Synthesis and Characterization of g-C₃N₄/Ag₃PO₄/TiO₂/PVDF Membrane with Remarkable Self-Cleaning Properties for Rhodamine B Removal

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Abstract: g-C₃N₄/Ag₃PO₄/TiO₂ nanocomposite materials were loaded onto a polyvinylidene fluoride (PVDF) membrane using a phase inversion method to obtain a photocatalytic flat membrane for dye removal. The morphology, structure, and photocatalytic activity of the g-C₃N₄/Ag₃PO₄/TiO₂ nanoparticles and composite membrane were evaluated. The g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membrane exhibited superior morphology, hydrophilic properties, and antifouling performance compared with the raw PVDF membrane. Four-stage filtration was performed to evaluate the self-cleaning and antifouling capacity of the g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membrane. Upon irradiating the composite membrane with visible light for 30 min, its irreversible fouling resistance (Rir) was low (9%), and its flux recovery rate (FRR) was high (71.0%) after five filtration cycles. The removal rate of rhodamine B (RhB) from the composite membrane under visible light irradiation reached 98.1% owing to the high photocatalytic activity of the membrane, which was superior to that of raw PVDF membrane (42.5%). A mechanism of photocatalytic composite membranes for RhB degradation was proposed. Therefore, this study is expected to broaden prospects in the field of membrane filtration technology.

Keywords: g-C₃N₄/Ag₃PO₄/TiO₂ nanocomposite; photocatalytic membrane; self-cleaning; membrane fouling; dye

1. Introduction

Rhodamine B (RhB) is one of the most popular dyes for printing, textile, and leather industries, which could cause pollution to the environment if not treated appropriately. Traditional physical methods, such as physical adsorption, coagulation, and chemical oxidation, and biological methods have been unable to achieve the efficient treatment of dye wastewater. Membranes with good selectivity, high efficiency, and excellent stability are widely used to treat municipal drinking water and wastewater. Membranes with good selectivity, high efficiency, and excellent stability are widely used to treat municipal drinking water and wastewater. However, membrane fouling and further treatment of concentrated contaminant solutions are bottlenecks that have hindered the development of membrane separation technologies [1,2]. Surface modifications, which increase the hydrophilicity and improve the self-cleaning ability of membranes, are effective methods for enhancing the antifouling properties of membranes. Polyvinylidene fluoride (PVDF) has been widely employed in many areas because it involves a simple preparation process, can be easily modified, presents high strength, and is inexpensive [3,4]. However, PVDF membranes should be modified to confer on them hydrophilic properties and improve their anti-pollution performance. Among the various modification methods studied, the introduction of inorganic nanocomponents into PVDF membranes is an effective approach because nanoparticles present surface and interface effects; moreover, a small amount of dopant can confer on membranes many new functions. Recently, doping PVDF membranes with nanoparticles with photocatalytic properties, such as Fe(NO)₃ [5],...
were evaluated. The renewability of the composite membrane over repeated RhB pho-
tocatalytic degradation and rejection rate of the composite membrane for RhB in solution
were evaluated. Since photocatalysts can effectively degrade contaminants in solu-
tions and on the membrane surface, photocatalyst-loaded membranes present outstanding
removal efficiency and remarkable anti-pollution performance [19,20].

Graphitic carbon nitride (g-C₃N₄), which primarily comprises C and N, presents
remarkable application potential owing to its excellent photocatalytic performance and
chemical stability. However, the photocatalytic activity of pure g-C₃N₄ has the disadvan-
tages of a high carrier recombination rate, sparse adsorption sites, and active sites above
450 nm, which result in a volatile photocatalytic efficiency [21,22]. The recombination rate
of photogenerated carriers in composites fabricated using two or more semiconductors (or
heterojunction structures) is lower than that of their individual components; therefore, the
photocatalytic performance of composites is superior to that of their individual components.
Numerous semiconductor materials, such as MoO₃ [23], TiO₂ [24], ZnO [25], SnO₂ [26],
ZrO₂ [27], BIOI [28], Ag₃PO₄ [29–31], and graphene oxide (GO) [8,32], were coupled with
g-C₃N₄ to accelerate the separation of photogenerated electron–hole pairs and increase
the bandgap energy. Among them, Ag₃PO₄ has been applied as a highly effective compo-
und for the visible-light-driven photodegradation of various organic pollutants in an
aqueous solution; however, it is prone to photocorrosion in practical applications. The
electric field that typically forms upon coupling g-C₃N₄ with Ag₃PO₄ can significantly
increase the transfer rate of photogenerated charge carriers [29]. The simultaneous addi-
tion of TiO₂ and Ag₃PO₄ to g-C₃N₄ inhibits the photocorrosion of Ag₃PO₄ because the band
positions of TiO₂ and Ag₃PO₄ match. Furthermore, other methods aimed at im-
proving photocatalytic activity by combining g-C₃N₄ with Ag₃PO₄ and other Ag-based
compounds or TiO₂ to form heterojunctions have been successfully developed. Abbasi-Asl
et al. [30] prepared a TiO₂/Ag₃PO₄/g-C₃N₄ semiconductor composite and used it for
the degradation of metronidazole (MNZ). The photodegradation efficiency of the com-
posite nanoparticles for MNZ reached 97.18% under optimal experimental conditions.
The comparison experiment showed that the photocatalytic efficiency of ternary compos-
ites (TiO₂/Ag₃PO₄/g-C₃N₄) was far better than that of pure and binary samples. Cui
et al. [22] fabricated g-C₃N₄/Ag₃PO₄/PVDF photocatalytic porous membranes using a
phase inversion method and utilized them for RhB removal. The removal efficiency of the
g-C₃N₄/Ag₃PO₄/PVDF membrane for RhB reached 97%, which was superior to those of the
g-C₃N₄/PVDF and pure PVDF membranes (85% and 41%, respectively).

In this study, a novel type of hydrophilic PVDF membrane loaded with g-C₃N₄/Ag₃PO₄/
TiO₂ photocatalytic nanocomposite was prepared via blending and phase inversion. The
morphology, structure, and photocatalytic activity of the g-C₃N₄/Ag₃PO₄/TiO₂ nanoparticles
and composite membrane were characterized and evaluated. A four-stage filtration
experiment was used to evaluate the membrane performance for the separation of bovine
serum albumin (BSA) and the membrane self-cleaning mechanism. Additionally, the pho-
tocatalytic degradation and rejection rate of the composite membrane for RhB in solution
were evaluated. The renewability of the composite membrane over repeated RhB pho-
tocatalytic degradation and adsorption cycles was also evaluated. A mechanism of photocatalytic
composite membranes for RhB degradation was proposed.

