Easy conversion of BiOCl plates to flowers like structure to enhance the photocatalytic degradation of endocrine disrupting compounds

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Abstract
Endocrine disrupting chemicals (EDCs) are exogenous agents that interfere with the synthesis, secretion, transport, binding action and elimination of the natural hormones in our body. Bisphenol A (BPA), one of the well-known emerging pollutants, is widely used as an industrial ingredient in polycarbonate plastic products. BPA can be released into aquatic environments through domestic and industrial wastewater discharge. Development of cost-effective technologies for the removal of BPA is currently a priority R&D area. BiOCl microstructures materials were successfully prepared via a hydrothermal method and evaluated for the photocatalytic degradation of Bisphenol A via under UV-B light. The prepared BiOCl microstructures were characterised using XRD, DRSUV−vis, SEM, EDS and XPS analyses. SEM results demonstrated that the morphology of these BiOCl nanostructured materials could easily be modified from microplates to microflowers by altering the solution stirring speed during synthesis. XRD analysis showed that the product could be indexed to the tetragonal phase of BiOCl. The band gap energies determined by DRUV−vis were estimated to be 3.36 eV and 3.32 eV for microflowers and microplates respectively. EDS analysis confirmed the presence of three elements bismuth, oxygen and chlorine in the BiOCl. The microflowers exhibited enhanced photocatalytic performance because of the higher adsorption capacity and presence of more active sites compared to BiOCl microplates.

1. Introduction

Providing clean water to satisfy human needs in an era of the growing world population and massive industrial development is a grand challenge of the 21st century [1]. Water pollution due to the release of harmful substances from various anthropogenic processes has resulted in some footprints of these substances in water bodies throughout the world [2]. Consumption of polluted water can prompt ailments and sicknesses that have negative health impacts on humans and other living organisms [3]. Endocrine disrupting chemicals (EDCs) are among the exogenous chemicals capable of interfering and mimicking the hormonal action of living organisms. Bisphenol A (BPA) is one of the most common and well-known endocrine disrupting chemicals. 5–6 and is widely used as an intermediate in the production of polycarbonate and epoxy resins. BPA ends up in a variety of consumer goods such as plastic bottles and canned food liners [4, 5].

Traditional physical wastewater treatment methods have the major disadvantage of transferring the pollutants from one phase to another, which require subsequent treatment or disposal. On the other hand, biological treatments take a long time for the effluent to reach the required standards and produce a large quantity of sludge, which normally cannot be reused [6, 7]. Advanced oxidation processes (AOPs) have emerged as more effective and sustainable alternative techniques for the complete removal of pollutants in wastewater.
2. Experimental

2.1. Materials
Analytical grade Bismuth nitrate pentahydrate Bi(NO₃)₃·5H₂O, 98%. Nitric acid HNO₃, 99%, Potassium chloride KCl, 99%, were purchased from Sigma-Aldrich and were employed as received without additional purification. The chemical sample bisphenol was obtained from the Sigma-Aldrich and used without further purification. The molecular structure of bisphenol is shown in scheme 1. Deionized, doubly distilled water was used for the preparation of all solutions.

2.2. Synthesis of BiOCl microstructures
In a typical procedure for the synthesis of BiOCl microflowers and microplates, of Bismuth nitrate pentahydrate Bi(NO₃)₃·5H₂O (0.2425 g) was dissolved in of HNO₃ (50 ml) and dropwise added to of potassium chloride (0.0821 g) dissolved in of distilled water (20 ml) using a burette with fast stirring. This was followed by a non-stirring period of 2 h. The resulting solution was transferred into an autoclave and placed in an oven at 160 °C for 12 h. After that, the white powder obtained was dried at 80 °C for 12 h and then collected for characterization.

