Decoration of Au nanoparticles onto BiOCl sheets for enhanced photocatalytic performance under visible irradiation for the degradation of RhB dye

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ABSTRACT
Plasmonic photocatalysts are promising candidates for use in the degradation of pollutants. Their ability to degrade a wide range of organic pollutants stems from key properties such as high visible light absorption, the ability to generate hot electrons and the formation of a Schottky barrier that facilitates effective separation of charge carriers. In the present work, we synthesised bismuth oxychloride sensitised with gold nanoparticles (NPs, 20–50 nm) via a two-step chemical process at low temperature. The fabricated Au/BiOCl powder was evaluated in the degradation of Rhodamine B (RhB) dye under visible light irradiation. The photocatalytic performance of the Au/BiOCl hybrid was almost double that of pristine BiOCl. This enhanced performance was attributed to electron transfer from BiOCl to Au via the formation of heterojunctions at the BiOCl/Au interface. Additionally, the surface plasmon resonance effect of the Au NPs provided high optical absorbance in the visible spectrum. TEM (transmission electron microscopy) analysis indicated the presence of polar (010) facets on the BiOCl sheets, which also contributed to dramatically improving their photocatalytic performance. The degradation time of the Au/BiOCl hybrid was 200 min compared with 320 min for pure BiOCl.

KEYWORDS
Bismuth oxychloride; Au nanoparticles; photocatalysis; exposed facets; surface plasmon resonance effect

1. Introduction
Semiconductor heterogeneous photocatalysts, eg ZnO/CdS, TiO₂/CdSe, are of interest because of their low cost and utility in applications such as water purification.[1–6] These photocatalysts have a band gap energy structure in which electron-hole pair formation takes place in the conduction and valence bands. It is believed that when organic molecules contact these catalyst surfaces, the induced redox reactions act to degrade the compounds. However, present plasmonic photocatalysts exhibit low absorbance, generating few charge carriers. Additionally, the high recombination rate, arising from the presence of structural defects, reduces photocatalytic activity. The separation of electron-hole pairs is essential to overcome this problem and improve photocatalytic efficiency.[7,8]
Numerous single-component semiconductor photocatalysts have been reported, including TiO$_2$, ZnO and CdS. Bismuth oxychloride (BiOCl) is a promising photocatalyst for the detoxification of water.[9–16] In addition to its suitable optical and electrical properties, BiOCl displays a unique, layered tetragonal [Cl–Bi–O–Bi–Cl]$_n$ structure with nonbonding interactions through the Cl atoms along the c-axis. In the BiOCl crystalline structure, four Bi–Cl atoms form opposing tetragonal pyramidal faces. The layers are perpendicular to the internal static electric field, which can be separated into photo-induced electron-hole pairs.[17,18] Not only its unique structure properties but also its two-dimensional structures can improve photosensitised catalytic activities due to excellent charge movements. It leads to reduce recombination rate and shows higher photodegradation activity.[19–21] According to the literature, the generation of an internal static electric field in the BiOCl structure could reduce recombination losses. Decoration of the BiOCl structure with metal nanoparticles (NPs) has been shown to improve the photocatalytic decomposition of organic contaminants.[22,23] Different crystalline facets can exhibit different photocatalytic performance. Recent research has focused on those facets of the BiOCl crystal structure that display superior photocatalytic activity.[24,25] Jiang et al. (2012) studied BiOCl nanosheets with exposed (001) and (010) facets. The performance of the different facets depended on the internal electric fields.[26] Li et al. (2014) reported that oxygen vacancies on the {001} facets of BiOCl nanosheets could be sustained under visible light.[27] Wang et al. (2012) reported that BiOCl nanosheets with {001} facets presented greater photosensitised degradation because of the high oxygen atom density on those facets.[28]

