Enhanced photocatalytic activity of novel α-Bi$_2$O$_3$@g-C$_3$N$_4$ composites for the degradation of endocrine-disrupting benzophenone-3 in water under visible light

Abiyu Kerebo Berekute$^{1,2}$, Kuo-Pin Yu$^{1,2,*}$ and Yi-Hsueh Brad Chuang$^3$

Abstract

The commonly used benzophenone-3 (BP-3) as ultraviolet filter ingredients is an endocrine-disrupting chemical that has received particular attention owing to its environmental ubiquity, and it poses a threat to aquatic biota and human health. In this study, novel α-Bi$_2$O$_3$@g-C$_3$N$_4$ nanocomposites with different α-Bi$_2$O$_3$ contents and enhanced photocatalytic activity were synthesized by a mixing calcination method. The as-synthesized photocatalysts were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, ultraviolet–visible diffuse reflectance spectroscopy, N$_2$ adsorption/desorption isotherm analysis, electrochemical impedance spectroscopy, photoluminescence spectroscopy and electron paramagnetic resonance (EPR) spectroscopy. The 1 wt% α-Bi$_2$O$_3$@g-C$_3$N$_4$ composite exhibited the highest rate constant of 0.42 h$^{-1}$ for photocatalytic degradation of BP-3, which was up to 6.3 times higher than that of g-C$_3$N$_4$ (0.07 h$^{-1}$). The enhanced photocatalytic activity might be due to the enhanced separation of photogenerated electron-hole (e$^-$/h$^+$) charge pairs and suppression of e$^-$/h$^+$ recombination. Scavenging experiments suggested that OH, h$^+$ and O$_2$ worked together in the α-Bi$_2$O$_3$@g-C$_3$N$_4$ photocatalytic process. The EPR spectra demonstrated that the α-Bi$_2$O$_3$@g-C$_3$N$_4$ composites generated considerably more O$_2^-$ and OH than g-C$_3$N$_4$. Finally, cyclic degradation experiments showed the reusability of 1 wt% α-Bi$_2$O$_3$@g-C$_3$N$_4$ for BP-3 removal.

Keywords: α-Bi$_2$O$_3$@g-C$_3$N$_4$, Z-scheme heterojunction, Photocatalytic degradation, Ultraviolet filter

1 Introduction

Benzophenone-3 ((2-hydroxy-4-methoxyphenyl)phenylmethanone, BP-3) has received special attention owing to its extensive use, ubiquity, persistence as a contaminant, potential ecotoxicity to aquatic biota and health risks to humans [1, 2]. BP-3 is widely used in cosmetics as a sunscreen ingredient, industrial products and food contact materials; it is commonly used to protect skin from sunburn and materials from possible UV light-induced photochemical degradation [3, 4]. BP-3 may be introduced to aquatic environments directly through human recreational activities such as swimming and indirectly by wastewater treatment plant (WWTP) effluents, which indicates that conventional wastewater treatment processes do not effectively remove BP-3 [5, 6].

Several studies have shown the incomplete removal of BP-3 in conventional WWTPs. For example, Liu et al.
reported BP-3 concentrations up to 2086 ng L⁻¹ in the influent and up to 153 ng L⁻¹ in the effluent, with a removal efficiency of 92% [7], while Wick et al. reported maximum BP-3 concentrations up to 720 ng L⁻¹ in the influent [8], and Langford et al. reported maximum BP-3 concentrations up to 1915 ng L⁻¹ in the effluent [9]. Similarly, Li et al. reported BP-3 concentrations up to 722 ng L⁻¹ in the influent and up to 664 ng L⁻¹ in the effluent, with a removal efficiency of only 9%, and Tsui et al. mentioned maximum BP-3 concentrations up to 371.3 ng L⁻¹ in the influent and up to 115.8 ng L⁻¹ in the effluent, with a removal efficiency of 69% [10, 11].

Advanced oxidation processes (AOPs) involving heterogeneous photocatalysts can effectively remove BP-3 from WWTP effluent. AOPs utilize chemical oxidation based on the in-situ generation of free radicals (hydroxyl radical (·OH), superoxide radical (·O²⁻), etc.) that nonselectively react with emerging organic contaminants and are capable of completely degrading them into carbon dioxide and water [12, 13]. Heterogeneous photocatalysts have received particular interest owing to their low cost, nontoxicity, efficiency, lack of secondary pollution and environmental friendliness [14–16]. Wang et al. reported the photocatalytic degradation of BP-3 using PbO@TiO₂ and Sb₂O₃@TiO₂ composites and showed optimal removal efficiencies of up to 87% and 80%, respectively [17]. Zuniga-Benitez et al. reported the photo-degradation of BP-3 using UV + TiO₂ treatment with an optimal remnant efficiency of 62% [18].

Recently, metal-free graphitic carbon nitride (g-C₃N₄) has been considered for use as a metal-free π-conjugated photocatalyst with an appropriate bandgap energy (~2.7 eV). It has attracted considerable attention for organic pollutant degradation, hydrogen production, carbon dioxide reduction and atmospheric purification owing to its high thermochemical stability, 2D optical structure, suitable electronic properties and inexpensive synthesis [19, 20]. The more negative conduction potential edge of g-C₃N₄ (~1.22 eV vs. normal hydrogen electrode (NHE)) is enough for the reduction of the adsorbed oxygen (O₂/·O₂⁻) redox couple (~0.33 eV vs. NHE) to produce ·O₂⁻. However, the photocatalytic efficiency of pristine g-C₃N₄ catalysts is low because of the fast recombination of photoinduced e⁻ and h⁺, limited delocalized conductivity, low quantum efficiency and narrow visible light absorption range [21, 22]. Consequently, to improve the photocatalytic performance, the application of various strategies, such as heterojunction formation, surface modification, metal or anion doping and use of dye-sensitized photocatalysts, is important. Among the aforementioned strategies, heterojunction formation efficiently suppresses charge carrier recombination, leads to excellent e⁻ and h⁺ separation and promotes the redox capacity of photogenerated carriers, thus enhancing the photocatalytic performance of the materials [23–25].

