



In-situ, grafted, and nonselective synthesis of Ag–TiO₂/SBA-15: Differences in catalyst properties and photocatalytic performance

Choi W

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Abstract

Materials with comparable nominal compositions can exhibit different functional properties when their synthesis histories produce different spatial organization and interfacial coupling. This study examines that process–structure–property relationship by comparing *in-situ*, grafted, and nonselective Ag–TiO₂/SBA-15 photocatalysts prepared with comparable nominal Ag/Ti precursor compositions and evaluated under identical photocatalytic conditions. XRD, FTIR, XPS, UV–Vis diffuse reflectance, and photoluminescence analyses showed that the *in-situ* material had relatively sharper anatase reflections, the strongest Ti–O–Si-related band, a Ti³⁺-related contribution not clearly resolved in the other materials, enhanced visible-light absorption, and the lowest steady-state photoluminescence emission. These differences were accompanied by a consistent performance ranking of *in-situ* > grafted > nonselective across chemically distinct substrates. The *in-situ* catalyst exhibited apparent rate constants of $0.0194 \pm 0.0005 \text{ min}^{-1}$ for methylene blue and $0.0108 \pm 0.0004 \text{ min}^{-1}$ for phenol ($n = 3$), ~ 1.6 times those of the grafted catalyst and 2.2–2.5 times those of the nonselective catalyst. During polyethylene treatment, the median diameter of the recovered $\geq 2 \text{ }\mu\text{m}$ particle fraction decreased from 41.8 ± 0.7 to $26.5 \pm 0.5 \text{ }\mu\text{m}$ after 6 h, while $88.0 \pm 2.5\%$ of the initial particle-size-reduction performance was retained after five cycles. The convergence of structural, optical, and functional measurements supports the materials-science hypothesis that concurrent formation of active and supporting phases can generate a more functionally integrated composite than post-synthesis combination. Because thermal treatment, hydrothermal processing, and templating also differed among protocols, the advantage cannot be assigned to incorporation route alone. Moreover, absorbance loss does not establish mineralization, and particle-size redistribution does not establish polymer destruction. The findings identify synthesis history and interfacial organization as material design variables warranting direct quantitative investigation.

Keywords

Ag–TiO₂/SBA-15, Mesoporous silica, *In-situ* synthesis, Post-synthesis grafting, Visible-light photocatalysis, Synthesis route, Metal support interactions, Polyethylene microplastics, Particle-size reduction, Photocatalyst reusability

Woosung Choi, University High School, 4771 Campus Drive, Irvine, California 92612, USA.
woosungchoi38@gmail.com

1. Introduction

Continued urbanization and industrialization have increased environmental pollution and intensified demands on energy, water, and other resources (1). Alongside climate change, the accumulation of microplastics and persistent organic pollutants presents interconnected environmental challenges that existing treatment methods do not adequately address (1). Industrial wastewater is an important pathway through which organic contaminants enter and accumulate in rivers, lakes, and oceans (2).

For example, the Citarum River was described in 2020 as one of the world's most polluted rivers, with textile and dye-manufacturing facilities identified as major sources of persistent organic pollutants and heavy metals that accumulated in the river and its sediments (3). In the United States, wastewater associated with petroleum refining and petrochemical production, paper manufacturing and coating, and pharmaceutical manufacturing has similarly been reported to contain phenolic and other aromatic organic pollutants (4). A 2022 report from the United States Environmental Protection Agency documented phenol, chlorophenol, benzene, toluene, aniline, and azo dyes in wastewater from oil-refining facilities in Texas and Louisiana (5). Many of these persistent compounds are toxic and may enter aquatic organisms, accumulate within food webs, and ultimately contribute to human exposure (6).

Many of these pollutants contain aromatic ring structures that confer high chemical stability and resistance to biodegradation (7). Photocatalysis has therefore attracted attention as a treatment strategy because photoexcited catalysts can promote the transformation of persistent organic

pollutants and, under favorable conditions, their mineralization to CO_2 and H_2O (7). Upon absorbing light of sufficient energy, a photocatalyst generates electron-hole pairs that can participate in surface redox reactions and produce reactive oxygen species (ROS) (8). These ROS can attack organic pollutants through successive oxidation reactions, potentially leading to ring opening and eventual mineralization (8). Because photocatalysts can be recovered and reused, they may reduce chemical consumption, secondary waste generation, and treatment costs (8).

TiO_2 is among the most widely used semiconductor photocatalysts because of its low toxicity, chemical stability, and relatively low production cost (9). However, anatase TiO_2 has a wide bandgap of ~ 3.2 eV and is primarily activated by ultraviolet light at wavelengths below about 387 nm, which constitutes only a small fraction of the solar spectrum (9). Its limited utilization of visible light therefore constrains photocatalytic performance under natural irradiation (9). In addition, rapid recombination of photogenerated electron-hole pairs reduces the number of charge carriers available for surface oxidation and reduction reactions (10).

One strategy for addressing these limitations is to incorporate metals or conductive metal nanoparticles into TiO_2 (11). Silver nanoparticles can act as electron acceptors at the Ag- TiO_2 interface, promoting charge separation and suppressing electron-hole recombination under suitable conditions (11). Because the Fermi level of Ag lies below the conduction band of TiO_2 , interfacial electron transfer can produce a Schottky barrier that inhibits electron back-

transfer and prolongs the availability of charge carriers for surface reactions (11). Ag nanoparticles also exhibit localized surface plasmon resonance, in which conduction electrons oscillate collectively in response to particular wavelengths of visible light and enhance the local electromagnetic field (12). When coupled with TiO_2 , this plasmonic response can extend the light-harvesting capability of the composite and promote visible-light-driven interfacial excitation and charge transfer (12). Ag therefore functions not simply as an added component but as an interfacial electron mediator and plasmonic light-harvesting domain, potentially improving the photooxidation of pollutants such as phenols, azo dyes, and antibiotics.

To improve the practical performance of photocatalysts, a support material can be used to limit nanoparticle aggregation and active-site blockage while promoting reactant adsorption and transport (13). SBA-15 is an ordered mesoporous silica with a hexagonally arranged pore structure, high surface area, and surface silanol groups that can facilitate the dispersion and anchoring of TiO_2 and Ag nanoparticles (13). Confinement within or association with the mesoporous framework may restrict excessive particle growth, reduce aggregation, and improve access of reactants to catalytic sites. The pore structure may also influence internal light scattering and the local optical environment (13). In addition, native Si–OH groups and introduced functionalities such as $-\text{NH}_2$ and $-\text{SH}$ can provide anchoring sites for metal or oxide species and thereby modify their interfacial organization and charge-transfer behavior (13). SBA-15 can therefore function not merely as an inert carrier but as a structural and interfacial scaffold that

may improve catalyst dispersion, light utilization, activity retention, and reusability.

Photocatalytic performance can vary substantially with the method used to incorporate metal and metal-oxide species into the support (Figure 1). Post-synthesis grafting or impregnation is comparatively straightforward and adaptable to various metals, but uneven deposition may promote particle aggregation, pore blockage, and loss of accessible surface area (14). In contrast, *in-situ* synthesis introduces the metal or oxide precursors during formation of the SBA-15 framework, potentially enabling more uniform dispersion and closer contact between the active phase and the support (14). This approach, however, requires tighter control of synthesis variables such as pH and temperature (15).

Studies using post-synthesis deposition of TiO_2 onto SBA-15 have shown that low TiO_2 loadings followed by calcination can improve dye-removal rates, whereas higher loadings may promote surface aggregation and pore obstruction, thereby increasing diffusion limitations and indicating an optimum loading range (16). By comparison, incorporation of the Ti precursor during SBA-15 formation has been reported to produce more uniformly dispersed TiO_2 nanodomains while preserving a high-surface-area support structure (17). These structural differences were accompanied by faster initial photocatalytic responses than those obtained using post-grafting or impregnation, consistent with improved active-phase dispersion and interfacial organization.

Previous studies therefore suggest that Ag– TiO_2 /SBA-15 is a promising photocatalytic

system. At the Ag–TiO₂ interface, Ag can promote charge separation and suppress electron–hole recombination, while its surface plasmon resonance can enhance the local electromagnetic field under visible-light irradiation and increase photoexcitation within the composite (16). SBA-15 can further improve active-phase dispersion and pollutant access through its ordered mesoporous structure and high surface area, potentially reducing aggregation of Ag–TiO₂ domains. Together, these features may facilitate the generation and utilization of reactive oxygen species such as •O₂[−] and •OH during pollutant oxidation.

However, direct comparisons of *in-situ* and grafted Ag–TiO₂/SBA-15 materials prepared with comparable nominal compositions and evaluated under common irradiation conditions

remain limited (18, 19). Consequently, it is unclear how synthesis history influences active-phase dispersion, metal–support interactions, optical response, charge-carrier behavior, photocatalytic performance, and activity retention. Addressing this question is important for designing catalysts that balance activity, durability, process complexity, and cost for particular wastewater applications. The present study therefore compares *in-situ*, grafted, and nonselective Ag–TiO₂/SBA-15 synthesis protocols using common characterization methods and photocatalytic testing conditions. Its novelty lies in examining whether different routes for assembling comparable nominal constituents produce distinct structural, optical, and functional material states, rather than assuming that final nominal composition alone determines photocatalytic performance.

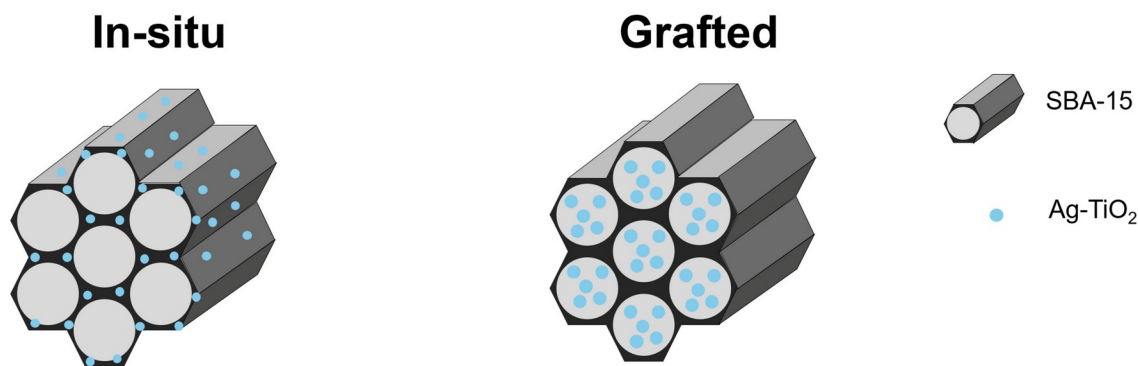


Figure 1. Proposed schematic illustration of the *in-situ* and grafted Ag–TiO₂/SBA-15 catalysts. Schematic showing how Ag–TiO₂ active sites are distributed on the SBA-15 depending on the synthesis route. In the *in-situ* catalyst, Ag–TiO₂ are embedded inside the SBA-15 channels through co-assembly. In the grafted catalyst, Ag–TiO₂ is mainly deposited on the external surface of the pre-formed SBA-15 by post-synthetic impregnation.

Ultimately, the research synthesized Ag–TiO₂/SBA-15 using two different methods. These selective (*in-situ*, grafted) and nonselective catalysts were then analyzed using X-ray Diffraction (XRD), UV/Vis diffuse reflectance spectroscopy, Photoluminescence

spectroscopy (PL), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), and Scanning Electron Microscopy (SEM) were used to systematically identify their surface properties and light response characteristics. Methylene blue (MB),

phenol, and polyethylene (PE) decomposition experiments were performed in order to compare the practical photocatalytic performance under visible light. In addition, the catalyst structure, kinetic parameters, and photodecomposition results were compared to identify mutually consistent trends associated with synthesis route, catalytic activity, and durability, and to suggest a suitable catalyst design for use in target wastewaters.

2. Methods

2.1 Catalyst synthesis

2.1.1 *Synthesis of grafted Ag-TiO₂/SBA-15*

Commercial SBA-15 powder (Sigma-Aldrich, 400mg) was preprocessed for 2 h at 200 °C to evaporate residual moisture and organic impurities. The above step was performed by placing the SBA-15 powder in a heat-resistant crucible on a hot plate stirrer. After this step, titanium isopropoxide (Sigma-Aldrich, 0.493 mL) and isopropyl alcohol (Sigma-Aldrich, 4.93 mL) were added to the preprocessed SBA-15 to form the Ti precursor solution. To prevent hydrolysis, acetylacetone (0.086 mL) was mixed for complex formation reaction, and was refluxed and stirred for 24 hours at room temperature. Subsequently, 1 mL of deionized water was dropped to aid partial hydrolysis of the Ti precursor, and the solution was stirred under the same conditions for another 24 h. Reflux reaction was performed using a hot plate stirrer at room temperature. After completion, the powder containing TiO₂ on the surface of SBA-15 was collected and mixed thoroughly with the Ag precursor solution (Sigma-Aldrich, Ag 1 mol% compared to Ti). The mixed solution is then stirred for 6 h at 60 °C to let Ag⁺ attach

to the surface of TiO₂/SBA-15. The resulting solution was then slowly evaporated to obtain the solid sample. The solid sample was heated to 300–400 °C in an open atmosphere and was calcinated for 2 h, finally producing grafted Ag-TiO₂/SBA-15.

2.1.2 *Synthesis of in-situ Ag-TiO₂/SBA-15*

Pluronic P123 (Sigma-Aldrich 0.67 g), 5 mL of deionized water, and 2 M HCl (Sigma-Aldrich, 20 mL) were dissolved and stirred at room temperature to produce a uniformly even solution. This step was to construct the template solution for the formation of the SBA-15 structure. Following this step, a silica precursor tetraethyl orthosilicate (TEOS (Sigma-Aldrich), 1.5 mL) was dropped into the solution while isopropanol (Sigma-Aldrich, 4.93 mL) and titanium isopropoxide (TTIP (Sigma-Aldrich), 0.493 mL) were added. To prevent premature hydrolysis, acetylacetone (0.086 mL) was mixed for complex formation reaction, and was refluxed and stirred for 24 hours at room temperature. In the next step, AgNO₃ (0.05 M, 0.33 mL) solution was added so that the final composition of Ag was 1 mol% compared to Ti. The AgNO₃ solution was only added after the addition of acetylacetone to minimize the chance of AgCl precipitation. Subsequently, the solution was stirred at 40 °C to a homogeneous sol state. The sol was placed in a Teflon-lined autoclave and underwent hydrothermal reaction for 48 h at 100 °C. In this stage, the uniform structure of SBA-15 was formed, while TiO₂ and Ag particles were intended to be incorporated within the SBA-15 framework during co-assembly. After the reaction, the powder was collected, rinsed, and dried. An electric furnace was used to heat the powder to 540 °C. The powder was then calcined for 3 h, removing the

template P123, solidifying and stabilizing the SBA-15 support while also crystallizing TiO_2 to finally obtain *in-situ* Ag- TiO_2 /SBA-15.

