoclinic reference pattern; interplanar spacings were obtained from Bragg's law and coherent-domain lengths from the Scherrer relation [20,21]. Field-emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray spectroscopy (EDS) were performed using a ZEISS Sigma microscope (Carl Zeiss, Germany) after drop-casting each colloid onto a clean silicon substrate and drying at room temperature. EDS verified the presence of tungsten (W), oxygen (O), carbon (C), and nitrogen (N). Transmission electron microscopy (TEM) was performed using a Zeiss EM10C microscope (Carl Zeiss, Germany) operated at 100 kV. Diluted colloids were deposited onto carbon-coated copper grids and

dried under ambient conditions. Atomic force microscopy (AFM) was performed using an NTEGRA atomic force microscope (NT-MDT, Russia) to examine the 2D and 3D surface topography of the deposited nanohybrids. Hydrodynamic particle-size distributions were measured by dynamic light scattering (DLS), and zeta potentials were determined using a Malvern Panalytical Zetasizer (Malvern Panalytical, UK) at 25 °C after 10 min sonication. Each measurement was repeated three times and the average was reported. DLS describes dispersed particles and aggregates in liquid, whereas TEM and AFM describe features in dried specimens [22].

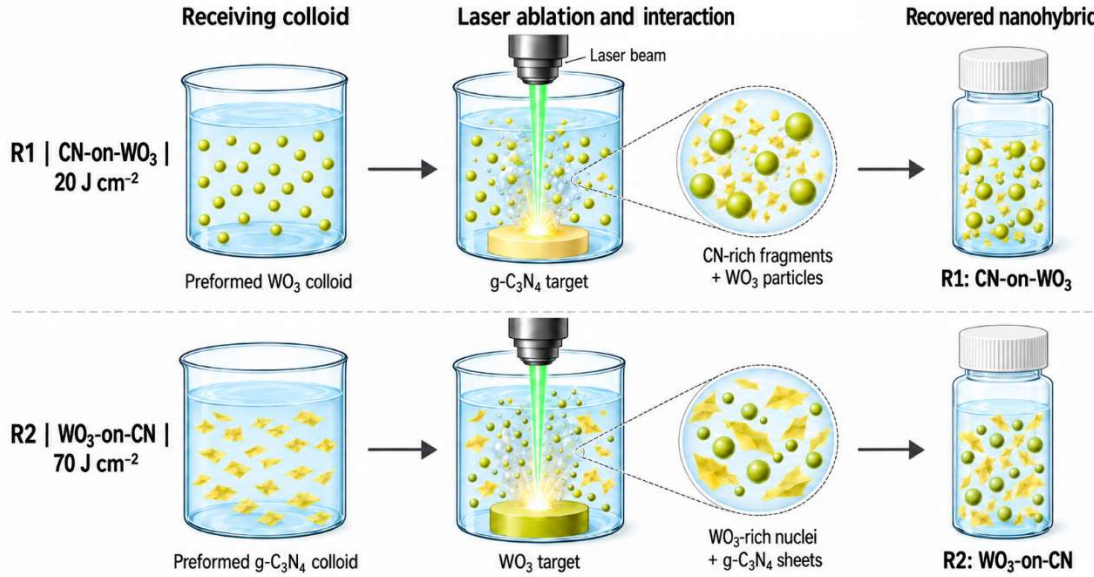


Figure 1. Schematic illustration of the reciprocal sequential PLAL synthesis routes. R1: ablation of g-C₃N₄ at 20 J cm⁻² in a preformed WO₃ colloid produces WO₃@g-C₃N₄. R2: ablation of WO₃ at 70 J cm⁻² in a preformed g-C₃N₄ colloid produces g-C₃N₄@WO₃.

2.3. Optical and MB-degradation analysis

Optical spectra of the colloidal suspensions were recorded using a JASCO V-780 UV-Vis-NIR spectrophotometer (JASCO Corporation, Japan) over 200–1200 nm. The absorption coefficient, α , was calculated from the measured absorbance using:

$$\alpha = \frac{2.303A}{l} \quad (1)$$

where A is the measured absorbance and l is the optical path length of the cuvette. The optical transition energies were estimated using the Tauc relation [23]:

$$(\alpha h\nu)^{1/n} = C(h\nu - E_g) \quad (2)$$

where h is Planck's constant, ν is the photon frequency, $h\nu$ is the photon energy, C is a proportionality constant, E_g is the optical transition energy, and n is the transition exponent. For a direct allowed transition, $n = 0.5$; therefore, $(\alpha h\nu)^2$ was plotted as a function of $h\nu$. Two distinct linear regions were extrapolated to $(\alpha h\nu)^2 = 0$ to determine the lower- and higher-energy optical transitions of each WO₃/g-C₃N₄ nanohybrid [23].

Photocatalytic degradation of an aqueous methylene blue (MB) solution with an initial concentration of 4 mg L⁻¹ was evaluated under xenon-lamp irradiation for 180 min, with UV-Vis spectra recorded at 30 min intervals. The absorbance at 664 nm was used throughout the kinetic analysis. Assuming proportionality between absorbance and MB concentration, the normalized concentration was calculated as:

$$\frac{C_t}{C_0} = \frac{A_{664,t}}{A_{664,0}} \quad (3)$$

where C_0 and C_t are the MB concentrations at the initial time and irradiation time t , respectively, while $A_{664,0}$ and $A_{664,t}$ are the corresponding absorbance values measured at 664 nm. The degradation efficiency, η , was calculated using:

$$\eta = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \quad (4)$$

The apparent photocatalytic kinetics were evaluated using the pseudo-first-order expression:

$$\ln\left(\frac{C_0}{C_t}\right) = k_{app}t \quad (5)$$

where k_{app} is the apparent pseudo-first-order rate constant (min^{-1}) and t is the irradiation time (min). The same monitoring wavelength and kinetic treatment were applied to both nanohybrids to provide a direct architecture-dependent comparison [24–29].