Herein, two or more semiconductors with appropriate bandgap energies are combined to fabricate type II heterojunction photocatalysts. Such photocatalysts can be formed by photogenerated electrons being transferred from the conduction band of photosystem I (PSI) to the valence band (VB) of photosystem II (PSII), while the hole is transferred in the opposite direction due to the potential difference between the conduction band and the VB edges. This potential difference improves the charge separation efficiency and suppresses recombination, which is favorable for photocatalytic performance. However, these merits are at the expense of the reduction abilities of PSI and oxidation abilities of PSII [26–28].

Regarding a Z-scheme photocatalytic system, the photoexcited electrons in the conduction band of PSII, which stem from visible light irradiation, may recombine with holes in the VB of PSI. Therefore, the conduction band edge of PSII should be lower than that of PSI, and the VB edge of PSI should be higher than that of PSII. Thus, strong oxidative holes and reductive electrons can be generated in the two different bands, thereby resulting in enhanced photocatalytic activity [25, 29].

Currently, a number of bismuth-containing semiconductors, such as bismuth oxide (Bi₂O₃), BiVO₄, Bi₂WO₆ and BiOX (X = Cl, Br, I), are available. As a preeminent semiconductor, Bi₂O₃, which has a band gap of ~2.8 eV, has received increasing attention owing to its nontoxicity, thermal stability, environmental friendliness, outstanding visible light absorption and strong oxidation when used as a photocatalyst. It has been reported that Bi₂O₃ exhibits six polymorphs, α, β, γ, δ, ε and ω phases. Among them, α-Bi₂O₃ has a monoclinic structure and is stable under ambient pressure and temperature conditions [27, 30, 31]. The more positive valence potential edge of α-Bi₂O₃ (2.89 eV vs. NHE) is enough for the oxidation of the water H₂O/OH redox couple (2.72 eV vs. NHE) and hydroxyl ion OH⁻/·OH redox couple (2.40 eV vs. NHE) to produce ·OH radicals. Therefore, considering the matching band gap alignments and appropriate band edge potentials of semiconductors, α-Bi₂O₃ is a promising candidate for integration with g-C₃N₄ to construct a direct Z-scheme heterojunction.

In the present study, we synthesized α-Bi₂O₃@g-C₃N₄ photocatalysts with different weight percentages of α-Bi₂O₃ through a mixing-calcination method. The objective of our study was to investigate the photocatalytic activity of the as-synthesized samples for the degradation of BP-3 and the effects of α-Bi₂O₃ doping on the photocatalytic properties of g-C₃N₄ catalysts. The as-synthesized samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray
photoelectro spectroscopy (XPS), Fourier transform infrared (FT-IR) spectroscopy, (ultraviolet–visible diffuse reflectance spectroscopy (UV-Vis DRS), N₂ adsorption/desorption isotherm analysis, electrochemical impedance spectroscopy (EIS) and photoluminescence (PL) spectroscopy. Furthermore, a possible reaction mechanism was proposed based on the energy band positions and electron paramagnetic resonance (EPR) spectroscopy and trapping experimental findings. Finally, the reusability of the best-performing photocatalyst in the photocatalytic process was also investigated.

2 Materials and methods

2.1 Chemicals

All chemicals, including melamine powder (C₃H₆N₆, 99.5%), bismuth (III) nitrate pentahydrate (Bi (NO₃)₃·5H₂O), isopropanol (IPA, C₃H₈O, 99.9%), superoxide dismutase (SOD, 99%), ammonium oxalate (AO, 99.9%), BP-3 (98%), barium sulfate (BaSO₄, 99%), and methanol (CH₃OH, 99.9%), were purchased from Sigma–Aldrich. All reagents and precursors were used as received without further purification, and deionized water was used in this study.

2.2 Synthesis of the α-Bi₂O₃@g-C₃N₄ photocatalyst

α-C₃N₄ was synthesized according to a previously reported method [32]. In a typical synthesis procedure, 5 g of melamine (C₃H₆N₆) was placed in a crucible with a cover. The crucible was heated in a tube furnace with a nitrogen atmosphere for 2 h, reaching a temperature of 520 °C at a heating rate of 10 °C min⁻¹. Further treatment was performed at 540 °C for 2 h. When 0.05, 0.1, 0.3 and 0.5 g Bi (NO₃)₃ were used, the obtained yellow solids were ground into powders and labeled 0.5 wt% α-Bi₂O₃@g-C₃N₄, 1 wt% α-Bi₂O₃@g-C₃N₄, 3 wt% α-Bi₂O₃@g-C₃N₄ and 5 wt% α-Bi₂O₃@g-C₃N₄. A schematic illustration of the synthesis method is shown in Fig. S1 of Supplemental Materials.

2.3 Material characterization

2.3.1 Physicochemical characterization

Physicochemical characterization of the as-synthesized samples was obtained using SEM, SEM-EDS, TEM, XRD, XPS and FT-IR spectroscopy, and N₂ adsorption and desorption isotherms. The crystal structure and phase composition of the as-synthesized samples were studied by XRD using a Bruker D2 Phaser diffractometer (Japan). The X-ray powder diffractometer was operated at 10 kV and used a Cu Kα radiation source with a wavelength of 1.5406 Å. The morphologies and elemental composition of the samples were studied by field-emission SEM (FE-SEM; JEOL JSM-7600F, Tokyo, Japan), in which the microscope was equipped with energy dispersive spectroscopy (EDS) and operated at an accelerating voltage of 15 kV, and TEM (JEOL JEM 1400Plus electron microscope, Tokyo, Japan). XPS measurements were performed with a Thermo VG Scientific XPS (ESCALAB 250, England). Moreover, all the binding energies were calibrated with respect to the C 1s peak of the adventitious carbon at 284.9 eV. FT-IR spectra of the as-synthesized samples were recorded on a JASCO-4200 spectrometer at room temperature with KBr as a reference sample. N₂ adsorption and desorption isotherm curves were obtained with a Micromeritics system at 77.35 K (Autosorb-Iq-MP, Quantachrome Instruments).