2.1.3 Synthesis of nonselective Ag- TiO_2 /SBA-15

Commercial SBA-15 powder (Sigma-Aldrich, 400 mg) was pretreated at 200 °C for 2 h to remove residual moisture and organic species. Activated SBA-15 was dispersed in isopropanol (Sigma-Aldrich, 4.93 mL), followed by the addition of titanium isopropoxide (Sigma-Aldrich, 0.493 mL) to prepare the Ti precursor solution. To prevent hydrolysis of Ti, acetylacetone (Sigma-Aldrich, 0.086 mL) was added as a stabilizing agent. Subsequently, Ag and Ti precursors were co-introduced into the same beaker. A 0.05 M AgNO_3 aqueous solution was used as the Ag precursor, and the added volume (0.33 mL) was adjusted such that the Ag content was 1 mol% relative to Ti. The resulting suspension was refluxed under stirring at room temperature for 24 h, after which 1 mL of distilled water was added dropwise to induce controlled hydrolysis. The mixture was stirred for an additional 24 h under the same conditions. The solvent then slowly evaporated on a hot plate maintained at 60 °C to obtain solid powder. The recovered solid was centrifuged, washed three times with distilled water, and dried overnight at 80 °C. Finally, the dried powder was calcined in air at 300–400 °C for 2 h to yield nonselective Ag- TiO_2 /SBA-15.

2.2 Catalyst characterization

2.2.1 UV/Vis Diffuse Reflectance Spectroscopy

UV–Vis diffuse reflectance spectroscopy (DRS) was conducted to analyze the optical properties of the synthesized Ag- TiO_2 /SBA-15 catalysts, particularly the bandgap energy and visible-light

absorption enhancement. Measurements were performed on a PerkinElmer Lambda 1050 UV–Vis–NIR spectrophotometer (USA) in the wavelength range of 250–800 nm using BaSO_4 as the reference. The scan rate was 600 nm·min⁻¹. Reflectance data were converted to absorption coefficients using the Kubelka–Munk function. In addition, the surface plasmon resonance (SPR) band of Ag nanoparticles (typically observed around 400–500 nm) was analyzed to quantitatively confirm the enhancement in visible-light activity. Three independent measurements were performed for each catalyst ($n = 3$). The optical band-gap energy (E_g) was independently determined from each measurement using Tauc plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$, and the resulting E_g values were reported as mean $\pm$ standard deviation. The 0–0 transition energy ($E_{0,0}$) was determined from the intersection of the normalized UV–Vis absorption and PL emission spectra for each independent measurement and was also reported as mean $\pm$ standard deviation.

2.2.2 Photoluminescence Spectroscopy (PL)

Photoluminescence spectra were recorded using a LabRAM HR Evolution Visible–NIR spectrometer (HORIBA, Japan) to evaluate the effect of Ag loading on charge recombination and defect state formation in TiO_2 . The excitation wavelength was set to 325 nm, and measurements were performed at room temperature. Three independent measurements were performed for each catalyst under identical instrumental conditions ($n = 3$). The emission intensity was numerically integrated over 450–700 nm, and the integrated PL emission area was used for quantitative comparison among the catalysts. Integrated areas were reported as mean $\pm$ standard deviation. Lower steady-state PL

intensity was interpreted as being consistent with reduced radiative electron–hole recombination rather than as a direct measurement of charge-carrier lifetime.

2.2.3 X-ray Diffraction (XRD)

XRD analysis was performed to examine the mesoporous structure of SBA-15 and to identify the crystalline phases of TiO₂ (anatase and rutile). Measurements were carried out on an Empyrean diffractometer (Panalytical, Netherlands) using Cu K α radiation ($\lambda = 1.5406$ Å) operated at 40 kV and 30 mA. Diffraction patterns were recorded over a 2θ range of 10–80° at a scan rate of 0.01°/s. The obtained data were used to evaluate the crystallinity of TiO₂, the uniformity of Ag/TiO₂ dispersion within SBA-15, and the possible formation of metallic Ag⁰ or Ag₂O phases. Three independent samples were analyzed for each synthesis route ($n = 3$). For crystallite-size estimation, the anatase (101) reflection near $2\theta = 25.3^\circ$ was analyzed separately for each XRD pattern, and its full width at half maximum (FWHM) was determined. The crystallite size was then calculated independently for each replicate using the Scherrer equation, $D = K\lambda/(\beta\cos\theta)$, with $K = 0.9$. The resulting FWHM and crystallite-size values were reported as mean $\pm$ standard deviation. Because Scherrer analysis provides an approximate coherent-domain size, these values were interpreted as crystallite-size estimates rather than exact particle dimensions.

2.2.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was performed to verify the integrity of the SBA-15 framework, the formation of Ti–O–Si bonds, and the presence of surface functional groups such as –OH or C=O.

Measurements were conducted in ATR (Attenuated Total Reflectance) mode using a Nicolet iS50 spectrometer (Thermo Fisher, USA). Spectra were collected over the range of 4000–400 cm^{–1} with a resolution of 2 cm^{–1}, and 64 scans were accumulated for each sample to ensure signal reliability.

2.2.5 Scanning Electron Microscopy (SEM)

The morphology, particle size, and surface roughness of the catalysts were observed using a SU8600 field-emission scanning electron microscope (Hitachi, Japan). Measurements were conducted under an accelerating voltage of 5–20 kV and a beam current of 10–100 pA. No conductive coating (Pd or Pt) was applied in order to preserve the native surface structure.

2.2.6 X-ray Photoelectron Spectroscopy (XPS)

XPS analysis was performed to identify the chemical states of Ti, O, and Ag in the three catalysts, and to determine the interfacial bonding between Ag–TiO₂ and the SBA-15 framework. The spectra were obtained on a NEXSA spectrometer (Thermo Fisher Scientific, USA) using Al K α radiation ($h\nu = 1486.6$ eV). C 1s, O 1s, Ti 2p, and Ag 3d spectra were acquired for each sample. The measured spectra were analyzed with the Advantage software (Thermo Fisher Scientific). For the calibration of the binding energy, the sp² adventitious carbon peak in the C 1s spectrum was set to 284.8 eV.

2.3 Evaluation of photocatalytic activity

2.3.1 Methylene Blue (MB) degradation

The photocatalytic activity of Ag–TiO₂/SBA-15 was first evaluated by determining the degradation of methylene blue (Sigma-Aldrich),

a representative organic dye with a characteristic π - π^* transition at $\lambda_{\text{max}} \approx 664$ nm. A $10 \text{ mg}\cdot\text{L}^{-1}$ MB aqueous solution (50 mL) was prepared in a 100 mL beaker, followed by the addition of 50 mg of the catalyst. The suspension was stirred in the dark for 30 min to reach adsorption equilibrium, which also served as the dark control to check the concentration change from adsorption alone. The mixture was then irradiated under a 500 W tungsten-halogen lamp equipped with a cutoff filter ($\lambda > 420$ nm) while being magnetically stirred at room temperature. The lamp-to-reactor distance was fixed at 10 cm, the irradiance at the sample surface was $\sim 100 \text{ mW}/\text{cm}^2$, and the reaction temperature was maintained at 27.5 ± 0.5 °C during irradiation. Aliquots (2 mL) were withdrawn at 10 min intervals (0–60 min), centrifuged at $1520 \times g$ for 5 min to remove the catalyst, and analyzed using a UV-Vis spectrophotometer (PerkinElmer Lambda 1050, USA) at 664 nm.

A separate dark-control reactor containing the same MB concentration and catalyst loading was subjected to the same initial 30 min dark-equilibration period and subsequently maintained without irradiation for an additional 60 min. Samples were collected at the same time points as in the photocatalytic experiment. As a photolysis control, the same MB solution was irradiated under the identical light condition without any catalyst, so that the direct photolysis of MB under visible light could be measured. Photocatalytic, dark-control, and photolysis experiments were independently repeated three times ($n = 3$). The concentration ratio (C/C_0) was determined from absorbance values, and apparent rate constants (k_{app}) were calculated based on a pseudo-first-order kinetic model. Because MB removal was evaluated from the

decrease in absorbance at 664 nm, the measurement was interpreted as apparent MB removal/decolorization rather than direct evidence of complete mineralization.

2.3.2 Phenol oxidation

To further assess the oxidation capability of the catalysts, phenol (100 ppm) was used as a model non-biodegradable organic pollutant. A 30 mL aliquot of the phenol solution was mixed with 50 mg of catalyst and stirred in the dark for 30 min to establish adsorption equilibrium, which was used as the dark control for the adsorption contribution. Photocatalytic oxidation was conducted under the same visible-light conditions ($\lambda > 420$ nm, 500 W tungsten-halogen lamp, 10 cm lamp-to-reactor distance, $\sim 100 \text{ mW}/\text{cm}^2$ irradiance, and 27.5 ± 0.5 °C). Samples (2 mL) were collected at predetermined time intervals (0–60 min), centrifuged, and analyzed by UV-Vis spectroscopy at $\lambda_{\text{max}} = 270$ nm.

A separate dark-control reactor containing the same phenol concentration and catalyst loading was subjected to the same initial 30 min dark-equilibration period and then maintained without irradiation for an additional 60 min, with samples collected at the same time points as in the photocatalytic experiment. A photolysis control without catalyst was also carried out under the same light condition to check the direct photolysis of phenol. Photocatalytic, dark-control, and photolysis experiments were independently repeated three times ($n = 3$). The temporal concentration changes were fitted to a pseudo-first-order kinetic model ($\ln(C_0/C) = k_{\text{app}} \cdot t$) to calculate rate constants, enabling a quantitative comparison of the *in-situ*, grafted, and nonselective samples. Because phenol was monitored only by absorbance at 270 nm, where

oxidation intermediates may also contribute, the measured decrease was treated as apparent phenol-associated absorbance loss rather than selective quantification of parent phenol or direct evidence of mineralization.

2.3.3 PE microplastic particle-size change

To evaluate the applicability of the catalysts toward solid-phase organic pollutants, polyethylene (PE) microplastics (Sigma-Aldrich), which have high chemical stability and are difficult to biodegrade, were selected as a model substrate. A total of 50 mg of catalyst was dispersed in 100 mL of distilled water, and 0.01 g of PE microplastics was added to adjust the final PE concentration to 0.1 g/L. The mixture was stirred under dark conditions for 10 min so that the PE and catalyst were uniformly dispersed, and visible light was then irradiated under the same conditions described above (500 W tungsten-halogen lamp, $\lambda > 420$ nm, 10 cm lamp-to-reactor distance, ~ 100 mW/cm² irradiance, and 27.5 ± 0.5 °C). To prevent changes in the composition of the reaction suspension caused by repeated sampling and to secure a sufficient amount of PE for laser diffraction analysis, independent reaction systems were prepared for each measurement time. Separate 100 mL reaction systems were terminated at 0, 2, 4, and 6 h, and the entire 100 mL suspension from each reaction system was used for PE recovery and particle-size analysis. Three independent reactions were performed for each catalyst and each measurement time ($n = 3$).

After irradiation, the entire reaction suspension was subjected to density separation before PE recovery to minimize interference from suspended Ag-TiO₂/SBA-15 catalyst particles.

The suspension was transferred to a density-separation vessel, and an aqueous NaI (Sigma-Aldrich) solution was added to establish a separation medium with a density of 1.50 g/cm³. The sample was gently inverted for 5 min and then allowed to stand for 30 min without centrifugation. The lower-density PE particles were preferentially retained in the upper floating fraction, whereas the denser inorganic catalyst particles preferentially settled toward the lower fraction. The entire PE-rich upper fraction was collected to minimize selective sampling within the recovered particle population. The collected upper fraction was subsequently vacuum-filtered through a 2 μ m membrane filter to recover the PE particles. The particles retained on the membrane were washed five times with deionized water to remove residual NaI and remaining loosely associated catalyst particles. The recovered particles were then redispersed in deionized water by gentle mixing. Ultrasonication was not used during sample preparation to minimize additional mechanical fragmentation of the PE particles. Because PE was recovered using a 2 μ m membrane, the particle-size analysis represents the recovered PE fraction ≥ 2 μ m; particles or degradation products smaller than the membrane cutoff were not included in the particle-size distribution analysis. The particle-size distribution of PE was measured using a Mastersizer 3000 particle size analyzer (Malvern Panalytical, UK) based on laser diffraction. The recovered PE suspension was introduced into a Hydro MV wet dispersion unit (120 mL) connected to the Mastersizer 3000, using deionized water as the dispersant. Measurements were performed at a pump speed of 2500 rpm and an obscuration of 5–10%, without ultrasonication. Particle-size distributions were calculated using the Mie

scattering model with refractive indices of 1.52 for PE and 1.33 for water and an absorption index of 0.01 for PE. The same dispersion and optical settings were maintained for all samples and controls.

Particle-size distributions were expressed on a volume basis, and $D_v(10)$, $D_v(50)$, and $D_v(90)$ were recorded. $D_v(10)$, $D_v(50)$, and $D_v(90)$ represent the particle diameters below which 10%, 50%, and 90% of the cumulative particle volume are present, respectively. Among these parameters, $D_v(50)$ was defined as the volume-based median particle diameter and was used as the primary parameter for comparing changes in PE particle size among the catalysts. Instrumental measurements were repeated three times for each independent sample, and the

average of the three measurements was used as the value for that independent experiment. The final results were expressed as mean $\pm$ standard deviation (mean $\pm$ SD) from three independently conducted photocatalytic experiments ($n = 3$).

For the control experiments, a photolysis control exposed to the same light conditions without catalyst and dark controls containing each catalyst without light irradiation were prepared. All control samples underwent the same density separation, filtration, washing, redispersion, and laser diffraction analysis procedures as the irradiated samples. The PE particle-size reduction was calculated using the initial $D_v(50)$ and the $D_v(50)$ after each irradiation time according to

$$\eta_{\text{size}}(\%) = \frac{D_{v(50),0} - D_{v(50),t}}{D_{v(50),0}} \times 100 (\%)$$

where $D_{v(50),0}$ is the initial volume-based median particle diameter of PE and $D_{v(50),t}$ is the volume-based median particle diameter after irradiation time t . Since this parameter represents a change in the particle-size distribution rather than a direct measurement of PE mass loss or complete mineralization, it was defined as particle-size reduction rather than absolute degradation efficiency.