2.3. Characterization of the BiOCl microstructures
The crystalline properties of BiOCl microcrystals were studied by x-ray diffraction (XRD) using a Bench x-ray diffractometer (Model: MiniFlex 600) x-ray diffractometer equipped with graphite monochromatised CuKα radiation (λ = 1.540 Å) and NaI(Tl) detector. The absorption spectra of the as-prepared samples were recorded on a DRUV–vis diffuse reflectance spectroscopy (Jasco V670) in the wavelength range of 200–1000 nm, using BaSO₄ as a reference. The morphological features were examined by field-emission scanning electron microscope (JEOL, Japan (Model: JSM 7800F)). The maximum working voltage of 30 kV was achieved at a maximum resolution of 0.8 nm, and a working distance of 10 mm was used during the measurements. The
chemical states and relative surface compositions of the samples were studied using multi-probe x-ray photoelectron spectroscopy (XPS) (Omicron Nanotechnology, Germany) and a software package (Casa Software Ltd) was used to analyse the XPS data. The binding energies of the obtained spectra were calibrated with respect to the intrinsic carbon C1 peak at 284.6 eV.

2.4. Photocatalytic degradation studies
All photoreaction experiments were carried out in a photocatalytic reactor system which consists of a cylindrical borosilicate glass reactor vessel with an effective volume of 250 ml, a cooling water jacket, and a UV-B lamp (8 W medium-pressure mercury lamp (Institute of Electric Light Source, Beijing) positioned axially at the centre as a visible light. The reaction temperature was kept at 25 °C by circulating the cooling water. A special glass frit as an air diffuser was fixed at the reactor to disperse air into the solution uniformly. Photocatalytic activities of the prepared samples were examined by the degradation of Bisphenol A under UV-B light irradiation. For each run, the slurry was freshly prepared by adding 0.250 and 0.500 g of catalyst into 250 ml of 10 ppm aqueous BPA. The slurry was stirred in the dark for about an hour to establish the adsorption-desorption equilibrium. Aliquots were then sampled at fixed time intervals and filtered using syringe filter (0.45 μm) to remove any suspended particles. The filtrate was analysed on a UV-vis spectrophotometer.

3. Results and discussion

3.1. XRD analysis
The crystalline properties of prepared BiOCl samples were investigated through x-ray diffraction analysis figure 1. According to the JCPDS card No.006–0249, both samples were indexed to the tetragonal crystal phase. In addition, the grain sizes and other crystal parameters of the synthesized BiOCl were measured using the Maud Software with Cif card number 1011175 [32]. The space groups and lattice parameters of the samples were identified as P4/nmm, a = b = 3.89 Å, c = 7.37 Å and α = β = γ = 90° where the grain sizes were 94.6 nm for microplates and 296.3 nm for microflower structures. The increase in grain size was attributed to low molecular diffusion rate (without stirring) in the case of microflowers that allowed the growth of the grain size compared to the microplate, which was vigorously stirred allowing more seeds to form with small grain sizes. The observed diffraction peaks at 2θ values of 11.98°, 24.10°, 25.86°, 32.50°, 33.45°, 40.90°, 46.64°, 49.70°, 54.10°, 55.12° and 58.60° correspond to the respective miller indices (001), (002), (101), (110), (102), (112), (200), (113), (211), (104) and (212) planes respectively. All results perfectly concur with previously reported observations of similar materials [33].

3.2. Optical properties and band gap analysis
Band gap energies of the samples were determined from diffuse reflectance measurements by UV-vis spectrophotometer. The diffuse reflectance UV-vis spectra of the synthesized samples are shown in figure 2. The optical band gap was calculated according to the Tauc equation as follows [34]:

![Figure 1. X-ray diffraction patterns of BiOCl samples.](image-url)
where $\alpha$, $\nu$, $A$, and $E_g$ are the absorption coefficient, light frequency, proportionality constant and band gap, respectively. The band gap energy is estimated from the extrapolation of the straight region of the $\alpha hv^{1/2}$ versus energy graph to the $x$-axis. The band gap values for the microplate and microflower structures were 3.41 and 3.43 eV, respectively. The small difference in the band gap energy values was ascribed to the difference in the morphology of the synthesised materials. Therefore, any enhancement in the photocatalytic performance will be due to the morphology, surface area and surface defects differences [35].