2. Material and Methods

2.1. Materials

Commercial PVDF (MW 200,000 Da) was purchased from Guangdong Zhan Yang Co.,
Ltd. (Guangzhou, China). Melamine, titanium dioxide, N₃,N-dimethylacetamide (DMAc),
polyvinylpyrrolidone (PVP), silver nitrate (AgNO₃), disodium phosphate (Na₂HPO₄), BSA,
RhB, and hydrochloric acid (HCl) were acquired from Aladdin.
2.2. Synthesis of g-C₃N₄

g-C₃N₄ was prepared via melamine pyrolysis using a one-step synthesis method. Melamine (10 g) was added to a porcelain crucible with a lid and calcinated at 550 °C under a heating rate of 5 °C/min in a muffle furnace for 2 h, and then it was cooled to 25 °C. The obtained milky yellow powder was purified with a 1.0 M HCl solution at 150 °C under a heating rate of 3 °C/min for 4 h. Eventually, the fabricated solid was collected through centrifugation, followed by drying, and ground into a uniform powder using an agate mortar and pestle prior to further use [31,33].

2.3. Synthesis of g-C₃N₄/Ag₃PO₄/TiO₂ Nanocomposites

Ag₃PO₄ was synthesized via precipitation. g-C₃N₄/Ag₃PO₄/TiO₂ composite nanoparticles were prepared simultaneously as follows: 0.4 g of g-C₃N₄, 1.0 g of PVP, and 0.4 g of TiO₂ were added to 80 mL of distilled water (suspension 1). After 15 min of intermittent ultrasonication, the suspension was subjected to magnetic stirring for 30 min. Next, 5.1 g AgNO₃ was added to suspension 1 (mixture 2). Thereafter, 100 mL of a 0.1 mol/L Na₃HPO₄ solution was added dropwise to mixture 2 using a burette. After the mixture was stirred for 3 h in the dark, a yellow sediment was separated via centrifugation, followed by rinsing three times with water and ethanol, alternately. Lastly, the residue was dried to a constant weight in a vacuum oven at 50 °C.

2.4. Preparation of Photocatalytic Composite Membranes

PVDF-based photocatalytic membranes using PVP as the pore former were synthesized by blending g-C₃N₄/TiO₂/Ag₃PO₄ nanoparticles with PVDF using phase inversion technique. In brief, 1.5 g of g-C₃N₄/TiO₂/Ag₃PO₄ nanoparticles, 2.0 g of PVP, and 40.0 g of DMAC were added to a 250 mL beaker placed in a 60 °C oil bath, and the reactants were stirred at a constant speed until the mixture became transparent. Thereafter, 7.5 g of PVDF powder was added to the beaker step by step with continuous stirring for 6 h at 60 °C to form a homogeneous and transparent casting mixture. Next, the mixture was placed in a vacuum-drying oven for 12 h at 60 °C to remove air bubbles. After degassing at 20 °C and 70% humidity, the dopant mixture was uniformly spread on a clean glass plate using a coater with 200 μm gap. The glass plate was allowed to rest in ambient air for 30 s, and then it was placed in a coagulation bath at 20 °C. Lastly, the prepared membrane was placed in ultrapure water for 24 h. Figure 1 shows the schematics of the preparation of the nanoparticles and the photocatalytic composite membranes.

![Schematics of nanocomposite synthesis and membrane preparation.](image)

2.5. Characterization of the g-C₃N₄/Ag₃PO₄/TiO₂ Nanocomposites

The crystalline structure and phase purity of the photocatalyst powders were analyzed using an Ultima4 (Rigaku) X-ray diffraction (XRD) instrument. The morphology of the
photocatalyst powders was evaluated using a JSM 7001F (JEOL) SEM apparatus. An F-4500 (Hitachi Corp.) photoluminescence (PL) spectrometer was used to investigate the photochemical properties of the samples.

2.6. Membrane Characterization

The roughness and morphology of the membrane surfaces were evaluated using the SEM JSM 7001F (JEOL, Tokyo, Japan) and a Dimension Icon (Bruker, Madison, WI, USA) AFM device, respectively. TGA experiments were conducted using a Q500IR (TA Instruments, New Castle, DE, USA) system. The interfacial interactions and crystallinity in the membranes were analyzed using an IS10 (Thermo Fisher, Waltham, MA, USA) FTIR spectrometer. The mechanical performance of the membranes was measured using a CMT4204 electronic universal testing machine (XinSanSi, Shanghai, China) at room temperature. The hydrophilic performance of the membranes was estimated by testing their water contact angles with an OCA 40 (Dataphysics, San Jose, CA, USA) goniometer. The sessile drop technique with dynamic contact angle measurement was used, and contact angles were measured for 30 s [34].

2.7. Basic Properties of Membranes

2.7.1. Permeability Measurements

The prepared membranes were placed in a dead-end stirred ultrafiltration cup to evaluate their permeability (Figure 2). The effective filtration area of the ultrafiltration cup was 50.2 cm$^2$. Permeability measurements were performed under an operating pressure of 0.1 MPa, as follows: The membrane was pre-pressured with deionized water until the permeate flux and operating pressure were stabilized. The volume of deionized water passing through the membrane was determined within 5 min. The permeate flux was calculated as follows:

$$J_0 = \frac{V}{At}$$

where $J_0$ is initial permeate flux of deionized water (L/(m$^2$ h)), $V$, $A$, and $t$ are the volume of deionized water collected within 5 min (L), effective filtration area (m$^2$), and time employed during filtration (h), respectively.

![Figure 2. Schematic of dead-end stirred ultrafiltration cup setup.](image-url)
The pore size and porosity of the membrane were measured by a weighing method. The operation process and calculation formula were similar to the existing reports [35]. The porosity ($\varepsilon$) was calculated as follows:

$$\varepsilon = \frac{m_w - m_d}{\rho_b \times V_d}$$  \hspace{1cm} (2)

where $m_d$ and $m_w$ are the weight of the membrane before and after immersion in n-butanol, $\rho_b$ is the density of n-butanol, and $V_d$ is the dry membrane volume.

2.7.2. Membrane reusability

After the membranes were pre-pressurized with deionized water, the feed solution was changed to a 0.2 g/L BSA solution, and the stable flux values ($J_{pf}$) were calculated using Equation (1). The concentration of BSA in the permeate was determined after 30 min, and the rejection of BSA (R) was calculated as follows:

$$R(\%) = (1 - \frac{C}{C_0}) \times 100\%$$  \hspace{1cm} (3)

where $C_0$ (mg/L) and $C$ (mg/L) are related to the contaminant concentrations before and after filtration, respectively.

