Photo-reduction of bromate in drinking water by metallic Ag and reduced graphene oxide (RGO) jointly modified BiVO₄ under visible light irradiation

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Abstract
Bromate (BrO₃⁻), an oxyhalide disinfection by-product (DBP) in drinking water, has been demonstrated to be carcinogenic and genotoxic. In the current work, metallic Ag and reduced graphene oxide (RGO) co-modified BiVO₄ was successfully synthesized by a stepwise chemical method coupling with a photodeposition process and applied in the photo-reduction of BrO₃⁻ under visible light irradiation. In this composite, metallic Ag acted as an electron donor or mediator and RGO enhanced the BrO₃⁻ adsorption onto the surface of catalysts as well as an electron acceptor to restrict the recombination of photo-generated electron-hole pairs. The Ag@BiVO₄@RGO composite exhibited greater photo-reduction BrO₃⁻ performance than pure BiVO₄, Ag@BiVO₄ and RGO@BiVO₄ under identical experimental conditions: initial BrO₃⁻ concentration 150 mg/L, catalyst dosage 0.5 g/L, pH 7.0 and visible light (λ > 420 nm). The photoluminescence spectra (PL), electron-spin resonance (ESR), photocurrent density (PC) and electrochemical impedance spectroscopy (EIS) measurements indicated that the modified BiVO₄ enhanced the photo-generated electrons and separated the electron-hole pairs. The photocatalytic reduction efficiency for BrO₃⁻ removal decreased with the addition of electron quencher K₂S₂O₈, suggesting that electrons were the primary factor in this photo-reduction process. The declining photo-reduction efficiency of BrO₃⁻ in tap water should attribute to the consumption of photo-generated electrons by coexisting anions and the adsorption of dissolved organic matter (DOM) on graphene surface. The overall results indicate a promising application potential for photo-reduction in the DBPs removal from drinking water.

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1. Introduction

Over the past decades, BrO₃⁻ originated from the chlorination or ozonation process in bromide-containing water has received a growing concern due to its carcinogenic and genotoxic properties (Von Gunten and Oliveras, 1998; Butler et al., 2005). The specified maximum contaminant level (MCL) of BrO₃⁻ for drinking water is 10 µg/L in the US and European countries (Wu et al., 2013; Weinberg et al., 2003), the same MCL is also explicitly stipulated in drinking water sanitary standard (GB 5749-2006) and drinking natural mineral water (GB 8537-2008) in China (Xu et al., 2012). To meet the strict limitation, the reduction of BrO₃⁻ to innocuous Br⁻ was proven to be efficient means. The reducing materials under study included biological activated carbon (Kirisits et al., 2001), ferrous ions (Chitrakar et al., 2011), zero-valent iron (Wang et al., 2009), layered double hydroxides (LDHs) (Zhong et al., 2013), activated carbon felt electrodes (Kishimoto and Matsuda, 2009) and Pd/Al₂O₃ catalyst (Chen et al., 2010). However, long reaction time, strict reaction condition and high risk to produce secondary pollutants limited the application of these reducing materials in practice, thus it is of a great necessity to develop a novel and economical alternative for bromate reduction.

Recently, photo-reduction technology has been implemented and emerged as a potential technology to remove BrO₃⁻ ions in drinking water (Zhang et al., 2010b; Peldszus et al., 2004). As a
typical photocatalyst, TiO₂ and its related photocatalysts had been successfully used in bromate removal from water under UV irradiation (Noguchi et al., 2003). For example, Mills and his co-workers demonstrated that bromate ions in tap water were totally reduced by Pt/TiO₂ catalyst under UV irradiation of 254 nm (Mills et al., 1996). Huang et al. reported graphene-TiO₂ composite photocatalyst showed a larger photo-reduction capacity of BrO₃⁻ than pure TiO₂, because graphene as an acceptor enhanced the photo-generated electrons from the photo-excited P25 and increased the charge transportation (Huang et al., 2014). According to previous studies (Zhao et al., 2011), the primary reactions for modified TiO₂ (M-TiO₂) should be listed as follows:

\[
\begin{align*}
\text{M-TiO}_2 + \text{UV} & \rightarrow \text{M-TiO}_2 (\text{e}^-) + \text{M-TiO}_2 (\text{h}^+) \quad (1) \\
\text{M-TiO}_2 (\text{h}^+) + \text{OH}^- & \rightarrow \text{OH} \quad (2) \\
\text{BrO}_3^- + \text{e}^- + 6\text{H}^+ & \rightarrow \text{Br}^- + 3\text{H}_2\text{O} \quad (3)
\end{align*}
\]

where electron (e⁻) is a strong reducer, M-TiO₂ possessed better electron-hole pairs separation under UV light, as compared with pure TiO₂. It could be inferred that electrons played a vital role in the photo-reduction system and appropriate modifications to single-component photocatalyst might enhance the corresponding photocatalytic activity.

Considering the cost and convenience in practical application, numerous attempts were devoted to the exploration of visible-light photocatalyst. Monoclinic BiVO₄ (m-BiVO₄) with a band gap energy of 2.4 eV, responsible to visible light, has been found to be a perfect visible-light material for degradation of organic contaminants and purification of wastewaters (Park et al., 2013b; Rao et al., 2014; Zhong et al., 2011). A relatively low mobility of photo-generated charges for pure BiVO₄ hindered the separation of electron-hole pairs, presenting as an unsatisfactory photocatalytic activity (Jo et al., 2012). Appropriate modifications always could improve the separation of charge carriers for pure BiVO₄, the methods employed usually included: (I) heterojunction construction (Hong et al., 2011), (II) ions doping (Obregon and Colon, 2014), (III) morphologies control (Dong et al., 2014b), (IV) loading noble metal doping (Ge, 2008), and (V) interface effect (Li et al., 2015). Photo-oxidation mechanism via photo-generated holes and other oxidative active species (O₂ or OH) were majorly detected in current studies, while the research on the photo-reduction induced by electrons generated from BiVO₄ or modified BiVO₄ was fewer and the application of oxylhalide disinfection by-product (DBP) reduction was seldom reported.

Herein, reduced graphene oxide (RGO) was chosen as the sub-strate to support BiVO₄ owing to its unique two-dimensional carbon structure (sp²-hybridized type), excellent conductivity and large surface area (Zhang et al., 2010a, 2015). Highly conductive reduced graphene oxide could be regarded as the ideal co-catalysts to improve various semiconductor photocatalysts. RGO could not only serve as an excellent electron acceptor to restrict the recombination of photo-generated electron-hole pairs, but also adsorb a large volume of BrO₃⁻ on the surface of catalyst, which was regarded as the ideal co-catalysts to combine with other semiconductor photocatalysts. In addition, a small amount of metallic Ag co-doped photocatalysts were proven to be effective in oriented migration of photo-generated electrons. For example, Sun et al. successfully deposited Ag nanoparticles onto [101] facets of TiO₂ nanocrystals and possessed superior photocatalytic reduction activity to nitrate (Sun et al., 2016). Vanitha et al. fabricated a novel Ag decorated CeO₂/RGO as an efficient supercapacitor (Vanitha et al., 2015). For these reasons, metallic Ag and RGO were chosen to modify BiVO₄ in this study. The co-modified BiVO₄ overcame the common drawbacks of single-component photocatalyst and achieved higher charge-separation efficiency. Thus the photo-reduction of BrO₃ under visible light over Ag@BiVO₄@RGO photocatalyst should be feasible and valuable. To the best of our knowledge, the relevant study has never been reported.