Gold (Au) is a more stable metal than silver in terms of its thermal and electrical conductivity and chemical activity.[29,30] In particular, its strongest absorption under visible light stems from a surface plasmon resonance (SPR) effect.[31,32] This effect results from the interaction between photons and nano-sized metal particles. These effects have recently been applied to photocatalysis as a way to promote charge carrier generation. [33–36] Gold particles have been used in numerous applications such as catalysis, cancer diagnostics and chemical sensors because of their extraordinary activity.[37] There are few reports concerning the various synthetic approaches to Au/BiOCl photocatalysts. [38–40] Kim et al. (2014) discussed the morphological differences between BiOCl and BiOCl$_x$I$_{1-x}$ prepared in water and ethylene glycol with respect to Ag- and Au-doping conditions.[41] Michel et al. (2012) reported that nanostructured BiOCl doped with Au NPs could be used in gas sensors.[42] Lin et al. (2014) reported synthesising BiOCl with Au NPs on different facets using a chemical reduction method.[43] It is clear that different synthetic routes to BiOCl decorated with Au NPs yield catalysts with different photocatalytic performance. However, the photocatalytic efficiency of Au/BiOCl is currently insufficient for commercial device fabrication because of poor optical absorbance, a high rate of recombination and a low surface area. Moreover, the fabrication process is complex and sometimes requires high temperatures. Therefore, we focused on enhancing the surface area and reducing the recombination rate of these systems by adding Au NPs to BiOCl sheets. Moreover, we synthesised products using a simple hydrothermal process at low temperature.

Herein, we report the synthesis of Au/BiOCl using a hydrothermal method and an assisted sonication method. The microstructure revealed circular Au NPs on BiOCl sheets, which enhanced the surface area. The Au/BiOCl hybrid exhibited a higher photocatalytic activity than did pure BiOCl toward Rhodamine B (RhB) under visible
light irradiation. Separation of charge carriers increased and the recombination of photo-generated electron-hole pairs decreased because of the exposed BiOCl \{001\} facets in this structure and the SPR effect of the Au NPs. This prepared material could be used in water purification devices.

## 2. Experimental section

### 2.1. Synthesis of BiOCl sheets

BiOCl with a sheet structure was grown using a hydrothermal method at relatively low temperature. Bismuth oxynitrate powder (Bi(NO₃), 0.478 g) was added to 5 mL of nitric acid (HNO₃) with constant stirring. Potassium chloride (KCl, 0.074 g) and hexamethylenetetramine (HMTA, 0.85 g) powders were added to the solution. Finally, distilled water (30 mL) was poured into the solution. Poly(vinylpyrrolidone) (PVP, 0.5 g) powder was added to the solution to control the surface morphology. After constant stirring at room temperature for ca. 5 h, the solution was transferred into a Teflon-lined stainless steel autoclave and maintained at 150 °C for 1 h in a box furnace. After completion of the hydrothermal reaction, the autoclave was allowed to cool at room temperature in air and the BiOCl powder was obtained by filtration.

### 2.2. Synthesis of BiOCl decorated with Au nanoparticles

Au NPs were prepared by the Turkevich method.\[44,45\] In brief, gold chloride hydrate powder (0.050 g) was added to distilled water (300 mL) with stirring. The temperature was gradually increased to the boiling point of the solution and it was left to boil for 30 min. Then, a solution of trisodium citric dihydrate (C₆H₅Na₃O₇, 0.3423 g in 30 mL) was added. Boiling was continued until the colour of the solution changed from transparent to pale red. The change in colour indicated the formation of Au NPs. To prepare Au/BiOCl, BiOCl powder (0.050 g) was added to the Au nanoparticle solution (25 mL) in a vial. The suspension was then sonicated for 1 h to improve the dispersion and to attach the Au NPs onto the BiOCl sheets. The Au/BiOCl powder was finally obtained by filtration.

### 2.3. Photocatalytic activity

Photocatalytic performance was evaluated by degrading RhB (Junsei, Japan) dye solution under illumination with a halogen lamp (100 W). The RhB solution was prepared by dissolving RhB powder (0.008 g) in deionised water (2000 mL) and mixing for 2 h. The solution was stored in a dark location. Each experiment consisted of first mixing powdered catalyst (0.1 g, BiOCl or Au/BiOCl) with the RhB solution (250 mL) for 30 min to completely dissolve the solids before irradiation. Then, the solution was exposed to visible light while stirring. Aliquots (3–4 mL) were collected into vials every 20 min during irradiation time for spectrophotometric analysis. For comparison, 100 mg of TiO₂ Degussa (P25) powders are used for photocatalytic activity under the same condition.
2.4. Characterisation