Subsequently, the fouled membrane was rinsed repeatedly with deionized water, and its permeate flux ($J_{rw}$) was recorded after 10 min. Lastly, the membrane was illuminated using a Xe lamp, and the water flux ($J_w$) was determined after 30 min. This process was repeated five times. The flux recovery ratio (FRR), total fouling ratio ($R_t$), reversible fouling ratio ($R_r$), and irreversible fouling ratio ($R_{ir}$) of the membranes were calculated as follows:

$$\text{FRR} = \frac{J_w}{J_0} \times 100\%$$  \hspace{1cm} (4)

$$R_t = \frac{J_0 - J_{pf}}{J_0} \times 100\%$$  \hspace{1cm} (5)

$$R_r = \frac{J_w - J_{pf}}{J_0} \times 100\%$$  \hspace{1cm} (6)

$$R_{ir} = \frac{J_0 - J_w}{J_0} \times 100\%$$  \hspace{1cm} (7)

2.7.2. Removal of RhB Using the Photocatalytic Membrane

A 10 mg/L solution of RhB, which was used to simulate wastewater, was filtered using an ultrafiltration cup and the photocatalytic membrane under the illumination of a 300 W Xe lamp. During this process, a piece of 420 nm cutoff filter was applied to cover the top of the ultrafiltration cup. The system was kept in dark for 30 min to reach adsorption equilibrium before light illumination. During the visible light illumination, 3 mL of permeate solution was collected from the ultrafiltration cup every 7.5 min and analyzed using an ultraviolet (UV)–visible (Vis) spectrophotometer at 554 nm to determine the concentration of residual RhB. The rejection of RhB was calculated using Equation (3). The time evolution of the concentration of RhB was fitted using the following pseudo-first-order kinetic equation:

$$\ln \frac{C}{C_0} = -kt$$  \hspace{1cm} (8)

where $k$ (min$^{-1}$) represents the rate constant and $t$ is the time employed during filtration.

3. Results and Discussion

3.1. Characterization of the g-C$_3$N$_4$/Ag$_3$PO$_4$/TiO$_2$ Nanocomposites

SEM images of g-C$_3$N$_4$, Ag$_3$PO$_4$/TiO$_2$, and g-C$_3$N$_4$/Ag$_3$PO$_4$/TiO$_2$ are shown in Figure 3. A two-dimensional, micrometer-sized, solid agglomerated structure of g-C$_3$N$_4$
was homogeneously formed (Figure 3a). g-C3N4 presented a typical thin lamellar structure of graphite-phase C3N4 with distinct folds, which conferred on it its large specific surface area. Ag3PO4 comprised 300–500 nm spheres, which connected tightly with the ultra-thin g-C3N4 layers (Figure 3b). The Ag3PO4/TiO2 nanoparticles presented a regular spherical shape similar to that of the pure Ag3PO4 particles that attached to the g-C3N4 sheets (Figure 3c,d).

Figure 3. SEM images of (a) g-C3N4, (b) Ag3PO4/TiO2, and (c,d) g-C3N4/Ag3PO4/TiO2.

Figure 4a shows the XRD patterns of pure g-C3N4, Ag3PO4/TiO2, and g-C3N4/Ag3PO4/TiO2. The characteristic peaks in the XRD pattern of pure g-C3N4 at 2θ = 27.8° (strong) and 12.6° (weak) were attributed to the (002) and (100) planes of g-C3N4, respectively [36]. The peaks at 20.80°, 29.68°, 33.31°, 36.59°, 42.54°, 47.78°, 52.60°, 55.05°, 57.29°, 61.62°, 65.81°, 69.94°, 71.89°, and 73.85° in the XRD pattern of Ag3PO4 corresponded to planes (110), (200), (210), (211), (220), (310), (222), (320), (321), (400), (330), (420), (421), and (322), respectively, of cubic-phase Ag3PO4. No impurity peaks were present in the XRD patterns of the samples, and the sharp peaks indicate good crystallization of the samples [33]. It is noteworthy that in the ternary catalyst, the (002) and (100) planes of g-C3N4 disappeared, while the diffraction peak of Ag3PO4 was more prominent, which indicated that the crystal of Ag3PO4 grew. As shown in Figure 4b, it was clear that the PL peak intensity of C3N4 was the highest, that is, the photogenerated electron–hole recombination of its monomer was the easiest. However, the spectral PL intensity of g-C3N4/Ag3PO4/TiO2 composites was significantly suppressed in comparison to g-C3N4 or Ag3PO4/TiO2, which showed that the ternary composite catalyst had the highest photogenerated current-carrying separation efficiency and the lowest recombination rate of the photogenerated charge carriers [37]. That is to say, the composite of g-C3N4/Ag3PO4/TiO2 can effectively improve the diffusion rate and charge mobility of photogenerated charge.
Figure 4. (a) XRD patterns and (b) PL spectra of g-C₃N₄, Ag₃PO₄/TiO₂, and g-C₃N₄/Ag₃PO₄/TiO₂.

3.2. Membrane Characterizations

3.2.1. Membrane Morphology

Figure 5a,b show the SEM images of the surface and cross-section of the raw PVDF membrane, respectively, whereas Figure 5c,d show those of the g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membrane. Surface and cross-sectional images were used to study the dispersion of nanoparticles on the PVDF membrane and probe the thickness and homogeneity of the coating layer. As shown in Figure 5a,c, the raw PVDF membrane displayed a cavity-like structure, and the composite membrane presented a dense top layer supported by a porous layer in the surface image. All cross-sections of membranes showed an asymmetric microscopic porous structure and spongy layers surrounding a finger-like macroscopic cavity. By contrast, the finger-like pore wall of the composite membrane appeared rougher and more porous. The addition of nanoparticles to PVDF promoted the demixing rate by increasing the thermodynamic instability of the membrane. During phase inversion, g-C₃N₄/Ag₃PO₄/TiO₂ nanoparticles strongly adsorbed water molecules, which provided abundant sites for the infiltration of water molecules and led to pore formation in the surface layer of the membrane.