3.3. SEM and EDS analysis

The morphologies of BiOCl microstructures were evaluated by scanning electron microscopy (SEM). Figure 3 shows the SEM images of the BiOCl obtained with vigorous stirring (figure 3(a)) and without stirring (figure 3(b)). A vigorous stirring of the precursor solution results in the formation of microplates while microflower structures were observed without stirring. The formation of microflower structures is attributed to low number of nucleation sites formed in the absences of stirring movement allowing the microplate structure to grow further. In general, the Van der Waals forces through Cl atoms in the atomic layers of [Cl–Bi–O–Bi–Cl] allow these sheets to packed on each other to form a 3D flower-like construction [36]. This microflower structure is expected to enhance the photocatalytic performance of synthesized BiOCl sample by providing more active sites to degrade the BPA [37]. The elemental composition of the microflower sample was confirmed through EDS analysis (figure 4). The sample was composed of three main elements; bismuth, oxygen and chlorine with an atomic ratio of Bi:O:Cl of 64.8:5.7:7.6 wt%. These results further confirmed the high purity of the synthesised BiOCl nanoflowers.
3.4. XPS analysis

The BiOCl microflower samples were examined through XPS technique to show the sample confirmation, elemental composition and chemical states. The XPS survey spectrum of BiOCl (figure 5) shows the presence of Bi, O and Cl as main elements that confirmed the high purity of the prepared samples. In general trace amount of carbon used to calibrate the instrument is detected around 284.23 eV. The high-resolution and core level peaks of Bi, O and Cl of BiOCl were analysed by CASA XPS software (figure 6). The XPS spectra for Bi shows doublet peaks at binding energy values around 164.9–170.1 eV and 447–470 eV representing Bi 4f and Bi 4d respectively. The Bi 4f doublet appears as two strong peaks with the splitting energy $\Delta = 5.2$ eV, which can be assigned to the Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$ of Bi$^{3+}$ (figure 6(b)). The Bi 4d doublet showed a peak split splitting energy, $\Delta$ of around 25 eV, again confirming the presence of Bi$^{3+}$ (figure 6(b)). The O and Cl peaks were also observed at binding energy value around 535 and 203.6 eV (figures 6(c) and (d)). These binding energies values are well matched with previously reported findings [38, 39].

3.5. Photocatalytic activity

Bisphenol A is known as a hard-to-degrade endocrine-disrupting chemical and was therefore selected as a model pollutant to determine the photocatalytic activity of the synthesised catalysts. The performance of the semiconductor photocatalytic microplates and microflowers was studied with the help of UV-vis absorption spectra by observing changes in the maximum absorbance of BPA at 278 nm (figure 7). The band intensity at 278 nm gradually declines with an increase in the irradiation time, indicating the degradation of the BPA with BiOCl microplates (figure 7(a)). The degradation was faster at higher photocatalyst loading of 500 mg with near

![Figure 4 EDS spectra of BiOCl sample.](image)

![Figure 5. XPS survey spectrum of BiOCl nanoflower.](image)
complete degradation being realised after 240 min of light exposure (figure 7(b)). These findings signify the importance of catalyst dosage optimization in photocatalytic experiments. The degradation efficiency is calculated using the equation:

\[
\text{% Degradation Efficiency} = \frac{(C_0 - C)}{C_0} \times 100
\]

where, \(C_0\) is the initial concentration of BPA and \(C\) is the concentration of BPA after treatment at time, \(t\). The maximum degradation efficiency BPA achieved after 90 min of illumination with UV-B light was 80.12% for the BiOCl microflowers compare to 60.7% for the BiOCl microplates at a catalyst dosage of 500 mg (figure 8). The experimental results showed enhancement photocatalytic activity for the microflowers, and this can be
attributed to the flower-like morphology, which offers more surface active sites and high adsorption capacity for the BPA. Photolysis showed barely any change in the concentration of the BPA, confirming the photostability of the pharmaceutical compound.