To evaluate the reusability of the photocatalysts without introducing centrifugation-related bias into the PE particle-size measurements, separate reactor series were prepared for catalyst recovery and particle-size analysis at each reuse cycle. For each catalyst, independent reactor series were established for the first through fifth reuse-cycle endpoints. In the reactor series designated for subsequent reuse, the catalyst was recovered

after irradiation by centrifugation at $5000 \times g$ for 10 min at room temperature. The PE-containing supernatant was carefully removed, and the recovered catalyst pellet was redispersed in 40 mL of deionized water and centrifuged again under the same conditions. This washing procedure was repeated three times. The recovered catalyst was then dried at 60°C for 12 h and reused in a fresh reaction suspension containing 100 mL of distilled water and 0.01 g of fresh PE microplastics. No fresh catalyst was added to compensate for catalyst loss during recovery. At the designated endpoint of each reuse cycle, a separate reactor from the corresponding catalyst lineage was terminated for particle-size analysis. The entire reaction suspension from this reactor was subjected directly to the same density-separation, membrane-filtration, washing, redispersion, and

laser-diffraction procedure described above. Thus, PE particle-size distributions at cycles 1–5 were determined from suspensions that had not undergone centrifugation prior to particle recovery. Reusability was evaluated from the $D_v(50)$ -based PE particle-size reduction at each cycle relative to that observed in the first cycle. Three independent reuse experiments were conducted for each catalyst ($n = 3$), and the results were expressed as mean $\pm$ standard deviation.

2.4 Statistical analysis

All quantitative results are reported as mean $\pm$ standard deviation (SD) from three independent experiments ($n = 3$), unless otherwise stated. Repeated instrumental measurements of the same sample were treated as technical replicates and were averaged to obtain a single value for each independent experiment. Differences among the *in-situ*, grafted, and nonselective catalysts in integrated PL emission area, optical band-gap energy (E_g), $E_{0,0}$, Scherrer crystallite size, and apparent photocatalytic rate constants (k_{app}) were evaluated by one-way analysis of variance (ANOVA), followed by Tukey's honestly significant difference (HSD) test for pairwise comparisons. For one-way ANOVA, the F statistic, corresponding degrees of freedom, p-value, and η^2 effect size were reported.

PE $D_v(50)$ data for the three catalyst synthesis routes were analyzed by two-way ANOVA using synthesis route (*in-situ*, grafted, and nonselective) and irradiation time (0, 2, 4, and 6 h) as factors. The catalyst-free photolysis control was analyzed separately and was not included as

a level of the synthesis-route factor. When a significant route $\times$ time interaction was observed, Tukey-adjusted pairwise comparisons among the three catalyst routes were performed separately within each irradiation time point. For two-way ANOVA, the F statistic, corresponding degrees of freedom, p-value, and partial η^2 were reported for each main effect and interaction.

Reusability data were analyzed by two-way ANOVA using catalyst type and reuse cycle as factors. The same reporting format was used for the main effects and catalyst type $\times$ reuse cycle interaction, including F values, degrees of freedom, p-values, and partial η^2 . Statistical significance was defined as $p < 0.05$. Statistical analyses were performed using Python.

3. Results

3.1 Characterization of Ag-TiO₂/SBA-15

UV–Vis diffuse reflectance spectra of the grafted, *in-situ*, and nonselective Ag-TiO₂/SBA-15 samples were obtained from three independent measurements for each catalyst ($n = 3$), and representative spectra are shown in Figure 2. All three samples exhibited a strong absorption band in the 380–400 nm range, corresponding to the band-gap transition of anatase TiO₂ (≈ 3.2 eV) (20). A broad absorption tail extending from 450 to 600 nm appeared in the *in-situ* sample, with a maximum overall absorption intensity across both UV and visible regions. The grafted sample showed moderate absorption in the visible range, and the nonselective sample displayed the weakest intensity in the same region.

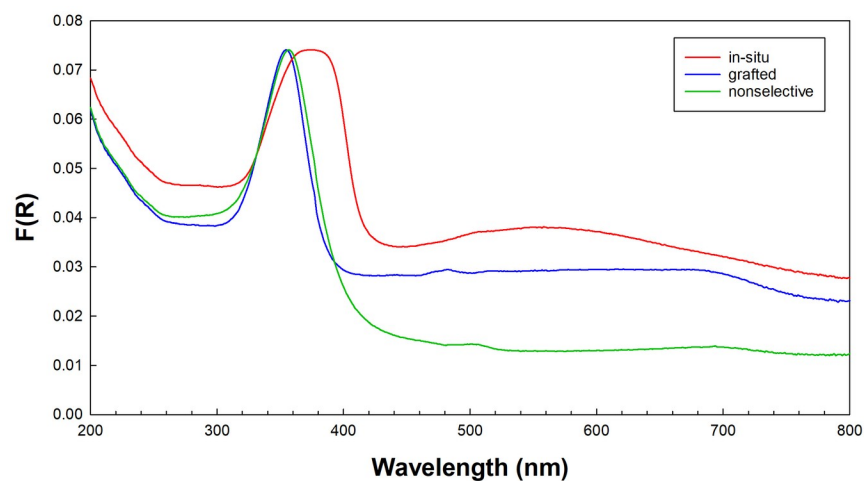


Figure 2. UV-Vis diffuse reflectance spectra of the three Ag-TiO₂/SBA-15 catalysts. Measured spectra were converted to the Kubelka-Munk function $F(R)$. All samples show the band-gap absorption of anatase TiO₂ near 380–400 nm. The *in-situ* sample shows an additional broad absorption tail at 450–600 nm, attributed to the surface plasmon resonance (SPR) of Ag nanoparticles.

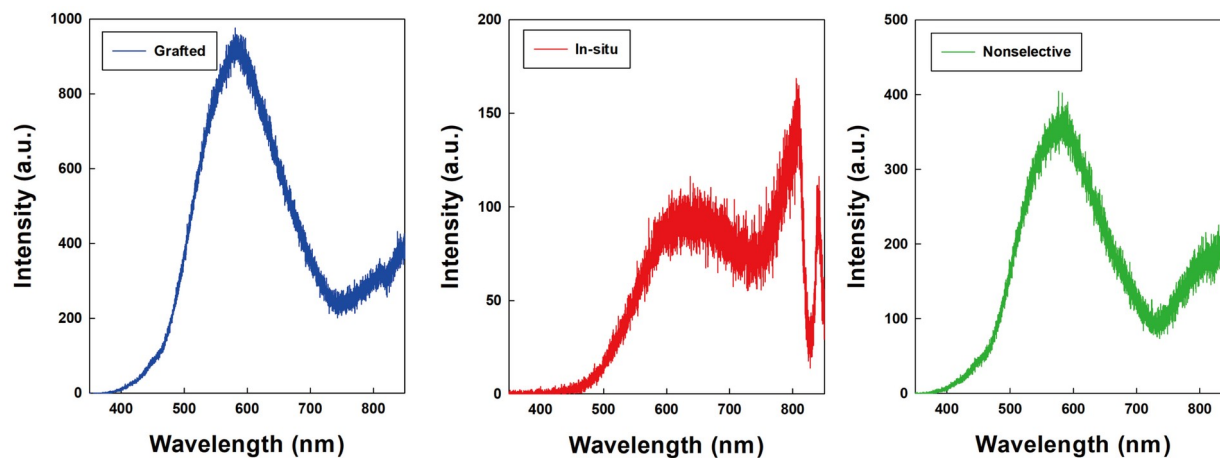


Figure 3. PL spectra of *in-situ* (red), grafted (blue), and nonselective (green) Ag-TiO₂/SBA-15 catalysts. All samples show broad emission centered at 520–560 nm. The emission intensity follows the order grafted > nonselective > *in-situ*, indicating that radiative electron-hole recombination is most strongly suppressed in the *in-situ* catalyst.

Photoluminescence spectra were measured at room temperature (Figure 3). All samples showed broad emission bands between 450 and 700 nm, with the main emission peak centered at 520–560 nm (21, 22). The integrated PL emission area over 450–700 nm were $1.29 \pm 0.06 \times 10^4$ a.u.·nm for the *in-situ* sample, $1.42 \pm 0.05 \times 10^5$ a.u.·nm for the grafted sample, and $5.35 \pm 0.20 \times 10^4$ a.u.·nm for the nonselective sample ($n = 3$). The integrated PL emission area

differed significantly among the three catalysts (one-way ANOVA, $F(2, 6) = 1335.87$, $p < 0.001$, $\eta^2 = 0.998$). Tukey's HSD test showed that the *in-situ* catalyst had a significantly lower integrated PL emission area than both the grafted and nonselective catalysts ($p < 0.001$ for both comparisons), while the nonselective catalyst also showed a significantly lower value than the grafted catalyst ($p < 0.001$).

The optical band-gap energies (E_g) of the three samples were determined from Tauc plots constructed by plotting $(\alpha h\nu)^{1/2}$ versus $h\nu$, based on the indirect transition nature of anatase TiO_2 (Figure 4a). The E_g values estimated from linear extrapolation of the absorption edge were 3.15 ± 0.01 eV for the grafted sample, 3.14 ± 0.01 eV for the nonselective sample, and 2.91 ± 0.02 eV for the *in-situ* sample ($n = 3$). A significant overall difference in E_g was observed among the three catalysts (one-way ANOVA, $F(2, 6) = 276.50$, $p < 0.001$, $\eta^2 = 0.989$). Tukey's HSD

test showed that the E_g of the *in-situ* catalyst was significantly lower than those of both the grafted and nonselective catalysts ($p < 0.001$ for both comparisons), whereas no significant difference was observed between the grafted and nonselective samples ($p = 0.593$). The 0–0 transition energies ($E_{0,0}$), defined as the intersection point between the normalized UV–Vis absorption and PL emission spectra, were also determined for each sample (Figure 4b). The $E_{0,0}$ values were 2.35 ± 0.01 eV for the nonselective sample, 2.24 ± 0.01 eV for the grafted sample, and 2.15 ± 0.01 eV for the *in-situ* sample ($n = 3$). The $E_{0,0}$ values differed significantly among the three catalysts (one-way ANOVA, $F(2, 6) = 301.00$, $p < 0.001$, $\eta^2 = 0.990$). Tukey's HSD test showed significant differences among all pairwise comparisons ($p < 0.001$). In all three samples, the $E_{0,0}$ values were lower than the corresponding E_g values obtained from the Tauc analysis.

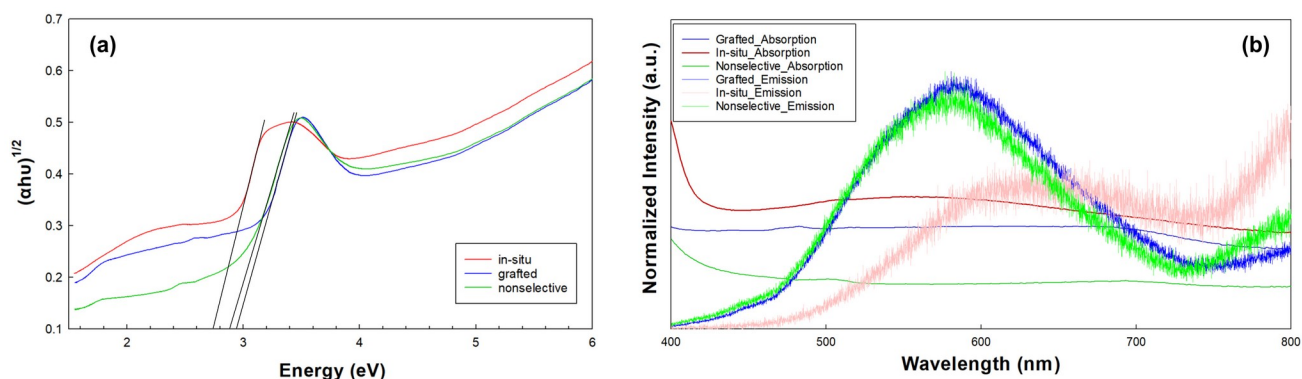


Figure 4. Tauc plots and 0–0 transition energy analysis. (a) Tauc plots of $(\alpha h\nu)^{1/2}$ versus photon energy. The optical band-gap energies (E_g) are 3.16 eV (grafted), 3.13 eV (nonselective), and 2.90 eV (*in-situ*). (b) Normalized UV–Vis absorption and PL emission spectra plotted on the same axis. The 0–0 transition energies ($E_{0,0}$) determined from the intersection are 2.34 eV (nonselective), 2.25 eV (grafted), and 2.14 eV (*in-situ*).

The crystalline structures of the synthesized catalysts were analyzed by XRD (Figure 5). All samples exhibited a broad peak near $2\theta \approx 22^\circ$, corresponding to the amorphous SiO_2 framework of SBA-15 (★) (23). Diffraction peaks at 25.3° , 37.8° , 48.0° , 54.2° , 62.8° , 69.6° , and 75.3° were

indexed to the (101), (004), (200), (211), (204), (220), and (215) planes of anatase TiO₂ (♥, JCPDS No. 21-1272) (24). A minor reflection at 27.4° was assigned to the (110) plane of rutile TiO₂ (25). Additional weak peaks at 38.1° and 44.3° corresponded to the (111) and (200) planes of metallic Ag (♠, JCPDS No. 04-0783) (24). In

the representative XRD patterns, the *in-situ* sample showed relatively sharper anatase reflections, whereas the grafted sample showed broader reflections. The nonselective sample showed an intermediate peak-broadening behavior.

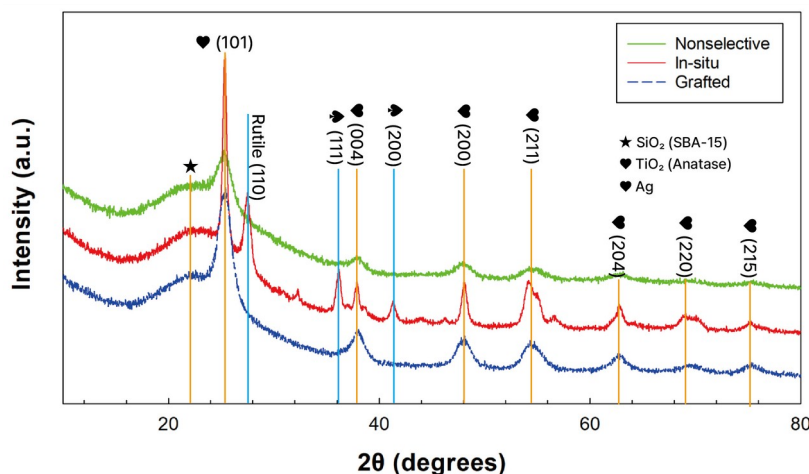


Figure 5. X-ray diffraction (XRD) patterns of the three Ag–TiO₂/SBA-15 catalysts. The broad peak at $2\theta \approx 22^\circ$ (★) corresponds to the SBA-15 silica framework. The peaks marked with ♥ (JCPDS No. 21-1272) are assigned to anatase TiO₂, and the weak peaks marked with ♠ (JCPDS No. 04-0783) are assigned to metallic Ag. A minor peak at 27.4° corresponds to rutile TiO₂. The *in-situ* sample shows the sharpest and most intense anatase reflections.