3. RESULTS AND DISCUSSION

3.1. Crystalline structure

The expanded XRD comparison defines the crystalline response of both nanohybrids against their pristine constituents (Figure 2). Pristine $\text{g-C}_3\text{N}_4$ displays a broad stacking-related maximum centered at approximately 25.1° with $d \approx 3.54 \text{ \AA}$, recording its short-range layered order. Pristine monoclinic WO_3 displays the characteristic triplet at approximately 23.16 , 23.64 , and 24.40° , assigned to the (002), (020), and (200) planes, respectively [20]. Both reciprocal nanohybrids retain this triplet: R1 $\text{WO}_3@\text{g-C}_3\text{N}_4$ exhibits reflections at 23.46 , 23.93 , and 24.71° , while R2 $\text{g-C}_3\text{N}_4@\text{WO}_3$ exhibits reflections at 23.31 , 23.78 , and 24.55° . The carbon-nitride stacking contribution remains broad and overlaps the WO_3 -dominated region, whereas EDS and TEM independently establish the carbon-nitride phase and its route-specific spatial distribution. The corresponding peak positions and derived structural parameters, including the interplanar spacing (d), full width at half maximum (FWHM), and Scherrer coherent-domain length (D), are summarized in Table 2.

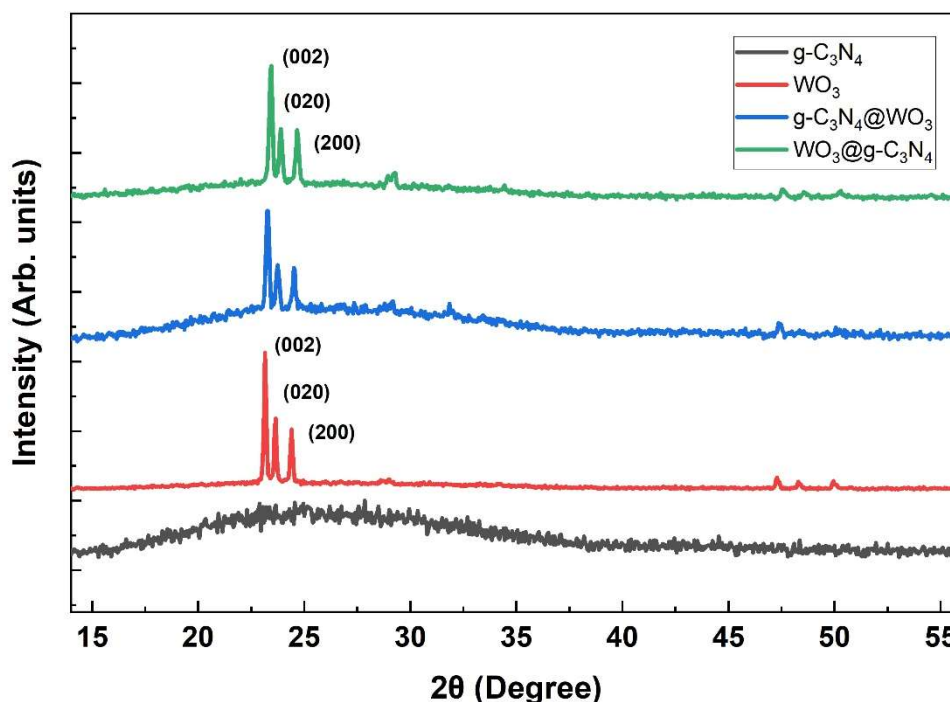


Figure 2. XRD patterns of pristine $\text{g-C}_3\text{N}_4$, pristine WO_3 , R1 $\text{WO}_3@\text{g-C}_3\text{N}_4$, and R2 $\text{g-C}_3\text{N}_4@\text{WO}_3$. The patterns are vertically offset for comparison of phase composition and peak positions.

Table 2. XRD peak positions of the pristine constituents and structural parameters of the monoclinic WO₃ reflections in the reciprocal nanohybrids.

Material/route	2 θ (°)	Feature / (hkl)	d (Å)	FWHM (°)	D (nm)
Pristine g-C ₃ N ₄	≈25.10	Stacking-related feature	≈3.540	—	—
Pristine WO ₃	≈23.16	(002)	≈3.837	—	—
	≈23.64	(020)	≈3.761	—	—
	≈24.40	(200)	≈3.645	—	—
R1 WO ₃ @g-C ₃ N ₄	23.46	(002)	3.789	0.17	48
	23.93	(020)	3.716	0.18	45
	24.71	(200)	3.601	0.17	47
R2 g-C ₃ N ₄ @WO ₃	23.31	(002)	3.813	0.17	47
	23.78	(020)	3.738	0.20	40
	24.55	(200)	3.623	0.15	53

Relative to pristine WO₃, all three R1 reflections shift 0.29–0.31° toward higher 2 θ and the R2 reflections shift 0.14–0.15°. The corresponding d-spacings contract by an average of approximately 1.22% in R1 and 0.61% in R2. Within the reciprocal pair, every R2 reflection lies 0.15–0.16° below the corresponding R1 reflection and its mean d-spacing is approximately 0.6% larger. These coherent shifts establish two different interfacial strain states: capture and shell formation around pre-existing WO₃ impose the stronger lattice contraction in R1, whereas direct WO₃ nucleation across the g-C₃N₄ receiving sheets preserves the less contracted oxide lattice in R2. The Scherrer lengths span 45–48 nm for R1 and 40–53 nm for R2, and both routes yield the same rounded mean of approximately 47 nm. Ablation order therefore changes lattice response and mesoscale assembly while preserving the mean WO₃ coherent-domain length. XRD, TEM, and AFM together connect crystal-scale interfacial strain with the core–shell morphology of R1 and the decorated particle-on-sheet morphology of R2 [21].