2.3.2 Photoelectrochemical characterization

Photoelectrochemical characterization of the as-synthesized samples was obtained using UV-Vis spectrophotometry, PL spectroscopy, EIS analysis and EPR spectroscopy. The absorbance, diffuse reflectance spectra and optical bandgap of each sample were assessed using a UV-Vis spectrophotometer (JASCO 760) with BaSO₄ as a reference sample. PL emission spectra were measured at room temperature on a JASCO FB-8500 fluorescence spectrophotometer. EIS was performed using an Autolab PGSTAT302N electrochemical test system (Metrohm Autolab B.V., Netherlands). EIS was performed for the as-synthesized samples with a standard three-electrode system that utilized Ag/AgCl and platinum strips as the reference and counter electrodes,
respectively. The working electrode was prepared by mixing 8 mg of the as-synthesized samples with 1 mg of polyvinylidene fluoride and 1 mg of carbon black, and then, 100 μL of a methyl-2-pyrrolidone was added. Thereafter, the slurry was coated on a 1 x 3 cm piece of nickel foam and dried at 60 °C for 12 h in a vacuum oven. The EIS spectra were recorded from 0.1 to 100 kHz at a current amplitude of 10 mV with a 0.5 M Na2SO4 aqueous solution as the electrolyte.

2.3.3 The measurement of reactive oxygen species (ROS)
A Bruker EPR spectrometer was used to measure the ROS in the presence of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) to further verify the generation of ROS in the photocatalytic systems. The samples were prepared as follows: 20 mg of the as-synthesized samples was dispersed in 1 mL of deionized water, and then, 80 μL of DMPO was introduced with a 3 min ultrasonic treatment, which was used to trap hydroxyl radicals (DMPO-•). The superoxide radicals (DMPO-•O2-) were determined by the same process except that the deionized water was replaced with methanol.

2.4 Photocatalytic degradation of BP-3
The photocatalytic activities of the as-synthesized g-C3N4 and α-Bi2O3@g-C3N4 composites were evaluated by using BP-3 as the organic contaminant. Briefly, the process was performed by dispersing 0.15 g of the as-prepared sample into 100 mL of a BP-3 solution at an initial concentration of 2 mg L⁻¹ and with the pH of the pristine solution. The solution was exposed to 24 W m⁻² visible light irradiation. After illumination time t, the solution was centrifuged, repeatedly washed with water and alcohol, dried at 60 °C for 12 h in a vacuum drying oven, and then, the solution was used again in the next experiment. The same procedure was repeated for all the remaining cycles.

3 Results and discussion
3.1 Characterization of the catalysts
The surface morphologies of the as-synthesized α-Bi2O3 and 1 wt% α-Bi2O3@g-C3N4 composite samples were studied by FE-SEM. According to Fig. 1a, α-Bi2O3 and 1 wt% α-Bi2O3@g-C3N4 composite exhibits an aggregated structure, and clearly, the surface structure of α-Bi2O3 in Fig. 1b exhibits thin sheet hierarchical microspheres. However, in Fig. 1c, Figs. S3a, S4a and S5a of the 1, 0.5, 3 and 5 wt% α-Bi2O3@g-C3N4 composite samples show the aggregated g-C3N4 structure covered by the thin sheet hierarchical microspheres of the α-Bi2O3 particles, confirming the formation of the α-Bi2O3@g-C3N4 composites [27, 35]. Small pores were observed on the surface structure of the α-Bi2O3@g-C3N4 composite; these pores might be due to the release of small molecular gases, specifically NO2 and H2O, during the mixing-calcination process. The elemental compositions of the 1, 0.5, 3 and 5 wt% α-Bi2O3@g-C3N4 composites were determined by EDS, and the results are shown in Fig. 1d, Figs. S3b, S4b and S5b. The EDS spectra reveal that the as-synthesized samples contain carbon (C), nitrogen (N), bismuth (Bi), and oxygen (O). Therefore, the EDS results confirm the presence of Bi, O, C, and N in the 1, 0.5, 3 and 5 wt% α-Bi2O3@g-C3N4 composites, further indicating the presence of both α-Bi2O3 and g-C3N4. Additionally, the elemental maps of the as-synthesized samples in Fig. 2a-d, Figs. S6, S7 and S8 confirm the presence of C, N, Bi, and O in the 1, 0.5, 3 and 5 wt% α-Bi2O3@g-C3N4 composites, respectively.

TEM was used for structural analysis and microstructural characterization of the as-synthesized α-Bi2O3@g-C3N4 composite samples. The synthesized samples show the aggregated g-C3N4 structure, and clearly, the surface structure of the α-Bi2O3@g-C3N4 composites [27, 35]. Small pores were observed on the surface structure of the α-Bi2O3@g-C3N4 composite; these pores might be due to the release of small molecular gases, specifically NO2 and H2O, during the mixing-calcination process. The elemental compositions of the 1, 0.5, 3 and 5 wt% α-Bi2O3@g-C3N4 composites were determined by EDS, and the results are shown in Fig. 1d, Figs. S3b, S4b and S5b. The EDS spectra reveal that the as-synthesized samples contain carbon (C), nitrogen (N), bismuth (Bi), and oxygen (O). Therefore, the EDS results confirm the presence of Bi, O, C, and N in the 1, 0.5, 3 and 5 wt% α-Bi2O3@g-C3N4 composites, further indicating the presence of both α-Bi2O3 and g-C3N4. Additionally, the elemental maps of the as-synthesized samples in Fig. 2a-d, Figs. S6, S7 and S8 confirm the presence of C, N, Bi, and O in the 1, 0.5, 3 and 5 wt% α-Bi2O3@g-C3N4 composites, respectively.

