Photocatalytic reduction of 4-nitroaniline in aqueous solution using BiOCl/BiOBr/rGO ternary heterojunction under simulated UV–visible light irradiation

Salama Alismaail¹ · Salwa Hussein Ahmed¹ · Maram Bakiro¹ · Ahmed Alzamly¹

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Abstract

BiOCl/BiOBr/rGO ternary heterojunctions were synthesized and characterized, and their photocatalytic activities were examined. Three different rGO mass ratios were incorporated into BiOCl_{75%}BiOBr_{25%}; 1% rGO, 3% rGO, and 5% rGO, respectively. The successful incorporation of rGO into the composites was confirmed using powder X-ray diffraction (PXRD). Furthermore, calculated band gap, elemental composition, and composites' morphology were investigated using UV–vis (UV–Vis) diffuse reflectance spectroscopy (DRS), energy-dispersive X-ray spectroscopy (EDX), and scanning electron microscopy (SEM), respectively. The photocatalytic activities of the ternary heterojunctions were evaluated toward the photocatalytic reduction of 4-nitroaniline (4-NA) in aqueous solution. Experimental results reveal that rGO incorporation enhances the activity of the prepared heterojunction photocatalysts, where photocatalyst containing 5% rGO exhibited the highest activity achieving rate of 0.84 min^{−1}.

✉ Ahmed Alzamly
ahmed.alzamly@uaeu.ac.ae

¹ Department of Chemistry, UAE University, P.O. Box 15551,
Al-Ain, UAE

Graphic abstract

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1 Introduction

p-Phenylenediamine (PPD) is an essential starting material for many commercial applications [1], such as dyes [2], antioxidants for rubber [3] aramid fibers [4], and thermoplastics materials [5]. *p*-Phenylenediamine is commonly produced through the catalytic hydrogenation of 4-nitroaniline (4-NA) [6]. Nonetheless, this process suffers from serious constraints of meticulous reaction requirements, expensive, and demanding procedures [7]. Therefore, developing an environmentally non-hazardous, economically efficient and less demanding processes for the synthesis of PPD is required [8].

The use of a photocatalyst semiconductor materials for photocatalytic organic transformations has been developed substantially over the past decade [9]. A few examples

for the utilization of water as a solvent in photocatalytic organic transformation have been reported [10–12]. Moreover, the use of visible light has gained considerable attention due to the use of a readily available solar light composed of approximately of ~52% visible light. Thus, fabricating of an efficient and selective visible-light-driven photocatalysts for organic transformations is of a great significance.

TiO₂ is among the photocatalysts investigated for the photoreduction of 4-nitroaniline to *p*-Phenylenediamine in aqueous medium [13]. Subsequently, an efficient reduction of 4-NA over heterogeneous semiconductor photocatalysts in aqueous suspension was reported [14–17]. Nevertheless, the band gap of the active phase (anatase) is 3.2 eV, limiting its absorption to only ~4% of ultraviolet radiation instead of the abundant visible light present in solar spectrum [18].

The photogenerated electron–hole pairs in semiconductor allow for separation and initiating the redox reactions at different sites of the photocatalysts [19]. The reaction efficiency dramatically decreases because of annihilation of charge carriers via electron–hole (e^- – h^+) recombination [20]. Accordingly, fabricating photocatalysts with enhanced separation efficiency of the photogenerated (e^- – h^+) pairs is crucial for facilitating the redox reactions [21, 22].

To date, many ternary heterojunctions have been reported in the literatures, and their enhanced photocatalytic activities were evident when compared with binary and single component systems [23–25]. For example, Rao et al. reported enhanced photocatalytic performance of C_3N_4 with layers of MoS_2 and nitrogenated rGO ternary heterojunction which attributed to the effective separation of the generated electron–hole pairs introduced by the internal electric field built by nitrogenated rGO interlayers [26]. Zhang et al. reported the synthesis ternary $Bi_2WO_6/Bi_{25}FeO_{40}/rGO$ heterojunction that presented higher photocatalytic activity due to the effective charge separation, better light absorption and large surface area [27]. Accordingly, ternary heterojunctions have the leverage to efficiently separate the photogenerated electron–hole pairs due to the synergistic effect of multi-components' heterojunction.