The photocatalytic degradation mechanism was proposed based on the discussion on the performance of the microflowers (figure 9). Under UV-B light irradiation, electrons are excited from the valance band to the conduction band of BiOCl simultaneously leaving holes in the valence band of the microflowers. The holes can scavenge H₂O molecules to form highly reactive OH⁻ radicals that can oxidise the BPA to the degradation by-products. The electrons, on the other hand, also scavenge O₂ to form superoxide radicals (O₂⁻) that can equally oxidise the BPA. The high surface area of microflowers provides active sites for these reactions to occur. BPA molecules adsorb onto the surface of BiOCl by electrostatic attraction and get mineralised by non-selective radicals.

4. Conclusion

A simple approach to fabricate BiOCl microstructures using the hydrothermal method was demonstrated. Plate- and flower-like microstructures were obtained by varying the precursor solution stirring rate. The XRD analysis confirmed the tetragonal phase of BiOCl. The band gap calculated through Tauc plots was estimated to be 3.36 and 3.32 eV for microflowers and microplates, respectively. EDS and XPS analyses revealed that the
samples were of high purity. Tuning the morphology of the BiOCl enhances the photocatalytic performance as the microflowers exhibited higher photocatalytic activity compared to the microplates. A degradation efficiency of 80% was observed within 4 h of UV-B irradiation using the BiOCl microflowers. Therefore, the adsorption of the target molecule on BiOCl surface is a crucial step toward efficient degradation of pollutants in water.

