Controlled Microwave-Assisted Synthesis of the 2D-BiOCl/2D-g-C₃N₄ Heterostructure for the Degradation of Amine-Based Pharmaceuticals under Solar Light Illumination

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ABSTRACT: Designing efficient 2D-bismuth oxychloride (BiOCl)/2D-g-C₃N₄ heterojunction photocatalysts by the microwave-assisted method was studied in this work using different amounts of BiOCl plates coupled with g-C₃N₄ nanosheets. The effects of coupling the 2D structure of g-C₃N₄ with the 2D structure of BiOCl were systematically examined by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy, X-ray diffraction, photoluminescence (PL), lifetime decay measurement, surface charges of the samples at various pH conditions, and UV–vis diffuse reflectance spectroscopy (UV–vis DRS). The prepared photocatalysts were used for the degradation of amine-based pharmaceuticals, and nizatidine was used as a model pollutant to evaluate the photocatalytic activity. The UV–vis DRS and other optical properties indicated the major effect of coupling of BiOCl with g-C₃N₄ into a 2D/2D structure. The results showed a narrowing in the band gap energy of the composite form, whereas the PL and lifetime analysis showed greater inhibition of the electron–hole recombination process and slightly longer charge carrier lifetime. Accordingly, the BiOCl/g-C₃N₄ composite samples exhibited an enhancement in the photocatalytic performance, specifically for the 10% BiOCl/g-C₃N₄ sample. Moreover, the zeta potential of this sample at different pH values was evaluated to determine the isoelectric point of the synthesized composite material. Consequently, the pH was adjusted to match the isoelectric point of the complex materials, which further enhanced the activity. Further degradation of pharmaceuticals was studied under solar light irradiation, and 96% degradation was achieved within 30 min.

1. INTRODUCTION

The research work nowadays is oriented toward treatment of wastewater and drinking water from various organic contamination, more specifically from pharmaceuticals and personal care products. Amine-based pharmaceuticals such as nizatidine, ranitidine, doxylamine, and carbinoxamine have attracted most researchers’ attention because of the ability of these compounds to produce toxic nitrogenous disinfection by-products (NDMPs), which are formed during the disinfection step. Unfortunately, in conventional wastewater treatment, some NDMPs have been detected after applying commonly used oxidants such as chlorine, chlorine dioxide, and potassium permanganate. However, most of the recent studies focused on the occurrence of NDMP compounds and the potential risk on the environment resulting from such compounds. On the other hand, only few studies have been undertaken photocatalytic degradation of amine-based pharmaceuticals as an alternative way of wastewater treatment.

The field of semiconductor photocatalysis has emerged as an innovative technology for application in many important fields such as water purification, environmental remediation, hydrogen evolution, optical sensing devices, energy harvesting, and storing devices. The idea of utilizing the abundantly available solar radiation for driving important chemical reactions has potential for large-scale industrial applications. Different types of semiconductor photocatalysts such as oxynitrides, sulphides, oxides, and metal-free semiconductors have been investigated.

The main issue with the excising photocatalysis materials can be summarized in two points; (1) possible use of the full solar spectrum, including the UV region along with the visible region and (2) the high recombination rate of photogenerated holes. This work described the synthesis of a BiOCl/g-C₃N₄ heterostructure and investigated its effect in enhancing the degradation of pharmaceuticals under solar light irradiation.
2. RESULTS AND DISCUSSION