In this work, Ag@BiVO₄@RGO photocatalyst was fabricated through chemical deposition of RGO and photo-reduction of Ag nanoparticles on the surface of pre-prepared BiVO₄. The prepared composites were employed as photocatalyst to reduce BrO₃ to Br⁻ under visible light irradiation. The effect of catalyst dosage, initial BrO₃ concentrations, initial pH and different water sources were investigated in details. The generation and transfer of electrons and separation of electron-holes pairs during the whole photocatalytic processes were measured by PL, PC and EIS to elucidate the mechanism of how the prepared photocatalysts enhanced photo-reduction of BrO₃.

2. Experimental

2.1. Materials and photocatalysts preparation

All reagents were used as received without further treatments. De-ionized water (18.25 MΩ cm) from Millipore system was used throughout all the experiments. BiVO₄ was fabricated by a previously reported method with minor modifications (Booshehri et al., 2014). In a typical synthesis procedure: 6 mmol of Bi(NO₃)₃·5H₂O was dissolved in 32 mL of HNO₃ (1 M). Afterwards the prepared NH₄VO₃ (keep the molar ratio of 1:1 with Bi(NO₃)₃·5H₂O) was added into the above solution. After being heated for 5 min and ultrasonicated for 40 min, CO(NH₂)₂ (3.0 g) was added and the resultant mixture was maintained at 80 °C for 24 h under oil bath condition. Finally, the product was collected by filtration, washed with de-ionized water and ethanol for several times and dried at 60 °C for 12 h.

The synthesis of RGO/1 wt%BiVO₄ was prepared as follows: 0.006 g of graphene oxide (GO) prepared according to modified Hummer's method (Gao and Wang, 2013) was dispersed into 50 mL of de-ionized water with 2 h ultrasonic treatment. After that, 0.6 g of BiVO₄ was added and continuously stirred for 2 h under laboratory condition. Subsequently, 1 mL of NH₃·H₂O and 3 mL of N₂H₄ were added in sequence. While being stirred for 4 h at 80 °C under water bath condition, the resulting sample was centrifuged, washed and dried at 60 °C for 12 h. Furthermore, Ag(1.0 wt%BiVO₄@RGO) was synthesized by a facile photo-reduction procedure. 0.25 g of BiVO₄@RGO and a certain amount (0.004 g) of AgNO₃ were dispersed into 10 mL de-ionized water. After that, 20 mL of methyl orange solution (20 mg/L) was added and kept 2 h stirring using a magnetic stirrer in the darkness. Then the mixture was exposed to a 300 W Xe lamp and irradiated for 1 h to photo-deposition of metallic Ag on the surface of BiVO₄@RGO. At last, the product was obtained by centrifugation, washing and vacuum drying.

2.2. Characterization

The as-prepared samples in the form of powder were collected and characterized by a Rigaku D/max 2500/pc X-ray diffractometer with Cu Kα radiation at a scan rate of 0.1° 20 s⁻¹. The XPS measurements were performed on a Thermo ESCALAB 250Xi spectrometer with Al Kα source. The photoluminescence (PL) spectra were recorded using a transient fluorescence spectrometer (Edinburgh FLsp920 full functional state). A zeta potential analyzer (Malvern) was used to measure the zeta potential of the samples under different pH conditions. Electron spin resonance (ESR) signals of spin-trapped paramagnetic species with 5, 5-dimethyl-1-
pyrroline N-oxide (DMPO) were detected using a Bruker ER200-SRC spectrometer under visible light irradiation (λ > 420 nm).

2.3. Photocatalytic activity test

In order to evaluate the photo-reduction performance of the as-prepared samples, photocatalytic removal of BrO₃⁻ ions were carried out under visible light irradiation using a 300 W Xe lamp (CEL-HXF300, China) with a 420 nm cut filter. The average light intensity striking the surface of reaction solution was about 100 mW cm⁻². In a typical experiment, 0.03 g of photocatalysts were homogeneously dispersed into 60 mL of BrO₃⁻ solution (150 μg/L) by ultrasonic bath for 10 min. Another 20 min dark stirring at room temperature was maintained for achieving the adsorption-desorption equilibrium. After that, the mixture was exposed to visible light, and 3 mL of solution was taken out at given time interval, centrifuged by 8000 rpm/min, filtrated by 0.22 μm membrane filter and analyzed the residual BrO₃⁻ by an ion chromatograph system ( Dionex ICS-900, USA) equipped with an AG-23 column with an AS-23 sampler.