X-ray diffraction (XRD; D/Max−2500/PC, Rigaku, USA; Cu Kα source) was conducted to examine the crystalline BiOCl and Au phases. Unique morphologies were discovered using scanning electron microscopy (SEM; S4800, Hitachi, Japan) and transmission electron microscopy (TEM; JEM 2100F, JEOL, Japan). Energy-dispersive spectroscopy (EDS) analysis was performed using an Oxford Instruments INCA instrument and a scanning range from 0 to 30 keV to determine the atomic percentages of the Au/BiOCl powder. Raman spectroscopy (Renishaw, USA; 532-nm laser) revealed the surface facet structure of BiOCl. Optical absorbance and photocatalytic activity were determined using ultraviolet−visible spectroscopy (UV−Vis; V650, JASCO, Japan). X-ray photoelectron spectroscopy (XPS; Sigma Probe, Thermo Fisher Scientific, UK; Al Kα source) was used to identify the chemical bonding states in BiOCl and Au/BiOCl.

3. Results and discussion

3.1. SEM analyses

Figure 1 shows the surface morphologies of pristine BiOCl and Au/BiOCl samples. Flower-like structures combined with sheets of BiOCl were found with an average size of

![Image](image_url)

**Figure 1.** SEM micrographs of (a) BiOCl, (b) Au/BiOCl and (c) EDS spectrum of Au/BiOCl; the table of elements is shown in the inset.
a few micrometers. The flower-like shapes are shown in Figure 1(a). The morphology of BiOCl can be altered from circular to flower-like using PVP surfactants.[46] This effectively increases the photocatalytic surface area of the material. Figure 1(b) shows that the Au/BiOCl hybrid had spherical Au NPs broadly distributed across the BiOCl sheets. The EDS analysis of Au/BiOCl in Figure 1(c) indicates the atomic percentages of the synthesised materials. Four elements, oxygen, chloride, gold, and bismuth, were identified. The atomic percentage of Au at 4.63% was lower than that of Bi, O, and Cl because of the small numbers of Au NPs. Furthermore, the atomic ratio on bismuth and chloride elements has confirmed to be nearly 1:1 ratio.[47,48] Therefore, we clearly confirm the successful formation of Au NPs on BiOCl sheets.

3.2. TEM analyses

The TEM micrograph in Figure 2 shows the distribution of Au NPs on a BiOCl sheet. Similar to the SEM micrographs, Figure 2(a) shows the branches of flower-like structure of BiOCl with an average size of 500 nm. As shown in Figure 2(b), spherical Au NPs were randomly distributed and deposited on the BiOCl sheets. The Au NPs were smaller than 50 nm in diameter, which is in good agreement with the particle size of a colloidal solution having a pale red colour.[49] In addition to this, high resolution transmission electron microscopy (HRTEM) image of Au/BiOCl sample shows the d-spacing of 0.26 nm for BiOCl and 0.23 nm for Au NPs, respectively. Figure 2(d) displays the selected-area electron diffraction (SAED) pattern of BiOCl structure, confirming the polycrystalline nature with orientation along (111), (200), (220), (311) and (222) planes. These planes match with the XRD peaks. As shown in Figure 2(e), the SAED pattern of Au NPs show single crystalline nature with the plane along (002) and (102) with an angle of 44°.

3.3. BET measurement

The N2 atmosphere adsorption and desorption isotherms for specific surface area are shown in Figure 3 using BET (Brunauer–Emmett–Teller) analysis. It follows IV type of isotherms with relative pressure vs. volume adsorption in hysteresis loop. Figure 3(a) displays pristine of BiOCl adsorption–desorption result with its surface area value of 15.01 m²g⁻¹. The specific surface area for pure BiOCl in other reference reveals 15.99 m²g⁻¹ value, which corresponds with that of as-prepared sample.[50] Figure 3(b) shows adsorption–desorption curve for Au/BiOCl hybrid having its surface area value of 17.84 m²g⁻¹, which is higher than that of pristine BiOCl. Hence, Au loading into BiOCl structure improved the surface area, resulting in more active sites for pollutant adsorption. This could improve the photocatalytic performance.