In this work, we report the fabrication of $BiOCl/BiOBr/rGO$ ternary heterojunctions. The enhanced photocatalytic reduction of 4-NA to PPD of the prepared ternary heterojunctions was compared to their binary system. To the best of the authors' knowledge, this is the first study on the construction of $BiOCl/BiOBr/rGO$ ternary heterojunctions photocatalyst and their use in photocatalytic reduction of 4-NA in aqueous solution. It worth mentioning that the reason for choosing $BiOCl_{75\%}BiOBr_{25\%}$ coupled with rGO is due to superior catalytic activity of $BiOCl_{75\%}BiOBr_{25\%}$ over $BiOCl_{25\%}BiOBr_{75\%}$ and $BiOCl_{50\%}BiOBr_{50\%}$ prepared composites.

2 Experimental

Bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), potassium chloride (KCl), acetic acid (CH_3COOH), potassium bromide (KBr), acetone (CH_3COCH_3), ethanol (CH_3CH_2OH), sodium borohydride ($NaBH_4$), 4-nitroaniline ($O_2NC_6H_4NH_2$), hydrazine hydrate ($NH_2NH_2 \cdot H_2O$), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), graphite powder (100+ mesh), sulfuric acid (H_2SO_4), and hydrogen peroxide (H_2O_2) were purchased from Sigma-Aldrich and used as received.

2.1 Synthesis of reduced graphene oxide (rGO)

Reduced graphene oxide (rGO) was synthesized applying modified Hummers' method using graphite powder as a starting material to produce graphene oxide followed by reduction to obtain the desired rGO. In a typical synthetic procedure: to a 2 g graphite powder, 60 mL of concentrated sulfuric acid was added followed by addition of 0.12 g $NaNO_3$. The mixture was kept under cooling and constant stirring for 1 h. To the mixture, an incremental addition of 6 g $KMnO_4$ was added followed by addition of 60 mL of deionized water (DW). The temperature of the reaction was raised to 90 °C and kept constant for an additional of 30 min. Afterward, 200 mL DW and 30 mL H_2O_2 were added to the mixture, and the obtained GO was washed with DW and 2 M HCl, and then filtered and left to dry in an oven at 100 °C. Dried GO was suspended in DW and hydrazine hydrate (5 mL) was added to reduce GO to rGO. After leaving the mixture to stir for 1 h, rGO was filtered and kept in oven for 24 h to dry.

2.2 Synthesis of $BiOCl$ and $BiOBr$ photocatalysts

Pure $BiOCl$ and $BiOBr$ were synthesized using coprecipitation method. For synthesizing $BiOCl$: 9.7 g of $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 150 mL 4 M acetic acid under constant stirring and heating at 80 °C. In a separate flask, 1.49 g of KCl was dissolved in 10 ml deionized water (DI). KCl solution was added dropwise to the $Bi(NO_3)_3 \cdot 5H_2O$ solution under constant stirring. A white powder formed. The reaction was kept stirring for 8 h at room temperature and then filtered and washed several times with DI water and ethanol then left to dry at 80 °C in an oven for 2 h. The obtained powder was then calcined at 400 °C for 2 h. Same steps was applied for the synthesis of $BiOBr$ by dissolving 2.38 g of KBr in DI water. The product was dried in an oven at 80 °C for 2 h followed by calcination at 150 °C for 2 h.

2.3 Syntheses of $BiOCl/BiOBr$ composites photocatalysts

Three different composites $BiOCl_{75\%}BiOBr_{25\%}$, $BiOCl_{50\%}BiOBr_{50\%}$, and $BiOCl_{25\%}BiOBr_{75\%}$ composites were synthesized by simple physical mixing in acetone. $BiOCl_{75\%}BiOBr_{25\%}$ was prepared mixing 75 mol % of $BiOCl$ with 25 mol % of $BiOBr$ in 10 mL acetone. The homogenous mixture was thoroughly mixed until acetone evaporated.

$\text{BiOCl}_{50\%}\text{BiOBr}_{50\%}$ and $\text{BiOCl}_{25\%}\text{BiOBr}_{75\%}$ were prepared adopting the same procedures. Prepared composites were then characterized and $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}$ was further used to prepare $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}/\text{rGO}$ heterojunction composites.