The average crystallite size (D) of anatase TiO₂ in each sample was estimated by applying the Scherrer equation, $D = K\lambda/(\beta\cos\theta)$, where $K = 0.9$, $\lambda = 1.5406 \text{ \AA}$ (Cu K α), β is the full width at half maximum (FWHM) of the diffraction peak in radians, and θ is the Bragg angle (26). The (101) peak of anatase at $2\theta = 25.3^\circ$ was selected as the reference reflection. The mean FWHM values were $1.41 \pm 0.07^\circ$ for the *in-situ* sample, $1.56 \pm 0.06^\circ$ for the nonselective sample, and $1.97 \pm 0.11^\circ$ for the grafted sample ($n = 3$). The corresponding Scherrer crystallite sizes were estimated as $5.78 \pm 0.29 \text{ nm}$ for the *in-situ* sample, $5.22 \pm 0.20 \text{ nm}$ for the nonselective sample, and $4.14 \pm 0.23 \text{ nm}$ for the grafted

sample. The estimated crystallite sizes differed significantly overall among the three catalysts (one-way ANOVA, $F(2, 6) = 35.34$, $p < 0.001$, $\eta^2 = 0.922$). Tukey's HSD analysis showed that the grafted sample had a significantly smaller estimated crystallite size than the *in-situ* ($p < 0.001$) and nonselective samples ($p = 0.004$). In contrast, the difference between the *in-situ* and nonselective samples was not statistically significant ($p = 0.068$).

The structural characteristics of the three composites were analyzed by FTIR spectroscopy (Figure 6). All samples exhibited Si–O–Si asymmetric stretching bands at $1176\text{--}1060 \text{ cm}^{-1}$

and a symmetric stretching band near 800 cm^{-1} . A broad absorption near 3440 cm^{-1} and a bending vibration at 1624 cm^{-1} were observed in all samples, corresponding to surface hydroxyl ($-\text{OH}$) groups and adsorbed molecular water, respectively (27). A band at approximately 973 cm^{-1} was assigned to $\text{Ti}-\text{O}-\text{Si}$ stretching (28). The intensity of this band differed across the three samples: the *in-situ* sample showed the strongest $\text{Ti}-\text{O}-\text{Si}$ peak, accompanied by a shoulder near 544 cm^{-1} (29). The intensity of the $\text{O}-\text{H}$ band at 3440 cm^{-1} was lowest in the *in-situ* sample. The grafted sample exhibited a moderate $\text{Ti}-\text{O}-\text{Si}$ peak and a weak signal near 544 cm^{-1} . The nonselective sample showed the weakest $\text{Ti}-\text{O}-\text{Si}$ band and the strongest $\text{O}-\text{H}$ stretching at 3440 cm^{-1} .

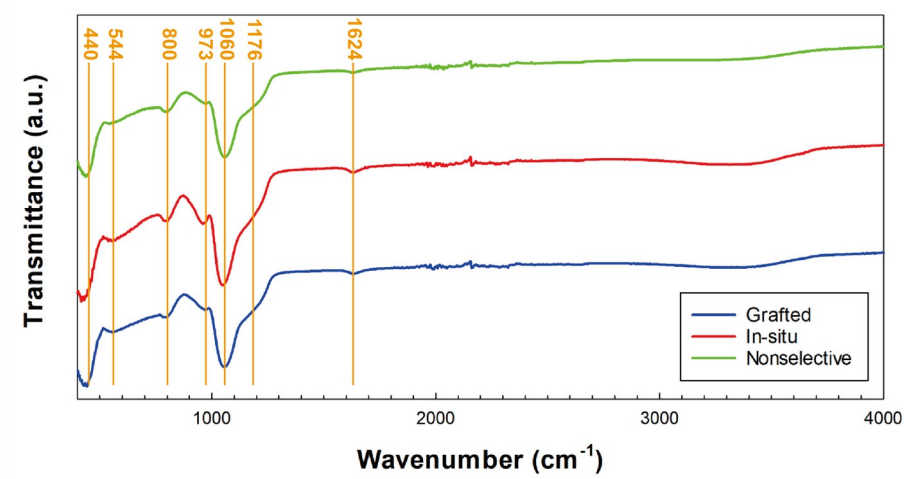


Figure 6. FTIR spectra of the three $\text{Ag}-\text{TiO}_2/\text{SBA-15}$ catalysts. All samples show $\text{Si}-\text{O}-\text{Si}$ stretching (1176 – 1060 and 800 cm^{-1}), surface $-\text{OH}$ (3440 cm^{-1}), and adsorbed-water bending (1624 cm^{-1}). The $\text{Ti}-\text{O}-\text{Si}$ stretching band at 973 cm^{-1} is most intense in the *in-situ* sample, together with a shoulder at 544 cm^{-1} assigned to $\text{Ag}-\text{O}$ or $\text{Ag}-\text{Ti}$ interfacial vibrations. The $-\text{OH}$ band intensity follows the opposite trend (nonselective > grafted > *in-situ*).

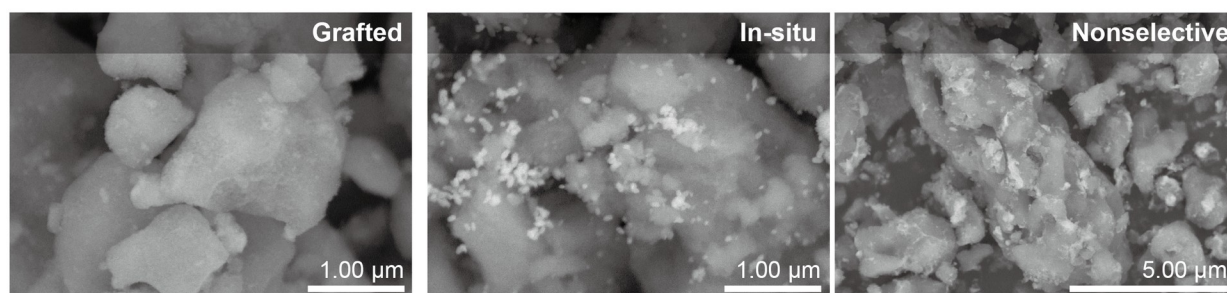


Figure 7. SEM images of grafted, *in-situ*, and nonselective $\text{Ag}-\text{TiO}_2/\text{SBA-15}$ catalysts. The bright dots correspond to $\text{Ag}-\text{TiO}_2$ and the dark regions to the SBA-15. The *in-situ* sample shows uniformly dispersed bright dots across the SBA-1, the grafted sample shows limited bright dots on the external surface, and the nonselective sample shows large and irregularly distributed bright regions, indicating localized aggregation.

The surface morphologies of the three composites were examined by SEM in

backscattered electron (BSE) mode, where the contrast distinguishes the silica matrix (low atomic number) from the Ag–TiO₂ domains (high atomic number) (Figure 7). The *in-situ* sample exhibited a uniform distribution of bright contrast regions across the SBA-15 framework. The grafted sample showed relatively smooth particle surfaces with limited bright Ag–TiO₂ domains visible on the external surface. The nonselective sample displayed large, non-uniformly distributed bright areas with irregular morphology.

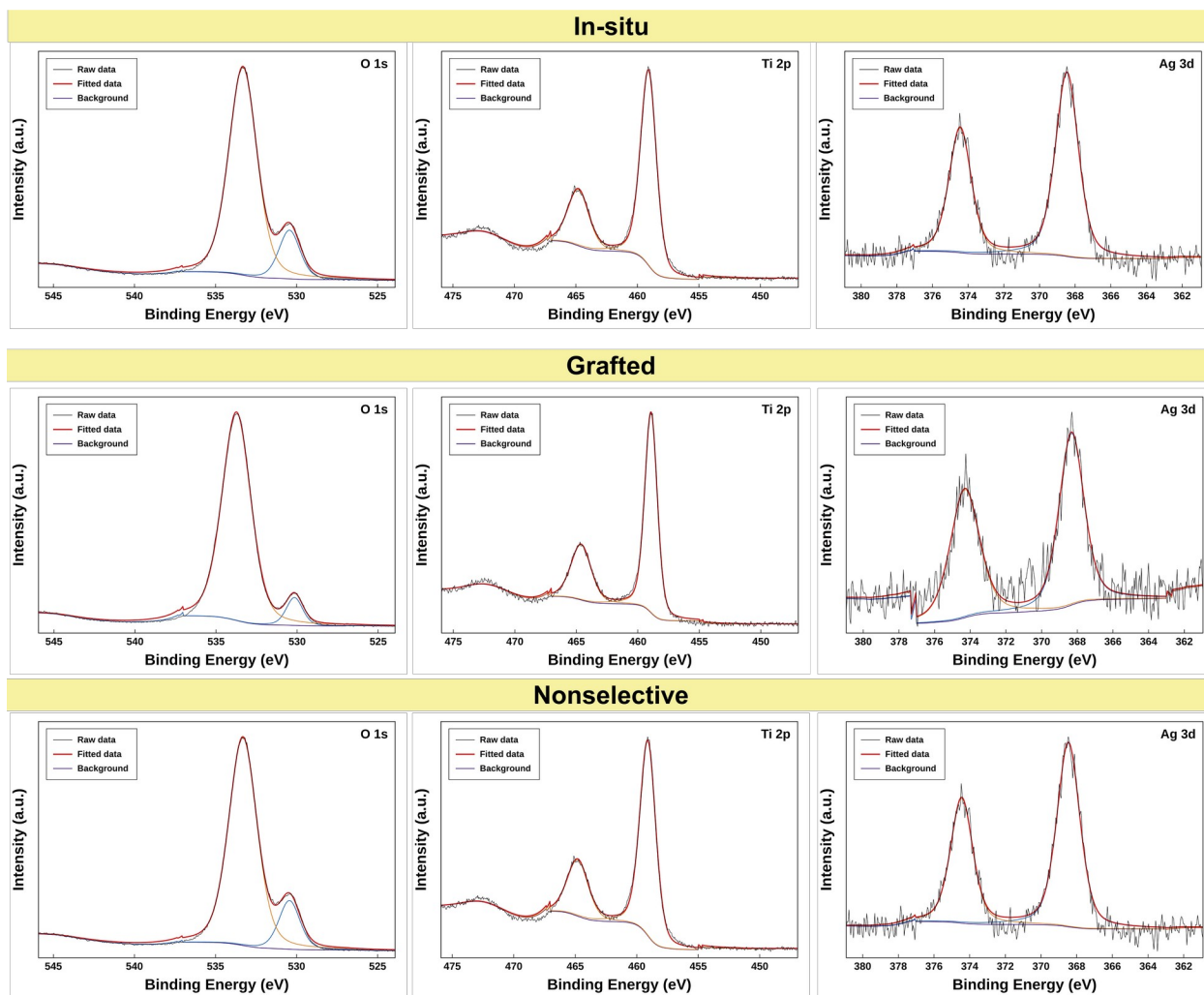


Figure 8. Representative XPS spectra of the *in-situ*, grafted, and nonselective Ag–TiO₂/SBA-15 catalysts. The O 1s, Ti 2p, and Ag 3d regions are shown for each sample, with the raw data, the fitted curve, and the background. In the Ti 2p region, all samples show the Ti⁴⁺ 2p_{3/2} and 2p_{1/2} peaks near 459 and 465 eV, and the *in-situ* sample shows a weak Ti³⁺ tail near 457–458 eV that is not clear in the other two samples. In the O 1s region, the large peak near 533 eV comes from the SiO₂ framework of SBA-15 and the smaller peak near 530 eV from the Ti–O–Ti lattice oxygen. In the Ag 3d region, all samples show the 3d_{5/2} and 3d_{3/2} peaks near 368 and 374 eV, close to metallic Ag⁰, and the Ag 3d signal of the grafted sample is noisy because of the low Ag content (1 mol% relative to Ti).

The chemical states of Ti, O, and Ag were examined by XPS (Figure 8). The Ti 2p spectra

of all three samples showed two main peaks near 459 eV and 465 eV, which are the $2p_{3/2}$ and $2p_{1/2}$ of Ti^{4+} in anatase TiO_2 , with a spin-orbit splitting of about 5.7 eV (30). In the *in-situ* sample, the $Ti\ 2p_{3/2}$ peak showed a weak tail on the lower binding energy side near 457–458 eV. This tail was not clear in the grafted and nonselective samples. The lower-binding-energy tail is consistent with a Ti^{3+} -related contribution (31); however, the relative Ti^{3+} fraction was not quantitatively determined. The O 1s spectra of all samples were made of a large peak near 533 eV and a smaller peak near 530 eV. The large peak originates from the Si–O of the SiO_2 framework of SBA-15, and the smaller peak originates from the lattice oxygen of Ti–O–Ti (32). The Ti–O–Si oxygen is reported near 531–532 eV, but in this study it was partially overlapped by the large SiO_2 peak, hence it could not be separated in the O 1s region. The Ag 3d spectra showed the $3d_{5/2}$ and $3d_{3/2}$ peaks near 368 eV and 374 eV in all samples, with a splitting of about 6.0 eV. These values are close to metallic Ag^0 (33). In the *in-situ* sample, the Ag $3d_{5/2}$ peak appeared at a slightly lower binding energy than in the grafted and nonselective samples. The Ag 3d signal of the grafted sample was noisy because the Ag content was low (1 mol% relative to Ti), hence the peak of the grafted sample was weak compared to the other two.

3.2 Comparative photocatalytic performance across model pollutants

The photocatalytic performance of the catalysts was first evaluated by methylene blue (MB) removal under visible-light irradiation (Figure 9a). In the photolysis control without catalyst, MB removal after 60 min was $3.0 \pm 0.3\%$ ($n = 3$). In the dark control with catalyst and no light, the removal after 60 min was $4.1 \pm 0.3\%$ for the

nonselective sample, $5.1 \pm 0.3\%$ for the grafted sample, and $6.3 \pm 0.4\%$ for the *in-situ* sample ($n = 3$). These values were substantially lower than those observed under photocatalytic irradiation, indicating that direct photolysis and dark adsorption made relatively small contributions to the overall MB removal. Plots of $\ln(C_0/C)$ versus time were linear for all three catalysts, consistent with a pseudo-first-order kinetic model ($R^2 > 0.997$ across the independent experiments). The apparent rate constants (k_{app}) were $0.0194 \pm 0.0005\ min^{-1}$ for the *in-situ* sample, $0.0121 \pm 0.0004\ min^{-1}$ for the grafted sample, and $0.0087 \pm 0.0003\ min^{-1}$ for the nonselective sample ($n = 3$). The synthesis route had a significant effect on k_{app} (one-way ANOVA, $F(2, 6) = 538.02$, $p < 0.001$, $\eta^2 = 0.994$), and Tukey's HSD test showed significant differences among the three catalysts ($p < 0.001$). The corresponding half-lives ($t_{1/2} = \ln 2/k_{app}$), calculated separately for each independent experiment, were $35.7 \pm 0.9\ min$, $57.3 \pm 1.7\ min$, and $79.7 \pm 2.8\ min$ for the *in-situ*, grafted, and nonselective samples, respectively. After 60 min, MB removal was $68.8 \pm 0.9\%$, $51.6 \pm 1.1\%$, and $40.7 \pm 1.1\%$ for the *in-situ*, grafted, and nonselective catalysts, respectively. Based on the mean k_{app} values, the apparent rate constant of the *in-situ* catalyst was ~ 1.60 times that of the grafted sample and 2.23 times that of the nonselective sample. Because MB removal was quantified from the decrease in absorbance at 664 nm, these results represent apparent MB removal/decolorization and do not by themselves demonstrate complete mineralization.