3.4. X-ray diffraction

XRD analyses were conducted to examine the crystallinity and phase orientation of the various materials. Figure 4 shows that the intense BiOCl peaks for the Au/BiOCl hybrid were in excellent agreement with those peaks for a BiOCl standard reference material (JCPDS #00–006–0249). The BiOCl lattice constants are \( a = 3.89 \) Å and \( b = 7.37 \) Å for tetragonal BiOCl.[51] The hydrothermal method that we used to fabricate the BiOCl is
Figure 2. TEM micrographs: (a) pristine BiOCl, (b) Au/BiOCl, (c) Au/BiOCl of d-spacing, (d) Au and (e) BiOCl SAED pattern.
a straightforward one that results in a highly crystalline product. The diffractogram of the Au/BiOCl hybrid shows that there was no change in the crystal structure of BiOCl. The Au peaks were in good agreement with standard data card values (JCPDS #01-071-4615). The peaks were of low intensity because of the relatively small amount of Au on the BiOCl sheets.

### 3.5. Raman spectroscopy

Raman spectroscopy was used to study the specific surface structures of the synthesised products (Figure 5). The BiOCl bands, found at three different wavenumbers, correspond...
Figure 4. XRD patterns of (a) BiOCl, (b) Au/BiOCl, (c) Au JCPDS card and (d) BiOCl JCPDS card.

Figure 5. Raman spectra of BiOCl and Au/BiOCl.
to the motion of halogen atoms on BiOCl surface.[52] Among them, the bands at 61 and 143 cm$^{-1}$ were attributed to an external and internal Bi–Cl stretching mode assigned as A$_{1g}$, respectively. The BiOCl band at 201 cm$^{-1}$ was assigned to an E$_{g}$ mode of Bi–Cl stretching. Generally, symmetric vibrations have a chance to get more intense Raman bands at 143 cm$^{-1}$ than asymmetric vibrations as observed in Figure 5.[53] Further, weak and broad bands at ca. 397 cm$^{-1}$ are caused by the motion of oxygen atoms, and were assigned to E$_{g}$ and B$_{1g}$ modes, respectively.[54] The bands at 397 cm$^{-1}$ were observed with slight blue-shift because of light-induced compressive stress in the Au NPs that were loaded onto the BiOCl sheets.[43,55–57] Au NPs absorb photons under irradiation and the photo-generated electrons transfer rapidly to the conduction band of BiOCl. Those electrons cause the vibration of local oxygen atoms that are compressively stressed by the surrounding grains.[58] These distinctive effects confirmed the existence of Au NPs on the BiOCl surface.

### 3.6. X-ray photoelectron spectroscopy

XPS analyses revealed the surface compositions and chemical states of the synthesised products (Figure 6). The peaks corresponded to the binding energies of Bi, O, Cl and Au. The Bi (4f) binding energies of pristine BiOCl with Au/BiOCl were compared to evaluate the effect of the decorative Au NPs. For BiOCl, two main peaks at 164.5 and 159.1 eV correspond to the Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$ orbitals of Bi$^{3+}$, respectively.[59] In case of Au/BiOCl, peaks at 164.4 and 159 eV were shown to be Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$, respectively. Those peaks have shifted to lower binding energy, revealing the apparent blue-shift of ca. 0.1 eV. The existence of shift shows that BiOCl structure accepts SPR electrons from Au NPs.[60] Therefore, the shift in binding energy of BiOCl loaded with Au NPs indicates strong interfacial interactions between Au and BiOCl relative to that of pristine BiOCl due to inducing electron transfer.[61,62]
3.7. Optical absorbance