2.4 Syntheses of $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}/\text{rGO}$ heterojunction composites

rGO heterojunction composites were prepared using three different mass ratios of rGO: 1%, 3%, and 5%. Where $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}/1\%$ rGO composite was prepared by physically mixing of 1.00 g of $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}$ composite and 0.01 g rGO in 10 mL acetone. The dried powder was then placed in an oven for 2 days at 150 °C. Same steps were

applied for the synthesis of the other two rGO ratio composites using 0.03 g and 0.05 g for $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}/3\%$ rGO and $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}/5\%$ rGO respectively.

3 Characterization techniques

3.1 Powder X-ray diffraction (PXRD)

X-ray diffraction spectra for synthesized photocatalysts were performed using a Shimadzu-6100 PXRD diffractometer installed with Cu-K α X-ray tube working at 40 kV voltage and current of 40 mA. The diffraction data were recorded in the 2θ angle range of 10–60° at 2°/min scanning rate where $\lambda = 1.542 \text{ \AA}$.

Fig. 1 XRD pattern for the prepared BiOCl, BiOBr, and $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}$

Fig. 2 XRD pattern for the prepared $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}$ and its three different rGO composites

Fig. 3 Tauc plot of pure $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}$ and different composites

Table 1 Physical properties and lattice parameters of $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}$ and $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}/\text{rGO}$ ternary composites

Sample		Lattice parameters				Pore size (nm)	Surface area (m^2/g)	Band gap (eV)
		$a=b$	c	$V \text{ \AA}^3$	$\alpha=\beta=\gamma$			
BiOCl	BiOCl	3.89	7.33	110.69	90	102.93	3.30	3.32
BiOBr	BiOBr	3.90	8.17	124.20	90	111.20	3.70	2.92
$\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}$	BiOCl	3.91	7.53	110.69	90	102.57	3.98	3.13
	BiOBr	3.94	8.32	129.53				
$\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}/1\%\text{rGO}$	BiOCl	4.38	8.54	163.91	90	115.16	5.23	3.12
	BiOBr	4.30	9.42	174.04				
$\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}/3\%\text{rGO}$	BiOCl	4.36	8.47	160.70	90	101.27	4.22	3.11
	BiOBr	4.32	9.33	174.58				
$\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}/5\%\text{rGO}$	BiOCl	4.35	8.44	159.88	90	112.02	4.68	3.05
	BiOBr	4.29	9.33	171.97				

3.2 UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS)

UV–Vis diffuse reflectance (UV–Vis DRS) analysis was used to calculate band-gap energies of the photocatalysts using Shimadzu UV-3600 UV–Vis spectrophotometer. Analysis was conducted in a wavelength range of (200–800 nm) and as a standard barium sulfate (BaSO_4) was used for baseline correction. Band-gap energies were calculated using UV–Vis DRS spectra by applying Tauc plot method [28] following Eq. (1):

$$(\alpha h\nu)^{\frac{1}{n}} = A(h\nu - E_g), \quad (1)$$

where α is absorption coefficient, $h\nu$ is frequency of light in eV, and A , E_g being a constant and band-gap energy value, respectively. The n value varies depending on the transition of the semiconductor photocatalyst, considering prepared photocatalysts are direct allowed, $n = 1/2$. E_g valued by extrapolating the linear fit of a plot of $(\alpha h\nu)^{1/n}$ vs. $(h\nu)$.

Fig. 4 BET analysis for the prepared BiOCl, BiOBr, BiOCl_{75%}BiOBr_{25%}, and BiOCl_{75%}BiOBr_{25%}/rGO ternary composites

3.3 Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS)

Synthesized photocatalyst were characterized using an FEI SEM Quanta Inspect S50 Scanning electron microscope equipped with EDS-Oxford INCA PENTA at a working voltage of 30 kV to study morphology and elemental compositions. Prior to the analysis, samples were placed on carbon tape on sample holder and coating with gold.

3.4 Surface area and porosity analyses

Surface area and porosity analyses were conducted using Quantachrome Autosorb-1 volumetric gas sorption using N₂ adsorption at 77 K. Samples were degassed before measurements at 150 °C for 2 h. Brunauer–Emmett–Teller (BET) was applied in calculating surface area; pore size was determined using the Barrett–Joyner–Halenda (BJH) analysis.

