Adsorption and degradation performance of Rhodamine B over BiOBr under monochromatic 532 nm pulsed laser exposure

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ARTICLE INFO

Article history:

Received 10 November 2010

Received in revised form 18 February 2011

Accepted 25 February 2011

Available online 3 March 2011

Keywords:

BiOBr

Photodegradation

532 nm-pulsed-laser

Sorption

Rhodamine B

ABSTRACT

The adsorption (under dark condition) and photodegradation behaviors of Rhodamine B molecules on BiOBr under visible (532 nm) pulsed laser exposure were studied and reported for the first time. The adsorption kinetics/isotherm behaviors and thermodynamic process (adsorption dynamical parameters) occurred on as-prepared BiOBr were investigated. The photodegradation mechanisms, effects of BiOBr dosage and pulsed laser energy on dye removal efficiency in the presence of BiOBr particles were studied as well. Furthermore, the photodegradation of other kinds of Rhodamine dyes such as Rhodamine 6G, Sulforhodamine B and Sulforhodamine 640 were initially investigated and compared under 532 nm pulsed laser exposure. The study also demonstrated that the dissolved oxygen plays a very significant role in the photo-catalytic decomposition of Rhodamine. The BiOBr catalyst was found intact even under acidified conditions showing good stability of the catalyst.

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1. Introduction

Photocatalytic degradation of pollutants on semiconductor compounds has become a promising approach to solve environmental problems during the last few decades [1,2]. Recently, as new kinds of visible-light-responsive photocatalysts, BiOBr has received much interest in the potential photocatalytic removal of contaminants from aqueous or gas phase [3–9].

It has been recently known that two different derivations (which are described below) lead to the definition of photocatalysis process [10,11]. In the first process (1.1), molecular A can be converted into molecular B through excited state of the catalyst, which has been widely considered as the dominant heterogeneous photocatalytic process. In the second process (1.2), the photoexcited molecular A can be converted into molecular B by the action of the photocatalyst.

It is worth mentioning that no data have been reported in the literature regarding the BiOBr-assisted photodegradation of dyes up till now. Nowadays, pulsed laser has been used in order to obtain high efficiencies in photocatalytic related applications such as pollutants degradation [12,13], water splitting [14] and anti-microbial reactions [15], because of the unique properties of laser radiations like monochromaticity, high intensity, and low beam divergence. In this present study, the adsorption and degradation of Rhodamine B (RhB) over BiOBr under 532 nm pulsed laser exposure is reported for the first time. Among bismuth oxyhalides compounds, BiOBr is a typical semiconductor with a band gap value of ~2.9 eV, and it cannot be excited by 532 nm pulsed laser with high monochromaticity. In this study, it was observed that RhB molecules which adsorbed on the BiOBr particles can be efficiently decomposed under pulsed laser exposure, and the photodegradation mechanism is discussed on the basis of the experiment results and the effects of BiOBr dosage and pulsed laser energy on removal efficiency have been investigated as well. Furthermore, the photodegradation behavior toward other kinds of Rhodamine series dyes, i.e. Rhodamine 6G (Rh6G), Sulforhodamine B (SRhB) and Sulforhodamine 640 (SRh640) were also investigated under 532 nm pulsed laser exposure.

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2. Experimental

2.1. Materials

Absolute ethanol, sodium bismuth oxide dihydrate ($\text{NaBiO}_3 \cdot 2\text{H}_2\text{O}$), hydrobromic acid (HBr, 40 wt%), tetraethyl orthosilicate (TEOS), hydrochloric acid (38%), AgNO_3 were purchased from Sinopharm Chemical Regent Co., Ltd. (China) and Rhodamine B dye was supplied by Chemical Agent Institute of Tianjin (China). The surfactant poly (ethylene oxide)-b-poly (propylene oxide)-b-poly (ethylene oxide) block copolymer $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (Pluronic P123) was provided by Sigma–Aldrich. The water used was distilled water, and all other chemicals except ammonium acetate and methanol (chromatographic pure, obtained from Sigma Aldrich) were of analytical grade and used as received without further purification.