Figure 5. SEM images of the (a) top surface and (b) cross-section of the raw PVDF membrane, and (c) top surface and (d) cross-section of the g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membrane.
Figure 6 shows the AFM images of the raw PVDF and g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membranes. Unlike the PVDF membrane, the g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membrane presented distinct ridges and valleys on its surface; furthermore, more holes were obtained on the surface of the composite membrane than on the surface of the raw PVDF membrane. The higher surface roughness of the composite membrane was attributed to the nodular structures that formed on the top layer of the membrane owing to the aggregation of the photocatalytic material. The Rₑ values of the raw PVDF and g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membranes were 93 and 309 nm, respectively, and the Rₑ values of the raw and composite membranes were 113 and 395 nm, respectively. These data indicated that the surface of the composite membrane was rougher than that of the raw membrane, which provided optimal conditions for adequate contact between photocatalytic materials and contaminants in solutions. This was attributed to the nodular structure generated via the aggregation of photocatalytic material on the membrane surface [8,38]. It was worth noting the results did not match with reference [15] which indicated that the addition of a ternary composite of Ag₃PO₄/GO/APTES decreased the roughness of PVDF membranes.

**Figure 6.** AFM images of surface of the (a,b) raw PVDF membrane and (c,d) g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membrane.

### 3.2.2. Basic Properties of Membranes

Some basic properties of two types of membranes are shown in Table 1 and Figure 7. The result of the porosity test was consistent with that of the SEM. The thickness of the composite membrane was higher than that of the raw membrane owing to the presence of nanoparticles. Tensile strength measurements were used to investigate the mechanical properties of raw and composite membranes. As shown in Table 1, the tensile stress of the g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membrane was lower than that of the raw PVDF membrane. That can be explained by the fact that more porous structures could decrease the membrane’s mechanical performance. Likewise, agglomeration resulting from excessive incorporation of g-C₃N₄/Ag₃PO₄/TiO₂ made the dispersion of particles in the polymer matrix nonuniform. When the membrane worked under the action of an external force, the
internal stress concentration polarization took place, resulting in the decreased mechanical performance [5].

Table 1. Characteristics of different membranes.

| Membrane           | Thickness (µm) | Porosity (%) | Tensile Strength (MPa) |
|--------------------|----------------|--------------|------------------------|
| raw membrane       | 176 ± 19       | 70 ± 7       | 9.3 ± 1.0              |
| composite membrane | 186 ± 17       | 85 ± 3       | 7.5 ± 1.9              |

Figure 7. (a) FTIR analysis, (b) TGA curves, and (c) dynamic contact angle of the raw PVDF and g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membranes.

As shown in Figure 7a, there are no obvious differences in the FTIR spectra between the raw and composite membranes. The obtained results show that relative overlapping is the dominant phenomenon in these spectra. The distinct peaks at 1440 and 1170 cm⁻¹ in the FTIR spectra of the raw PVDF and g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membranes were attributed to the C–H deformation vibration and the C–F vibration, respectively. Furthermore, the absence of the characteristic absorption peaks of Ag₃PO₄ in the FTIR spectra of the g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membrane was attributed to the relatively low amount of Ag₃PO₄ or overlap with other peaks [39].

Two types of membranes were heated at 15 °C/min at temperatures ranging from 25 °C to 700 °C. The TGA curves of the raw PVDF and g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membranes, which were used to evaluate the thermal stability of the membranes (Figure 7b), showed that the TGA curves of the raw and composite membranes were comparable, which was attributed to the decomposition and evaporation of small polymer fragments at high temperatures. The significant mass loss (72.3%) in the range of 306–473 °C was attributed to the thermal decomposition of the PVDF backbone. A distinct weight loss was exhibited in the TGA curve of g-C₃N₄/Ag₃PO₄/TiO₂/PVDF as the temperature was increased from 317 to 540 °C, and the weight loss rate was ~60.9% at 700 °C. The weight loss rate and quantity of the g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membrane were lower than those of the raw PVDF membrane. This was attributed to the addition of composite particles forming hydrogen or coordination bonds between organic macromolecular interactions, hindering the thermal...
motion of molecules and the movement of macromolecular chains. Consequently, the energy needed to break the bonds increased, and the thermal stability of the membrane increased [35]. Cacho-Bailo [40] obtained similar results by adding a metal–organic skeleton to polysulfone membranes.

Surface hydrophilicity is a critical factor for the anti-pollution performance of membranes. Generally, the lower the contact angle, the higher the membrane’s hydrophilic performance; in other words, the greater the resistance against fouling. The contact angle of the raw PVDF membrane (83.15°) was higher than that of the composite membrane (70.32°) (Figure 7c). This was attributed to the nanoparticles loaded on the top layer of the PVDF membrane. Overall, the addition of g-C_3N_4/Ag_3PO_4/TiO_2 to PVDF improved membrane hydrophilicity. Generally, the more hydrophilic composites added, the stabler and denser the hydration layer which could rule out more contaminant molecules was obtained. At the same time, hydrogen bonds formed between g-C_3N_4 and water molecules, which promoted the diffusion of water molecules in the membrane and weakened the adsorption of contaminants on the membrane surface [41,42]. The hydrophilicity improvement of the membrane also resulted from the hydroxyl radical produced by the composite nanoparticles. In addition, according to previous studies [43,44], surface roughness can improve membrane wettability owing to the formation of composite nanoparticle layers. A few contaminant molecules could accumulate in the “valleys” on the surface accordingly. These results were consistent with the aforementioned SEM and AFM results.

3.2.3. Antifouling Performance of Membranes

The ratios of reversible and irreversible fouling (R_r and R_i, respectively) to the total fouling (R_t) of the membranes are critical parameters for evaluating the antifouling performance of membranes (Figure 8a,b). R_r represents the fouling molecules that are tightly anchored to the membrane surface and trapped within its pores, whereas R_i primarily represents the foulant that is loosely bound to the membrane surface. Before visible light irradiation, the R_i values of the membranes were higher than the corresponding R_r values (Figure 8a,b), indicating that irreversible fouling was the predominant process. The R_r value of the composite membrane decreased considerably, from 61.1% to 8.9%, whereas the R_i value increased significantly, from 33.7% to 85.3%. For the composite membrane, a fraction of irreversible fouling was converted into reversible fouling. Notably, the R_r values of the g-C_3N_4/Ag_3PO_4/TiO_2/PVDF membrane were remarkably greater than those of the raw PVDF membrane under both experimental conditions. Therefore, the addition of photocatalytic nanomaterials to PVDF improved the antifouling ability of the raw PVDF membrane.

In practice, it is necessary to evaluate the antifouling properties of membranes. Therefore, we subjected both membranes to four-stage filtration experiments for five cycles. The FRR values of both membranes decreased gradually after each cycle (Figure 8c), which was attributed to the accumulation of irreversible sums and the adsorption of dirt in the membrane pores. However, the composite nanoparticles promoted the self-cleaning ability of the membrane and lowered the FRR value of the g-C_3N_4/Ag_3PO_4/TiO_2/PVDF membrane from 90.1% to 71.0%. In contrast, the FRR value of the raw PVDF membrane decreased from 78.9% to 50.3% after five filtration cycles. This was attributed to the photocatalytic performance and high hydrophilicity of the g-C_3N_4/Ag_3PO_4/TiO_2 nanoparticles on the membrane surface, which could prevent the accumulation of foulant on the membrane surface during filtration. The BSA rejection of the raw and composited membranes was higher than 90% during the five filtration cycles. The addition of g-C_3N_4/Ag_3PO_4/TiO_2 to PVDF increased the BSA rejection and flux of the PVDF membrane.