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References

[1] Qu X, Alvarez P J and Li Q 2013 Applications of nanotechnology in water and wastewater treatment Water Res. 47 3931–46
[2] Yang W, Song J, Higano Y and Tang J 2015 Exploration and assessment of optimal policy combination for total water pollution control with a dynamic simulation model J. Clean. Prod. 102 342–52
[3] Arenas-Sánchez A, Rico A and Vighi M 2016 Effects of water scarcity and chemical pollution in aquatic ecosystems: state of the art Sci. Total Environ. 572 390–403
[4] Santos J M, Pütz D A, Jurban M, Joakim A, Friedrich K and Kim H 2016 Differential BPA levels in sewage wastewater effluents from metro Detroit communities Environ. Monit. Assess. 188 585
[5] Guerra P, Kim M, Teslić S, Aalee M and Smyth S 2015 Biophenol-A removal in various wastewater treatment processes: operational conditions, mass balance, and optimization J. Environ. Manage. 152 192–200
[6] Grandclement C, Seyssieج E, Piram A, Wong-Wah-Chung P, Vanot G, Tilicas N, Roche N and Doumeng P 2017 From the conventional biological wastewater treatment to hybrid processes, the evaluation of organic micropollutant removal: a review Water Res. 111 297–317
[7] Sillanpää M, Nicbi M C, Matilainen A and Vepsäläinen M 2018 Removal of natural organic matter in drinking water treatment by coagulation: a comprehensive review Chem. Rev. 199 54–71
[8] Gil A, Galeano I A and Vicente MA 2019 Applications of Advanced Oxidation Processes (AOPs) in Drinking Water Treatment (Berlin: Springer)
[9] Al Balushi B S, Al Marzouqi F, Al Wahaibi B, Kuvarega A T, Al Kindy S M, Kim Y and Selvaraj R 2019 Controlled microwave-assisted synthesis of CdS–BiOCl/2D g-C3N4 heterostructure for the degradation of aniline-based pharmaceuticals under solar light illumination ACS Omega 4 4671–8
[10] Al Marzouqi F, Selvaraj R and Kim Y 2018 Thermal oxidation etching process of g-C3N4 nanosheets from their bulk materials and its photocatalytic activity under solar light irradiation Desalination. Water Treat. 116 267–76
[11] Al Ruqaishy M, Al Marzouqi F, Qi K, Liu S-Y, Karthikeyan S, Kim Y, Al-Kindy S M Z, Kuvarega A T and Selvaraj R 2018 Template-free preparation of TiO2 microspheres for photocatalytic degradation of pharmaceuticals in aqueous solution Desalination. Water Treat. 125537 F T H Al Sarihi 2018 Cerium-doped ZnO for photocatalytic degradation of pharmaceuticals in aqueous solution J. Photochem. Photobiol., A 342 2018 267–76
[12] Al Marzouqi F, Al Farsi B, Kuvarega A T, Al Lawati H A, Al Kindy S M, Kim Y and Selvaraj R 2019 Hydrothermal synthesis of CdS–BiOCl/2D g-C3N4 heterostructure for photocatalytic degradation of pharmaceuticals Appl. Surf. Sci. 457 539–65
[13] Al Marzouqi F, Al Farsi B, Kuvarega A T, Al Lawati H A, Al Kindy S M, Kim Y and Selvaraj R 2019 Controlled microwave-assisted synthesis of the 2D BiOCl/2D g-C3N4 heterostructure for the degradation of aniline-based pharmaceuticals under solar light illumination ACS Omega 4 4671–8
[14] Al Marzouqi F, Selvaraj R and Kim Y 2018 Thermal oxidation etching process of g-C3N4 nanosheets from their bulk materials and its photocatalytic activity under solar light irradiation Desalination. Water Treat. 116 267–76
[15] Al Ruqaishy M, Al Marzouqi F, Qi K, Liu S-Y, Karthikeyan S, Kim Y, Al-Kindy S M Z, Kuvarega A T and Selvaraj R 2018 Template-free preparation of TiO2 microspheres for the photocatalytic degradation of organic dyes Korean J. Chem. Eng. 35 2283–9
[16] Wetchakan K, Wetchakan N and Sakulsermsuk S 2018 An overview of solar/visible light-driven heterogeneous photocatalysis for water purification: TiO2- and ZnO-based photocatalysts used in suspension photoreactors J. Ind. Eng. Chem. 71 19–49
[17] Ahmad SN and Haider W 2018 Heterogeneous photocatalysis and its potential applications in water and wastewater treatment: a review Nanotechnology 29 342001
[18] Al Marzouqi F, Kim Y and Selvaraj R 2019 Shifting of the band edge and investigation of charge carrier pathways in the CdS/g-C3N4 heterostructure for enhanced photocatalytic degradation of levofloxacin New Journal of Chemistry 43 9784–92
[19] Meetani M A, Alajdeor A, Hisanodee S, Alhamadat A, Selvaraj R, Al Marzouqi F and Rauf M A 2019 Photocatalytic degradation of acetaminophen in aqueous solution by ZnO2, CdS, g-C3N4, catalyst and visible radiation Desalination. Water Treat. 138 270–9