Figure 7 compares the optical absorbance of the BiOCl and Au/BiOCl powders. The steeply sloping absorption of pure BiOCl plateaued at ca. 300 nm while that of Au/BiOCl reached a maximum at ca. 325 nm. The band gap energy for BiOCl was only 3.07 eV (Figure 7(d)). When Au NPs were added to the BiOCl sheets, the band gap changed to 384 nm with a calculated energy of 2.94 eV. The band gap energy for BiOCl decorated with Au NPs was lower than that of pristine BiOCl.[63,64] The narrow band gap is related to particle size. The absorbance data indicate that the plasmon resonance absorption of Au NPs appeared in the visible region at ca. 540 nm (Figure 7(c)). The band appears because of the oscillation of free conduction band electrons in the Au NPs.[65] The surface plasmon absorption band position also depends on particle size and the intensity of this absorption depends on the amount of Au particles.[66,67] Additionally, as shown in Figure 7(b) and 7(c), it demonstrates shift in absorption from 524 to 540 nm. Generally, wavelength ($\lambda_{\text{max}}$) and electron density ($n$) of metal NPs are related to each other according to following Equation (1) [68]:

$$\lambda_{\text{max}} = 4\pi c \left( \frac{2\varepsilon_0 m}{e^2 n} \right)^{1/2}$$

where $c$ (speed of light), $\varepsilon_0$ (vacuum permittivity), $e$ (charge of electron) and $m$ (mass of
electron). According to this formula, if the induced electrons transfer from Au NPs to conduction band of BiOCl, it reduces $n$, leading to the shift in $\lambda_{\text{max}}$. Thus, comparative analyses of the optical spectra confirmed the strong interaction between BiOCl and Au NPs which showed the surface plasmon absorption properties of the Au NPs.

### 3.8. Photocatalytic activities

The photocatalytic activities of the synthesised BiOCl and Au/BiOCl powders were assessed by monitoring the disappearance under visible light irradiation of the RhB dye absorption at ca. 550 nm (Figure 8). Figure 8(a) shows that pristine BiOCl exhibited a degradation time of ca. 300 min. Figure 8(b) shows the behaviour of the Au/BiOCl hybrid, whose degradation time was ca. 200 min. The presence of Au NPs clearly reduced the degradation time under identical reaction conditions. Figure 9(a) shows the degradation behaviour as a function of RhB dye concentration with different time. In the dark conditions, as-prepared catalysts have no degradation, indicating that RhB dye did not go through self-degradation during the photocatalytic activity and only Au NPs can be

![Figure 8](image-url). Photocatalytic activity of (a) pristine BiOCl and (b) Au/BiOCl.
affected on its activity. For comparison, photodegradation of TiO₂ Degussa (P25) was conducted under the same condition and there was no degradation. As shown in Figure 9(b), the experimental data was fitted with pseudo-second-order reaction model as the kinetics mechanism. Second-order equation is as follows (2);

\[
\frac{1}{[A_t]} = kt + \frac{1}{[A_0]}
\]  

(2)

\(A_0\) is the initial concentration of RhB \((t = 0)\) and \(A_t\) is the concentration of RhB at specific time. Those fitting data are shown in Figure 9(b). From that equation, we can clearly calculate the \(k\) value as \(3.07 \times 10^{-3}\) min⁻¹ of BiOCl and \(8.69 \times 10^{-3}\) min⁻¹ of Au/BiOCl, respectively. Based on higher kinetic rate constant for Au/BiOCl, we can estimate its good photocatalytic performance relative to that of pure BiOCl. Further, the surface-area-normalised degradation rate constants were calculated to explore the influence of surface area depending on photocatalytic activities.[69] The surface-area-normalised constants were calculated as kinetic constant divided by the specific surface area (Table 1). It exhibited

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**Figure 9.** Photodegradation of RhB dye under visible light irradiation. (a) Photodegradation as a function of RhB dye concentration and (b) fitting of data to pseudo-second-order kinetics.
values as $2.05 \times 10^{-4} \text{ min}^{-1} \text{m}^{-2} \text{g}$ and $4.87 \times 10^{-4} \text{ min}^{-1} \text{m}^{-2} \text{g}$ on BiOCl and Au/BiOCl, respectively. These results confirmed the improvement in photocatalytic activity of Au/BiOCl sample compared to that of pure BiOCl regardless of surface area. Scheme 1 illustrates a possible mechanism for the degradation of RhB dye by Au/BiOCl and it is compared with degradation mechanism for pure BiOCl. Figure 7 shows that the synthesised BiOCl absorbed only in the UV region. Visible light could not absorb and excite the BiOCl because of its high band gap energy. RhB cannot self-photolyse and is considered to be a photosensitiser. Au/BiOCl acts as an electron carrier and donor.[70]. The photodegradation process starts upon irradiation and the optical adsorption of RhB dye molecules, producing RhB$^*$ and ·RhB$^+$. During RhB$^*$ production, an electron from RhB$^*$ is injected into the conduction band of BiOCl to form BiOCl(e$^-$). That electron reacts with BiOCl-surface-attached O$_2$ molecules to produce oxygen radicals, O$_2$$. The radical cation of RhB$^+$ reacts with oxygen radicals, which eventually degrade the products. Additionally, Au nanoparticle is acted as an electron donor to the conduction band of BiOCl and it transfers the electrons via SPR effects. Consequently, Au NPs help photodegradation reaction to be faster and better, as