2.5 Influence of ROS scavengers on the photocatalytic process
An active species trapping experiment was performed by using the 1 wt% α-Bi2O3@g-C3N4 catalyst for the photodegradation of BP-3. The degradation process was observed by adding different active species quenchers. To do this, AO (5 mg), SOD (5 mg) and IPA (5 mL) were chosen as the quenchers of h⁺, •O2⁻ and •OH, respectively. The utilized method was similar to that of the previous photocatalytic activity test except when treated with the respective quenchers in the presence of BP-3.
Bi$_2$O$_3$ and 1 wt% α-Bi$_2$O$_3$@g-C$_3$N$_4$ composite samples. Figure 3a and b shows that the pure g-C$_3$N$_4$ sample displays a typical smooth surface with a layered sheet structure [20], and the pure α-Bi$_2$O$_3$ sample shows a dark image of nanoparticles, as demonstrated in Fig. 3c. The deposition of α-Bi$_2$O$_3$ on the surface of g-C$_3$N$_4$ is clearly observed in the TEM images of 1 wt% α-Bi$_2$O$_3$@g-C$_3$N$_4$, as shown in Fig. 3e. Numerous dark, particle-like structures are observed on the surface of g-C$_3$N$_4$. Consequently, the dark particles can be assigned to α-Bi$_2$O$_3$, and the gray part and layered sheet are assigned to g-C$_3$N$_4$. Since Bi has a higher atomic mass than C and N, the electron beam can penetrate g-C$_3$N$_4$ more easily than α-Bi$_2$O$_3$. High-resolution TEM was further performed to investigate the d-spacing of the as-synthesized catalysts, and the results are displayed in Fig. 3b, d and f. The 0.376 nm d-spacing of the lattice fringes corresponds to the (002) lattice plane of g-C$_3$N$_4$ (Fig. 3b), while the 0.401 nm d-spacing of the lattice fringes corresponds to the (021) lattice plane of α-Bi$_2$O$_3$ (Fig. 3d). In addition, Fig. 3f displays the presence of α-Bi$_2$O$_3$ and g-C$_3$N$_4$ phases and an interplanar spacing of 0.406 nm, which correspond to the (021) crystal plane of α-Bi$_2$O$_3$, further confirming the formation of heterojunctions in the as-synthesized sample.

The XRD patterns of the as-synthesized g-C$_3$N$_4$, α-Bi$_2$O$_3$, 0.5 wt% α-Bi$_2$O$_3$@g-C$_3$N$_4$, 1 wt% α-Bi$_2$O$_3$@g-C$_3$N$_4$, 3 wt% α-Bi$_2$O$_3$@g-C$_3$N$_4$ and 5 wt% α-Bi$_2$O$_3$@g-C$_3$N$_4$ catalysts are shown in Fig. 4a. The characteristic peaks of the g-C$_3$N$_4$ sample are indexed to the corresponding orthorhombic phase (PDF #89-8491) with lattice parameters of $a = 4.048$ Å, $b = 4.885$ Å and $c = 6.495$ Å. The g-C$_3$N$_4$ catalyst shows two diffraction peaks at $2\theta = 13.62$ and 27.44°, which can be indexed as the (001) and (002) planes, respectively. The weak peak at 13.62° corresponds to an interlayer d-spacing of 0.649 nm, which is related to the order of the tri-s-triazine in-plane structural repeating unit, and the strong peak at 27.44°, which corresponds to an interlayer d-spacing of 0.367 nm, is attributed to the long-range interlayer stacking of aromatic systems and/or graphitic sheets [36, 37]. The peaks of the α-Bi$_2$O$_3$ sample are related to the corresponding monoclinic phase (PDF #02-0498) with lattice parameters of $a = 5.830$ Å, $b = 8.140$ Å and $c = 7.480$ Å. The diffraction peaks located at $2\theta = 26.03$, 27.59, 33.53 and 46.53° are attributed to the (002), (121),
(202) and (041) planes, respectively. The peaks of α-Bi₂O₃, especially the peak at 27.59°, are very sharp, which suggests good crystallinity. The intensity of the XRD peaks of the α-Bi₂O₃@g-C₃N₄ composites decreases as the α-Bi₂O₃ content increases from 0.5 to 5 wt%, and the peak of α-Bi₂O₃ that is ascribed to the monoclinic phase is not identified. Therefore, the α-Bi₂O₃ particles are confirmed to be homogeneously dispersed on the surface of g-C₃N₄, which results in a significant decrease in the intensity of the (002) peaks of the composite catalysts. In addition, no new diffraction peaks are observed in the composite, which confirms that the composite contains only g-C₃N₄ and α-Bi₂O₃ [38, 39].

The crystallite sizes of g-C₃N₄, α-Bi₂O₃ and the 1 wt% α-Bi₂O₃@g-C₃N₄ composite are estimated to be 6.73, 14.18 and 4.47 nm, respectively.

The chemical bonding of the as-synthesized g-C₃N₄, α-Bi₂O₃ and α-Bi₂O₃@g-C₃N₄ composites with different weight percentages of α-Bi₂O₃ was investigated by FT-IR spectroscopy. The spectra are depicted in Fig. 4b. Regarding g-C₃N₄, the sharp peak centered at 808 cm⁻¹ can be assigned to the out-of-plane bending modes of the triazine units [23]. Moreover, the peaks located at 1560, 1412, 1321 and 1242 cm⁻¹ correspond to aromatic C–N stretching vibrations, whereas the peak located at 1641 cm⁻¹ is assigned to the C=N stretching vibration mode [40]. Additionally, the broad peak centered at 3000-3300 cm⁻¹ is associated with the stretching vibration mode of NH₂ or N-H groups, and the bending vibration of the O-H band resembles that of adsorbed water [37, 41]. The peak of α-Bi₂O₃ located at approximately 520 cm⁻¹ corresponds to the typical stretching vibration mode of the Bi–O bands of BiO₆ units [42].

Regarding the four α-Bi₂O₃@g-C₃N₄ composites, the peak of α-Bi₂O₃ centered at 520 cm⁻¹ is not observed in all composite samples, which might be due to its low content and weak vibrations. Similar trends have been reported by Huang et al. [43] and Wang et al. [44] regarding CeO₂@g-C₃N₄ and sulfur-doped@g-C₃N₄, respectively. However, strong peak intensities from g-C₃N₄ are observed in the 1240-1640 cm⁻¹ region when the α-Bi₂O₃ content in the composites is increased from 0.5 to 5 wt%.