[20] Qi K, Karthikeyan S, Kim W, Al Marzouqi F, Al-Khusaibi I S, Kim Y and Selvaraj R 2017 Hydrothermal synthesis of SnS2 nanocrystals for photocatalytic degradation of 2, 4, 6-trichlorophenol under white LED light irradiation Desalination. Water Treat. 92 108–15
[21] Zong J, Zhao Y, Ding L, Li H, Ma W, Chen C and Zhao J 2019 Opposite photocatalytic oxidation behaviors of BiOCl and TiO2 direct hole transfer vs. indirect OH oxidation Appl. Catalysis B 241 11620–6
[22] Wu S, Xiong J, Sun J, Hood Z D, Zeng W, Yang Z, Gu L, Zhang X and Yang S-Z 2017 Hydroxyl-dependent evolution of oxygen vacancies enables the regeneration of BiOCl photocatalyst ACS Applied Materials & Interfaces 9 16620–6
[23] Nguyen S D, Yeon J, Kim S-H and Halasymani P S 2011 BiO (IO)3; a new polar iodate that exhibits an aurivillius-type (Bi2O2)3+2 layer and a large SHG response JACS 133 12422–5
[24] Cong R, Sun J, Yang T, Li M, Liao F, Wang Y and Lin J 2011 Syntheses and crystal structures of two new bismuth hydroxyl borates containing [Bi2O2]3+2 layers: Bi2O3 [Bi2O2(OH)] and Bi2O3 [BO3(OH)] Inorg. Chem. 50 5098–104
[25] Al Abri R, Al Marzouqi F, Kuvarega A T, Meetani M A, Al Kindy S M, Karthikeyan S, Kim Y and Selvaraj R 2019 Nanostructured cerium-doped ZnO for photocatalytic degradation of pharmaceuticals in aqueous solution J. Photochem. Photobiol., A 112065
[26] Al-Fahdi T, Al Marzouqi F, Kuvarega A T, Mamba B B, Al Kindy S M, Kim Y and Selvaraj R 2019 Visible light active CdS@TiO2 core–shell nanostructures for the photodegradation of chlorophenols J. Photochem. Photobiol., A 374 75–83
[24] Fang J, Fan H, Tian H and Dong G 2015 Morphology control of ZnO nanostructures for high efficient dye-sensitized solar cells Mater. Charact. 108 51–7
[25] Al Marzouqi F, Al Adawi H, Qi K, Liu S-Y, Kim Y and Selvaraj R 2019 A green approach to the microwave-assisted synthesis of flower-like ZnO nanostructures for reduction of Cr (VI) Toxicological & Environ. Chem. 1–21
[26] Fang J, Fan H, Ma Y, Wang Z and Chang Q 2015 Surface defects control for ZnO nanorods synthesized by quenching and their anti-recombination in photocatalysis Appl. Surf. Sci. 332 47–54
[27] Arthur R, Ahern J and Patterson H 2018 Application of BiOX photocatalysts in remediation of persistent organic pollutants Catalysts 8 604–8
[28] Ye L 2016 BiOx (X = Cl, Br, and I) Photocatalysts Semiconductor Photocatalysis-Materials, Mechanisms and Applications (Intech Open)
[29] Ahern J, Fairchild R, Thomas J S, Carr J and Patterson H H 2015 Characterization of BiOX compounds as photocatalysts for the degradation of pharmaceuticals in water Appl. Catalysis B 179 229–38
[30] Lee G-J, Zheng Y-C and Wu J J 2018 Fabrication of hierarchical bismuth oxyhalides (BiOX, X = Cl, Br, I) materials and application of photocatalytic hydrogen production from water splitting Catal. Today 307 197–204
[31] He R, Zhang J, Yu J and Cao S 2016 Room-temperature synthesis of BiOCl with tailorable (0 0 1) facets and enhanced photocatalytic activity J. Colloid Interface Sci. 478 201–8
[32] Wang C-Y, Zhang Y-J, Wang W-K, Pei D-N, Huang G-X, Chen J-J, Zhang X and Yu H-Q 2018 Enhanced photocatalytic degradation of bisphenol A by Co-doped BiOCl nanosheets under visible light irradiation Appl. Catalysis B 221 320–8
[33] Gao X, Zhang X, Wang Y, Peng S, Yue B and Fan C 2015 Rapid synthesis of hierarchical BiOCl microspheres for efficient photocatalytic degradation of carbamazepine under simulated solar irradiation Chem. Eng. J. 263 419–26
[34] Tauc J, Grigorovic R and Vancu A 1966 Optical properties and electronic structure of amorphous germanium Physica Status Solidi (B) 15 627–37
[35] Huo Y, Zhang J, Miao M and Jin Y 2012 Solvothermal synthesis of flower-like BiOBr microspheres with highly visible-light photocatalytic performances Appl. Catalysis B 111 334–41
[36] Xu K, Xu X and Peng Z 2018 Facile synthesis and photocatalytic activity of La-doped BiOCl hierarchical, flower-like nano- / micro-structures Mater. Res. Bull. 98 103–10
[37] Cui Z, Mi L and Zeng D 2013 Oriented attachment growth of BiOCl nanosheets with exposed {1 1 0} facets and photocatalytic activity of the hierarchical nanostructures J. Alloys Compd. 549 70–6
[38] Wu T, Li X, Zhang D, Dong F and Chen S 2016 Efficient visible light photocatalytic oxidation of NO with hierarchical nanostructured 3D flower-like BiOCl/Br−x solid solutions J. Alloys Compd. 671 318–27
[39] Sun M, Zhao Q, Du C and Liu Z 2015 Enhanced visible light photocatalytic activity in BiOCl/SnO2 heterojunction of two wide band-gap semiconductors RSC Adv. 5 22740–52