2.4. Photo-electrochemical measurements

The photocurrent density (PC) and electrochemical impedance spectroscopy (EIS) spectra, were determined in a conventional three-electrode electrochemical cell with a working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE) as reference electrode. The working electrode was immersed in a sodium sulfate electrolyte solution (0.5 M) using CHI660C workstation and irradiated at a visible light. A 300 W Xe lamp served as the light source. The average light intensity was about 100 mW cm⁻². The available surface area of working electrodes for all photo-electrochemical tests was 0.25 cm².

3. Results and discussion

3.1. Characterization of as-prepared catalysts

The XRD patterns can provide information on the crystalline nature of the as-obtained photocatalysts, which are presented in Fig. S1 (Supplementary information). All patterns of samples exhibited sharp diffraction peaks, suggesting that high crystallinity was achieved. From Fig. S1A (Supplementary information), it could be deduced that all the peaks in the XRD pattern of BiVO₄ were indexed to monoclinic scheelite BiVO₄ phase (JCPDS File No. 14-0688) (Li et al., 2015). For Ag@BiVO₄, RGO@BiVO₄ and Ag@BiVO₄@RGO, no detectable diffraction peaks of silver species (38.1°, 44.2°, 64.4° and 77.4° for Ag (0) and 34.2° for Ag (1) (Liu et al., 2012) and RGO 2θ = 26° and 44° (Dong et al., 2014a) could be observed for the modified BiVO₄, possibly due to the relatively small dosage amount and low diffraction intensity of metallic Ag and RGO in the corresponding composites (Song et al., 2016). Fig. S1B (Supplementary information) showed the comparison of XRD patterns between the fresh and the used samples. No significant discrepancy was perceived in the crystal structure except the lower intensity of the XRD pattern after four cycles, validating high stability of Ag@BiVO₄@RGO under visible light irradiation.

The chemical states and the surface composition of Ag@BiVO₄@RGO composite powder were investigated by XPS analysis. Fig. S2A (Supplementary information) was a typical XPS survey spectrum of Ag@BiVO₄@RGO, which composed of Bi, O, V, Ag and C. Three characteristic peaks could be found in the high-resolution C1s spectrum (Fig. S2B, Supplementary information). The peak located at 284.6 eV could be assigned to the sp² bonded carbon (C-C) in graphene. The peak at 286.7 eV belonged to the oxygen containing functional groups (epoxy/hydroxyls, C–O) while the peak appeared at 288.5 eV was associated with the O–C=O species (carboxyl) (Zhang et al., 2015). As depicted in Fig. S2C (Supplementary information), Ag 3d spectrum displayed two characteristic peaks at 368.3 eV and 374.4 eV, corresponding to Ag 3d₅/₂ and Ag 3d₇/₂, respectively (Song et al., 2016). The weight ratio of metallic Ag in the Ag@BiVO₄@RGO composite was calculated to be 0.95 wt% according to the XPS spectrum, which was in good consistence with the preparation (1 wt% of metallic Ag photo-deposition). Other elements (Bi, V and O) analyses could be found in Fig. S3 (Supplementary information). In addition, the surface areas of pure BiVO₄ and Ag@BiVO₄@RGO composite were measured by BET test (Fig. S4, Supplementary information). Compared to pure BiVO₄ (surface area = 33.625 m²/g), Ag@BiVO₄@RGO nanocomposite displayed a higher surface area (64.321 m²/g), validating that the presence of RGO on the surface of BiVO₄ resulted in higher surface area.