The surface chemical compositions of g-C₃N₄, α-Bi₂O₃ and the 1 wt% α-Bi₂O₃@g-C₃N₄ composite were analyzed by XPS. Figure S9a shows the full survey XPS spectra of α-Bi₂O₃, g-C₃N₄ and 1 wt% α-Bi₂O₃@g-C₃N₄.

Fig. 2 EDS elemental mapping (a) C, (b) N, (c) Bi and (d) O of 1 wt% α-Bi₂O₃@g-C₃N₄
and N 1s XPS spectra of α-Bi₂O₃, g-C₃N₄ and 1 wt% α-Bi₂O₃@g-C₃N₄. Figure 5a shows the Bi 4f high-resolution spectra of α-Bi₂O₃ and 1 wt% α-Bi₂O₃@g-C₃N₄. The two peaks centered at 159.3 eV and 164.3 eV represent the 4f⁷/₂ and 4f⁵/₂ orbitals of trivalent Bi (Bi³⁺) in α-Bi₂O₃, respectively [33]. However, the binding energies of the Bi 4f⁷/₂ and Bi 4f⁵/₂ orbitals in 1 wt% α-Bi₂O₃@g-C₃N₄ shift to 158.3 eV and 163.3 eV, respectively, which indicates the formation of a heterojunction between g-C₃N₄ and α-Bi₂O₃ in the composite [40]. Figure 5b shows two strong peaks at 529.9 eV and 530.4 eV, which correspond to the carbon species adsorbed on the sample surface from the instrument and the sp²-hybridized bonded carbon in the heterocyclic aromatic ring (N–C= N) of the g-C₃N₄ lattice, respectively [43]. Compared with that of α-Bi₂O₃, the O 1s signal in of 1 wt% α-Bi₂O₃@g-C₃N₄ shows a positive shift, which also confirms the formation of a heterojunction between g-C₃N₄ and α-Bi₂O₃ in the composite.

The C 1s spectrum shown in Fig. 5c shows two peaks and binding energies at 284.9 eV and 288.6 eV, which correspond to the carbon species adsorbed on the sample surface from the instrument and the sp²-hybridized bonded carbon in the heterocyclic aromatic ring (N–C= N) of the g-C₃N₄ lattice, respectively [45]. As shown in Fig. 5c, the signal in the C 1s spectrum shifts to a lower binding energy after α-Bi₂O₃ loading, which further confirms the formation of heterojunctions. The binding energy of the adventitious carbon peak (284.9 eV) does not change after heterojunction formation.

The N 1s spectrum of g-C₃N₄ in Fig. 5d shows three peaks centered at 398.5, 399.3 and 399.5 eV, which are assigned to the tertiary N bonded to carbon atoms in the form of N-(C)₃ units, the sp²-hybridized aromatic N atoms bonded to carbon in the form of C-N=C, and amino groups with a hydrogen atom (C-N-H) and charging effects, respectively [19, 37]. As shown in Fig. 5d, the N 1s binding energy of 1 wt% α-Bi₂O₃@g-C₃N₄ exhibits a blueshift, which also suggests a possible
interaction between g-C_3N_4 and α-Bi_2O_3 in the composite. Generally, this kind of interaction promotes charge carrier separation and interparticle electron transfer, leading to the enhanced photocatalytic performance of 1 wt% α-Bi_2O_3@g-C_3N_4.

To investigate the surface physicochemical properties of the as-synthesized samples with respect to the surface area and pore size distribution, nitrogen adsorption-desorption isotherms were obtained. As shown in Fig. S9c, g-C_3N_4, α-Bi_2O_3, and the α-Bi_2O_3@g-C_3N_4 composites exhibit type IV isotherms with a type H3 hysteresis loop, as defined by International Union of Pure and Applied Chemistry; these results are characteristic of slit-like mesoporous materials [46].

Furthermore, the BET surface areas, pore volumes and pore diameters of the g-C_3N_4, α-Bi_2O_3, 0.5 wt% α-Bi_2O_3@g-C_3N_4, 1 wt% α-Bi_2O_3@g-C_3N_4, 3 wt% α-Bi_2O_3@g-C_3N_4 and 5 wt% α-Bi_2O_3@g-C_3N_4 samples are summarized in Table 1. The results suggest that α-Bi_2O_3 loading reduces the BET surface area of the composite.

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**Fig. 4** (a) XRD patterns and (b) FT-IR spectra of g-C_3N_4, α-Bi_2O_3 and the α-Bi_2O_3@g-C_3N_4 composites
samples, possibly due to the particle aggregation that occurs on the surface of g-C₃N₄. The BET surface area of 1 wt% α-Bi₂O₃@g-C₃N₄ is larger than that of 0.5 wt% α-Bi₂O₃@g-C₃N₄, 3 wt% α-Bi₂O₃@g-C₃N₄ and 5 wt% α-Bi₂O₃@g-C₃N₄. This phenomenon could be due to the different pore size distributions of the as-synthesized samples, as shown in Fig. S9d. Therefore, the high BET surface area of 1 wt% α-Bi₂O₃@g-C₃N₄ offers the possibility for efficient diffusion of the pollutant on the catalyst surface, which is beneficial for the photocatalytic reaction [45].

3.2 UV-Vis DRS analysis

The optical properties of the as-synthesized samples were measured by UV-Vis DRS. Figure 6a shows the
where α is the absorption coefficient, h is Planck’s constant, ν is the light frequency, A is a constant, $E_g$ is the bandgap energy, and n depends on the nature of the transition in a semiconductor (n = 1 for a direct transition and n = 4 for an indirect transition). The intrinsic $E_g$ values were determined by extrapolating the steepest portion of $(αν)^2$ = 0. The light absorption onset edges of g-C₃N₄, α-Bi₂O₃, 0.5 wt% α-Bi₂O₃@g-C₃N₄, 1 wt% α-Bi₂O₃@g-C₃N₄, 3 wt% α-Bi₂O₃@g-C₃N₄, and 5 wt% α-Bi₂O₃@g-C₃N₄ are approximately 450, 437, 453, 455, 459 and 463 nm, respectively, with $E_g$ values of 2.72, 2.8, 2.70, 2.69, 2.66 and 2.64 eV, respectively (Fig. 6b). The absorption spectra of the α-Bi₂O₃@g-C₃N₄ composites show a slight redshift, which is triggered by the α-Bi₂O₃ doped on the porous surface of g-C₃N₄, confirming the formation of heterojunctions between g-C₃N₄ and α-Bi₂O₃. Figure S9b shows that the optical bandgaps of the α-Bi₂O₃@g-C₃N₄ composites linearly decrease with an increasing concentration of α-Bi₂O₃, which may result from the interaction between g-C₃N₄ and α-Bi₂O₃.