The catalysts were further tested for apparent phenol removal under identical visible-light conditions (Figure 9b). In the photolysis control without catalyst, phenol removal after 60 min

was $2.8 \pm 0.2\%$ ($n = 3$). In the dark control, the removal was $1.6 \pm 0.1\%$ for the nonselective sample, $2.1 \pm 0.2\%$ for the grafted sample, and $2.6 \pm 0.2\%$ for the *in-situ* sample. As observed for MB, both direct photolysis and removal under dark conditions were small relative to those observed under visible-light photocatalytic conditions. Plots of $\ln(C_0/C)$ versus time showed linearity for all samples ($R^2 > 0.995$ across the independent experiments). The k_{app} were $0.0108 \pm 0.0004 \text{ min}^{-1}$ for the *in-situ* sample, $0.0067 \pm 0.0003 \text{ min}^{-1}$ for the grafted sample, and $0.0043 \pm 0.0002 \text{ min}^{-1}$ for the nonselective sample ($n = 3$). The differences in k_{app} among the three catalysts were statistically significant (one-way ANOVA, $F(2, 6) = 335.28$, $p < 0.001$, $\eta^2 = 0.991$; Tukey's HSD, $p < 0.001$ for all pairwise comparisons). The corresponding half-lives were

$64.2 \pm 2.4 \text{ min}$ for the *in-situ* sample, $103.6 \pm 4.6 \text{ min}$ for the grafted sample, and $161.4 \pm 7.5 \text{ min}$ for the nonselective sample. After 60 min, apparent phenol removal was $47.7 \pm 1.3\%$, $33.1 \pm 1.2\%$, and $22.7 \pm 0.9\%$ for the *in-situ*, grafted, and nonselective catalysts, respectively. Based on the mean k_{app} values, the apparent rate constant of the *in-situ* catalyst was ~ 1.61 times that of the grafted catalyst and 2.51 times that of the nonselective catalyst. Because phenol was monitored only by UV absorbance at 270 nm, where oxidation intermediates such as catechol and hydroquinone may also absorb, these values should be interpreted as apparent phenol-associated absorbance loss rather than selective quantification of parent phenol or evidence of mineralization.

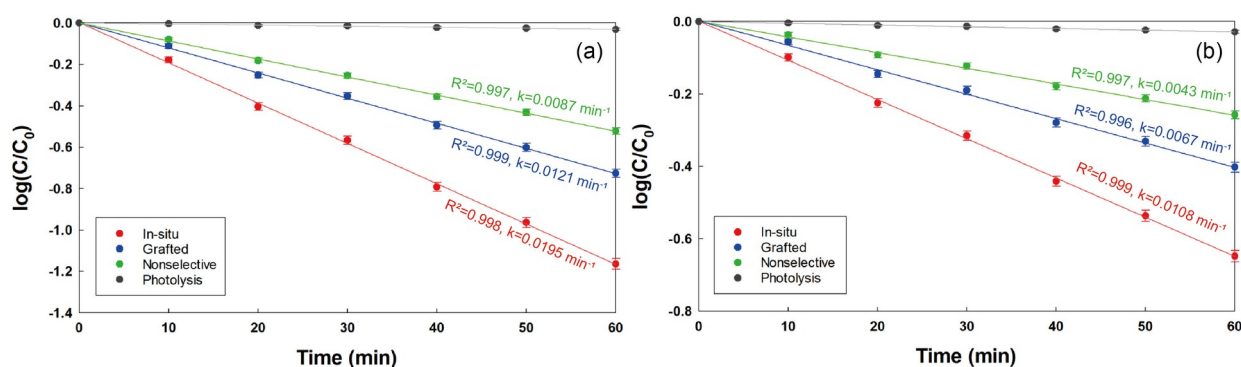


Figure 9. Pseudo-first-order kinetic plots for the photocatalytic degradation of (a) methylene blue (MB) and (b) phenol under visible-light irradiation ($\lambda > 420 \text{ nm}$, 500 W tungsten-halogen lamp). $\ln(C/C_0)$ is plotted against irradiation time. Linear fits gave $R^2 = 0.999$ for MB and $R^2 = 0.996\text{--}0.999$ for phenol. The apparent rate constants (k_{app} , the negative of the fitted slope) for MB are 0.0196, 0.0120, and 0.0086 min^{-1} and for phenol are 0.0109, 0.0066, and 0.0042 min^{-1} , in the order of *in-situ*, grafted, and nonselective. The *in-situ* catalyst shows $\sim 1.6\text{--}1.7$ times higher k_{app} than the grafted sample and 2.3–2.6 times higher than the nonselective sample.

For PE microplastics, changes in the particle-size distribution of the recovered PE fraction ($\geq 2 \mu\text{m}$) were analyzed by laser diffraction using a Mastersizer 3000 instead of DLS (Figure 10a). $D_v(10)$, $D_v(50)$, and $D_v(90)$ were monitored over

0–6 h, and the initial $D_v(50)$ of the PE particles was $41.8 \pm 0.7 \mu\text{m}$ ($n = 3$). In the photolysis control without catalyst, $D_v(50)$ decreased only slightly to $41.4 \pm 0.6 \mu\text{m}$ after 6 h, corresponding to a $1.0 \pm 0.5\%$ particle-size reduction. In the

dark controls with catalyst and no light, the $D_v(50)$ values after 6 h were $40.9 \pm 0.6 \mu\text{m}$ for the nonselective sample, $40.5 \pm 0.5 \mu\text{m}$ for the grafted sample, and $40.1 \pm 0.5 \mu\text{m}$ for the *in-situ* sample. These changes were smaller than those observed under photocatalytic irradiation. Under visible-light irradiation, the initial $D_v(50)$ of $41.8 \pm 0.7 \mu\text{m}$ decreased after 6 h to $34.9 \pm 0.6 \mu\text{m}$ for the nonselective catalyst, $31.2 \pm 0.5 \mu\text{m}$ for the grafted catalyst, and $26.5 \pm 0.5 \mu\text{m}$ for the *in-situ* catalyst ($n = 3$). These changes corresponded to $D_v(50)$ -based particle-size reductions of $16.5 \pm 1.2\%$, $25.4 \pm 1.3\%$, and $36.6 \pm 1.4\%$ for the nonselective, grafted, and *in-situ* catalysts, respectively. Two-way ANOVA showed significant main effects of synthesis route, $F(2, 24) = 172.10$, $p < 0.001$, partial $\eta^2 = 0.935$, and irradiation time, $F(3, 24) = 553.66$, $p < 0.001$, partial $\eta^2 = 0.986$. A significant synthesis route $\times$ irradiation time interaction was also

observed, $F(6, 24) = 27.22$, $p < 0.001$, partial $\eta^2 = 0.872$. Following the significant interaction, Tukey-adjusted pairwise comparisons among the three catalyst routes were performed separately within each irradiation time point. No differences were observed among the conditions at 0 h ($p = 1.000$). At 2 h, the *in-situ* condition differed significantly from the grafted ($p = 0.011$) and nonselective ($p < 0.001$) conditions, whereas the grafted and nonselective conditions were not significantly different ($p = 0.096$). At 4 h, all three catalyst conditions differed significantly from one another ($p \leq 0.0024$), and at 6 h all pairwise differences among the three catalysts were significant ($p < 0.001$). These measurements demonstrate a shift in the recovered $\geq 2 \mu\text{m}$ PE particle-size distribution and should not be interpreted as direct evidence of polymer destruction, chemical oxidation, mass loss, or mineralization.

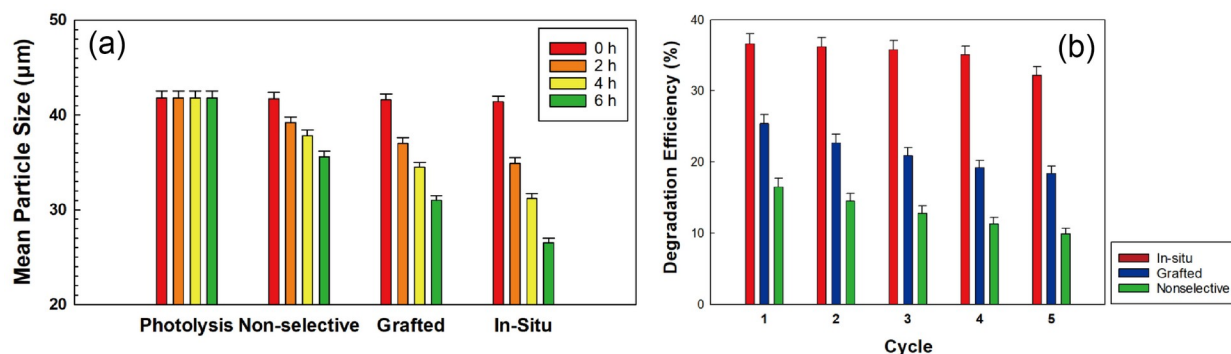


Figure 10. Changes in polyethylene (PE) microplastic particle size and catalyst reusability under visible-light irradiation. (a) Volume-based median particle diameter, $D_v(50)$, of the recovered PE fraction, measured by laser diffraction using a Mastersizer 3000. The initial $D_v(50)$ was $41.8 \pm 0.7 \mu\text{m}$. After 6 h, $D_v(50)$ was $41.4 \pm 0.6 \mu\text{m}$ in the catalyst-free photolysis control and decreased to $34.9 \pm 0.6 \mu\text{m}$ with the nonselective catalyst, $31.2 \pm 0.5 \mu\text{m}$ with the grafted catalyst, and $26.5 \pm 0.5 \mu\text{m}$ with the *in-situ* catalyst. These values correspond to $D_v(50)$ -based particle-size reductions of $1.0 \pm 0.5\%$, $16.5 \pm 1.2\%$, $25.4 \pm 1.3\%$, and $36.6 \pm 1.4\%$, respectively. (b) $D_v(50)$ -based PE particle-size-reduction performance over five consecutive treatment cycles. After five cycles, the *in-situ* catalyst retained $88.0 \pm 2.5\%$ of its initial particle-size-reduction performance, compared with $72.4 \pm 3.2\%$ for the grafted and $60.0 \pm 3.9\%$ for the nonselective catalyst. Data are presented as mean $\pm$ SD from three independent experiments ($n = 3$).

The reusability of the catalysts was evaluated over five consecutive PE treatment cycles

(Figure 10b). Because PE mass loss or complete mineralization was not directly measured, reusability was evaluated using $D_v(50)$ -based particle-size reduction rather than absolute degradation efficiency. In the first cycle, the particle-size reductions were $36.6 \pm 1.4\%$ for the *in-situ* catalyst, $25.4 \pm 1.3\%$ for the grafted catalyst, and $16.5 \pm 1.2\%$ for the nonselective catalyst. After five cycles, these values decreased to $32.2 \pm 1.2\%$, $18.4 \pm 1.0\%$, and $9.9 \pm 0.8\%$, respectively. Accordingly, the retained particle-size-reduction activity after five cycles was $88.0 \pm 2.5\%$ for the *in-situ* catalyst, $72.4 \pm 3.2\%$ for

the grafted catalyst, and $60.0 \pm 3.9\%$ for the nonselective catalyst ($n = 3$). Two-way ANOVA showed significant main effects of catalyst type, $F(2, 30) = 1436.82$, $p < 0.001$, partial $\eta^2 = 0.990$, and reuse cycle, $F(4, 30) = 36.70$, $p < 0.001$, partial $\eta^2 = 0.830$. The catalyst type $\times$ reuse cycle interaction was not statistically significant, $F(8, 30) = 2.00$, $p = 0.082$, partial $\eta^2 = 0.347$. The photolysis and dark-control results, together with the k_{app} , half-lives, PE particle-size changes, and retained activity after repeated use, are summarized for direct comparison across the three catalysts (Table 1).

Table 1. Control responses, apparent kinetic parameters, PE particle-size changes, and five-cycle performance retention of Ag–TiO₂/SBA-15 catalysts

Test	Photolysis control (no catalyst)	Dark control (catalyst, no light)	<i>In-situ</i>	Grafted	Nonselective
Methylene blue	$3.0 \pm 0.3\%$ removal (60 min)	$6.3 \pm 0.4\%$ / $5.1 \pm 0.3\%$ / $4.1 \pm 0.3\%$ removal	$k_{app} = 0.0194 \pm 0.0005 \text{ min}^{-1}$ $t_{1/2} = 35.7 \pm 0.9 \text{ min}$	$k_{app} = 0.0121 \pm 0.0004 \text{ min}^{-1}$ $t_{1/2} = 57.3 \pm 1.7 \text{ min}$	$k_{app} = 0.0087 \pm 0.0003 \text{ min}^{-1}$ $t_{1/2} = 79.7 \pm 2.8 \text{ min}$
Phenol	$2.8 \pm 0.2\%$ removal (60 min)	$2.6 \pm 0.2\%$ / $2.1 \pm 0.2\%$ / $1.6 \pm 0.1\%$ removal	$k_{app} = 0.0108 \pm 0.0004 \text{ min}^{-1}$ $t_{1/2} = 64.2 \pm 2.4 \text{ min}$	$k_{app} = 0.0067 \pm 0.0003 \text{ min}^{-1}$ $t_{1/2} = 103.6 \pm 4.6 \text{ min}$	$k_{app} = 0.0043 \pm 0.0002 \text{ min}^{-1}$ $t_{1/2} = 161.4 \pm 7.5 \text{ min}$
PE microplastics	$D_v(50)$: $41.8 \pm 0.7 \rightarrow 41.4 \pm 0.6 \mu\text{m}$ (6 h)	$D_v(50)$, 6 h: 40.1 ± 0.5 / 40.5 ± 0.5 / $40.9 \pm 0.6 \mu\text{m}$	$D_v(50) = 26.5 \pm 0.5 \mu\text{m}$ $36.6 \pm 1.4\%$ size reduction	$D_v(50) = 31.2 \pm 0.5 \mu\text{m}$ $25.4 \pm 1.3\%$ size reduction	$D_v(50) = 34.9 \pm 0.6 \mu\text{m}$ $16.5 \pm 1.2\%$ size reduction
PE reusability	—	—	$88.0 \pm 2.5\%$ retained (after cycle 5)	$72.4 \pm 3.2\%$ retained (after cycle 5)	$60.0 \pm 3.9\%$ retained (after cycle 5)

The endpoint performances are further compared using MB and phenol removal after 60 min and $D_v(50)$ -based PE particle-size reduction after 6 h, allowing the relative treatment efficiencies of the *in-situ*, grafted, and nonselective catalysts to be evaluated across chemically distinct substrates (Table 2).