4 Photocatalytic activity

The photocatalytic activity of prepared composites was assessed through the photoreduction of 4-NA under light irradiation as a model reaction. A 4-nitroaniline solution of

1×10^{-4} M concentration was prepared. 100 mL of the solution was transferred into round flask (250 mL), and 100 mg of the photocatalyst was added; measured pH value was 6.5. The solution was purged with N₂ gas for 10 min and positioned 13 cm from a 500 W Halogen lamp (OSRAM HALOLINE), with wavelength range of 380–780 nm [29]. Prior to irradiation, reaction was kept for a period of 1 h for adsorption–desorption equilibrium followed by the addition of 3 mg of NaBH₄. Reaction was conducted at room temperature; however, the halogen lamp produces heat estimated at around ~70 °C. At selected time intervals, 3 mL from the solution was collected and filtered, and their absorptions were measured using UV–Vis.

5 Results and discussion

5.1 Powder X-ray diffraction spectroscopy (PXRD)

The PXRD patterns of the prepared BiOCl, BiOBr and BiOCl/BiOBr composites are presented in Fig. 1 and Figure S1. BiOCl_{75%}BiOBr_{25%} exhibited diffraction peaks correspond to both BiOCl and BiOBr (Fig. 1) which indexed to (JCPDS file no. 78–0348) and (JCPDS No: 09–0393) database, respectively. Pure rGO shows a broad peak at 26.3°

Fig. 5 SEM images for BiOCl, BiOBr, BiOCl_{75%}BiOBr_{25%}, and BiOCl_{75%}BiOBr_{25%}/rGO ternary composites **a** Pure BiOCl, **b** Pure BiOBr, **c** BiOCl_{75%}BiOBr_{25%}, **d** BiOCl_{75%}BiOBr_{25%}/1%rGO, **e** BiOCl_{75%}BiOBr_{25%}/3%rGO, and **f** BiOCl_{75%}BiOBr_{25%}/5%rGO

with a calculated crystal size of 3.99 nm, and therefore, in the prepared ternary system BiOCl_{75%}BiOBr_{25%}/rGO, a tiny shoulder peak coincides at one of the mean peaks of BiOCl

at 25.94° (Fig. 2). The low intensity of the peak is ascribed to the low amount of rGO in the three prepared composites. All prepared composites exhibited diffraction peaks

Fig. 6 EDX of BiOCl_{75%}BiOBr_{25%}, BiOCl_{75%}BiOBr_{25%}/rGO ternary composites: **a** BiOCl_{75%}BiOBr_{25%}, **b** BiOCl_{75%}BiOBr_{25%}/1%rGO, **c** BiOCl_{75%}BiOBr_{25%}/3%rGO, and **d** BiOCl_{75%}BiOBr_{25%}/5%rGO

Table 2 Weight and atomic percentage of BiOCl_{75%}BiOBr_{25%}/rGO composites

Samples	Weight %					Atomic %				
	O	Bi	Cl	Br	C	O	Bi	Cl	Br	C
BiOCl _{75%} BiOBr _{25%}	9.34	75.66	7.28	7.73	—	46.79	29.01	16.45	7.75	—
BiOCl _{75%} BiOBr _{25%} /1%rGO	13.06	47.48	4.73	4.46	30.27	21.75	6.05	3.55	1.49	67.15
BiOCl _{75%} BiOBr _{25%} /3%rGO	10.27	64.65	6.37	6.46	12.26	28.75	13.86	8.04	3.62	45.73
BiOCl _{75%} BiOBr _{25%} /5%rGO	11.53	54.72	5.20	5.22	23.33	22.97	8.35	4.68	2.08	61.92

attributed to BiOCl, BiOBr, and rGO with no extra peaks for any impurities present in the sample.

5.2 UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS)

Figure S2 and Fig. 3 show Tauc plots of BiOCl, BiOBr, BiOCl_{75%}BiOBr_{25%}, and BiOCl_{75%}BiOBr_{25%}/rGO composites. Calculated band-gap energy of the prepared ternary system and BiOCl_{75%}BiOBr_{25%} indicate that there is not much change in calculated band-gap energies. However, system containing 5%rGO showed a bit lower band-gap energy value of 3.05 eV (Table 1).