2.1. XRD Analysis. The crystalline properties of the prepared BiOCl, g-C3N4, and various BiOCl/g-C3N4 composite samples were investigated by XRD. The XRD pattern of the obtained samples is shown in Figure 1. The g-C3N4 sample had two unique diffraction peaks at 13.1° and 27.4° corresponding to the (100) and (002) planes of g-C3N4, respectively. The BiOCl sample peaks were indexed to the tetragonal crystal phase with diffraction peaks obtained 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° which correspond to the respective miller indices of (001), (002), (101), (110), (102), (112), (200), (113), (211), (104), and (212) planes, respectively. All results perfectly matched with previously reported studies (JCPDS card no. 006-0249). For the prepared BiOCl/g-C3N4 composite structure, the diffraction peaks of BiOCl are clearly observable, as well as the typical peak for g-C3N4 (002), indicating the coupling between BiOCl and g-C3N4 where the intensity of the (002) diffraction peak decreased along with the increasing number of BiOCl microplates on the surface of g-C3N4. Moreover, the grain sizes of the synthesized structures were measured using the Maud Software with Cif card number 1011175. For BiOCl sample, the space group and lattice parameters of the samples were P4/mmm, a = b = 3.89 Å, c = 7.37 Å, and α = β = γ = 90° and the grain sizes of 94.6, 90.1, 60.1, and 51.8 nm were found for pure BiOCl, 50% BiOCl/g-C3N4, 30% BiOCl/g-C3N4, and 10% BiOCl/g-C3N4 samples, respectively. The decrease in grain size values could be attributed to the presence of a limited concentration of a BiOCl precursor preventing further growth of the microplate. It was also observed that no other peaks are identified in XRD patterns, indicating the high purity of the BiOCl/g-C3N4 heterostructure.

2.2. UV-vis DR Spectra and Band Gap Analysis. The UV-vis diffuse reflectance spectra of the synthesized samples are shown in Figure 2a. From the figure, the absorption edge of BiOCl sample was approximately 364 nm, which is in the UV range, whereas the fundamental absorption edge of the g-C3N4 material was about 450 nm, which is considered to be in the visible light range. Moreover, the coupling of the BiOCl sample with g-C3N4 showed a red shift of the band edge absorption up to 476 nm, which is expected to enhance the visible light photocatalytic performance of the heterostructure. The optical band gap was calculated according to the following Tauc equation

$$\alpha h \nu = A (h \nu - E_g)^{n/2}$$

where α, η, A, and E_g are the absorption coefficient, light frequency, proportionality constant, and band gap, respectively, where the n value is equivalent to 4 because of the essential absorption of both g-C3N4 and BiOCl in an indirect transition between bands. Therefore, the band gap energy is estimated from the slope drawn near to the band edge of (αhν)^1/2 versus hν plots as shown in Figure 2b. The band gap values for BiOCl, g-C3N4, 50% BiOCl/g-C3N4, 30% BiOCl/g-C3N4, and 10%
BiOCl/g-C\textsubscript{3}N\textsubscript{4} samples were 3.40, 2.76, 2.77, 2.70, and 2.60 eV, respectively. All composite forms of BiOCl/g-C\textsubscript{3}N\textsubscript{4} showed lower band gap values when compared to pure BiOCl. Moreover, the 10% BiOCl/g-C\textsubscript{3}N\textsubscript{4} sample exhibited a smaller band gap value compared to all samples including g-C\textsubscript{3}N\textsubscript{4}. This observation could point to the sufficient overlapping of the lowest unoccupied molecular orbital (LUMO) of g-C\textsubscript{3}N\textsubscript{4} and the conduction band of BiOCl shorting the initial band gap values of each g-C\textsubscript{3}N\textsubscript{4} and BiOCl separately.30,55

2.3. Scanning Electron Microscopy and EDS Analysis.

The morphologies of g-C\textsubscript{3}N\textsubscript{4}, BiOCl, and BiOCl/g-C\textsubscript{3}N\textsubscript{4} samples prepared by the microwave-assisted method were determined by scanning electron microscopy (SEM). Figure 3\textsubscript{a,b} shows the SEM images of pure g-C\textsubscript{3}N\textsubscript{4} and pure BiOCl samples. The g-C\textsubscript{3}N\textsubscript{4} image shows sheet-like microstructures, whereas the BiOCl product consists of a microplate structure. Moreover, the fabrication of BiOCl in the presence of g-C\textsubscript{3}N\textsubscript{4} does not change the microplate structure of BiOCl obtained in the absence of g-C\textsubscript{3}N\textsubscript{4} (Figure 3c−e). The number of BiOCl microplates on the surface of the g-C\textsubscript{3}N\textsubscript{4} sheet increased because of increase in the percentage of the BiOCl precursor from 10% up to 50%. However, the 2D/2D type of composite is expected to enhance the photocatalytic performance of the

Figure 2. (a) UV−vis diffuse reflectance spectra of the obtained samples; (b) the corresponding Tauc plot of the samples.