3.2.4. Photocatalytic Properties of Membranes

Figure 9a,b show the photocatalytic degradation efficiency and kinetic model of RhB, respectively. The blank test demonstrated that RhB rejection did not change in the absence of a membrane, so the photodecomposition of RhB was negligible.
Figure 8. (a) The antifouling property and (b) the ratio of irreversible fouling to reversible fouling of the membranes, and (c) the flux recovery ratio and rejection of BSA (initial BSA concentration of 300 mg/L, pH = 6.9).

Figure 9. (a) Membrane performance for the photocatalytic degradation of RhB, (b) kinetic model for the photocatalytic degradation of RhB, and (c) changes in the UV–Vis spectra of RhB with reaction time (initial RhB concentration of 10 mg/L, pH = 6.4).
The amount of RhB decreased only by 42.5% after 120 min of filtration using the raw PVDF membrane (Figure 9a). RhB removal by the raw PVDF membrane occurred exclusively via absorption. In contrast, the degradation efficiency of the g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membrane for RhB was significantly higher (98.1%) under visible light irradiation. The kinetic equation \(-\ln(C/C_0) = kt\) was used to evaluate the photodegradation of RhB (Figure 9b). The k value of the raw PVDF membrane (0.00549 min\(^{-1}\)) was negligible as it was approximately seven times lower than that of the composite membrane (0.03618 min\(^{-1}\)) under the same experimental conditions. These results indicate that the g-C₃N₄/Ag₃PO₄/TiO₂ coating improved the photocatalytic activity of the PVDF membrane. The UV–Vis absorption spectra of an RhB solution subjected to photodegradation using the g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membrane under visible light irradiation for 90 min are shown in Figure 9c. The maximum absorption peaks at 554 nm declined significantly, consistent with the results shown in Figure 9a.

The membranes were used to remove RhB for five cycles, and the experimental data provided information about the reusability and stability of the g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membrane. The removal rates of RhB using the composite membrane and a dead-end stirred ultrafiltration cup under visible light irradiation for five cycles were 98.1%, 97.0%, 96.5%, 95.6%, and 95.3%, respectively (Figure 10a). After five cycles, the photocatalytic performance of the composite membrane was still as excellent as in its original state. The low attenuation rate after the five experimental cycles indicates the excellent stability and regeneration capacity of the composite membrane, for the reason that the g-C₃N₄/Ag₃PO₄/TiO₂ nanoparticles are stably bound in the membrane without loss.

![Figure 10](image-url) (a) Photocatalytic activity and (b) cycling test and reusability of g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membranes under visible light irradiation for five cycles (initial RhB concentration of 10 mg/L, pH = 6.4).

### 3.3. Mechanism of the g-C₃N₄/Ag₃PO₄/TiO₂/PVDF Membrane

The photodegradation mechanism of RhB by the C₃N₄/Ag₃PO₄/TiO₂/PVDF membrane is shown in Figure 11. First, RhB molecules were electrostatically adsorbed onto the surface and within the pores of the membrane. Subsequently, the C₃N₄/Ag₃PO₄/TiO₂ nanoparticles became excited under visible light irradiation and photogenerated electrons and holes migrated to the surface of the nanocomposite.

According to previous studies [30,45,46], the bandgap energies of C₃N₄, Ag₃PO₄, and TiO₂ are approximately 2.76, 2.31, and 3.20 eV, respectively. The conduction band (CB) of g-C₃N₄ (−1.16 eV) is more negative than those of TiO₂ (−0.29 eV) and Ag₃PO₄ (−0.299 eV); therefore, superoxide radicals (•O₂⁻) can be generated as the photoinduced electrons in the CB of g-C₃N₄ reduce the absorbed O₂. Similarly, the electrons in the CB of TiO₂ migrated to Ag₃PO₄. Furthermore, the valence band (VB) potential of Ag₃PO₄ (+2.61 eV) was more positive than those of g-C₃N₄ (+1.60 eV) and the H₂O/•OH pair (+2.38 eV); therefore, •OH active species can be formed via the oxidation of H₂O by the holes in the VB of Ag₃PO₄ [47]. Subsequently, the strong oxidizing radicals (•O₂⁻ and •OH) and...
photogenerated holes could thoroughly oxidize RhB into CO₂ and H₂O. In addition, Ag⁺
ions can be reduced to metallic Ag with the help of generating enough energy, which can
be excited by Ag₃PO₄ and g-C₃N₄ under light irradiation. The photogenerated electrons
in the CB of Ag₃PO₄ can be transferred to metallic Ag via the constructed Ag bridge
and bind to the holes in the VB of g-C₃N₄ [47,48]. According to previously published
papers [49–51], the hybrid C₃N₄/Ag₃PO₄/TiO₂ ternary composite photocatalyst had a
higher electron–hole pair separation efficiency and a lower recombination rate than the
binary composite photocatalyst.

![Figure 11. Photocatalytic degradation process in the g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membrane.](image)

4. Conclusions

In summary, g-C₃N₄/Ag₃PO₄/TiO₂ nanocomposites were prepared and used as
precursors to fabricate g-C₃N₄/Ag₃PO₄/TiO₂/PVDF photocatalyst membranes using the
phase inversion method. The g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membrane presented excellent
self-cleaning properties and high RhB removal performance during membrane separation
and photodegradation. Therefore, our results demonstrated that the nanocomposites
improved the antifouling and self-cleaning performance of the membrane. Furthermore,
the visible-light-driven photocatalytic degradation of RhB on the membrane surface by
the g-C₃N₄/Ag₃PO₄/TiO₂ nanoparticles conferred the composite membrane’s excellent
self-cleaning ability and remarkable regeneration capacity.