### 3.3 Photocatalytic activity evaluation

Figure 7a shows that approximately 20% of BP-3 is removed by adsorption in the dark, and the photocatalytic activity of pristine g-C₃N₄ is relatively low, with only 55% of BP-3 being photocatalytically degraded. However, the α-Bi₂O₃@g-C₃N₄ composites show higher photocatalytic activity than pristine g-C₃N₄, and the 1 wt% α-Bi₂O₃@g-C₃N₄ composite shows the optimal removal efficiency, decomposing 92% of BP-3. Notably, the photocatalytic efficiencies for the photodegradation of BP-3 decrease by 5 and 14% for 3 wt% α-Bi₂O₃@g-C₃N₄ and 5 wt% α-Bi₂O₃@g-C₃N₄, respectively. This phenomenon may be due to the excess loading of α-Bi₂O₃ decreasing the BET areas and the photoinduced charge transfer efficiency (as shown in the EIS results), thus leading to poor photocatalytic performance.

The Langmuir–Hinshelwood (L–H) kinetic model equation (Eq. (3)) is widely used to describe photocatalytic kinetics:

$$ r = \frac{\frac{dC}{dt}}{K_{L-H} C + \frac{K_{L-H} C}{1 + K_{L-H} C}} $$

where $r$ is the photocatalytic reaction rate, $k_{L-H}$ is the reaction rate constant, $K_{L-H}$ is the adsorption constant of BP-3 on the surface of a photocatalyst, and C is the concentration of BP-3. Due to the low concentration of BP-3, i.e., the value of $K_{L-H}$ C is << 1, the photocatalytic degradation of BP-3 can be simplified to the common pseudo-first-order kinetics equation (Eq. (4)) shown below [49]:

$$ \frac{dC}{dt} = k_{app} C $$

where $k_{app}$ ($h^{-1}$) is the apparent photocatalytic rate constant or pseudo-first-order rate constant. This constant can be determined from the slope of -ln ($C_t/C_0$) versus the irradiation time plot (Fig. 7b), in which $C_0$ is the initial concentration of BP-3 in the aqueous solution at time zero and $C_t$ is the concentration of BP-3 at irradiation time t (h). The apparent photocatalytic rate constants of different photocatalysts for the degradation of BP-3 are summarized in Fig. 7b. Accordingly, the highest $k_{app}$ is found with
1 wt% $\alpha$-Bi$_2$O$_3@g$-C$_3$N$_4$. The synergistic effect between the binary phases in 1 wt% $\alpha$-Bi$_2$O$_3@g$-C$_3$N$_4$ results in better photogenerated electron-hole ($e^-$-$h^+$) charge separation, thus inhibiting $e^-$ and $h^+$ recombination.

3.4 PL and EIS spectral analysis

To examine the recombination processes of the photoinduced $e^-$ and $h^+$ of the as-synthesized photocatalysts, PL spectroscopy was employed, and the spectra are shown in Fig. 8a. Herein, the PL spectra of bare g-C$_3$N$_4$, $\alpha$-Bi$_2$O$_3$ and the $\alpha$-Bi$_2$O$_3@g$-C$_3$N$_4$ composites were obtained with an excitation wavelength of 300 nm (~4.08 eV) to elucidate the recombination processes of the photogenerated $e^-$-$h^+$ pairs. As shown in Fig. 8a, pristine g-C$_3$N$_4$ has the highest PL peak intensity, which is due to its faster rate of $e^-$-$h^+$ recombination; therefore, it
shows the lowest photocatalytic activity [50]. The PL intensity of bare $\alpha$-Bi$_2$O$_3$ is the lowest and is almost negligible. Hence, the PL peak intensity of the composite is lower than that of pristine g-C$_3$N$_4$, which confirms the formation of heterojunctions and indicates efficient charge separation from the CB of g-C$_3$N$_4$ to the CB of the $\alpha$-Bi$_2$O$_3$ nanocluster. Therefore, the recombination process of the photoinduced charge carriers in the $\alpha$-
Bi$_2$O$_3$@g-C$_3$N$_4$ composites is significantly hampered, which might be favorable for improving the photocatalytic activity of the composites [41].

To further demonstrate the photoinduced charge transfer efficiency and recombination processes of the as-synthesized catalysts, EIS measurements were performed. Figure 8b shows the Nyquist impedance plots of g-C$_3$N$_4$, α-Bi$_2$O$_3$ and the α-Bi$_2$O$_3$@g-C$_3$N$_4$ composites. A smaller arc radius indicates a lower charge transfer resistance ($R_t$) and a more facile charge transfer process at the electrode/electrolyte interface [51]. Notably, 1 wt% α-Bi$_2$O$_3$@g-C$_3$N$_4$ exhibits a smaller arc radius than the other as-synthesized samples. This result suggests that 1 wt% α-Bi$_2$O$_3$@g-C$_3$N$_4$ has a better photoinduced charge transfer efficiency and a lower recombination rate of photoinduced charge carriers [52, 53]. This scenario could be beneficial for the photocatalytic performance of 1 wt% α-Bi$_2$O$_3$@g-C$_3$N$_4$.