Figure 3. SEM images of (a) g-C\textsubscript{3}N\textsubscript{4}, (b) BiOCl, (c) 10% BiOCl/g-C\textsubscript{3}N\textsubscript{4} sample, (d) 30% BiOCl/g-C\textsubscript{3}N\textsubscript{4} sample, and (e) 50% BiOCl/g-C\textsubscript{3}N\textsubscript{4} sample.

Figure 4. Elemental composition of the (a) 10% BiOCl/g-C\textsubscript{3}N\textsubscript{4} sample; (b−f) color contrast of the individual elements Bi, Cl, O, N, and C.
material because of increased area of interaction. 48 In order to study the elemental distribution of BiOCl particles on the surface of g-C3N4 sheets, the elemental mapping analysis was performed as shown in Figure 4a. Quantitative analysis of the scanned area revealed a concentrated presence of Bi, O, and Cl, whereas the BiOCl particles were located as shown in Figure 4b-d and the presence of C and N was spread all over the scanned area as shown in Figure 4e,f. Moreover, the elemental composition of the prepared heterostructure sample was measured by energy-dispersive X-ray spectroscopy (EDX) analysis (Figure 5a). It is observed that the sample was composed mainly of five main elements: carbon, nitrogen, bismuth, oxygen, and chlorine. The atomic ratios of Bi/O/Cl/C/N were 9.5:3.5:1.2 wt %:45:40.8. These results further confirm the high purity of the produced BiOCl/g-C3N4 structure. The particle size distribution of BiOCl is shown in Figure 5b, and the average particle size was about 0.25 μm.

2.4. Optical Properties. The PL emission peak is mainly considered to result from the recombination process of the photogenerated electrons and holes pairs. In general, increase in PL emission peak intensity indicates a higher recombination rate for photogenerated electrons and holes. 56,57 Figure 6a shows the PL emission spectra of g-C3N4, BiOCl, and BiOCl/g-C3N4 composite samples. All samples were exposed to an excitation process at a wavelength of 370 nm at room temperature and the main emission peak observed at about 450 nm. The BiOCl sample, no emission peak was detected because of insufficient excitation energy for such a high band gap energy sample (3.4 eV). For the other samples, the PL intensities of g-C3N4 reduced dramatically after coupling it with BiOCl plates, indicating the inhabitation of the recombination process of free charge carriers in the heterostructure samples. Moreover, the 10% BiOCl/g-C3N4 and 30% BiOCl/g-C3N4 showed the lowest PL peak intensity when compared to other samples. Time-resolved PL measurement was performed in order to understand the photo-generated recombination process. The fitting of the normalized decay curves is shown in Figure 6b. The average fluorescence lifetime results of g-C3N4, 10% BiOCl/g-C3N4, 30% BiOCl/g-C3N4, and 50% BiOCl/g-C3N4 samples were 1.31, 1.95, 3.59, and 3.14 ms respectively. The 10% BiOCl/g-C3N4 sample showed a longer charge carrier lifetime compared to other samples. This enhancement in lifetime can be attributed to the formation of BiOCl/g-C3N4 heterojunction, which prevent fast photogenerated electrons and holes recombination.