The photocatalytic performance of the g-C₃N₄/Ag₃PO₄/TiO₂/PVDF membrane has
been improved compared to previous studies of TiO₂-based photocatalytic membranes.
Mericq et al. [52] demonstrated that the TiO₂ nanoparticles improved the structure of the
membrane as well as its antifouling performance under UV irradiation. Zhang et al. [41]
found that Ag/g-C₃N₄ membranes degraded a maximum of 77% of methyl orange in
100 min. Cui et al. [22] fabricated g-C₃N₄/Ag₃PO₄/PVDF membranes for RhB removal
(97%), which were superior to those of g-C₃N₄/PVDF and pure PVDF membranes (85%
and 41%, respectively). It is worth noting that they did not take the mechanical properties
of the membrane and the exudation of nanoparticles into account. In fact, the incorporation
of g-C₃N₄/Ag₃PO₄/TiO₂ which resulted in the decreased mechanical performance of the
membrane cannot be ignored. Hence, the further improvement of the mechanical strength
of the membrane is one of the keys to the application of photocatalytic membranes in the
future. Overall, this study can expand the application of g-C₃N₄/Ag₃PO₄/TiO₂ as an ad-
vanced membrane material and the use of composite membranes for wastewater treatment.
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References

1. Zhou, A.; Jia, R.; Wang, Y.L.; Sun, S.H.; Xin, X.D.; Wang, M.Q.; Zhao, Q.H.; Zhu, H.H. Abatement of sulfadiazine in water under a modified ultrafiltration membrane (PVDF-PVP-TiO$_2$-dopamine) filtration-photocatalysis system. *Sep. Purif. Technol.* 2020, 234, 116099. [CrossRef]

2. Li, X.; He, S.B.; Feng, C.L.; Zhu, Y.K.; Pang, Y.; Hou, J.; Luo, K.; Liao, X.S. Non-competitive and competitive adsorption of Pb$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$ ions onto SDS in process of micellar-enhanced ultrafiltration. *Sustainability* 2018, 10, 92. [CrossRef]

3. Wan, J.; Huang, J.H.; Yu, H.B.; Liu, L.S.; Shi, Y.H.; Liu, C.H. Fabrication of self-assembled 0D-2D Bi$_2$MoO$_6$-g-C$_3$N$_4$ photocatalytic composite membrane based on PDA intermediate coating with visible light self-cleaning performance. *J. Colloid Interface Sci.* 2021, 601, 229–241. [CrossRef] [PubMed]

4. Lan, T.; Huang, J.H.; Ouyang, Y.C.; Yi, K.X.; Yu, H.B.; Zhang, W.; Zhang, C.Y.; Yi, S.Z. QQ-PAC core-shell structured quorum quenching beads for potential membrane antifouling properties. *Enzym. Microb. Technol.* 2021, 148, 109813. [CrossRef]

5. Yang, C.Y.; Wang, P.; Li, J.N.; Wang, Q.; Xu, P.; You, S.J.; Zheng, Q.Z.; Zhang, G.S. Photocatalytic PVDF ultrafiltration membrane blended with visible-light responsive Fe(III)-TiO$_2$ catalyst: Degradation kinetics, catalytic performance and reusability. *Chem. Eng. J.* 2021, 417, 129340. [CrossRef]

6. Naseem, S.; Wu, C.M.; Motora, K.G. Novel multifunctional Rb$_3$WO$_3$@Fe$_3$O$_4$ immobilized Janus membranes for desalination and synergic-photocatalytic water purification. *Desalination* 2021, 517, 115256. [CrossRef]

7. Huang, X.Z.; Liu, H.W.; Zhang, X.; Jiang, H.R. High Performance All-Solid-State Flexible Micro-Pseudocapacitor Based on Hierarchically Nanostructured Tungsten Trioxide Composite. *ACS Appl. Mater. Interfaces* 2015, 7, 27845–27852. [CrossRef] [PubMed]

8. Shi, Y.H.; Huang, J.H.; Zeng, G.M.; Cheng, W.J.; Hu, J.L.; Shi, L.X.; Yi, K.X. Evaluation of self-cleaning performance of the modified g-C$_3$N$_4$ and GO based PVDF membrane toward oil-in-water separation under visible-light. *Chemosphere* 2019, 230, 40–50. [CrossRef]

9. Kolesnyk, I.; Kujawa, J.; Bubela, H.; Konovalova, V.; Burban, A.; Cyganiuk, A.; Kujawski, W. Photocatalytic properties of PVDF membranes modified with g-C$_3$N$_4$ in the process of Rhodamines decomposition. *Sep. Purif. Technol.* 2020, 250, 117231. [CrossRef]

10. Huang, J.H.; Hu, J.L.; Shi, Y.H.; Zeng, G.M.; Cheng, W.J.; Yu, H.B.; Gu, Y.L.; Shi, L.X.; Yi, K.X. Evaluation of self-cleaning and photocatalytic properties of modified g-C$_3$N$_4$ based PVDF membranes driven by visible light. *J. Colloid Interface Sci.* 2019, 541, 356–366. [CrossRef]

11. Chen, X.J.; Huang, G.; Li, Y.P.; An, C.J.; Feng, R.F.; Wu, Y.H.; Shen, J. Functional PVDF ultrafiltration membrane for Tetrabromobisphenol-A (TBBPA) removal with high water recovery. *Water Res.* 2020, 181, 115952. [CrossRef] [PubMed]

12. Zhang, Y.Q.; Liu, P.L. Preparation of porous ZrO$_2$ solid superacid shell/void/TiO$_2$ core particles and effect of doping them on PVDF membranes properties. *Chem. Eng. Sci.* 2015, 135, 67–75. [CrossRef]

13. Chen, X.J.; Huang, G.; An, C.J.; Feng, R.F.; Wu, Y.H.; Huang, C. Plasma-induced PAA-ZnO coated PVDF membrane for oily wastewater treatment: Preparation, optimization, and characterization through Taguchi OA design and synchrotron-based X-ray analysis. *J. Membr. Sci.* 2019, 582, 70–82. [CrossRef]

14. Ayyar, S.; Dinh, T.T.L.; Ahn, Y.H. Enhanced antifouling performance of PVDF ultrafiltration membrane by blending zinc oxide with support of graphene oxide nanoparticle. *Chemosphere* 2020, 241, 125068. [CrossRef] [PubMed]

15. Zhang, R.; Li, Y.; Cai, Y.; Han, Y.; Zhang, T.Q.; Liu, Y.; Zeng, K.L.; Zhao, C. Photocatalytic Poly(vinylidene fluoride) membrane of Ag$_3$PO$_4$/GO/APTES for water treatment. *Colloids Surf. A* 2020, 597, 124779. [CrossRef]

16. Fan, G.D.; Chen, C.G.; Chen, X.L.; Li, Z.S.; Bao, S.L.; Luo, J.; Tang, D.S.; Yan, Z.S. Enhancing the antifouling and rejection properties of PVDF membrane by Ag$_3$PO$_4$-GO modification. *Sci. Total Environ.* 2021, 801, 149611. [CrossRef]