3.2. Reciprocal morphology and local composition

The FE-SEM images show two different route-specific assembly states (Figure 3). R1 WO₃@g-C₃N₄ contains heterogeneous aggregates built from fused, rounded features separated by open interparticle voids. This morphology develops when carbon-nitride fragments capture and bridge pre-existing WO₃ particles, producing a shell-rich aggregate network after deposition. R2 g-C₃N₄@WO₃ forms a finer and more continuous granular texture. The dense distribution of small surface domains across the carbon-nitride support records the high nucleation population generated during the 70 J cm^{−2} WO₃ ablation step. This distinction suggests that the two enhanced pathways control the mode of assembly, not just the amount of one component.

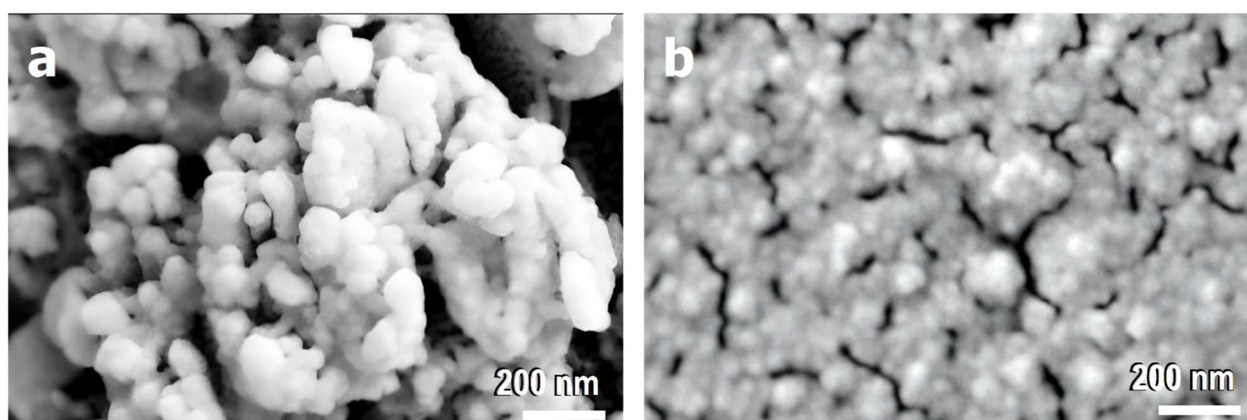


Figure 3. FE-SEM images in standardized route order: (a) R1 CN-on-WO₃ and (b) R2 WO₃-on-CN. Scale bars: 200 nm.

EDS detects W, O, C, and N in both products (Figure 4), confirming that the oxide and carbon-nitride phases coexist within the sampled nanohybrid regions. The R1 spectrum combines the W/O response of the preformed cores with the C/N response of the subsequently generated surrounding phase. The R2 spectrum combines the C/N response of the receiving sheets with the W/O response of the deposited domains. This elemental

coexistence, interpreted together with the reversed synthesis order, FE-SEM texture, and TEM contrast, establishes $\text{WO}_3@\text{g-C}_3\text{N}_4$ for R1 and $\text{g-C}_3\text{N}_4@\text{WO}_3$ for R2. The Au signal originates from the conductive coating/support.

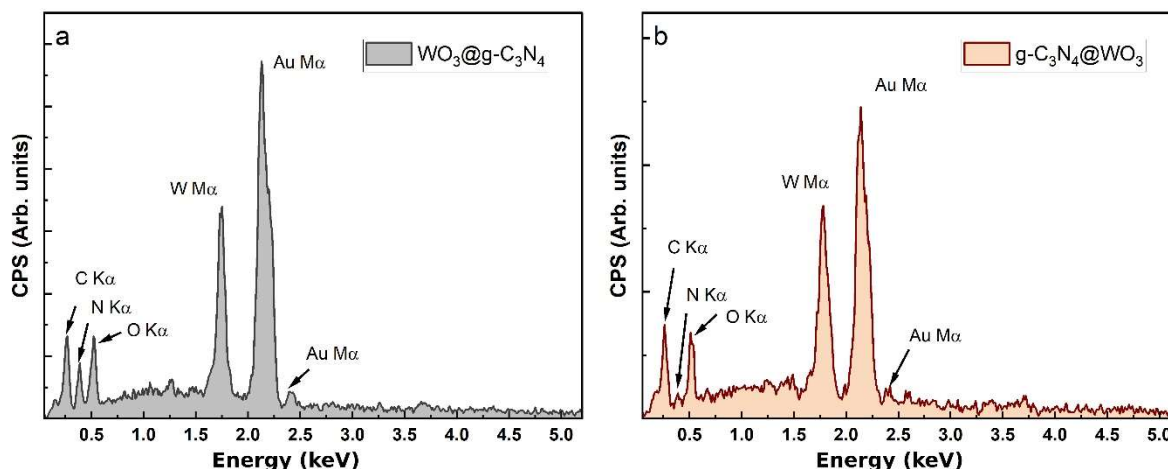


Figure 4. EDS spectra of (a) R1 $\text{WO}_3@\text{g-C}_3\text{N}_4$ and (b) R2 $\text{g-C}_3\text{N}_4@\text{WO}_3$. W, O, C, and N are detected; the Au signal originates from the conductive coating/support.