Overall, the same performance ranking, *in-situ* > grafted > nonselective, was observed across three physicochemically distinct substrates: the cationic dye MB, the neutral aromatic compound phenol, and the solid polymer PE. However, the measured endpoints differ in meaning: MB and phenol were evaluated from changes in UV/Vis absorbance, whereas PE was evaluated from

changes in the recovered particle-size distribution.

Table 2. Cross-substrate comparison of apparent MB and phenol removal and PE particle-size reduction by Ag–TiO₂/SBA-15 catalysts

Substrate	Photolysis control	Dark control	In-situ	Grafted	Nonselective
Methylene blue (60 min)	3.0 ± 0.3% removal	6.3 ± 0.4% / 5.1 ± 0.3% / 4.1 ± 0.3% removal	68.8 ± 0.9% removal	51.6 ± 1.1% removal	40.7 ± 1.1% removal
Phenol (60 min)	2.8 ± 0.2% removal	2.6 ± 0.2% / 2.1 ± 0.2% / 1.6 ± 0.1% removal	47.7 ± 1.3% removal	33.1 ± 1.2% removal	22.7 ± 0.9% removal
PE microplastics (6 h)	1.0 ± 0.5% size reduction	D _v (50), 6 h: 40.1 ± 0.5 / 40.5 ± 0.5 / 40.9 ± 0.6 μm	36.6 ± 1.4% reduction D _v (50) = 26.5 ± 0.5 μm	25.4 ± 1.3% reduction D _v (50) = 31.2 ± 0.5 μm	16.5 ± 1.2% reduction D _v (50) = 34.9 ± 0.6 μm

4. Discussion

4.1 Synthesis route and structural integration

The instrumental analyses results show that the synthesis route is closely related to how Ag and TiO₂ are incorporated into the SBA-15, and how strongly Ag and TiO₂ interact at the molecular level. From the FTIR analysis (Figure 6), the *in-situ* sample showed the strongest Ti–O–Si stretching peak at 973 cm⁻¹, which is consistent with a greater contribution of Ti–O–Si interfacial bonding in this sample. However, because FTIR peak intensity is influenced by several experimental and structural factors, this observation alone does not quantitatively determine the degree of chemical integration. As illustrated in the schematic figure of the *in-situ* catalyst (Figure 1), Ag–TiO₂ species are intended to become integrated with the silica framework during co-assembly rather than being introduced only after the formation of SBA-15. Moreover, the FTIR showed a shoulder peak near 544 cm⁻¹ that was most apparent in the *in-situ* sample. This feature has been associated with metal–oxygen or interfacial vibrations in related systems (29), and is therefore consistent with,

but does not independently prove, stronger Ag–TiO₂–silica interfacial interactions. The XPS Ag 3d result also provides complementary evidence of differences in the electronic environment of Ag. In the *in-situ* sample, the Ag 3d^{5/2} peak appeared at a slightly lower binding energy than in the other two samples (Figure 8), which may reflect altered electronic interactions between Ag and the surrounding oxide phases. Because the magnitude of this shift was small, it should not by itself be interpreted as direct evidence of a specific Ag–Ti bonding configuration.

The XRD results also demonstrate synthesis-dependent differences in TiO₂ crystallization (Figure 5). The *in-situ* sample displayed relatively sharp anatase reflections, with a mean crystallite size of 5.78 ± 0.29 nm, whereas the crystallite sizes of the grafted and nonselective samples were 4.14 ± 0.23 and 5.22 ± 0.20 nm, respectively (n = 3). The grafted sample had a significantly smaller estimated crystallite size than both the *in-situ* and nonselective samples, whereas the difference between the *in-situ* and nonselective samples was not statistically significant (p = 0.068). Therefore, the small

difference between the latter two samples should not be assigned mechanistic significance. Although these dimensions are within the nanometer scale expected for TiO_2 domains associated with mesoporous supports, XRD alone cannot establish whether individual crystallites are located inside the SBA-15 channels or on the external surface. Direct confirmation of pore confinement would require complementary pore-structural or spatial characterization such as N_2 adsorption and TEM.

Furthermore, such results were also observed from the SEM-BSE images (Figure 7). In the *in-situ* sample, bright contrast regions consistent with higher-atomic-number Ag/Ti-containing domains were uniformly dispersed on the SBA-15 particles. The nonselective catalyst displayed large and irregularly distributed bright regions, characteristic of localized aggregation. The grafted Ag– TiO_2 /SBA-15 showed few bright regions on the external surface. Because SEM-BSE cannot separate external deposition from pore-confined incorporation, this observation alone does not confirm where the Ag– TiO_2 is located in the grafted sample. But when it is considered together with the smaller crystallite size and the weaker Ti–O–Si peak of the grafted sample, the few bright regions are more likely to originate from a lower amount of well-integrated Ag– TiO_2 rather than from a large amount confined inside the channels. Three different synthesis routes (*in-situ*, grafted, and nonselective) thus produce three different distributions of Ag and TiO_2 with respect to the SBA-15, and these structural differences additionally also appear in the optical, electronic, and catalytic properties described in the following sections.

4.2 Optical and electronic consequences of structural integration

The optical analysis shows that the synthesis route also affects the optical properties of the three catalysts. From the UV/Vis DRS analysis, the Tauc band gap (E_g) of the three samples was obtained (Figure 4). The *in-situ* sample's $E_g = 2.91 \pm 0.02$ eV, was significantly lower than the grafted (3.15 ± 0.01 eV) and nonselective (3.14 ± 0.01 eV) samples ($n = 3$, $p < 0.001$ for both comparisons). No significant difference in E_g was observed between the grafted and nonselective samples ($p = 0.593$). A decrease of about 0.23–0.24 eV in the *in-situ* sample cannot be explained by only one reason. Several factors may contribute, including changes in Ti–O–Si bonding, defect-related electronic states, and electronic coupling between TiO_2 and metallic Ag (22). The presence of a Ti^{3+} -related contribution is suggested by the XPS Ti 2p result, where the *in-situ* sample showed a weak tail near 457–458 eV that was not clearly resolved in the other two samples (Figure 8). However, the relative Ti^{3+} fraction was not quantitatively determined, so a higher Ti^{3+} concentration in the *in-situ* catalyst cannot be established from the present XPS data. Moreover, the *in-situ* DRS spectrum showed a strong absorption tail in the 450–600 nm region, consistent with visible-light absorption involving Ag-related plasmonic and/or interfacial electronic contributions (12, 22).

The $E_{0,0}$ values provide additional information. The values of $E_{0,0}$ followed the order nonselective (2.35 ± 0.01 eV) > grafted (2.24 ± 0.01 eV) > *in-situ* (2.15 ± 0.01 eV) ($n = 3$), with significant differences among all three catalysts ($p < 0.001$). In every sample, $E_{0,0}$ was lower than the corresponding E_g . The $E_g - E_{0,0}$ differences

indicate the presence of lower-energy optical transitions that are not represented by the Tauc band-edge estimate and may involve defect- or interface-related states (34). However, the specific electronic states responsible for these transitions cannot be identified from steady-state absorption and emission measurements alone. The lower E_g and $E_{0,0}$ of the *in-situ* sample are therefore consistent with its enhanced response to visible-light excitation, rather than constituting direct evidence for a particular charge-transfer pathway.

The PL data further demonstrate substantial differences in steady-state radiative recombination behavior (Figure 3). The integrated PL emission areas over 450–700 nm were $1.29 \pm 0.06 \times 10^4$ a.u.·nm for the *in-situ* catalyst, $1.42 \pm 0.05 \times 10^5$ a.u.·nm for the grafted catalyst, and $5.35 \pm 0.20 \times 10^4$ a.u.·nm for the nonselective catalyst ($n = 3$; $p < 0.001$). The *in-situ* sample exhibited the lowest emission intensity, which is consistent with reduced steady-state radiative electron–hole recombination. This result does not directly demonstrate a longer carrier lifetime because time-resolved PL was not performed. The grafted sample showed the highest PL intensity, suggesting comparatively greater radiative recombination under the measurement conditions. The nonselective sample showed an intermediate PL intensity. These differences are compatible with synthesis-dependent interfacial charge-transfer behavior, but the exact charge-transfer pathway and carrier lifetime require time-resolved measurements for direct confirmation.

4.3 Structure–activity correlation in photocatalytic degradation

The photocatalytic results followed the same overall ranking observed across the structural and optical measurements. In the methylene blue (MB) and phenol removal experiments, the *in-situ* catalyst's k_{app} values of $0.0194 \pm 0.0005 \text{ min}^{-1}$ and $0.0108 \pm 0.0004 \text{ min}^{-1}$, respectively ($n = 3$) were the highest. The k_{app} values of the grafted catalyst were $0.0121 \pm 0.0004 \text{ min}^{-1}$ and $0.0067 \pm 0.0003 \text{ min}^{-1}$, respectively, while those of the nonselective catalyst were $0.0087 \pm 0.0003 \text{ min}^{-1}$ and $0.0043 \pm 0.0002 \text{ min}^{-1}$. Therefore, the pollutant removal followed the order *in-situ* > grafted > nonselective, and was additionally non-dependent on pollutant chemical characteristics. The same order was also observed later in the particle-size reduction of PE. In addition, because the changes observed in the photolysis and dark controls were smaller than those under the irradiated catalyst conditions, substrate-specific adsorption or direct photolysis alone cannot explain this consistent performance order. However, because separate adsorption-isotherm experiments were not performed, differences in adsorption characteristics among the catalysts cannot be completely excluded.

For all three catalysts, the k_{app} value derived from phenol-associated absorbance loss was ~ 49 –56% of the MB k_{app} value for the same catalyst. This slower apparent removal rate can be related to differences in the structure and reaction behavior of the substrates. Phenol is generally known to be oxidized through multiple hydroxylation and ring-opening steps through intermediates such as catechol and hydroquinone (35). However, because these intermediates were not directly analyzed in this study, this pathway is a mechanistic interpretation based on previous studies rather than a result directly confirmed in the present experiment. In addition, catechol,

hydroquinone, and other aromatic intermediates may contribute to absorbance in the UV region. Therefore, the decrease at 270 nm cannot selectively distinguish parent phenol disappearance from intermediate formation and should not be interpreted as direct evidence of phenol mineralization.

The PE microplastic experiment revealed the same catalyst-efficiency ranking for a solid substrate. The initial $D_v(50)$ of PE was $41.8 \pm 0.7 \mu\text{m}$, and after 6 h of irradiation it decreased to $26.5 \pm 0.5 \mu\text{m}$ with the *in-situ* catalyst, $31.2 \pm 0.5 \mu\text{m}$ with the grafted catalyst, and $34.9 \pm 0.6 \mu\text{m}$ with the nonselective catalyst. These correspond to $D_v(50)$ -based particle-size reductions of $36.6 \pm 1.4\%$, $25.4 \pm 1.3\%$, and $16.5 \pm 1.2\%$, respectively ($n = 3$). PE is chemically stable, has few functional groups that can easily initiate radical attack, and absorbs very little water (36). Although photocatalytic oxidation and fragmentation of PE have been reported in previous studies, the present experiment did not directly measure chemical oxidation of the polymer. The optical analysis and PL results in this study are consistent with the greater particle-size change observed with the *in-situ* catalyst, but they do not establish the chemical mechanism responsible for this change. ROS generation, oxygen-containing functional groups on the PE surface, molecular-weight changes, mass loss, and PE mineralization were not directly measured. Therefore, the observed decrease in $D_v(50)$ in this study should be interpreted strictly as a shift toward smaller particle sizes in the recovered $\geq 2 \mu\text{m}$ PE fraction, rather than evidence of complete PE degradation or mineralization.

The reuse experiment also showed the same

order among the catalysts. After five consecutive PE treatments, the retained particle-size-reduction performance was $88.0 \pm 2.5\%$ for the *in-situ* catalyst, $72.4 \pm 3.2\%$ for the grafted catalyst, and $60.0 \pm 3.9\%$ for the nonselective catalyst ($n = 3$). The relatively strong Ti–O–Si-related signal observed by FTIR and the other structural-analysis results are consistent with the possibility that stronger interaction between the catalyst and support contributed to the retention of performance. However, Ag leaching, structural changes in the catalyst after repeated use, and catalyst mass loss during the recovery process were not quantitatively measured. Accordingly, these results establish synthesis-protocol-dependent differences in operational performance retention, while the mechanisms responsible for those differences remain unresolved.

4.4 Synthesis history as a materials-design variable

To compare the photocatalytic performance of the catalysts prepared in this study with previous studies, the k_{app} values of the three catalysts were compared with those of previously reported Ag–TiO₂ and TiO₂/SBA-15 systems. Liang et al. (38) reported a k_{app} of 0.011 min^{-1} for grafted Ag–TiO₂/SBA-15 in MB degradation. Naik et al. (39) reported a k_{app} of 0.009 min^{-1} for TiO₂/SBA-15 nanocomposites prepared by an aqueous synthesis method. These values provide reference points for comparison with the results of this study. However, because pollutant concentration, catalyst loading, wavelength and intensity of irradiation, and reactor structure differ among studies, there are limitations in directly comparing the k_{app} values.

The k_{app} for MB removal for the *in-situ* Ag–

TiO₂/SBA-15 was $0.0194 \pm 0.0005 \text{ min}^{-1}$, which is $\sim 1.8\text{--}2.2$ times higher than the values reported in the two studies above. The k_{app} for phenol treatment was $0.0108 \pm 0.0004 \text{ min}^{-1}$, which was higher than the $0.004\text{--}0.008 \text{ min}^{-1}$ range reported for previous Ag–TiO₂ systems (40). Because the present phenol value was derived from UV absorbance at 270 nm rather than from chromatographic quantification, this comparison should be interpreted as evaluating apparent kinetic responses rather than direct mineralization rates. Therefore, comparison with previously reported systems indicates that the *in-situ* catalyst achieved competitive photocatalytic performance under the conditions evaluated. However, because experimental conditions differed among studies, these comparisons do not establish that the present catalyst is intrinsically superior to previously reported systems. Nevertheless, the mutually consistent trends across XRD, FTIR, UV–Vis DRS, PL, XPS, SEM, photocatalytic activity, and reusability support the interpretation that the *in-situ* protocol produced distinct interfacial and optical characteristics associated with higher photocatalytic performance under the conditions evaluated.