17. Safarpour, M.; Khataee, A.; Vatanpour, V. Effect of reduced graphene oxide/TiO$_2$ nanocomposite with different molar ratios on the performance of PVDF ultrafiltration membranes. *Sep. Purif. Technol.* 2015, 140, 32–42. [CrossRef]
18. Sakkar, S.; Muthukumar, S.; Jegatheesan, V. Factors affecting the degradation of remazol turquoise blue (RTB) dye by titanium dioxide (TiO$_2$) entrapped photocatalytic membrane. *J. Environ. Manag.* 2020, 272, 111090. [CrossRef]

19. Che, H.N.; Liu, L.H.; Che, G.B.; Dong, H.J.; Liu, C.B.; Li, C.M. Control of energy band, layer structure and vacancy defect of graphitic carbon nitride by intercalated hydrogen bond effect of NO$_3$– toward improving photocatalytic performance. *Biochem. Eng. J.* 2019, 159, 209–219. [CrossRef]

20. Yu, H.B.; Huang, J.H.; Jiang, L.B.; Yuan, X.Z.; Yi, K.X.; Zhang, W.; Zhang, J.; Chen, H.Y. Steering photo-excitons towards active sites: Intensified substrates affinity and spatial charge separation for photocatalytic molecular oxygen activation and pollutant removal. *Chem. Eng. J.* 2019, 368, 127334. [CrossRef]

21. Cai, G.H.; Wang, J.P.; Wu, X.Q.; Zhan, Y.Y.; Liang, S.J. Scalable one-pot synthesis of porous 0D/2D C$_3$N$_4$ nanocomposites for efficient visible-light driven photocatalytic hydrogen evolution. *Appl. Surf. Sci.* 2018, 459, 224–232. [CrossRef]

22. Cui, Y.H.; Yang, L.L.; Meng, M.J.; Zhang, Q.; Li, B.R.; Wu, Y.L.; Zhang, Y.L.; Lang, J.H.; Li, C.X. Facile preparation of antifouling g-C$_3$N$_4$/Ag$_2$PO$_4$ nanocomposite photocatalytic polynvinilidene fluoride membranes for effective removal of rhodamine B. *Korean J. Chem. Eng.* 2019, 36, 236–247. [CrossRef]

23. Liu, L.S.; Huang, J.H.; Yu, H.B.; Wan, J.; Liu, L.Y.; Yi, K.X.; Zhang, W.; Zhang, C.Y. Construction of MoO$_3$ nanoparticles / g-C$_3$N$_4$ nanosheets 0D/2D heterojunction photocatalysts for enhanced photocatalytic degradation of antibiotic pollutant. *Chemosphere* 2021, 282, 131049. [CrossRef] [PubMed]

24. Ni, S.; Fu, Z.; Li, L.; Ma, M.; Liu, Y. Step-scheme heterojunction g-C$_3$N$_4$/TiO$_2$ for efficient photocatalytic degradation of tetracycline hydrochloride under light. *Colloids Surf. A.* 2022, 649, 129475. [CrossRef]

25. Sun, Q.; Sun, Y.; Zhou, M.; Cheng, H.; Chen, H.; Dorus, B.; Lu, M.; Le, T. A 2D/3D g-C$_3$N$_4$/ZnO heterojunction enhanced visible-light driven photocatalytic activity for sulfonamides degradation. *Ceram. Int.* 2022, 48, 7283–7290. [CrossRef]

26. Van, K.N.; Hsu, H.T.; Nguyen Thi, V.N.; Le Thi, T.L.; Truong, D.H.; Truong, T.T.; Dao, N.N.; Vo, V.; Tran, D.L.; Vasquez, Y. Facile construction of S-scheme SnO$_2$/g-C$_3$N$_4$ photocatalyst for improved photocatalytic efficiency. *Chemosphere* 2022, 289, 131320. [CrossRef] [PubMed]

27. Khezami, L.; Ben Aissa, M.A.; Modwi, A.; Ismail, M.; Guesmi, A.; Algethimi, F.K.; Ben Ticha, M.; Assadi, A.A.; Nguyen-Tri, P. Harmonizing the photocatalytic activity of g-C$_3$N$_4$ nanosheets by ZrO$_2$ stuffing: From fabrication to experimental study for the wastewaster treatment. *Biochem. Eng. J.* 2022, 182, 108411. [CrossRef]

28. Yin, C.; Liu, Y.L.; Lv, X.Y.; Lv, S.Y.; Cheng, H.; Kang, X.R.; Li, X. Carbon dots as heterojunction transport mediators effectivelly enhance BiOI/g-C$_3$N$_4$ synergistic persulfate degradation of antibiotics. *Appl. Surf. Sci.* 2022, 601, 154249. [CrossRef]

29. Raeisi-Kheirabadi, N.; Nezamzadeh-Ejhieh, A. A Z-scheme g-C$_3$N$_4$/Ag$_2$PO$_4$ nanocomposite: Its photocatalytic activity and capability for water splitting. *Int. J. Hydrog. Energy* 2020, 45, 33381–33395. [CrossRef]

30. Abbasi-Asl, H.; Sabzehei, M.M.; Ghedi, M. Efficient degradation of metronidazole antibiotic by TiO$_2$/Ag$_2$PO$_4$/g-C$_3$N$_4$ ternary composite photocatalyst in a continuous flow-loop photoreactor. *J. Environ. Sci.* 2021, 9, 105963. [CrossRef]

31. Liu, L.; Qi, Y.H.; Lu, J.R.; Lin, S.L.; An, W.J.; Liang, Y.H.; Cui, W.Q. A stable Ag$_3$PO$_4@g$-C$_3$N$_4$ hybrid core@shell composite with enhanced visible light photocatalytic degradation. *Appl. Catal. B Environ.* 2016, 183, 133–141. [CrossRef]

32. Ikreeedegh, R.R.; Tahir, M. Facile fabrication of well-designed 2D/2D porous g-C$_3$N$_4$–GO nanocomposite for photocatalytic photocatalytic methane reforming (DRM) with CO$_2$ enhanced syngas production under visible light. *Fuel* 2021, 305, 121558. [CrossRef]

33. He, P.Z.; Song, L.M.; Zhang, S.J.; Wu, X.Q.; Wei, Q.W. Synthesis of g-C$_3$N$_4$/Ag$_3$PO$_4$ heterojunction with enhanced photocatalytic performance. *Mater. Res. Bull.* 2014, 51, 432–437. [CrossRef]