TEM directly reveals the architecture determined by the order of ablation (Figure 5). R1 contains repeated near-spherical objects with an electron-dense central region surrounded by a lower-contrast carbon-nitride-rich periphery. The recurrence of this core-periphery geometry across the field establishes a $\text{WO}_3@\text{g-C}_3\text{N}_4$ core-shell morphology. R2 exhibits a fundamentally different arrangement: electron-dense WO_3 domains are anchored across folded, low-contrast $\text{g-C}_3\text{N}_4$ sheets, producing a decorated particle-on-sheet heterostructure. The stronger contrast of the WO_3 domains follows their greater mass thickness and tungsten content, while the extended low-contrast regions define the carbon-nitride support [30]. Thus TEM reveals the essential structural difference between shell formation in R1 and surface decoration in R2.

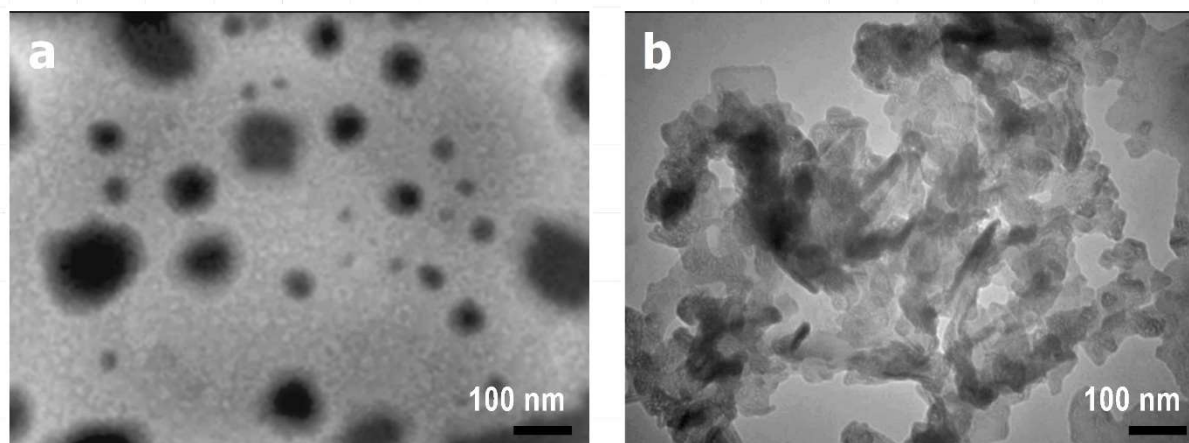


Figure 5. TEM images of (a) R1 $\text{WO}_3@\text{g-C}_3\text{N}_4$ showing the core-shell morphology and (b) R2 $\text{g-C}_3\text{N}_4@\text{WO}_3$ showing the particle-on-sheet morphology.

3.3. Electrokinetic charge and AFM topography

R1 and R2 exhibit zeta potentials of -46.3 and -41.7 mV, respectively. The large negative magnitudes establish strong electrostatic repulsion and stable aqueous dispersion under the measurement conditions [22]. The 4.6 mV shift also tracks external phase identity. R1 exposes a carbon-nitride-rich shell and consequently retains the more negative surface response, whereas WO_3 decoration in R2 partially covers the carbon-nitride surface and shifts the electrokinetic potential toward less negative values. Zeta potential thus supports the surface arrangement identified by TEM and EDS. The corresponding AFM topography and particle-size distributions are presented in Figures 6 and 7.