### 3.5 Possible photocatalytic mechanisms

The CB and VB potential edge positions of semiconductor materials determine their oxidation and reduction abilities; these positions can be calculated by empirical equations (Eqs. (5) and (6)) [40].
Herein, the $E_{VB}$ and $E_{CB}$ are the VB and CB potentials, respectively; $x$ is the absolute electronegativity of the corresponding semiconductor material, which can be obtained by determining the arithmetic mean of the electron affinity and first ionization potential of the constituent atoms ($5.99 \text{ eV for } \alpha$-Bi$_2$O$_3$ and $~4.64 \text{ eV for } g$-C$_3$N$_4$)\cite{42,54}; $E^e$ is the free electron energy on the hydrogen scale ($~4.5 \text{ eV vs. NHE}$); and $E_g$ is the bandgap energy of the semiconductors. The calculated values of the $E_{VB}$ and $E_{CB}$ edge positions are estimated to be $~1.50$ and $~2.89 \text{ eV}$ for the as-synthesized $g$-C$_3$N$_4$ and $~1.22$ and $~0.09 \text{ eV}$ for the as-synthesized $\alpha$-Bi$_2$O$_3$, respectively.

When the 1 wt$\%$ $\alpha$-Bi$_2$O$_3@g$-C$_3$N$_4$ is illuminated, both $g$-C$_3$N$_4$ and $\alpha$-Bi$_2$O$_3$ can produce a photoexcited $e^--h^+$ pair (Eq. (7)). The photoexcited $e^-$ in the CB of $\alpha$-Bi$_2$O$_3$ and photoinduced $h^+$ in the VB of $g$-C$_3$N$_4$ can recombine, causing the accumulation of $e^-$ in the CB of $g$-C$_3$N$_4$ and $h^+$ in the VB of $\alpha$-Bi$_2$O$_3$; this behavior results in strong oxidation and reduction for the photodegradation of BP-3 (Eq. (8)).
The reduction potential of CB in g-C₃N₄ is ~-1.22 eV vs. NHE, which is more negative than the standard redox potential of O₂/•O₂⁻ (~-0.33 eV vs. NHE) [55]. The photoexcited electrons in the CB of g-C₃N₄ can reduce adsorbed oxygen molecules to •O₂⁻ (Eq. (10)) or cause •O₂⁻ to react with hydrogen ions and e⁻ to produce H₂O₂ (Eq. (11)), which can be further reduced to generate •OH (Eq. (12)). In addition, the oxidation potential of the VB in α-Bi₂O₃ (~2.89 eV vs. NHE) is more positive than the standard redox potential of •OH/H₂O (~2.72 eV vs. NHE) [56]. Thus, photoinduced h⁺ in the VB of α-Bi₂O₃ on the surface of the catalyst can react with H₂O to generate •OH (Eq. (9)). Additionally, the remaining h⁺ in the VB of α-Bi₂O₃ on the surface of the catalyst directly oxidizes BP-3.

To further elucidate the mechanism of the photocatalytic reaction and verify the reactive species responsible for the degradation of BP-3, reactive species scavenging experiments were conducted. The results of the scavenging study with the 1 wt% α-Bi₂O₃@g-C₃N₄ composite are shown in Fig. 9. The figure shows that when IPA, AO and SOD are used as quenchers, the photodegradation rate of BP-3 decreases from 92% under normal conditions to 51, 56 and 78%, respectively, and the k_app for the photocatalytic degradation of BP-3 by the 1 wt% α-Bi₂O₃@g-C₃N₄ composite decreases from 0.42 h⁻¹ in the
absence of scavengers to 0.06, 0.07 and 0.14 h\(^{-1}\) in the presence of IPA, AO and SOD, respectively (Fig. 9b). Thus, the presence of IPA, AO and SOD significantly affects the photocatalytic process. Therefore, the generated \(\cdot \text{OH}, \cdot \text{h}^+\) and \(\cdot \text{O}_2^-\) work together to degrade BP-3 (Eq. (13)).

To ascertain the Z-scheme heterojunction and further confirm the involvement of ROS (\(\cdot \text{OH}\) and \(\cdot \text{O}_2^-\)) in the photocatalytic system, EPR measurements were performed. As depicted in Fig. 10a and b, the characteristic peaks of the \(\cdot \text{OH}\) and \(\cdot \text{O}_2^-\) radicals were not detected prior to light exposure, whereas the typical characteristic peaks of \(\cdot \text{O}_2^-\) and \(\cdot \text{OH}\) radicals were observed when the sample was illuminated. This result suggests that \(\cdot \text{O}_2^-\) and \(\cdot \text{OH}\) radicals play significant roles in the photocatalytic process. As shown in Fig. 10a, the typical characteristic peak of \(\cdot \text{OH}\) radicals for g-C\(_3\)N\(_4\) does not appear under dark and illuminated conditions owing to the photogenerated holes on g-C\(_3\)N\(_4\) having an inadequate oxidation potential for producing OH radicals. This result reveals that the VB potential edge of g-C\(_3\)N\(_4\) is 1.50 eV, which is lower than the ~2.72 eV standard redox potential of \(\cdot \text{OH}/\text{H}_2\text{O}\). However, g-C\(_3\)N\(_4\) can facilitate the generation of \(\cdot \text{OH}\) radicals on the surface of 1 wt% \(\alpha\-\text{Bi}_2\text{O}_3@g\-\text{C}_3\text{N}_4\). As seen in Fig. 10b, the \(\cdot \text{O}_2^-\) EPR signal intensity of 1 wt% \(\alpha\-\text{Bi}_2\text{O}_3@g\-\text{C}_3\text{N}_4\) is stronger than that of g-C\(_3\)N\(_4\). This result shows that more \(\cdot \text{O}_2^-\) radicals are generated on the surface of 1 wt% \(\alpha\-\text{Bi}_2\text{O}_3@g\-\text{C}_3\text{N}_4\) than on the surface of g-C\(_3\)N\(_4\). Additionally, Figs. S12a, S13a and S14a show the 0.5 wt% \(\alpha\-\text{Bi}_2\text{O}_3@g\-\text{C}_3\text{N}_4\), 3 wt% \(\alpha\-\text{Bi}_2\text{O}_3@g\-\text{C}_3\text{N}_4\), and 5 wt% \(\alpha\-\text{Bi}_2\text{O}_3@g\-\text{C}_3\text{N}_4\) composites dispersed in methanol (for DMPO-\(\cdot \text{O}_2^-\)), while Figs. S12b, S13b and S14b show the 0.5, 3, and 5 wt% \(\alpha\-\text{Bi}_2\text{O}_3@g\-\text{C}_3\text{N}_4\) composites dispersed in water (for DMPO-\(\cdot \text{OH}\)). Thus, it can be inferred that the photocatalysis of the as-synthesized sample follows the Z-scheme photocatalytic mechanism, which not only delays charge carrier recombination but also preserves strong redox potentials to effectively degrade pollutants.