| Samples | Kinetic constant \([\text{min}^{-1}]\) | Before normalised surface area \([\text{m}^2/\text{g}]\) | After normalised surface area \([\text{min}^{-1}\text{m}^{-2}\text{g}]\) |
|---------|---------------------------------|----------------|----------------|
| BiOCl   | $3.07 \times 10^{-3}$          | 15.01          | $2.05 \times 10^{-4}$          |
| Au/BiOCl| $8.69 \times 10^{-3}$          | 17.84          | $4.87 \times 10^{-4}$          |

**Scheme 1.** Proposed degradation mechanism of RhB dye molecules by (a) only BiOCl and (b) Au nanoparticles loaded on BiOCl sheets.
shown in Figure 9(a). Further mechanism equations of Au/BiOCl in detail, can be shown below Equations (3)–(9).[23,61,71]:

\[
\begin{align*}
\text{BiOCl} + \text{hv} & \rightarrow \text{BiOCl} + (e^- + h^+) \\
\text{Au} + \text{hv} & \rightarrow \text{Au} + (e^- + h^+) \\
\text{RhB} + \text{hv} & \rightarrow \text{RhB}^+ \\
\text{RhB}^+ + \text{BiOCl} & \rightarrow \text{RhB}^+ + e^- \\
\text{O}_2 & \rightarrow e^- \rightarrow \cdot\text{O}_2^- \\
\text{O}_2^- + \cdot\text{RhB}^+ & \rightarrow \text{Degradation} \\
h^+ + \text{RhB} & \rightarrow \text{Degradation}
\end{align*}
\]

3.9. Reusability test

Photostability is a crucial factor to be applied in diverse fields. The recycle test of Au/BiOCl hybrid sample has been conducted up to three consecutive cycles under same condition, as shown in Figure 10. Clearly, there is no substantial change or reduction in the photocatalytic performance, indicating good stability of the present photocatalysts until two cycles. Moreover, the stability decreased slightly after third cycle, compared to former cycle degradations, indicating the minimal change in performance. In addition to this, we measured XRD pattern of the same powder after recycle test as shown in Figure 11. The same peak positions for Au and BiOCl structure before and after recycling test, were observed in XRD analysis. It seems that Au NPs were not exfoliated after the recycling test. Therefore, Au/BiOCl can be reused in photocatalysis fields, due to its excellent stability.

Figure 10. Reusability cycle test of Au/BiOCl composite under visible illumination with 3 times same process.
4. Conclusions

A heterogeneous semiconductor photocatalyst, BiOCl decorated with Au NPs (Au/BiOCl), was synthesised via a simple process using only hydrothermal and assisted sonication methods. SEM and TEM analyses revealed spherical Au NPs smaller than 50 nm in diameter attached to the (010) facets of thin sheets of BiOCl. XRD analyses indicated high crystallinity with clearly defined peaks for both BiOCl and Au. Raman bands at 201 and 397 cm\(^{-1}\) were blue-shifted relative to pristine BiOCl, consistent with light-induced compressive stress of the Au NPs. Optical absorbance measurements confirmed an SPR effect caused by the Au NPs. The SPR absorption is caused by the oscillation of electrons and is dependent on the Au particle size. The RhB dye degradation time with Au/BiOCl was ca. 200 min and ca. 300 min for pristine BiOCl. Thus, decorating BiOCl sheets with Au NPs greatly improved the photocatalytic activity under visible light irradiation over that of pristine BiOCl.

Disclosure statement

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