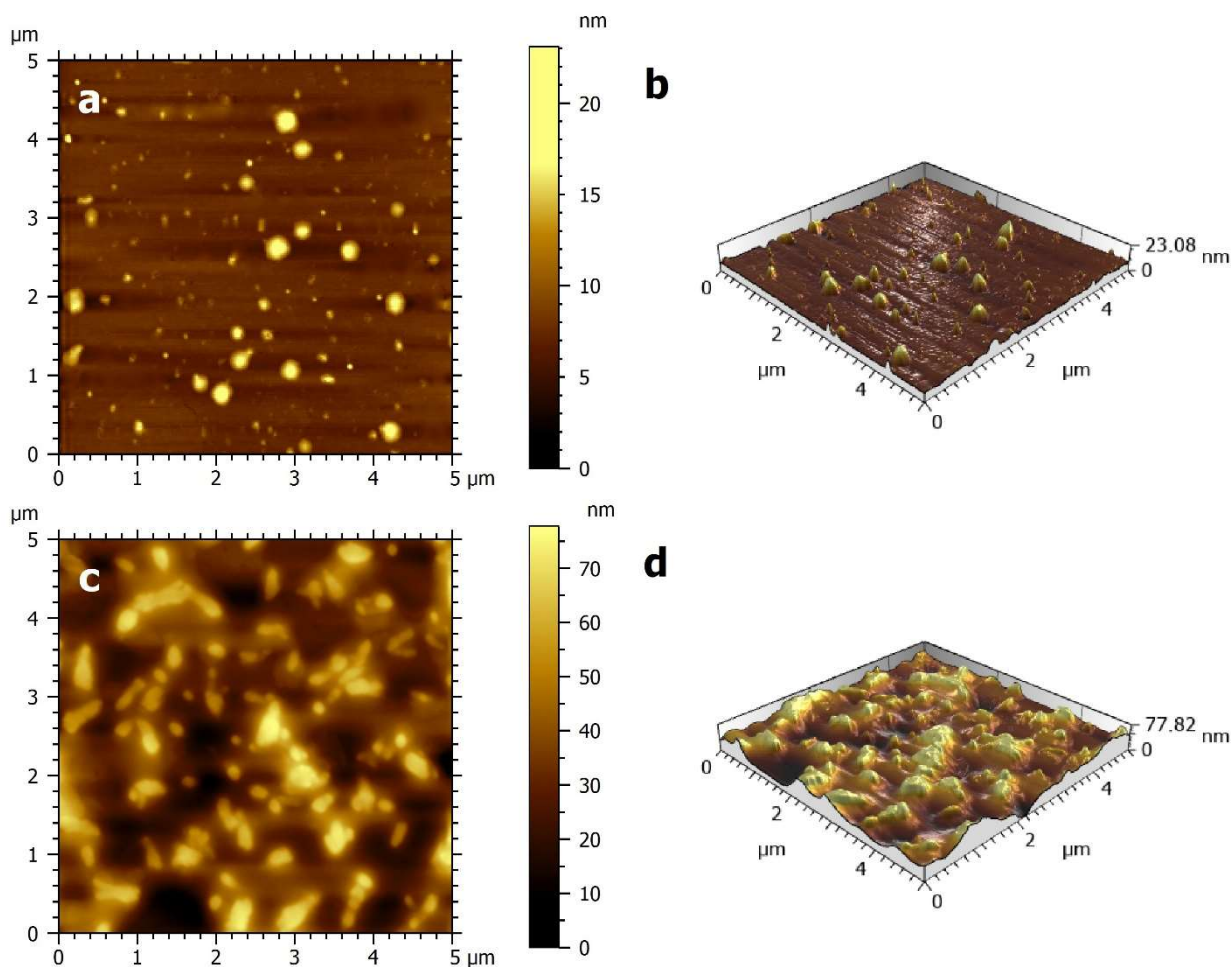


Figure 6. AFM topography of (a, b) R2 $\text{g-C}_3\text{N}_4@\text{WO}_3$ and (c, d) R1 $\text{WO}_3@\text{g-C}_3\text{N}_4$, shown as corresponding 2D and 3D surface profiles.

AFM reproduces the architectural contrast on deposited surfaces. R2, shown in Figure 6a and b, contains discrete raised domains on a comparatively flat background with a displayed vertical range of 23.08 nm, matching WO_3 decoration of $\text{g-C}_3\text{N}_4$ sheets. R1, shown in Figure 6c and d, presents a continuous irregular relief with a displayed vertical range of 77.82 nm, matching shell-mediated wrapping, bridging, and drying of core-shell particles. The AFM segmentations give a mean particle size of 82.5 nm for R2 and 74.1 nm for R1. These particle assembly dimensions are larger than the approximately 47 nm XRD coherent domains because each AFM feature incorporates interfacial assembly and deposition. The combined height and particle-size information distinguishes a laterally extended decorated surface in R2 from a vertically rougher core-shell aggregate network in R1 [31].

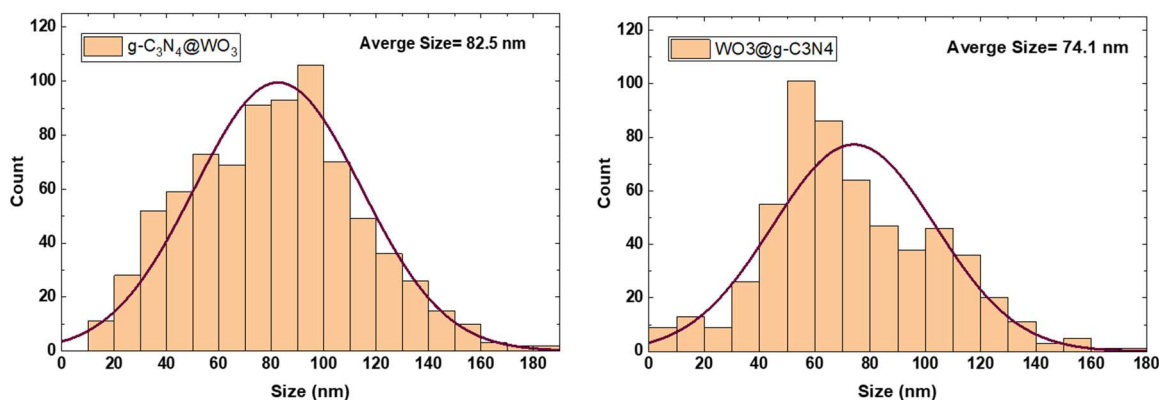


Figure 7. AFM-derived particle size distributions of (a) R2 $\text{g-C}_3\text{N}_4@\text{WO}_3$ and (b) R1 $\text{WO}_3@\text{g-C}_3\text{N}_4$, with mean particle sizes of 82.5 and 74.1 nm, respectively.

3.4. Ablation-order-directed formation mechanism

Sequence-dependent morphology is governed by the coupling of solvent-conditioned interfacial affinity with nonequilibrium PLAL kinetics. A comparison of the dry-solid surface energies alone does not determine the spreading coefficient. For carbon nitride spreading over WO_3 in water, the relevant relation is $S = \gamma(\text{WO}_3/\text{water}) - [\gamma(\text{g-C}_3\text{N}_4/\text{water}) + \gamma(\text{WO}_3/\text{g-C}_3\text{N}_4)]$; the solid-liquid and solid-solid interfacial terms, together with facet termination, defects, charge, and hydration, define the sign of S . Classical Frank-van der Merwe and Volmer-Weber labels do not describe this liquid-confined process because they classify heteroepitaxial layer and island deposition through surface/interface energetics [32]. Sequential PLAL instead couples ablated-fragment capture, solution-phase nucleation, and cavitation-bubble transport. Density-functional calculations on $\text{WO}_3/\text{g-C}_3\text{N}_4$ junctions establish interfacial charge redistribution and strong non-bonding/electrostatic interaction between the phases [33], providing the thermodynamic basis for their adhesion. This framework assigns the sequence-dependent assembly to interface-specific energetics rather than to an assumed sign of the spreading coefficient.