5.3 BET surface analysis for BiOCl_{75%}BiOBr_{25%} and BiOCl_{75%}BiOBr_{25%}/rGO ternary composites

The specific area of BiOCl_{75%}BiOBr_{25%} and BiOCl_{75%}BiOBr_{25%}/rGO ternary composites was evaluated according to N₂ adsorption–desorption isotherm analysis. Prepared photocatalysts possess H3 hysteresis loop in the range of 0.75–1.0 P/P₀ indicating the presence of slit-shape pores, as shown Fig. 4 and Table 1 [30, 31]. Surface area of the photocatalysts was calculated to be 3.98 m²/g, 5.2270 m²/g, 4.2235 m²/g, 4.6756 m²/g for BiOCl_{75%}BiOBr_{25%}, 1% rGO, 3% rGO, and 5% rGO, respectively. The addition of rGO increased surface area of BiOCl_{75%}BiOBr_{25%}; however, no trend was observed for surface area as rGO load increased in the composites.

Fig. 7 UV-Vis absorption of 4-NA under visible light irradiation as a function of time in the presence of **a** $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}$, **b** $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}/5\%\text{rGO}$, **c** NaBH_4 , and **d** TiO_2 photocatalysts

5.4 Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analyses

SEM images were applied to examine the morphology of the prepared pure BiOCl , BiOBr , and $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}$ and $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}/\text{rGO}$ ternary composites (Fig. 5). Both pure BiOCl and BiOBr exhibit same flakes-like morphology; however, $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}$ composite does not show any distinctive morphology where it exhibits agglomerated rock like morphology. As for $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}/\text{rGO}$ ternary composites, it is observed that increasing rGO percent in the composites cause no change in morphology, where different composites show same agglomerated particles. Indicating that rGO has no effect in morphology which attributed to the low rGO content present in to the composites [32].

The elemental composition of the prepared photocatalysts was confirmed using EDX. As shown in Fig. 6, the existence of Bi, O, Cl, Br, and C with no extra peaks proving the

purity of the composites. Table 2 presents the atomic and weight percent of each element, and the high percentage of C in the composites is attributed to the use of carbon tape during the analysis.

5.5 Photocatalytic activity of the $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}$ composite and $\text{BiOCl}_{75\%}\text{BiOBr}_{25\%}/\text{rGO}$

Figure 7 and Figure S3 display the photoreduction of 4-NA to PPD using prepared composites under simulated visible light irradiation as a function of time. Reaction was monitored by observing the decrease in absorbance

Table 3 Calculated photocatalytic rate constants for the conversion of 4-NA to PPD

Photocatalyst composite	Rate (min^{-1})	% Conversion
Pure BiOCl ^a	0.11 ± 0.02	88.6
Pure BiOBr ^a	0.20 ± 0.03	98.9
BiOCl _{75%} BiOBr _{25%} ^a	0.29 ± 0.09	99.4
BiOCl _{50%} BiOBr _{50%} ^a	0.21 ± 0.06	97.6
BiOCl _{25%} BiOBr _{75%} ^a	0.23 ± 0.06	98.5
BiOCl _{75%} BiOBr _{25%} ^b	NR	NR
BiOCl _{75%} BiOBr _{25%} /1%rGO ^a	0.59 ± 0.2	100
BiOCl _{75%} BiOBr _{25%} /3%rGO ^a	0.82 ± 0.1	99.17
BiOCl _{75%} BiOBr _{25%} /5%rGO ^a	0.84 ± 0.1	98.80
BiOCl _{75%} BiOBr _{25%} /5%rGO ^b	NR	NR
NaBH ₄ ^c	0.038 ± 0.06	41.3
TiO ₂ ^a	0.028 ± 0.05	17.6

^aNaBH₄ was added to the reaction before light irradiation^bReaction was conducted without the addition of NaBH₄^cNo photocatalysts was added to 4-NA solution, ^c Reaction was started after the addition of NaBH₄ only. NR; no reaction

maxima at 380 nm that indicates the reduction of 4-NA; moreover, two new peaks at 283 nm and 305 nm appeared as irradiation time increases indicating the formation of PPD. BiOCl_{75%}BiOBr_{25%} exhibited higher photocatalytic activity compared to BiOCl_{25%}BiOBr_{75%} and BiOCl_{50%}BiOBr_{50%}, and therefore, it was further synthesized incorporating rGO. As shown in Table 3, rate constant increases as rGO load increases in the sample.