Apart from the comparison of absolute performance, a main feature of this study is that three synthesis methods, *in-situ*, grafted, and nonselective, were systematically compared under similar nominal Ag/Ti compositions and identical photocatalytic testing conditions. Most previous studies reported either grafted Ag–TiO₂ or *in-situ* Ag–TiO₂ separately, making a direct comparison between different synthesis methods difficult. In this study, the three catalysts were characterized using the same analytical methods and evaluated under the same visible-light

photocatalytic conditions. As a result, differences in E_g , $E_{0,0}$, integrated PL emission, crystallite size, k_{app} , PE particle-size reduction, and reuse performance differences could be attributed to synthesis method. This shows that the overall synthesis process is an important design variable when designing Ag–TiO₂/SBA-15 photocatalysts. However, because the heat-treatment and hydrothermal-treatment conditions were not identical among the three synthesis methods, the observed differences cannot be explained only by the effect of the incorporation step.

4.5 Limitations and future work

Although the *in-situ* Ag–TiO₂/SBA-15 in this study showed good photocatalytic performance, there are still several limitations that should be acknowledged.

First, the synthesis route was not isolated as the only variable in this study. The *in-situ* catalyst was prepared with a hydrothermal treatment and calcination at 540 °C, while the grafted and nonselective catalysts were prepared without hydrothermal treatment and calcined at 300–400 °C. The hydrothermal treatment and the higher calcination temperature can affect the TiO₂ crystallinity, the crystallite size, the Ti–O–Si condensation, the defect concentration, and the Ag dispersion. Hence the better performance of the *in-situ* catalyst cannot be assigned to the incorporation route alone. This study compares the complete synthesis protocols rather than the effect of the incorporation route by itself. A more rigorous comparison would need control experiments in which the grafted and nonselective catalysts are calcined at the same 540 °C, and this is left for future work.

Second, the *in-situ* catalyst was made from a P123-templated SBA-15 route, while the grafted and nonselective catalysts used commercial SBA-15. Hence the comparison also includes the difference in the template-directed assembly, not only the incorporation route. This study assumed that the 540 °C calcination fully removes the P123 template, but the complete removal was not checked by TGA, Raman, or elemental analysis. If some carbonaceous species remain, they may also affect the optical and photocatalytic properties. Therefore, whether the superior activity of the *in-situ* catalyst originates from the incorporation route, the template-directed mesostructure, or both cannot be fully separated in the present design.

Third, the behavior of the catalyst suspensions was not separately analyzed. Because Ag–TiO₂/SBA-15 was used as a powder catalyst dispersed in water in this study, differences in aggregation, sedimentation, and colloidal stability among the three catalysts may have affected the actual illuminated surface area, contact between pollutants and catalysts, and mass transfer. Therefore, in future studies, sedimentation profiles, hydrodynamic particle size, or zeta potential should be measured to determine whether suspension behavior contributes to the observed differences in performance.

Fourth, MB and phenol were quantified using single-wavelength UV/Vis absorbance rather than compound-specific chromatographic analysis. Loss of MB absorbance at 664 nm primarily reflects decolorization or apparent removal and does not demonstrate complete degradation or mineralization. Similarly, absorbance at 270 nm is not fully selective for

parent phenol because aromatic oxidation intermediates may contribute to the same UV region. Liquid Chromatography-Mass Spectroscopy (LC-MS) analysis would be required to distinguish parent-compound disappearance from intermediate formation, while total organic carbon (TOC) analysis would be required to quantify mineralization.

Fifth, the PE analysis has limitations arising from particle recovery and particle-size measurement. Density separation using NaI was used to preferentially separate the lower-density PE from the higher-density inorganic catalyst, but complete recovery of PE and complete removal of catalyst particles were not separately verified. Therefore, heteroaggregates in which PE and catalyst were strongly associated may not have been completely separated. In addition, because a 2 µm membrane was used, the reported D_v(10), D_v(50), and D_v(90) represent only the recovered PE fraction larger than 2 µm. Particles and degradation products smaller than 2 µm were excluded from the analysis. Therefore, the laser diffraction results quantify changes in the recovered PE particle-size distribution rather than total PE mass loss or mineralization. Chemical oxidation of PE was also not established because carbonyl-index FTIR or XPS measurements of treated PE, molecular-weight analysis, oxidation-product identification, and mass-loss or TOC/CO₂ measurements were not performed. Moreover, a shift toward smaller PE particles should not automatically be interpreted as an environmental benefit, because fragmentation may increase the abundance and mobility of smaller microplastic particles.

Sixth, the photocatalytic experiments in this study were performed using a single laboratory-

scale visible-light source. The lamp-to-reactor distance, irradiance, and temperature were controlled at 10 cm, $\sim 100 \text{ mW/cm}^2$, and $27.5 \pm 0.5 \text{ }^\circ\text{C}$, respectively. However, in the actual environment, the wavelength distribution and intensity of sunlight change over time, and real wastewater contains various organic and inorganic substances together. Therefore, the photocatalytic performance obtained under the laboratory light source cannot be directly extended to performance in the actual environment. In future studies, experiments using a solar simulator and real wastewater samples are needed.

In addition, the reuse experiment in this study was performed for only five cycles. Therefore, the short-term retention of catalyst performance can be confirmed, but this is not sufficient to claim long-term durability for industrial use. Also, because no fresh catalyst was added to compensate for the amount lost after catalyst recovery, the decrease in performance over repeated cycles may include not only deactivation of the catalyst itself but also physical catalyst loss during centrifugation, washing, and transfer. The amount of Ag leached into the solution was also not measured. Therefore, to evaluate long-term durability, quantitative analysis of Ag leaching using ICP-MS together with more than 20 reuse cycles is needed.

Finally, the mechanistic interpretation of this study is mainly based on steady-state characterization such as UV/Vis DRS, PL, FTIR, and XRD. These analyses can indirectly infer charge behavior, but they cannot directly measure actual charge transfer over time. ROS generation and oxidation products on the PE surface were also not directly analyzed.

Therefore, future studies should directly analyze charge-transfer pathways and radical species using transient absorption spectroscopy and *in-situ* EPR, and the chemical changes of treated PE should also be measured.

In future work, matched control catalysts in which calcination temperature, hydrothermal treatment, SBA-15 source, and nominal composition are independently controlled should first be prepared. This would allow the effect of the incorporation route itself to be separated from the other synthesis variables identified in this study. Long-term reuse performance, Ag leaching, suspension stability, and mass and chemical changes of PE should also be quantitatively examined. The catalyst should then be applied to a continuous-flow photoreactor rather than a batch reactor and evaluated under conditions closer to actual wastewater treatment. Finally, computational methods such as DFT and kinetic Monte Carlo (kMC) can be used together with experiments to analyze the metal–support interaction at the Ag–TiO₂/SBA-15 interface at the atomic level (40, 41).

4.6 Perspective: Co-formation as a Materials-Design Principle

The findings of this study may be viewed in the context of a broader materials-design principle: components that are integrated during material formation can exhibit properties that are not reproduced by physically mixing or sequentially depositing the same nominal constituents. Final composition describes which components are present, but it does not fully describe their spatial organization, interfacial contact, electronic coupling, or accessibility. Consequently, two materials with comparable nominal

compositions may perform differently because their synthesis histories produce different functional structures.

This principle is observed in several fields. In pharmaceutical technology, co-processed excipients can exhibit better flow, compressibility, disintegration, and reduced segregation than physical mixtures of the same excipients because joint processing modifies particle architecture and component distribution (42). Similarly, hot-melt extrusion and other amorphous-solid-dispersion methods can disperse drug molecules within a polymeric phase, producing dissolution behavior that cannot generally be reproduced by simply mixing the crystalline drug and polymer (43). Pharmaceutical cocrystals likewise demonstrate that organized solid-state association can generate properties distinct from those of the corresponding physical mixture (44). In polymer nanocomposites, *in-situ* formation can improve nanoscale filler dispersion and interfacial contact relative to post-formation blending, thereby changing electrical, mechanical, and transport properties (45).

A closely related principle operates in heterogeneous catalysis. Catalytic activity is not determined solely by the quantity of an active component but also by the structure of the active-component-support interface. Metal-support interactions can modify local electronic states, adsorption behavior, charge transfer, resistance to particle migration, and the accessibility of active sites (46). Because many of these effects occur over nanometre or atomic-length scales, they may not be predicted from bulk composition alone. Co-assembly during support formation may therefore generate interfacial environments

and spatial distributions that cannot be completely recreated by grafting active species onto a preformed support.

The present results are consistent with this wider process-structure-property framework. Although the three Ag-TiO₂/SBA-15 protocols used comparable nominal Ag/Ti precursor compositions, the *in-situ* protocol introduced the Ti and Ag precursors during formation of the mesoporous silica structure. This provided an opportunity for the active and supporting phases to develop concurrently rather than being combined only after formation of the SBA-15 support. The relatively stronger Ti-O-Si-related FTIR feature, altered XPS contribution, enhanced visible-light absorption, lower steady-state PL emission, and consistently greater apparent photocatalytic response of the *in-situ* material are compatible with the formation of a more functionally integrated composite.

The present experiment does not establish which particular structural feature produced this advantage. It also cannot completely separate co-assembly from the effects of hydrothermal treatment, calcination temperature, or SBA-15 preparation. Nevertheless, the agreement among multiple independent observations supports a testable hypothesis: the performance advantage of the *in-situ* protocol arises not merely from the presence of Ag, TiO₂, and SBA-15, but from the history-dependent organization of their interfaces. In this interpretation, the material is not simply the sum of its components; its synthesis pathway determines the interfacial state through which those components interact.

Future studies should therefore compare matched materials using equivalent thermal histories and

precursor contents while progressively varying the stage at which Ag and Ti species are introduced. Spatially resolved elemental mapping, nitrogen adsorption, transmission electron microscopy, quantitative Ti–O–Si analysis, time-resolved spectroscopy, and leaching measurements could then determine whether increasing integration during material formation predicts dispersion, interfacial coupling, charge separation, activity, and reuse stability. Such experiments would move the field from comparing named synthesis routes toward identifying measurable degrees of interfacial integration.

5. Conclusion

This study shows that Ag–TiO₂/SBA-15 cannot be adequately described by nominal composition alone. Although the three materials were prepared with comparable nominal Ag/Ti precursor compositions and evaluated under the same photocatalytic conditions, they did not behave as interchangeable combinations of Ag, TiO₂, and silica. Instead, the in-situ, grafted, and nonselective protocols produced a persistent functional hierarchy of in-situ > grafted > nonselective across methylene blue, phenol, and polyethylene particle-size experiments. The central conclusion is therefore not merely that one catalyst performed better than the others, but that the pathway by which the components were assembled appears to have created materially different functional states.

The observed advantage is not explained simply by the nominal identities or proportions of the constituents. One possible explanation could involve the organization of those constituents across multiple length scales. Introducing Ag and Ti precursors while the SBA-15 framework is

forming may alter their spatial distribution, degree of confinement, interfacial contact with silica, aggregation state, and accessibility to reactants. It may also change the density or character of Ti–O–Si linkages, Ag–TiO₂ electronic coupling, Ti³⁺ or oxygen-vacancy-related states, crystallite development, pore accessibility, and the distances over which photogenerated charge carriers must migrate. None of these properties is specified by bulk composition alone. They are products of synthesis history and may collectively determine whether the resulting material behaves as an integrated composite or as supported phases that remain comparatively segregated.

The agreement among structural, optical, and functional observations makes this interpretation plausible. The in-situ material combined Ti–O–Si-related, XPS, optical-absorption, photoluminescence, and XRD differences with the highest apparent response for three chemically distinct substrates. Because methylene blue is a cationic dye, phenol is a neutral aromatic compound, and polyethylene is a solid hydrophobic polymer, the repeated ranking is less readily explained by a single substrate-specific interaction. It instead points toward a more general difference in the material, such as interfacial organization, charge behavior, active-phase dispersion, accessible surface structure, or suspension behavior. The present evidence does not identify which of these possibilities is dominant, but it narrows the scientific question from whether the protocols produce different performance to which history-dependent material property mediates that difference.

Alternative explanations must nevertheless

remain open. The in-situ material underwent hydrothermal treatment, higher-temperature calcination, and template-directed SBA-15 formation, whereas the grafted and nonselective materials used commercial SBA-15 and different thermal histories. The observed superiority could therefore arise from co-assembly, thermal processing, pore architecture, crystallite development, residual template-derived species, actual rather than nominal Ag/Ti loading, colloidal stability, or some interaction among these variables. These are not merely experimental nuisances. From a materials-science perspective, they are candidate formation variables that may define the final functional material. The present study compares complete synthesis protocols and therefore establishes protocol-level superiority under the conditions tested, rather than isolating incorporation route as the sole causal factor.

The findings consequently support a broader process–structure–property hypothesis: when active and supporting phases develop concurrently, the resulting interfaces may acquire properties that cannot be reproduced by depositing or physically combining the same constituents after support formation. Similar behavior is found in co-processed excipients, amorphous solid dispersions, pharmaceutical cocrystals, polymer nanocomposites, and supported metal catalysts, where joint formation produces functional properties not predictable from a simple inventory of components. In this framework, an Ag–TiO₂/SBA-15 catalyst is not only a mixture of Ag, TiO₂, and mesoporous silica. It is a history-dependent material whose performance may depend on how, when, and under what conditions its interfaces were created.

The present measurements define this hypothesis but do not yet prove its microscopic mechanism. Absorbance loss for methylene blue and phenol does not establish complete degradation or mineralization, while the polyethylene results demonstrate redistribution toward smaller particles in the recovered $\geq 2 \mu\text{m}$ fraction rather than polymer destruction, oxidation, or mass loss. Similarly, steady-state photoluminescence, FTIR, XPS, XRD, and SEM provide mutually consistent but indirect evidence of altered interfacial and electronic structure. The conclusions should therefore be understood as internally convergent rather than mechanistically definitive.

The decisive next experiment is not simply to repeat the photocatalytic tests, but to decompose “synthesis route” into measurable formation variables. A matched factorial design should independently vary the stage of Ag and Ti introduction, SBA-15 source, hydrothermal treatment, calcination temperature, and calcination duration while holding actual elemental loading constant. ICP-MS or XRF, nitrogen sorption, TEM with elemental mapping, quantitative surface analysis, zeta potential, time-resolved spectroscopy, EPR measurements of reactive species, and leaching analysis could then determine whether performance follows actual loading, pore structure, dispersion, defect chemistry, suspension stability, or degree of interfacial integration. Compound-specific chromatography and total organic carbon analysis should establish whether improved apparent removal corresponds to parent-compound disappearance or mineralization, while chemical, molecular-weight, and mass-balance measurements are required to determine whether polyethylene undergoes oxidation or

merely fragmentation.

The most important outcome of this study is therefore a shift in the design question. Future work should move beyond asking which named synthesis route performs best and instead ask which measurable degree of interfacial integration is created by that route and whether it predicts function across materials and substrates. If such a relationship is confirmed under matched conditions, interfacial integration could become a controllable design variable for Ag–TiO₂/SBA-15 and other multicomponent materials. The present study provides the

comparative evidence and testable framework needed to pursue that transition from composition-based formulation to synthesis-history-based materials design.