R1 begins with suspended monoclinic WO_3 particles that serve as abundant capture templates. Ablation of $\text{g-C}_3\text{N}_4$ at its optimized 20 J cm^{-2} condition injects nanoscale, sheet-like carbon-nitride fragments into the confined plume and cavitation bubble. The established WO_3 -carbon-nitride interfacial attraction promotes attachment, while the fragments conform to, bridge, and progressively cover the curved WO_3 surfaces. Time-resolved PLAL measurements show that primary species form during bubble expansion and subsequently undergo collision, agglomeration, redeposition, and release during bubble collapse [11]. In the preformed WO_3 colloid, these repeated collisions are biased toward the oxide-particle population; over 100 pulses, cumulative fragment capture and compaction generate the carbon-nitride-rich periphery resolved by TEM and the rough, bridged relief measured by FE-SEM and AFM. Sequential ablation into a pre-existing nanoparticle colloid is independently established as a seed-directed route to core-shell assembly [13], and chemically prepared $\text{WO}_3@ \text{g-C}_3\text{N}_4$ systems confirm that intimate carbon-nitride shells can form around WO_3 cores [6].

R2 changes the dominant kinetic pathway from fragment capture and conformal wrapping to particle nucleation followed by surface capture. The first-stage $\text{g-C}_3\text{N}_4$ colloid presents extended sheets, while ablation of WO_3 at its optimized 70 J cm^{-2} condition generates a dense W/O-containing plume. Rapid cooling and supersaturation within the cavitation bubble promote the nucleation of numerous compact WO_3 primary particles [11]. These particles are subsequently transported during bubble expansion and collapse toward the $\text{g-C}_3\text{N}_4$ sheets, where interfacial attraction promotes their attachment as discrete surface domains. Repeated pulses increase the density of these domains and the available junction perimeter without producing a continuous conformal layer. This nucleation-and-capture pathway accounts for the decorated 2D/3D architecture observed by TEM and is consistent with reported WO_3 -loaded $\text{g-C}_3\text{N}_4$ nanosheets containing discrete WO_3 nanoparticles [4].

The two pre-optimized fluences are therefore integral components of the route design. At 20 J cm^{-2} , carbon-nitride fragment production combined with pre-existing, high-curvature WO_3 capture surfaces favors cumulative conformal assembly. At 70 J cm^{-2} , WO_3 primary-particle nucleation combined with the broad capture area of $\text{g-C}_3\text{N}_4$ sheets favors discrete decoration. Ablation order selects the template encountered by the second-phase species, while target-specific fluence selects whether those species arrive predominantly as flexible fragments or compact nuclei. This coupled thermodynamic-kinetic mechanism explains the common mean WO_3 coherent-domain length alongside the reciprocal TEM architectures, route-dependent zeta potential, and distinct AFM topography. The process therefore converts one chemical pair into two reproducible interfacial architectures without surfactants or post-synthesis assembly. Independent PLAL studies confirm this parameter-structure relation: varying fluence changes the structural and morphological state of WO_3 nanoparticles [34], laser energy modifies the morphology and optical response of carbon nanostructures produced in water [35], and liquid-phase laser ablation of CsPbI_3 demonstrates fluence-controlled evolution of aspect ratio, lattice strain, crystallite size, and optical behavior [36].

3.5. Optical response and dual transition energies

The transmittance spectra distinguish the optical responses produced by the two reciprocal architectures (Figure 8a). Both nanohybrids exhibit a steep near-UV transition followed by a broad visible-to-near-infrared plateau. R1 $\text{WO}_3@ \text{g-C}_3\text{N}_4$ reaches approximately 57–59% transmittance across much of this region, whereas R2 $\text{g-C}_3\text{N}_4@ \text{WO}_3$ remains at approximately 46–50%. The 8–10 percentage-point reduction observed for R2 indicates stronger optical extinction, which can be associated with the distribution of discrete WO_3 domains over the $\text{g-C}_3\text{N}_4$ sheets and enhanced particle-sheet scattering. Such processing-dependent modification of semiconductor morphology and optical response has also been reported in oxide-based systems, where changes in synthesis conditions altered grain size, transmittance, and optical band gap [37].

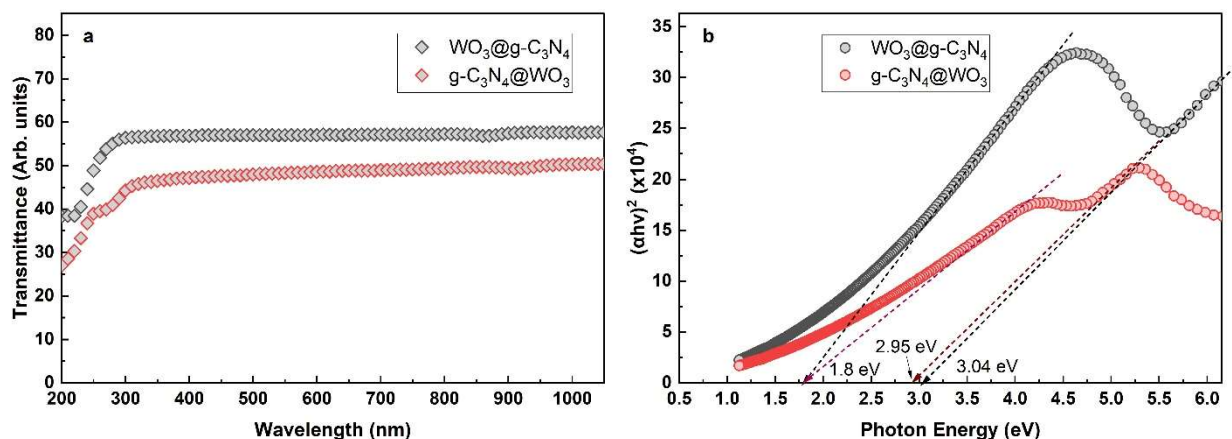


Figure 8. Optical properties of the reciprocal nanohybrids: (a) transmittance spectra and (b) direct-transition Tauc plots, $(\alpha h\nu)^2$ versus $h\nu$. The estimated transition energies are 1.80 and 3.04 eV for R1 and 1.80 and 2.95 eV for R2.