It is reported that the spectral absorption range would directly influence the number of photo-generated electrons and holes (Chen et al., 2016), so the optical absorption properties of pure BiVO₄ and modified BiVO₄ samples were investigated by UV–vis diffuse reflectance spectra (DRS). As displayed in Fig. S2D (Supplementary information), the bare BiVO₄ exhibited an absorption edge at ca. 517 nm with an edge band of 2.4 eV. An improved visible-light absorption capability was found in the presence of metallic Ag, RGO and the combination of two others on the surface of BiVO₄. The co-modified BiVO₄ (Ag@BiVO₄@RGO) presented the maximal visible-light absorption edge, which could be assigned to the grafting of RGO and the SPR effect of metallic Ag. The result demonstrated that the co-effect was an effective method to enhance the visible light performance of single semiconductor.

Moreover, the edge band calculation result of BiVO₄ was illustrated in Fig. S5 (Supplementary information). The band gap (Eg) of a semiconductor could be calculated by the following formula (Wang et al., 2015):

\[
a(\nu) = A(\nu - E_g)^{n/2}
\]

where \(a\), \(h\), \(\nu\), \(E_g\) and \(A\) are indicative to the absorption coefficient, Planck constant, light frequency, band gap energy, and a constant, respectively. Among them, \(n\) is determined by the type of optical transition of a semiconductor (\(n = 1\) for direct- and indirect-band-gap semiconductors, respectively). The \(n\) value for pure BiVO₄ was 4, and the corresponding energy band gap was measured to be about 2.4 eV.

3.2. Photo-reduction of BrO₃⁻ under visible light irradiation

In order to detect the photocatalytic performance of the as-prepared samples, experiments of BrO₃⁻ reduction were carried out under visible light irradiation. As shown in Fig. 1A, BrO₃⁻ concentrations decreased with the increasing irradiation time in the presence of pure BiVO₄ and modified BiVO₄ photocatalysts. Furthermore, it could be observed that modified BiVO₄ exhibited much superior photocatalytic activity than pure BiVO₄. Within the irradiation time of 120 min, BrO₃⁻ concentration decreased from 150 μg/L to 43 μg/L for pure BiVO₄ whereas it reduced to 12 μg/L and 2 μg/L for Ag@BiVO₄ and RGO@BiVO₄, respectively. Benefiting from the co-effect of Ag and RGO, BrO₃⁻ was almost reduced (99.1%) completely by Ag@BiVO₄@RGO composite in 90 min. Conversely, bromide concentrations in solution also increased with irradiation time. The total bromine contents maintained over 98% (Fig. S6, Supplementary information), suggesting that only photo-reduction process happened in the photocatalytic system.