34. Rosman, N.; Norharyati Wan Salleh, W.; Aqilah Mohd Razali, N.; Nurain Ahmad, S.Z.; Hafiza Ismail, N.; Aziz, F.; Harun, Z.; Fauzi Ismail, A.; Yusof, N. Ibuprofen removal through photocatalytic filtration using antifouling PVDF-ZnO/Ag$_2$O/Ag$_2$O nanopaticles/g-C$_3$N$_4$ nanocomposites for high-efficiency water clean. *Sci. Total Environ.* 2020, 737, 139818. [CrossRef] [PubMed]

35. Pan, T.D.; Liu, Y.; Li, Z.J.; Fan, J.; Wang, L.; Liu, J.; Shou, W. A Sm-doped Egeria-densa-like ZnO nanowires@PVDF nanofiber membrane for high-efficiency water clean. *Chem. Asian J.* 2022, 17, 257–269. [CrossRef]

36. Lan, Z.A.; Zhang, G.G.; Wang, X.C. A facile synthesis of Br-modified g-C$_3$N$_4$ semiconductors for photocoredox water splitting. *Appl. Catal. B Environ.* 2016, 192, 116–125. [CrossRef]

37. Li, S.Y.; Zhang, M.; Qu, Z.H.; Cui, X.; Liu, Z.Y.; Piao, C.C.; Li, S.G.; Wang, J.; Song, Y.T. Fabrication of highly active Z-scheme Ag/g-C$_3$N$_4$-Ag$_2$PO$_4$ (1 1 0) photocatalyst photocatalyst for visible light photocatalytic degradation of levofloxacin with simultaneous hydrogen production. *Biochem. Eng. J.* 2020, 208, 122394. [CrossRef]

38. Arumugham, T.; Aminmodu, R.G.; Kallekkal, N.J.; Rana, D. Nano CuO/g-C$_3$N$_4$ sheets-based ultrafiltration membrane with enhanced interfacial affinity, antifouling and protein separation performances for water treatment application. *J. Environ. Sci.* 2019, 82, 57–69. [CrossRef]

39. Shao, L.Q.; Jiang, D.L.; Xiao, P.; Zhu, L.M.; Meng, S.C.; Chen, M. Enhancement of g-C$_3$N$_4$ nanosheets photocatalysis by synergistic interaction of ZnS microsphere and RGO inducing multistep charge transfer. *Appl. Catal. B Environ.* 2016, 198, 200–210. [CrossRef]

40. Cacho-Bailo, F.; Télechea, C.; Coronas, J. Interactive Thermal Effects on Metal–Organic Framework Polymer Composite Membranes. *Mater. Today Proc.* 2021, 42, 69–74. [CrossRef]

41. Zhang, M.Y.; Liu, Z.Y.; Gao, Y.; Shu, L. Ag modified g-C$_3$N$_4$ composite entrapped PES UF membrane with visible-light-driven photocatalytic antifouling performance. *RSC Adv.* 2017, 7, 42919–42928. [CrossRef]
42. Seyyed Shahabi, S.; Azizi, N.; Vatanpour, V. Synthesis and characterization of novel g-C$_3$N$_4$ modified thin film nanocomposite reverse osmosis membranes to enhance desalination performance and fouling resistance. *Sep. Purif. Technol.* **2019**, *215*, 430–440. [CrossRef]

43. Chen, J.X.; Li, Z.Y.; Wang, C.B.; Wu, H.; Liu, G. Synthesis and characterization of g-C$_3$N$_4$ nanosheet modified polyamide nanofiltration membranes with good permeation and antifouling properties. *RSC Adv.* **2016**, *6*, 112148–112157. [CrossRef]

44. Ravichandran, K.; Sindhuja, E. Fabrication of cost effective g-C$_3$N$_4$+Ag activated ZnO photocatalyst in thin film form for enhanced visible light responsive dye degradation. *Mater. Chem. Phys.* **2019**, *221*, 203–215. [CrossRef]

45. Mamba, G.; Mishra, A.K. Graphitic carbon nitride (g-C$_3$N$_4$) nanocomposites: A new and exciting generation of visible light driven photocatalysts for environmental pollution remediation. *Appl. Catal. B Environ.* **2016**, *198*, 347–377. [CrossRef]

46. Du, Y.E.; Li, W.X.; Bai, Y.; Huangfu, Z.W.; Wang, W.J.; Chai, R.D.; Chen, C.D.; Yang, X.J.; Feng, Q. Facile synthesis of TiO$_2$/Ag$_3$PO$_4$ composites with co-exposed high-energy facets for efficient photodegradation of rhodamine B solution under visible light irradiation. *RSC Adv.* **2020**, *10*, 24555–24569. [CrossRef]

47. Lv, J.L.; Dai, K.; Zhang, J.F.; Lu, L.H.; Liang, C.H.; Geng, L.; Wang, Z.L.; Yuan, G.Y.; Zhu, G.P. In situ controllable synthesis of novel surface plasmon resonance-enhanced Ag$_2$WO$_4$/Ag/Bi$_2$MoO$_6$ composite for enhanced and stable visible light photocatalyst. *Appl. Surf. Sci.* **2017**, *391*, 507–515. [CrossRef]

48. Liu, W.; Shen, J.; Yang, X.F.; Liu, Q.Q.; Tang, H. Dual Z-scheme g-C$_3$N$_4$/Ag$_3$PO$_4$/Ag$_2$MoO$_4$ ternary composite photocatalyst for solar oxygen evolution from water splitting. *Appl. Surf. Sci.* **2018**, *456*, 369–378. [CrossRef]

49. Dong, Z.F.; Wu, Y.; Thirugnanam, N.; Li, G.L. Double Z-scheme ZnO/ZnS/g-C$_3$N$_4$ ternary structure for efficient photocatalytic H$_2$ production. *Appl. Surf. Sci.* **2018**, *430*, 293–300. [CrossRef]

50. Wen, J.Q.; Xie, J.; Chen, X.B.; Li, X. A review on g-C$_3$N$_4$-based photocatalysts. *Appl. Surf. Sci.* **2017**, *391*, 72–123. [CrossRef]

51. Yu, H.B.; Huang, J.H.; Jiang, L.B.; Leng, L.J.; Yi, K.X.; Zhang, W.; Zhang, C.Y.; Yuan, X.Z. In situ construction of Sn-doped structurally compatible heterojunction with enhanced interfacial electric field for photocatalytic pollutants removal and CO$_2$ reduction. *Appl. Catal. B Environ.* **2021**, *298*, 120618. [CrossRef]

52. Méricq, J.P.; Mendret, J.; Brosillon, S.; Faur, C. High performance PVDF-TiO$_2$ membranes for water treatment. *Chem. Eng. Sci.* **2015**, *123*, 283–291. [CrossRef]