The direct-transition Tauc plots resolve two linear optical regimes in each nanohybrid (Figure 8b). R1 $\text{WO}_3@\text{g-C}_3\text{N}_4$ exhibits transition energies of 1.80 and 3.04 eV, while R2 $\text{g-C}_3\text{N}_4@\text{WO}_3$ exhibits transition energies of 1.80 and 2.95 eV. The paired transitions express the two-component electronic response of the coupled $\text{WO}_3/\text{g-C}_3\text{N}_4$ network rather than a single-phase absorption edge [3–8,23]. The common 1.80 eV lower-energy transition establishes a coupled optical channel in both reciprocal architectures. R2 displays the lower higher-energy transition and stronger overall attenuation, while R1 retains a fully accessible visible-light response through the same 1.80 eV channel. The photocatalytic ranking therefore separates optical attenuation from productive interfacial utilization: the lower transmittance of R2 records stronger extinction, whereas the continuous core-shell contact and external carbon-nitride-rich surface of R1 convert the optical excitation into the faster MB-removal reaction. This interpretation is reinforced by WO_3 studies linking processing-dependent morphology with optical response [38]. Multicomponent nanohybrids likewise exhibit multiple accessible optical transitions or bandgap regimes when strongly coupled constituents coexist, as reported for several hybrid and double-heterojunction semiconductor systems [39–41].

3.6. Photocatalytic degradation and structure–performance relationship

The corrected time-dependent spectra show a continuous decrease across the complete MB absorption envelope for both nanohybrids (Figure 9). Each initial spectrum contains a dominant band at approximately 660–665 nm and a shorter-wavelength contribution at approximately 610–620 nm. R1 presents these contributions as a broader, more strongly overlapped envelope, whereas R2 resolves the shorter-wavelength shoulder more distinctly. The larger fractional contraction of the R1 envelope throughout irradiation directly matches its higher final degradation efficiency. This behavior reflects strong dye capture at the negatively charged carbon-nitride-rich shell and rapid reaction at the continuous $\text{WO}_3/\text{g-C}_3\text{N}_4$ interface. Irradiation reduces both spectral components monotonically without generating a new dominant visible band. The fixed 664 nm response therefore tracks the dominant MB chromophore consistently across both routes and provides a common basis for the degradation and kinetic analysis [24,28]. Independent PLAL work on a $\text{ZnO}/\text{CuO}/\text{Al}_2\text{O}_3$ heterostructure likewise establishes MB degradation by a laser-generated multicomponent photocatalyst [42].

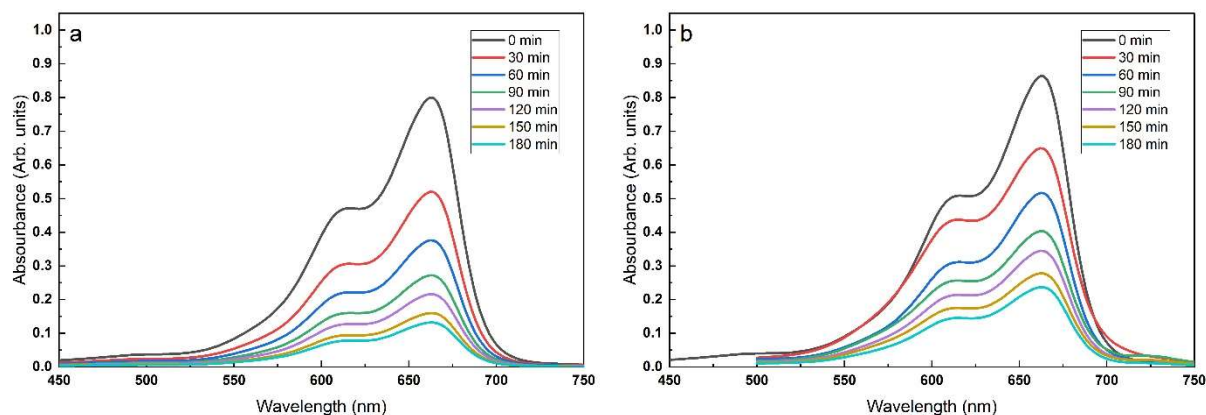


Figure 9. Time-dependent UV–Vis absorption spectra of MB during photocatalytic degradation using (a) R1 $\text{WO}_3@\text{g-C}_3\text{N}_4$ and (b) R2 $\text{g-C}_3\text{N}_4@\text{WO}_3$ under xenon-lamp irradiation. Spectra were recorded at 30 min intervals.

The corrected conversion profiles establish faster MB removal by R1 throughout irradiation (Figure 10a). R1 reaches approximately 35, 52, 66, 74, 80, and 83% degradation at 30–180 min, while R2 reaches approximately 24, 39, 52, 61, 67, and 71% over the same period. The 52% conversion is used here only as a common kinetic benchmark: R1 reaches approximately 52% degradation after 60 min, whereas R2 requires approximately 90 min to reach the same conversion. The maximum degradation after 180 min is 83% for R1 and 71% for R2. Consistently, the apparent pseudo-first-order rate constant of R1 ($1.00 \times 10^{-2} \text{ min}^{-1}$) is approximately 42% higher than that of R2 ($7.03 \times 10^{-3} \text{ min}^{-1}$), providing a more quantitative measure of the photocatalytic advantage of the core-shell architecture.