2.2. Preparation of as prepared BiOBr

The preparation method for BiOBr with sheet morphology (supplementary information, Fig. S1) is described as follows, first $\text{NaBiO}_3 \cdot 2\text{H}_2\text{O}$ powders were completely dissolved into HBr aqueous solution, then the precipitation (BiOBr) with light yellow was obtained after adding enough amount of distilled water in the solution mentioned above. After stirring for 30 min, the resulted products were separated by centrifugation, washed by absolute ethanol and distilled water, and dried at 80°C for 10 h in air. The ordered mesoporous silica of SBA-15 was prepared according to prescribed method reported in the literature [16].

2.3. Characterization of BiOBr samples

The crystal structures of the BiOBr samples before and after photochemical reaction were determined by X-ray diffractometer (XRD, Bruker D8 ADVANCE) with 2θ scope of $10\text{--}70^\circ$ using $\text{Cu-K}\alpha$ X-ray source ($\lambda = 0.15418\text{ nm}$). The scanning electron microscopy (SEM) and high resolution-transmission electron microscopy (HRTEM) images of as-prepared BiOBr were recorded on a JSM 7401 field emission gun-scanning electron microscope and JEM-200CX transmission electron microscope, respectively. Fourier transform infrared spectra (FT-IR) were recorded at room temperature using a Nicolet NEXUS 670 FT-IR spectrophotometer. Diffuse reflectance spectroscopy (DRS) analysis was performed at room temperature on a Shimadzu UV 3600 spectrophotometer.

2.4. Sorption (batch) experiments

Batch experiments were performed in order to examine and calculate the sorption kinetics/equilibrium and chemical thermodynamic parameters. One hundred (100) mg of the BiOBr was mixed with 200 mL RhB aqueous solution with a known initial concentration, in a 250 mL flask and the mixture shaken in an orbital shaker (150 rpm) at a constant temperature. The mixture was centrifuged at 4000 rpm in a centrifugation machine after batch sorption experiments so that the absorbance of RhB can be determined at 554 nm by means of UV–vis spectrophotometer (VARIAN Cary 100). The concentrations of the solutions were determined using linear regression equation.

2.5. Photocatalytic activity evaluation

The experimental setup for photochemical study was described in our earlier publications [17,18]. 532 nm laser radiations were generated from the second harmonic of the Spectra Physics Nd: YAG laser (Model GCR 250) with a pulse width of $\sim 8\text{ ns}$. The high power laser beam with wavelength of 532 nm was used as the light

Table 1

Kinetic parameters of the pseudo-second-order and intra-particle diffusion models for RhB adsorption on BiOBr at different temperatures.

Temperature (K)	Pseudo second order kinetic model		
	q_e ($\mu\text{mol g}^{-1}$)	k_2 ($\text{g } \mu\text{mol}^{-1} \text{ h}^{-1}$)	r^2
302 ± 1	9.19466	11.95258	0.98313
313 ± 1	6.24563	18.42789	0.88795
323 ± 2	2.34198	22.55334	0.98138

source. The diameter of laser beam was expanded to $\sim 1.0\text{ cm}$ so that the destructive effect of radiation can be avoided. After the photochemical reaction, the slurry of reaction mixture was taken out and centrifuged (4000 rpm) to remove BiOBr at certain intervals, and the concentrations of RhB aqueous was determined by UV–vis spectrophotometer. Meanwhile, the concentration of RhB in the solutions was determined by high-performance liquid chromatography (HPLC). The samples were analyzed using the method adopted by Kai et al. [19]. Briefly speaking, HPLC runs were performed using Waters HPLC instrument equipped with UV–vis diode array detector using a C18 inverted phase column ($150\text{ mm} \times 4.6\text{ mm i.d.}$, Phenomenex). Ammonium acetate and methanol were used as mobile phase. The gradient elution was programmed as follows: Methanol was obtained at 55% and this proportion was kept for 10 min, then linearly increased to 65% during 0.5 min, then maintained at 65% for 12.5 min and then back to 55% in the last 1 min. The flow rate was 1.0 mL/min , and sample injection volume was $50\text{ } \mu\text{L}$. The photonic efficiency (PE) of the photochemical reaction was also calculated according to the following expression:

Photonic efficiency (%)

$$= \frac{\text{Number of dye molecules decomposed/time}}{\text{Number of photons of wavelength } \lambda \text{ absorbed/time}} \times 100 \quad (3)$$

$$\text{Number of photons of wavelength } \lambda \text{ absorbed} = \frac{P_L t}{h\nu} \quad (4)$$

where P_L is the laser power in Watt (J/s), t the time in second, h is the Planck's constant and ν is the frequency of the incident laser. Hence the PE can be calculated by dividing of total number of dyes molecules decomposed with total number of photons of the laser incident on the sample.

3. Results and discussion

Adsorption kinetics is one of the most significant characters which describe the adsorption behavior. In this study, the pseudo-second-order adsorption kinetic model was adopted to evaluate and calculate the solute uptake rate and the corresponding thermal dynamical parameters. The pseudo-second-order adsorption kinetic equation can be written as follows [20]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{k_2 q_e} = \frac{1}{v_0} + \frac{t}{q_e} \quad (5)$$

where q_t ($\mu\text{mol g}^{-1}$) is the adsorption capacity at specific contact time, k_2 ($\text{g } \mu\text{mol}^{-1} \text{ h}^{-1}$) the pseudo-second-order kinetic constant, q_e ($\mu\text{mol g}^{-1}$) the amount of RhB adsorbed on BiOBr at equilibrium, and v_0 ($\mu\text{mol g}^{-1} \text{ h}^{-1}$) represents the initial adsorption rate.

Fig. 1a depicts the dependence of adsorption capacity under different temperatures toward RhB molecules over BiOBr on the contact time and the corresponding fitting curves are also depicted in the same figure. It was found that the initial adsorption rates increase dramatically in the first 3 h for the adsorption temperatures of 303 K, 313 K and 323 K, respectively. And the adsorption-desorption equilibrium can be reached after shaking the solution for 4 h. In addition, as presented in Fig. 1a and Table 1, the decrease of adsorption capacity at equilibrium with increase in

Fig. 1. The variations of adsorption capacity of RhB (with different initial concentrations) as a function of contact time over BiOBr semiconductor compound (a), plots $\ln k_2$ (b) and $\ln K_C$ (c) vs. $1/T$ for adsorption of RhB molecules ($C_0 = 7$ ppm, $T = 302 \pm 2$ K, adsorbent dosage = 0.01 g/200 mL).

temperature can be clearly noticed, demonstrating the exothermic nature of the adsorption process.

It has been widely reported [21,22] that the pseudo-second-order kinetic rate constant of RhB adsorption can be described as a function of temperature by the Arrhenius type relationship which is expressed as follows:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (6)$$

where k_2 ($\text{g mg}^{-1} \text{h}^{-1}$) is the pseudo-second-order kinetic constant, E_a the Arrhenius activation energy (kJ mol^{-1}), A the Arrhenius factor, R the gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$) and T is the temperature of the solution. Therefore, the E_a was calculated by plotting $\ln k_2$ versus $1/T$ (as depicted in Fig. 1b) and obtained E_a (kJ mol^{-1}) of $0.357 \text{ kJ mol}^{-1}$ demonstrate the physical sorption property [22].