Composite of highest rGO percent (BiOCl_{75%}BiOBr_{25%}/5% rGO) exhibited the highest rate of 0.84 min^{-1} that can be ascribed to the role of rGO in trapping electrons by acting as a sheet, hence minimizing the recombination rate. An attempt to evaluate the photocatalytic performance at higher rGO loading (up to 10%) showed dramatic decrease in the photocatalytic performance which may be attributed to the strong absorption of rGO to incident light at higher load [33]. All prepared composites exhibited excellent conversion percentage > 98% after 20 min. Two control reactions were conducted (1) reaction with only NaBH₄ to understand its role in the reduction process and (2) reduction using TiO₂ used as a benchmark photocatalyst in the field. TiO₂ exhibited the lowest rate constant of 0.028 min^{-1} compared to the prepared visible light active composites which come as a no surprise, since it is a UV active photocatalyst. Moreover, the use of NaBH₄ only with no photocatalysts present showed low-rate constant emphasizing the role of the photocatalyst for the reaction to complete. C/C_0 vs. time graph shows the change in concentration of 4-NA under visible light irradiation using various photocatalysts for 20 min (Fig. 8). According to Fig. 9, conversion of 4-NA to PPD follows the first-order kinetics, where straight lines were obtained for the collected experimental data upon drawing the change of $\ln(C/C_0)$ with time (20 min). Moreover, calculated rate constant for the prepared samples is presented in Table 3. Owing to the accessibility of excited electrons (e^-) in the conduction band (CB) of the photocatalyst and electron holes (h^+) in

Fig. 8 Kinetics plot of $\ln C/C_0$ over time of BiOCl_{75%}BiOBr_{25%}, BiOCl/BiOBr/rGO composites, NaBH₄, and TiO₂ photocatalysts

Fig. 9 Proposed mechanisms for the conversion of 4-NA

the valence band (VB), the reduction of 4-NA is proposed to proceed through the following mechanism. When the photocatalyst absorbs light with energy higher than the band gap of the photocatalyst, electrons migrate from VB to CB creating electron–hole pairs. These photogenerated charges transfer to rGO sheet, and hence reduce recombination rate and extend the life of the photo-induced charge pairs providing electrons for the reduction of the nitro-group. The oxidation of water molecules at the holes created at the VB afford more electrons for the reduction of 4-NA to PPD. As proposed by Moghanlou et al. [34], the oxidation of water molecules at the holes created at the VB afford more electrons for the reduction of 4-NA to PPD. Accordingly, reaction mechanism is proposed in Fig. 10. Moreover, NaBH_4 act as sacrificial electron donor for the photogenerated holes, and thus facilitate charge transfer for the reduction of 4-NA [35].

5.6 Conclusion

In conclusion, pure BiOCl, BiOBr, and various BiOCl/BiOBr composites were prepared. BiOCl_{75%}/BiOBr_{25%} composite exhibited the highest activity compared to the other prepared ratios. BiOCl_{75%}/BiOBr_{25%} was further

investigated incorporating three different ratios of rGO. The successful incorporation of rGO into BiOCl_{75%}/BiOBr_{25%} composite was confirmed by PXRD and other analytical techniques. As shown, upon increasing rGO loading, no significant changes were observed on the band gap and morphology for the prepared composites photocatalysts. The photocatalytic activity was evaluated for the photoreduction of para-nitroaniline to p-phenylenediamine. Results show that as percent rGO increases in the composite, reaction rate increases which could be attributed to the enhanced separation of charge carriers. This study is emphasizing on the role of rGO in trapping electrons and inhibiting the recombination of the photogenerated electron–hole pairs hence afford more electrons for the reduction of 4-NA.

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Declarations

Conflict of interest There are no conflicts to declare.

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