2.5. Isoelectric Point. Knowing the isoelectric point of photocatalysis is a very important factor to determine the electrostatic interaction behavior between the catalyst and the pollutant. 58 The isoelectric point could be determined by varying the pH value of photocatalyst suspension where the pH value resulting in the zero net charge of the photocatalyst is known as the isoelectric point. Thus, in order to check the surface charges of the obtained samples, their zeta potentials were analyzed. The zeta potentials of BiOCl, g-C3N4, and 10% BiOCl/g-C3N4 were −4.56, −24.08, and −21.34 mV respectively. The zeta potential values of BiOCl, g-C3N4, and 10% BiOCl/g-C3N4 as a function of pH values are shown in Figure 7. As observed, the measured potential continuously declined with an increase in pH. The isoelectric points of BiOCl, g-C3N4, and 10% BiOCl/g-C3N4 were observed at pH values 3.84, 3.62, and 3.72 respectively. Moreover, Dumanovic et al, reported that the protonation process of nizatidine occurs in neutral media at a pH value of 5−8. 39 The pH of the resulting solution after mixing nizatidine with water was 5.6.

Figure 5. (a) EDX spectrum of the BiOCl/g-C3N4 sample; (b) histogram of the average particle size distribution.

Figure 6. (a) PL spectra of g-C3N4, BiOCl, and g-C3N4/BiOCl samples; (b) time-resolved fluorescence decay spectra of the obtained sample.

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Therefore, all prepared samples were negatively charged at the time of the experiment.

2.6. Photocatalytic Activity Studies. The degradation of nizatidine using the BiOCl/g-C3N4 composite was investigated primarily under a light-emitting diode (LED) single wavelength (365 nm) light irradiation. The degradation profile of nizatidine was followed with the help of a UV–vis spectrophotometer as shown in Figure 8a. Figure 8b represents the concentration changes of nizatidine concentration with time starting from an initial concentration of 5 mg/L of the nizatidine aqueous solution at pH = 5.6. Moreover, a control experiment was performed to check the effect of the LED light on the pharmaceutical compound in the absence of the prepared catalyst. The initial concentration remained almost the same in the absence of the catalyst, indicating that nizatidine is very photostable. However, the degradation was dramatically enhanced after the addition of the prepared catalyst. Among the prepared samples, the pure BiOCl and pure g-C3N4 samples showed the lowest degradation performance. As expected, the BiOCl/g-C3N4 composite samples exhibited superior photocatalytic performance. The 10% BiOCl/g-C3N4 showed the best performance among all the prepared samples. The enhancement noticed for the 10% BiOCl/g-C3N4 sample could be attributed to the coupling of the two semiconductors, which results in the narrowing of the band gap energy along with an effective separation of the charge carriers as shown in UV–vis DRS and PL results. Moreover, the photocatalytic performance was further enhanced by adjusting the pH from 5.6 to 3.7 to reach an IEP of the 10% BiOCl/g-C3N4 sample as estimated from zeta potential results in Figure 8c. This further enhancement may be attributed to the improved interaction obtained between nizatidine and the 10% BiOCl/g-C3N4 catalyst. To confirm the above statement, another experiment was carried out at pH 10. At a higher pH, the photocatalytic performance of 10% BiOCl/g-C3N4 dropped down, which was expected because at a higher pH level the catalyst and the pollutant are negatively charged, resulting in a poor interaction.59 A final test was performed under natural solar irradiation and the degradation dramatically increased to reach 96% within 30 min compared to the LED 365 nm of 120 min (Figure 8d). Finally, to investigate the stability of the 10% BiOCl/g-C3N4 sample, the photodegradation experiment was repeated five times under the same conditions. After each cycle, the sample was washed then collected and kept to dry overnight in an oven for the next run. Compared to the fresh sample, the recycled samples showed an acceptable stability in nizatidine degradation. Figure 9 shows that the photodegradation efficiencies of 10% BiOCl/g-C3N4 remained almost the same after the second cycle. A schematic
For the degradation of nizatidine as an amine-based pharmaceutical model under solar light irradiation. The sample with 10% BiOCl to g-C3N4 ratio showed the highest photocatalytic activity. The degradation under solar irradiation reached 96% within 30 min. Moreover, the prepared composite showed reasonable stability after the second run of recycling. Therefore, applying the 10% BiOCl/g-C3N4 for the degradation of the amine-based pharmaceutical can be taken into consideration as an alternative method for removal of such pollutants during water treatment.