The spontaneity during the adsorption process can dramatically affect the Gibbs free energy change (ΔG°) which can be expressed as follows:

$$\Delta G^\circ = -RT \ln K_C \quad (7)$$

Eq. (1.5) clearly shows the definition of ΔG° , where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$), T is the absolute temperature, and K_C represents the equilibrium constant which can be expressed as the ratio of adsorption amount (at equilibrium) to the equilibrium concentration. The dependence of equilibrium constant of K_C on adsorption temperature can be expressed as follows [23,24]:

$$\frac{d(\ln K_C)}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (8)$$

$$\ln K_C = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (9)$$

where ΔH° and ΔS° are respectively the standard enthalpy and entropy change, except the adsorption equilibrium of K_C , universal gas constant of R and absolute temperature of T . ΔH° and ΔS° were obtained (as listed in Table 2) from the slope and intercept of the van't Hoff plot linear plot of $\ln K$ versus $1/T$ (Fig. 1c).

The obtained negative and small values of ΔG° at 302 and 313 K further implied the spontaneous process and physisorption (generally in the range of -20 to 0 kJ mol^{-1}) nature during the adsorption process [22]. However, the positive value of ΔG° at 323 K was found, demonstrating the adsorption process under such temperature was not a spontaneous process, namely, the adsorption reaction might possibly gain energy from an external source. The negative value of ΔH° and ΔS° obtained indicated the exothermic irreversible characteristic of the adsorption of RhB on BiOBr.

Adsorption isotherm is another significant approach to evaluate the adsorption capacity of adsorbents as well as initially understand the interactions between adsorbate-adsorbent. To investigate the isothermal behavior for RhB adsorption on BiOBr, typical isothermal models i.e. Langmuir and Freundlich models, were adopted. For Langmuir model, the adsorption can be expressed as follows [25]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (10)$$

where q_e is the adsorption amount at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the aqueous solution (mg L^{-1}), q_m the maximum adsorption capacity (mg g^{-1}) and K_L is the constant related to the free energy of adsorption (L mg^{-1}).

The Freundlich model for adsorption of RhB adsorption on BiOBr can be written as follows [26]:

$$q_e = K_F C_e^{1/n} \quad (11)$$

where K_F ($\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$) and n are two constants indicating the relative adsorption capacity and the intensity of the adsorption, respectively. The symbols q_e and C_e represents the adsorption

Table 2

Thermodynamic parameters for the adsorption of RhB on BiOBr.

Temperature (K)	E_a (kJ mol ⁻¹)	K_C	r^2	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)	r^2
302 ± 1	0.357	3.00063	0.9746	-2.75895	-68.027	-215.161	0.9427
313 ± 1		1.66954		-1.33379			
323 ± 2		0.5051		1.83414			

Table 3

Parameters of Langmuir and Freundlich adsorption isothermal models toward RhB molecules on BiOBr at 302 ± 1 K.

Langmuir model			Freundlich model		
q_m (μmol g ⁻¹)	K_L (L μmol ⁻¹)	r^2	K_F (μmol ^{1-1/n} L ^{1/n} g ⁻¹)	n	r^2
13.66263	0.11099	0.95122	1.42276	1.31459	0.9272

amount at equilibrium (mg g⁻¹) and equilibrium concentration of the aqueous solution (mg L⁻¹), respectively. Fig. 2 depicts the isothermal scatters and fitting curves for the adsorption capacity at equilibrium as a function of equilibrium concentration of the bulk solution, and the related fitting results are listed in Table 3. From the fitting coefficients comparison, it was found that both the Langmuir and Freundlich models can describe the adsorption isotherms occurred on the BiOBr ($r^2 > 0.9$), but which model can better describe the adsorption phenomenon depends upon the relative values of the fitting coefficients. The adsorption isotherm can be fitted better through the Langmuir model ($r^2 = 0.95122$) than the Freundlich model ($r^2 = 0.9272$), thus the possible monolayer adsorption of RhB molecules occurred on BiOBr could be initially deduced because the Langmuir model assumes monolayer coverage of adsorbate on a homogenous surface of adsorbent. The fitting result by employing Freundlich model demonstrated the close-to-linear property where constant of n^{-1} is 0.76 (for a linear isotherm, $n^{-1} = 1$) probably due to the low concentration of RhB selected in the present study.