The photo-reduction of BrO₃⁻ in this study followed the pseudo-first-order kinetic model. The rate constant (k) could be calculated...
by the following equation (Zhong et al., 2013):
\[
\ln \left( \frac{C_t}{C_0} \right) = -k t
\]
where \(C_0\) and \(C_t\) are the concentration of BrO\(_3^-\) at the time of 0 and \(t\), respectively ([μg/L]), and \(k\) represents the rate constant (min\(^{-1}\)). The corresponding plots of \(-\ln(C_t/C_0)\) vs. \(t\) exhibited a good linearity, and corresponding kinetic plots and first-order reactions parameters for pure BiVO\(_4\) and modified BiVO\(_4\) were distinctly depicted in Fig. 1B and Table 1, respectively. By considering the correlation coefficients \(R^2\), it could be found that the reduction of BrO\(_3^-\) over all prepared samples obeyed well the first-order reaction toward BrO\(_3^-\) concentrations \(R^2 > 0.97\). The rate constant over Ag@BiVO\(_4@RGO\) for the reduction of BrO\(_3^-\) was 0.1174 min\(^{-1}\), which was as 8.1, 4.4 and 2.6 times higher than those reductions by pure BiVO\(_4\), Ag@BiVO\(_4\) and Ag@BiVO\(_4@RGO\), respectively. Based on the above analysis, it could be concluded that photo-reduction of BrO\(_3^-\) under visible light by BiVO\(_4\) was feasible and appropriate modifications were in favor of achieving better BrO\(_3^-\) removal efficiency. Table 2 presents some results of the previous studies on BrO\(_3^-\) reduction by photocatalysis, most of these procedures were concentrated on the conversion of BrO\(_3^-\) to Br\(^-\) under acidic and alkali conditions, as more H\(^+\) or OH\(^-\) in the solution would play a negative role in the photo-reduction process. Deep insight into the zeta potential of as-synthesized Ag@BiVO\(_4@RGO\) composite is presented in Fig. 2C. The reduction of BrO\(_3^-\) by Ag@BiVO\(_4@RGO\) composite is presented in Fig. 2B. When initial BrO\(_3^-\) concentrations increased from 100 μg/L to 300 μg/L, the corresponding BrO\(_3^-\) reduction efficiencies decreased. The reduction efficiency reached at 99.9% at the initial BrO\(_3^-\) concentration of 100 μg/L, whereas this value was only 33.6% at the concentration of 300 μg/L under identical condition. The same observation was also made in previous study (Wang et al., 2015). Lower photon adsorption on catalyst particles should be responsible for the missing photocatalytic activity along with higher initial concentrations. Meanwhile, lower photon entering resulted in less electrons generation among the photocatalytic process, further to obtain an unsatisfying BrO\(_3^-\) reduction. From Fig. 2B, almost similar variations of BrO\(_3^-\) removal at the initial concentration of 100 μg/L and 150 μg/L were distributed, thus we chose concentration of 150 μg/L as the target concentration of BrO\(_3^-\) for the remaining explorations.

### 3.3. Effect of catalyst dosage

In view of economic condition, catalyst dosage was an important parameter for large-scale production. Results of residual BrO\(_3^-\) concentration in solutions against the amount of Ag@BiVO\(_4@RGO\) are depicted in Fig. 2A. A transparent trend distribution was found, the reduction ability firstly increased when the solid-to-solution ratio increasing from 0.167 g/L to 0.500 g/L, then decreased at 1.000 g/L and constantly declined at 1.667 g/L, suggesting an optimum catalyst dosage (0.500 g/L) existed in the photo-reduction procedure. Excess solid-to-solution ratio may lead to higher turbidity of the reaction system, resulting in worse light penetration through the BrO\(_3^-\) solution (Chen et al., 2016).

### 3.4. Effect of initial concentrations

The effect of initial BrO\(_3^-\) concentration on the bromate removal by Ag@BiVO\(_4@RGO\) composite is displayed in Fig. 2B. When initial BrO\(_3^-\) concentrations increased from 100 μg/L to 300 μg/L, the corresponding BrO\(_3^-\) reduction efficiencies decreased. The reduction efficiency reached at 99.9% at the initial BrO\(_3^-\) concentration of 100 μg/L, whereas this value was only 33.6% at the concentration of 300 μg/L under identical condition. The same observation was also made in previous study (Wang et al., 2015). Lower photon adsorption on catalyst particles should be responsible for the missing photocatalytic activity along with higher initial concentrations. Meanwhile, lower photon entering resulted in less electrons generation among the photocatalytic process, further to obtain an unsatisfying BrO\(_3^-\) reduction. From Fig. 2B, almost similar variations of BrO\(_3^-\) removal at the initial concentration of 100 μg/L and 150 μg/L were distributed, thus we chose concentration of 150 μg/L as the target concentration of BrO\(_3^-\) for the remaining explorations.