The main steps of the possible photocatalytic reaction mechanism are proposed as follows:

\[
\begin{align*}
\alpha\-\text{Bi}_2\text{O}_3@g\-\text{C}_3\text{N}_4 + \text{h}^+ &\rightarrow \alpha\-\text{Bi}_2\text{O}_3 (\text{e}^- + \text{h}^+) \\
+ g\-\text{C}_3\text{N}_4 (\text{e}^- + \text{h}^+) \\
\alpha\-\text{Bi}_2\text{O}_3 (\text{e}^- + \text{h}^+) &\rightarrow \alpha\-\text{Bi}_2\text{O}_3 (\text{h}^+) \\
+ g\-\text{C}_3\text{N}_4 (\text{e}^-) \\
2\text{h}^+ + 2\text{H}_2\text{O} &\rightarrow 2\cdot \text{OH} + 2\text{H}^+ 
\end{align*}
\]
\[ \text{O}_2 \text{(ads)} + e^- \rightarrow 2\text{O}_2^- \]  
(10)

\[ 2\text{O}_2^- + 2\text{H}^+ + e^- \rightarrow \text{H}_2\text{O}_2 \]  
(11)

\[ \text{H}_2\text{O}_2 + e^- \rightarrow \text{OH} + \text{OH}^- \]  
(12)

\[ \text{h}^+ + \cdot\text{O}_2^- + \cdot\text{OH} + \text{BP-3} \rightarrow \text{Intermediate product} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]  
(13)

From the obtained experimental and characterization results, a schematic illustration showing the possible photodegradation mechanism is proposed in Fig. 11.

To further confirm the photodegradation of BP-3, HPLC measurements were conducted. Figure S10d shows the HPLC chromatograms of BP-3 before and after photocatalytic degradation by the 1 wt% \( \alpha \)-Bi\(_2\)O\(_3@g\)-C\(_3\)N\(_4\) composite. The flow rate was 0.8 mL min\(^{-1}\), and the injection volume was 20 \( \mu \)L. Two major peaks are recorded for the 300 min photocatalytic degradation process. The peaks centered at 4.68 and 8.21 min correspond to BP-3 and an intermediate byproduct, respectively. The peak intensities of BP-3 and the intermediate byproduct significantly decrease during the photodegradation process, which indicates that both BP-3 and the intermediate byproducts degrade during photocatalysis. Generally, BP-3 is metabolized to 2,4-dihydroxybenzophenone and dioxynbenzene via demethylation and hydroxylation routes, respectively [18].

### 3.6 Photocatalyst reusability test

The reusability of catalysts is a very important parameter for their practical application. Herein, we investigated the reusability of the as-synthesized 1 wt% \( \alpha \)-Bi\(_2\)O\(_3@g\)-C\(_3\)N\(_4\) by performing four successive recycling runs, and the results are shown in Fig. 12. The removal efficiencies observed after the second, third and fourth recycling runs for BP-3 photodegradation decrease slightly by 4%, 6% and 8%, respectively. This decrease might be due to the loss of some catalyst during the washing, centrifugation and drying procedures and the active sites of the catalyst surface being covered by reactive chemicals. However, the apparent rate constant of 1 wt% \( \alpha \)-Bi\(_2\)O\(_3@g\)-C\(_3\)N\(_4\) after the fourth recycling test indicated a higher photocatalytic efficiency than that after the other runs. Therefore, the as-synthesized 1 wt% \( \alpha \)-Bi\(_2\)O\(_3@g\)-C\(_3\)N\(_4\) has good stability and favorable reusability, which promotes its practical applicability.

### 4 Conclusions

In this study, novel \( \alpha \)-Bi\(_2\)O\(_3@g\)-C\(_3\)N\(_4\) composites with different weight percentages (0.5, 1, 3 and 5 wt%) of \( \alpha \)-Bi\(_2\)O\(_3\) were synthesized by a mixing-calcination strategy. Among these photocatalysts, 1 wt% \( \alpha \)-Bi\(_2\)O\(_3@g\)-C\(_3\)N\(_4\) showed higher photocatalytic efficiency than the other photocatalysts for BP-3 degradation, exhibiting an optimal rate constant of 0.42 h\(^{-1}\), which is up to 6.3 times
higher than that of pristine g-C3N4. The improved photocatalytic performance can be attributed mainly to the enhanced photogenerated e−-h+ charge separation and suppressed e− and h+ recombination, which are dominant factors for improving the photocatalytic activity. More importantly, radical trapping experiments and EPR findings confirm that the active species •OH, h+ and •O2• work together to enhance the photocatalytic activity of the composite. The migration pattern of photogenerated carriers suggests a Z-scheme photocatalytic mechanism rather than a type II mechanism. The method presented in this study might be considered a promising approach for the removal of emerging organic pollutants.

5 Supplementary Information
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Additional file 1. Supplementary materials.

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Authors’ contributions
Abiyu Kerebo Berekute conducted the experiments and wrote the study. Kuo-Pin Yu and Yi-Hsu Chiang are Abiyu Kerebo Berekute's advisor and coadvisor, respectively. They provided research ideas and guidance for this study. All authors read and approved the final manuscript.

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Availability of data and materials
All data generated or analyzed during this study are available within the article and Supplementary Materials.

Declarations

Competing interests
The authors declare they have no competing interests.

Author details
1International PhD Program in Environmental Science and Technology, University System of Taiwan, Taipei 11221, Taiwan. 2Institute of Environmental and Occupational Health Sciences, National Yang Ming Chiao Tung University, Taipei 11221, Taiwan. 3Institute of Environmental Engineering, National Yang Ming Chiao Tung University, Hsinchu City 30010, Taiwan.
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