Fig. 3 depicts the photolysis, adsorption (dark) and degradation (with/without N₂ bubbles) of RhB molecules over BiOBr under 532 nm pulsed laser exposure as a function of exposure time. Almost no degradation was observed as the low energy of single photonic with the wavelength of 532 nm. The adsorption removal efficiency can be reached to 25% after reaction for 90 min under dark condition. The bandgap of BiOBr semiconductor is demonstrated at around 2.9 eV, implying such compound cannot be excited by the photons with the wavelength of 532 nm. However, it was found

that RhB molecules were effectively removed and decomposed over BiOBr under 532 nm pulsed laser exposure and the removal efficiency was tested at around 90% under the identical experimental conditions. In addition, it was found that the efficiency decreased to ~83% with N₂ bubbles, initially implying that the dissolved oxygen could play an important role during the photochemical reaction.

Fig. 4 depicts the UV-vis spectral changes of RhB aqueous solution as a function of reaction time in the process of BiOBr assisted photodegradation. It was found that absorbance of the absorption peak at 554 nm decreased dramatically as the photodegradation reaction proceeded. The UV-vis spectral variations also displayed an obvious wavelength shift of the band to shorter wavelengths. The wavelengths of the characteristic peaks were shifted from 554 nm to 548 nm under N₂ and 532 nm without N₂ bubbling, possibly because of the intermediate products of de-ethylated RhB molecules [27]. It should be noticed that no shift of the absorption band at 554 nm was observed after the photolysis (or photocatalysis) and adsorption for 90 min (as depicted in Fig. 5). The results were further confirmed by HPLC monitoring (as depicted in Fig. 6) and it was clearly found that the intensity of the chromatographic peak at retention time of ~19 min decreased after photodegradation, demonstrating that the RhB was effectively decomposed rather than simply bleached. Some other weak chromatographic signals with different retention times were observed, suggesting the formation of some other new molecule during the BiOBr-assisted photodegradation. Meanwhile, PE% values for the BiOBr-assisted photo-degradation of RhB were estimated and plotted as a function of laser exposure time for RhB removal. As shown

Fig. 2. Representative adsorption isotherm toward RhB molecules on as-prepared BiOBr and the fitting curves by means of Langmuir and Freundlich models ($T = 307 \pm 2$ K, adsorbent dosage = 0.01 g/200 mL).

Fig. 3. RhB was photolyzed, adsorbed under dark, photo-assisted degraded over BiOBr with and without N₂ bubbles under 532 nm pulsed laser irradiation as a function of irradiation time ($C_0 = 7$ ppm, dosage = 0.1 g/100 mL, laser energy = 131 mJ).

Fig. 4. UV-vis spectral variations of RhB aqueous solution during 532 nm pulsed laser-assisted degradation without (a) and with N_2 bubbles (b).

Fig. 5. UV-vis spectral comparison among the initial RhB solution, RhB solution photolyzed by 532 nm pulsed laser and adsorbed under dark for 90 min.

in Fig. 7, it was found that the PE increased at first and then decreased because of the fact that the degradation rate decreased with prolonging the reaction time (as shown in Fig. 3) which was caused by the decreasing of the photoexcited electron-hole recombination [12]. The highest PE value was estimated at 0.44% and 0.53% after 30 min of the reaction with and without N_2 bubbling respectively.