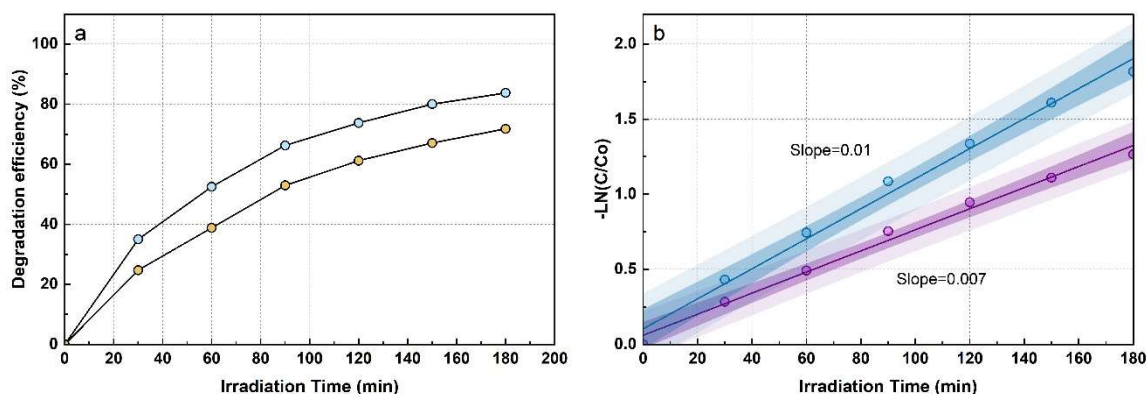


Figure 10. (a) MB degradation efficiency as a function of irradiation time and (b) corresponding pseudo-first-order kinetic plots for R1 $\text{WO}_3@\text{g-C}_3\text{N}_4$ and R2 $\text{g-C}_3\text{N}_4@\text{WO}_3$.

R1 outperforms R2 because its $\text{WO}_3@\text{g-C}_3\text{N}_4$ core-shell architecture combines continuous interfacial contact, favorable MB adsorption, and stable aqueous dispersion. The carbon-nitride-rich shell surrounds each WO_3 core and creates an extended radial heterojunction rather than isolated junction perimeters. Published $\text{WO}_3@\text{g-C}_3\text{N}_4$ core-shell systems identify this enlarged nanoscale interface as the origin of improved carrier mobility and electron-hole separation [6], while broader $\text{WO}_3/\text{g-C}_3\text{N}_4$ studies attribute enhanced photocatalysis to interfacial synergy, accessible surface area, and suitable band alignment [3]. In the present system, the R1 zeta potential of -46.3 mV is more negative than the -41.7 mV of R2. This difference strengthens electrostatic attraction between the R1 surface and cationic MB and maintains stronger repulsion between suspended nanohybrids; negatively charged WO_3 -based surfaces are established adsorption sites for cationic MB [24]. AFM supplies a complementary surface descriptor: the 77.82 nm vertical range of R1 is more than three times the 23.08 nm range of R2, creating a rough shell-mediated reaction surface with abundant adsorption and contact sites. The shared 1.80 eV transition gives both hybrids access to the same lower-energy optical channel, but R1 uses that excitation more effectively through continuous radial junction contact and dye enrichment at the outer shell. R2 produces stronger optical extinction, yet its discrete WO_3 domains provide a less continuous interface and a less negative external surface. The 42% rate enhancement of R1 is therefore the combined result of core-shell interfacial continuity, electrostatic MB concentration, rougher surface topography, and improved colloidal accessibility.

4. CONCLUSIONS

Sequential PLAL directs $\text{WO}_3/\text{g-C}_3\text{N}_4$ into two distinct nanohybrid architectures through deliberate coupling of ablation order and target-specific second-step fluence. R1, produced by ablating $\text{g-C}_3\text{N}_4$ at 20 J cm^{-2} in a WO_3 colloid, forms $\text{WO}_3@\text{g-C}_3\text{N}_4$ core-shell particles. R2, produced by ablating WO_3 at 70 J cm^{-2} in a $\text{g-C}_3\text{N}_4$ colloid, forms $\text{g-C}_3\text{N}_4@\text{WO}_3$ decorated sheets. Comparison with pristine $\text{g-C}_3\text{N}_4$ and WO_3 confirms phase retention and quantifies route-specific lattice response: R1 shows a $0.29\text{--}0.31^\circ$ higher-angle shift relative to pristine WO_3 , R2 shows a $0.14\text{--}0.15^\circ$ shift, and both maintain an average coherent-domain length of approximately 47 nm. Direct-transition Tauc analysis establishes two transition energies for each hybrid—1.80 and 3.04 eV for R1 and 1.80 and 2.95 eV for R2. Although R2 produces the lower transmittance, R1 delivers the stronger photocatalytic response: 83% MB degradation after 180 min with $k_{\text{app}} = 1.00 \times 10^{-2} \text{ min}^{-1}$, compared with 71% and $7.03 \times 10^{-3} \text{ min}^{-1}$ for R2. The 42% rate enhancement arises from the continuous radial $\text{WO}_3/\text{g-C}_3\text{N}_4$ interface, the more negative carbon-nitride-rich outer surface, the rougher shell-mediated topography, and stronger MB enrichment at the R1 reaction interface. Ablation order therefore functions as a direct morphology-control parameter, and the pre-optimized fluence of the second target establishes the fragmentation or nucleation regime required to construct the selected interface.

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