4. EXPERIMENTAL SECTION

4.1. Materials and Methods. The g-C3N4 samples were prepared by using melamine powder (M2659 ALDRICH). Analytical grade bismuth nitrate pentahydrate Bi(NO3)3·5H2O, 98%, nitric acid HNO3, 99%, and potassium chloride KCl, 99%, were purchased from Sigma-Aldrich and were used without further purification for the preparation of BiOCl. The g-C3N4 synthesis was done in a muffle furnace by directly heating melamine powder in a semi-closed system. One gram of melamine powder was placed into an alumina crucible and covered with a lid and then direct heating was applied by increasing the temperature to 550 °C at a heating rate of 20 °C/min for 3 h. The BiOCl/g-C3N4 composite samples were prepared through the microwave-assisted technique. BiOCl/g-C3N4 samples with three wt % ratios were prepared, which were 10, 30 and 50% (wt %/wt %). In a typical procedure for preparing the BiOCl/g-C3N4 composite, 0.2 g of g-C3N4 powder was dispersed in 40 mL of DI water and sonicated for 30 min and then depending upon the percentage, different amounts of Bi(NO3)3·5H2O and KCl were mixed and stirred for 2 h. The obtained solution was transferred into a microwave vessel and the microwave was maintained at 110 °C with a heating rate of 3 °C/min for 1 h. The product was then washed with water and ethanol. The pure BiOCl sample was obtained by the same method without g-C3N4.

4.2. Characterization. The crystalline phases of all the samples were examined by XRD analysis using a Miniflex600 X-ray diffractometer with graphite monochromatized Cu Kα radiation (λ = 1.540 Å) source. The sample morphologies were checked using a field emission scanning electron microscope (JSM-7800F JOEL, Japan) with a maximum working voltage of 30 kV, maximum resolution of 0.8 nm, and a working distance of 10 mm being used during measurements. UV–vis DRS measurements were conducted using the PerkinElmer Lambda 650S spectrometer. PL behavior was evaluated using a PerkinElmer LS 55 Luminescence Spectrometer. Lifetime decay measurement was done with help of EasyLife X equipped with 380 nm nanosecond pulsed LED’s. The surface charges of the samples at various pH conditions were measured by a Photol Otsuka Electronics.

4.3. Photocatalytic Activity Studies. Nizatidine is an amine-based pharmaceutical. It was chosen as a model pollutant to test the photocatalytic activity of the prepared samples. All photodegradation reaction experiments were carried out in a photocatalytic reactor batch system consisting of a cylindrical borosilicate glass reactor vessel with an effective volume of 500 mL. The experiment was carried out in the open atmosphere with an air diffuser fixed at the reactor to uniformly disperse oxygen into the solution. The reaction suspensions were prepared by adding 0.1 g of the prepared sample in 250 mL of aqueous nizatidine solution (0.4 mg/mL), with an initial concentration of 5 mg/L. The aqueous
suspension was then irradiated with Mic-LED-365 (from Prizmatix 420 mW with an average intensity 13.37 W/m²). Prior to illumination, the reaction suspensions were magnetically stirred for 30 min in the dark to ensure adsorption-desorption equilibrium between the photocatalyst and nitzadine. Upon illumination, 6 mL aliquots of suspension were taken from the reactor at scheduled time intervals. The sample was centrifuged at 8000 revolutions per minute (rpm) for 5 min and then filtered to remove the catalyst. The filtrate was analyzed on the UV–vis spectrophotometer to evaluate the degradation of nitzadine.

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**Notes**
The authors declare no competing financial interest.

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