From the results mentioned above, it is reasonable to believe that the band structure of both molecules, BiOBr and RhB in aqueous solution play an important role in the photochemical degradation process. To date, several methods have been adopted for the solid-based band/electronic structure measurement and speculation, such as ultraviolet photoelectron spectroscopy (UPS) [28], flatband-potential-determination based photoelectrochemical techniques [29–31], atom's Mulliken electronegativity theory [6,27,32–38] and density functional theory (DFT) calculation based on plane wave pseudo potential method [39–41]. The band-gap width, CB/VB of the catalysts series BiOX (X = F, Cl, Br, I) semiconductor were calculated by means of DFT method [42]. The atom's Mulliken electronegativity method, the CB/VB edge potentials of BiOBr have been calculated at 0.27 eV and 3.19 eV with respect to the vacuum level, respectively [6]. Fig. 8(a) depicts a possible mechanism for the BiOBr-assisted photodegradation under 532 nm pulsed laser exposure. It is reasonable to believe that the energy band(s) having the width equal or less than 2.33 eV (which can be excited by the photon with the wavelength of 532 nm) might exist in RhB molecules, and the photoexcited electrons would be injected from the highest occupied molecular orbital (HOMO) of the molecules to the CB of BiOBr, because of the over-potential between the CB edge of BiOBr and excited orbital of RhB. Thus the electrons injected from excited dye molecules to the CB of BiOBr will participate in the photochemical decomposition of RhB molecules which can diffuse from the bulk solution to the surface of BiOBr (such like the reduction of oxygen). Consequently the possible photodegradation pathways were proposed briefly as follows [43,44].

Reduction pathway:

Oxidation pathway:

Although our result have proved the effect of dissolved oxygen during the reaction which confirmed the contribution of the negative oxygen ion with oxidative ability in the photodegradation, the direct reduction process by excited electrons still cannot be neglected due to the reducing ability of the electrons located on CB and further investigation is needed to carry out to understand this phenomenon.

Here, it is worth noticing that some pioneering papers [45–48] regarding the photo-decarboxylation of ethanoic acid has demonstrated that some special molecules could be destabilized when adsorbed onto the surface of solid, and consequently the radiations that are ineffective for photodegradation in the absence of the solid are effective. Namely, the energy of photons becomes sufficient when the molecule is adsorbed. In order to investigate the existence of such effect in the current photodegradation process, ordered mesoporous silica (SBA-15) was selected because of

Fig. 6. HPLC chromatograms of the original RhB solution (1), after photodegradation for 90 min without (2)/with N₂ bubbles (3) under pulsed laser irradiation by using 254 nm (a) and 554 nm (b) as the detection wavelength.

its strong affinity toward to RhB molecules through static electric/hydrophilic interaction. As depicted in Fig. 8b, it was found the adsorption efficiency of RhB molecules over SBA-15 can reach to ~ 45% after contact time of 120 min under dark condition, but no obvious changes in RhB concentration and adsorption band (at 554 nm) was observed after light/laser was on, which proves that the effect of sorption-induced destabilization was not the real reason for the RhB decomposition over BiOBr under 532 nm pulsed laser irradiation.

The dependences of removal efficiency of RhB from aqueous solution on BiOBr dosage and incident laser energy were investigated as well and the corresponding results have been depicted in Fig. 9. From Fig. 9a which shows the dosage effect on the removal performance, the maximum removal efficiency of 89.3% (after 1 h reaction) was achieved under the dosage of 0.15 g/100 mL, by using laser energy of 131 mJ. As expected, it was found that as the dosage increases, the degradation efficiency increases, but the degradation rate decreases and almost reaches to saturation limit and this finding is in agreement with the previous reports [18,36]. From Fig. 9b which depicts the laser energy effect on the removal performance, the maximum removal efficiency of 94.6% (after 1.5 h reaction) was obtained under the dosage of 0.12 g/100 mL, using pulsed laser energy of 134 mJ. It was found that the removal effi-

Fig. 7. The plots of PE vs. laser exposure time for BiOBr-assisted photodegradation with (a) and without N₂ (b) bubbles.

Fig. 8. Possible mechanism of 532 nm pulsed laser assisted photodegradation of RhB molecules over BiOBr; (b) changes of RhB concentration over SBA-15 before and after light on ($C_0 = 7$ ppm, adsorbent dosage = 0.08 g/200 mL, laser energy = 131 mJ).

ciency can be increased by increasing the laser energy because the number of the excited RhB molecules increases with increasing the laser energy which can lead to the increase in the incident photons number.