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6. References

1. United Nations Environment Programme. (2019). *Global environment outlook GEO-6: Healthy planet, healthy people*. Cambridge University Press.
2. Luo, Y., Guo, W., Ngo, H. H., Nghiem, L. D., Hai, F. I., Zhang, J., Liang, S., & Wang, X. C. (2014). A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Science of the Total Environment*, 473–474, 619–641. <https://doi.org/10.1016/j.scitotenv.2013.12.065>
3. Marselina, M., Wibowo, F., & Mushfiroh, A. (2022). Water quality index assessment methods for surface water: A case study of the Citarum River in Indonesia. *Heliyon*, 8(7). <https://doi.org/10.1016/j.heliyon.2022.e09848>
4. Varjani, S., Joshi, R., Srivastava, V. K., Ngo, H. H., & Guo, W. (2020). Treatment of wastewater from petroleum industry: current practices and perspectives. *Environmental Science and Pollution Research*, 27(22), 27172–27180. <https://doi.org/10.1007/s11356-019-04725-x>
5. U.S. Environmental Protection Agency. (2022). *Industrial wastewater treatment technology database: Phenolic and aromatic compounds in refinery effluents* (EPA Report No. EPA-821-R-22-004).
6. Jiang, Y.-Y., Zeng, Y., Long, L., Guo, J., Lu, R.-F., Chen, P.-P., Pan, Z.-J., Zhang, Y.-T., Luo, X.-J., & Mai, B.-X. (2024). First report on the trophic transfer and priority list of liquid crystal monomers in the Pearl River Estuary. *Environmental Science & Technology*, 58(36), 16131–

16141. <https://doi.org/10.1021/acs.est.4c04962>

7. Chong, M. N., Jin, B., Chow, C. W., & Saint, C. (2010). Recent developments in photocatalytic water treatment technology: A review. *Water Research*, 44(10), 2997–3027. <https://doi.org/10.1016/j.watres.2010.02.039>

8. Fujishima, A., Rao, T. N., & Tryk, D. A. (2000). Titanium dioxide photocatalysis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 1(1), 1–21. [https://doi.org/10.1016/S1389-5567\(00\)00002-2](https://doi.org/10.1016/S1389-5567(00)00002-2)

9. Jiang, R., Li, B., Fang, C., & Wang, J. (2014). Metal/semiconductor hybrid nanostructures for plasmon-enhanced applications. *Advanced Materials*, 26(31), 5274–5309. <https://doi.org/10.1002/adma.201400203>

10. Schneider, J., Matsuoka, M., Takeuchi, M., Zhang, J., Horiuchi, Y., Anpo, M., & Bahnemann, D. W. (2014). Understanding TiO₂ photocatalysis: Mechanisms and materials. *Chemical Reviews*, 114(19), 9919–9986. <https://doi.org/10.1021/cr5001892>

11. Li, X., Yu, J., Low, J., Fang, Y., Xiao, J., & Chen, X. (2015). Engineering heterogeneous semiconductors for solar water splitting. *Journal of Materials Chemistry A*, 3(6), 2485–2534. <https://doi.org/10.1039/C4TA04461D>

12. Ninakanti, R., Dingenen, F., Borah, R., Peeters, H., & Verbruggen, S. W. (2022). Plasmonic hybrid nanostructures in photocatalysis: Structures, mechanisms, and applications. *Topics in Current Chemistry*, 380(5), 40. <https://doi.org/10.1007/s41061-022-00390-w>

13. Verma, P., Kuwahara, Y., Mori, K., Raja, R., & Yamashita, H. (2020). Functionalized mesoporous SBA-15 silica: recent trends and catalytic applications. *Nanoscale*, 12(21), 11333–11363. <https://doi.org/10.1039/D0NR00732C>

14. Santra, C., Shah, S., Mondal, A., Pandey, J. K., Panda, A. B., Maity, S., & Chowdhury, B. (2016). Synthesis, characterization of VPO catalyst dispersed on mesoporous silica surface and catalytic activity for cyclohexane oxidation reaction. *Microporous and Mesoporous Materials*, 223, 121–128. <https://doi.org/10.1016/j.micromeso.2015.10.046>

15. Yu, J., Wang, W., Cheng, B., & Su, B. L. (2009). Enhancement of photocatalytic activity of mesoporous TiO₂ powders by hydrothermal surface fluorination treatment. *The Journal of Physical Chemistry C*, 113(16), 6743–6750. <https://doi.org/10.1021/jp900136q>

16. Ulfa, M., Al Afif, H., Saraswati, T. E., & Bahruji, H. (2022). Fast removal of methylene blue

via adsorption-photodegradation on TiO₂/SBA-15 synthesized by slow calcination. *Materials*, 15(16), 5471. <https://doi.org/10.3390/ma15165471>

17. He, Z. Q., Wang, D., Fang, H. Y., Chen, J. M., & Song, S. (2014). Highly efficient and stable Ag/AgIO₃ particles for photocatalytic reduction of CO₂ under visible light. *Nanoscale*, 6(18), 10540–10544. <https://doi.org/10.1039/C4NR02450H>

18. Ma, J., Qiang, L. S., Tang, X. B., & Tang, D. Y. (2010). TiO₂/SBA-15: Rapid synthesis and photocatalytic performance. *Chinese Journal of Inorganic Chemistry*, 26(6), 963–969.

19. Jardim, A. A. M. L. F., Bacani, R., Gonçalves, N. S., Fantini, M. C. A., & Martins, T. S. (2017). SBA-15:TiO₂ nanocomposites: II. Direct and post-synthesis using acetylacetone. *Microporous and Mesoporous Materials*, 239, 235–243. <https://doi.org/10.1016/j.micromeso.2016.10.009>

20. Estrella-Pajulas, L. L., & Gamala, B. J. I. (2024). A review on the synthesis, characterization, and recent advancements of visible light-activated C-TiO₂ nanomaterials for environmental remediation. *Next Nanotechnology*, 6, 100082. <https://doi.org/10.1016/j.nxnano.2024.100082>

21. Kernazhitsky, L., Shymanovska, V., Gavrilko, T., Naumov, V., Fedorenko, L., & Kshnyakin, V. (2013). Photoluminescence and optical absorption of pure nanocrystalline TiO₂ anatase and rutile at room temperature. *Journal of Nano- and Electronic Physics*, 5(3), 1–7.

22. Hussain, A., Rauf, A., Ahmed, E., Khan, M. S., Mian, S. A., & Jang, J. (2023). Modulating optoelectronic and elastic properties of anatase TiO₂ for photoelectrochemical water splitting. *Molecules*, 28(7), 3252. <https://doi.org/10.3390/molecules28073252>

23. Barbero, B. (2017). *Synthesis and in-situ ATR studies of nanostructured titania photocatalysts for the degradation of aqueous organic pollutants* [Doctoral dissertation, Aston University]. Aston University Research Archive.

24. Stepanova, A., Tite, T., Ivanenko, I., Enculescu, M., Radu, C., Culita, D. C., Rostas, A. M., & Galca, A. C. (2023). TiO₂ phase ratio's contribution to the photocatalytic activity. *ACS Omega*, 8(44), 41664–41673. <https://doi.org/10.1021/acsomega.3c05890>

25. Kılıç, B., Gedik, N., Mucur, S. P., Hergul, A. S., & Gür, E. (2015). Band gap engineering and modifying surface of TiO₂ nanostructures by Fe₂O₃ for enhanced performance of dye sensitized solar cell. *Materials Science in Semiconductor Processing*, 31, 363–371. <https://doi.org/10.1016/j.mssp.2014.12.020>

26. Monshi, A., Foroughi, M. R., & Monshi, M. R. (2012). Modified Scherrer equation to estimate more accurately nano-crystallite size using XRD. *World Journal of Nano Science and Engineering*, 2(3), 154–160. <https://doi.org/10.4236/wjnse.2012.23020>
27. Pham, X. N., Pham, T. D., Nguyen, B. M., Tran, H. T., & Pham, D. T. (2018). Synthesis of Al-MCM-41@Ag/TiO₂ nanocomposite and its photocatalytic activity for degradation of dibenzothiophene. *Journal of Chemistry*, 2018(1), 8418605. <https://doi.org/10.1155/2018/8418605>
28. El Atti, O., Hot, J., Fajerwerg, K., Lorber, C., Lebeau, B., Ryzhikov, A., Kahn, M., Collière, V., Coppel, Y., Ratel-Ramond, N., Ménini, P., & Fau, P. (2024). Synthesis of TiO₂/SBA-15 nanocomposites by hydrolysis of organometallic Ti precursors for photocatalytic NO abatement. *Inorganics*, 12(7), 183. <https://doi.org/10.3390/inorganics12070183>
29. Cherif, Y., Azzi, H., Sridharan, K., Ji, S., Choi, H., Allan, M. G., Benaissa, S., Saidi-Bendahou, K., Dampsey, L., Ribeiro, C. S., Krishnamurthy, S., Nagarajan, S., Maroto-Valer, M. M., Kuehnel, M. F., & Pitchaimuthu, S. (2023). Facile synthesis of gram-scale mesoporous Ag/TiO₂ photocatalysts for pharmaceutical water pollutant removal and green hydrogen generation. *ACS Omega*, 8(1), 1249–1261. <https://doi.org/10.1021/acsomega.2c06657>
30. Cui, L., Ren, L., Chen, Z., Zhu, B., Xu, C., & Wei, G. (2026). Facile preparation of a plasmon-enhanced Ag-CuO/TiO₂ for the efficient visible-light-driven photodegradation of tetracycline hydrochloride. *Materials*, 19(11), 2189. <https://doi.org/10.3390/ma19112189>
31. Preethi, L. K., Antony, R. P., Mathews, T., Walczak, L., & Gopinath, C. S. (2017). A study on doped heterojunctions in TiO₂ nanotubes: an efficient photocatalyst for solar water splitting. *Scientific Reports*, 7(1), 14314. <https://doi.org/10.1038/s41598-017-14463-0>
32. Zhang, M., Yu, X., Lu, D., & Yang, J. (2013). Facile synthesis and enhanced visible light photocatalytic activity of N and Zr co-doped TiO₂ nanostructures from nanotubular titanic acid precursors. *Nanoscale Research Letters*, 8(1), 543. <https://doi.org/10.1186/1556-276X-8-543>
33. Jin, B. (2013). C@ Ag/TiO₂: A highly efficient and stable photocatalyst active under visible light. *World Journal of Nano Science and Engineering*, 3(1), 1–5. <https://doi.org/10.4236/wjnse.2013.31001>
34. Lettieri, S., Pavone, M., Fioravanti, A., Santamaria Amato, L., & Maddalena, P. (2021). Charge carrier processes and optical properties in TiO₂ and TiO₂-based heterojunction photocatalysts: A review. *Materials*, 14(7), 1645. <https://doi.org/10.3390/ma14071645>

35. Tao, Y., Cheng, Z. L., Ting, K. E., & Yin, X. J. (2013). Photocatalytic degradation of phenol using a nanocatalyst: The mechanism and kinetics. *Journal of Catalysts*, 2013, 364275. <https://doi.org/10.1155/2013/364275>
36. Nabi, I., Bacha, A.-U.-R., Li, K., Cheng, H., Wang, T., Liu, Y., Ajmal, S., Yang, Y., Feng, Y., & Zhang, L. (2020). Complete photocatalytic mineralization of microplastic on TiO₂ nanoparticle film. *iScience*, 23(7), 101326. <https://doi.org/10.1016/j.isci.2020.101326>
37. Tofa, T. S., Kunjali, K. L., Paul, S., & Dutta, J. (2019). Visible light photocatalytic degradation of microplastic residues with zinc oxide nanorods. *Environmental Chemistry Letters*, 17(3), 1341–1346. <https://doi.org/10.1007/s10311-019-00859-z>
38. Liang, L., Meng, Y., Shi, L., Ma, J., & Sun, J. (2014). Enhanced photocatalytic performance of novel visible light-driven Ag-TiO₂/SBA-15 photocatalyst. *Superlattices and Microstructures*, 73, 60–70. <https://doi.org/10.1016/j.spmi.2014.05.008>
39. Naik, B., Manoratne, C. H., Chandrashekhar, A., Iyer, A., Prasad, V. S., & Ghosh, N. N. (2013). Preparation of TiO₂, Ag-doped TiO₂ nanoparticle and TiO₂-SBA-15 nanocomposites using simple aqueous solution-based chemical method and study of their photocatalytical activity. *Journal of Experimental Nanoscience*, 8(4), 462–479. <https://doi.org/10.1080/17458080.2011.597435>
40. Li, N., Ma, Y., & Sun, W. (2024). Exploring the dynamics of charge transfer in photocatalysis: applications of femtosecond transient absorption spectroscopy. *Molecules*, 29(17), 3995. <https://doi.org/10.3390/molecules29173995>
41. Wei, B., Cui, X., Calatayud, M., Salahub, D. R., Dixon, D. A., & Pacchioni, G. (2025). Dynamic catalysis multiscale simulations for nonoxidative coupling of methane using light and heat. *ACS Catalysis*, 15(2), 832–845. <https://doi.org/10.1021/acscatal.4c04312>
42. Daraghmeh, N., Rashid, I., Al Omari, M. M. H., Leharne, S. A., Chowdhry, B. Z., & Badwan, A. (2010). Preparation and characterization of a novel co-processed excipient of chitin and crystalline mannitol. *AAPS PharmSciTech*, 11(4), 1558–1571. <https://doi.org/10.1208/s12249-010-9523-8>
43. Agrawal, A. M., Dudhedia, M. S., & Zimny, E. (2016). Hot melt extrusion: Development of an amorphous solid dispersion for an insoluble drug from mini-scale to clinical scale. *AAPS PharmSciTech*, 17(1), 133–147. <https://doi.org/10.1208/s12249-015-0425-7>

44. Al-Kazemi, R., Al-Basarah, Y., & Nada, A. (2019). Dissolution enhancement of atorvastatin calcium by cocrystallization. *Advanced Pharmaceutical Bulletin*, 9(4), 559–570. <https://doi.org/10.15171/apb.2019.064>
45. Baniasadi, H., Ramazani, A., & Javan Nikkhah, S. (2010). Investigation of in situ prepared polypropylene/clay nanocomposites properties and comparing to melt blending method. *Materials & Design*, 31(1), 76–84. <https://doi.org/10.1016/j.matdes.2009.07.014>
46. Shi, Y., Ma, Z. R., Xiao, Y. Y., Yin, Y. C., Huang, W. M., Huang, Z. C., Zheng, Y. Z., Mu, F. Y., Huang, R., Shi, G. Y., Sun, Y. Y., Xia, X. H., & Chen, W. (2021). Electronic metal–support interaction modulates single-atom platinum catalysis for hydrogen evolution reaction. *Nature Communications*, 12(1), Article 3021. <https://doi.org/10.1038/s41467-021-23306-6>