The stability of as-prepared BiOBr during the degradation of RhB was examined by measuring the XRD patterns of the sample after photodegradation. From the XRD results depicted in Fig. 10, no change of BiOBr crystal structure was observed and all the apparent peaks corresponding to the tetragonal structure of BiOBr (JCPDS Card No. 78-0348). Meanwhile, FT-IR measurement (supplementary information, Fig. S2) was adopted to evaluate the microstructure changes of BiOBr catalyst as well, and these results clearly demonstrated that the A_{2u} -type vibrations of Bi-O bond (at around 515 cm^{-1}) in BiOBr crystal did not change after photodegradation. DRS spectrum of BiOBr after photodegradation clearly shows a broad adsorption peak at ~ 530 nm possibly because of the de-ethylated RhB product (supplementary information, Fig. S3). In addition, a recent investigation carried out by Chen et al. [49] showed that Cl^- ions were dissolved in aqueous solution

during UV-induced photocatalytic degradation of Methyl orange because of the interaction between bonded Cl^- ions and photoexcited electrons. In the present study, no AgBr precipitate was detected by adding acidified $AgNO_3$ aqueous solution to the RhB solution after photodegradation for 90 min, demonstrating that bonded Br^- ions in BiOBr crystal were not dissolved in the solution. The results above clearly display the excellent chemical stability of as-prepared BiOBr. Rhodamine based dyes are a family of related chemical compounds represented by RhB and Rh6G, which have been used as dyes and their toxicity and solubility in water, methanol and ethanol have been widely confirmed [50]. Utilizing the BiOBr-assisted photodegradation properties under 532 nm pulsed laser exposure, the removal efficiencies toward dyes of Rh6G, SRhB and SRh640 were investigated as well and the results have been depicted in Fig. 11. It was noticed that all of the selected Rhodamine dyes can be effectively removed to different extent under the green laser ($\lambda = 532$ nm) exposure. Additionally, it was found that N_2 introduction into the photodegradation process can decrease the removal efficiency, which demonstrated the necessity

Fig. 9. Effects of photoassisted removal efficiency and adsorption peak of RhB solution on the BiOBr dosage (a, $C_0 = 7$ ppm, laser energy = 131 mJ, reaction time = 60 min) and incident laser energy (b, $C_0 = 7$ ppm, dosage = 0.12 g/100 mL; reaction time = 90 min).

Fig. 10. XRD patterns of BiOBr before and after photodegradation.

Fig. 11. Degradation comparison among different kinds of dye molecules over BiOBr under assistance of 532 nm pulsed laser exposure (dosage = 0.12 g/100 mL, $C_0 = 8$ ppm, reaction time = 1 h, laser energy = 131 mJ).

of the dissolved oxygen in the BiOBr-assisted photodegradation for achieving high removal efficiencies.

4. Conclusions

In this study, the adsorption and photodegradation process of RhB on BiOBr catalyst under 532 nm pulsed laser exposure has been investigated for the first time. The results clearly proved that the RhB molecules which were adsorbed on the surface of BiOBr can be effectively decomposed through the photochemical reaction and the dissolved oxygen is very essential during the photodegradation process. Furthermore, other kinds of Rhodamine dyes can be removed to various extents by this photo-degradation technique as well. This study also implied the possibility of degradation of dyes by the assistant of BiOBr under visible light exposure using monochromatic radiations from laser having the wavelength of 532 nm which could be beneficial for designing a photocatalytic reactor for removal of dyes and other organic pollutants for commercial applications using solar radiations in visible region.

Acknowledgements

This work was financially supported by Center of Excellence in Nanotechnology (CENT) and KFUPM through NSTIP program under Project #08-NAN93-4 funded by KACST, Natural Science Foundation of Jiangsu Province of China (No: BK2010497). We are also grateful to referee for bringing ref [45–48] to our attention.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [10.1016/j.apcata.2011.02.033](https://doi.org/10.1016/j.apcata.2011.02.033).

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