### 3.5. Effect of initial pH

The influence of initial pH for BrO\(_3^-\) reduction by Ag@BiVO\(_4@RGO\) composite is presented in Fig. 2C. The reduction of BrO\(_3^-\) was highly dependent on the pH value and the highest reduction rate was obtained at pH 7.0. It was unsuitable for BrO\(_3^-\) removal under acidic and alkali conditions, as more H\(^+\) or OH\(^-\) in the solution would play a negative role in the photo-reduction process. Deep insight into the zeta potential of as-synthesized Ag@BiVO\(_4@RGO\) (Table 3), potential became more negative with the increasing of initial pH values. The \(\xi\)-potentials at given pH values 3, 5, 7, 9, and 11 were 3.24 mV, -15.32 mV, -25.48 mV, -37.25 mV and -46.32 mV, respectively. As the pH was lowered, the functional groups were protonated and the corresponding proportion of the positive-charged surface increased. In basic condition, less BrO\(_3^-\) was adsorbed on the surface of the catalyst due to the intrinsic repulsion between the anions and the negative surface of Ag@BiVO\(_4@RGO\) by OH\(^-\) adsorption, indicating that less BrO\(_3^-\) could be reduced attributing to the less contacting probability. Furthermore, the generated active species (OH\(^-\), hydroxyl radical) also lead to the oxidation of Br\(^-\), which was in accordance with the previous finding (Park et al., 2013a; Von Gunten and Oliveras, 1998). The reactions between hydroxide ions and positive holes brought out

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(k) (min(^{-1}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiVO(_4)</td>
<td>0.0145</td>
<td>0.996</td>
</tr>
<tr>
<td>Ag@BiVO(_4)</td>
<td>0.0267</td>
<td>0.997</td>
</tr>
<tr>
<td>RGO@BiVO(_4)</td>
<td>0.0452</td>
<td>0.978</td>
</tr>
<tr>
<td>Ag@BiVO(_4@RGO)</td>
<td>0.1174</td>
<td>0.972</td>
</tr>
</tbody>
</table>
the forming of oxidation species. As for the reduction process in acidic condition, more electrons could transfer to the surface of Ag@BiVO4@RGO composite because of the autogenous attraction. As a result, the reduction efficiency in acidic condition was much better than that in basic condition. However, the increasing H⁺ could react with OH⁻, oxidation species such as (HO₂$^-$) could be formed and promoted the process of oxidation Br⁻ to BrO₃⁻ (Huang et al., 2014), leading to a relative low BrO₃⁻ removal efficiency.

According to the above-mentioned analysis, the optimum reduction condition could be observed at a neutral solution (pH 7.0), it was unbenevolent for degradation reaction of BrO₃⁻/CO₃ reduction predominantly ascribed to the formed oxidation radicals or less BrO₃⁻ adsorption under acidic or basic condition.

### 3.6. Photo-reduction of BrO₃⁻ in tap water

The photo-reduction of BrO₃⁻ by pure BiVO₄ and Ag@BiVO₄/RGO composite was also examined with the tap water originated from Xiang River and de-ionized water, respectively. As clearly illustrated in Fig. 2D, preferable BrO₃⁻ removal efficiencies by Ag@BiVO₄@RGO was achieved in both water sources, verifying that metallic Ag and RGO co-modified BiVO₄ exhibited a desirable reduction property in natural water. Nevertheless, the BrO₃⁻ removal in tap water was inhibited to some extent. The BrO₃⁻ removal efficiency in de-ionized water could achieve 99.1% within the irradiation time of 90 min, while it needed 120 min to reach the same effect for tap water. The similar phenomenon was found for

### Table 2

Summary of photocatalytic reduction of BrO₃⁻ ions over previous studies.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Light source (nm)</th>
<th>Catalysis dosage (g/L)</th>
<th>BrO₃⁻ concentration (µg/L)</th>
<th>pH</th>
<th>k for pseudo-first-order (10⁻³ min⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/TiO₂</td>
<td>UV/254</td>
<td>0.4</td>
<td>50</td>
<td>8.1</td>
<td>9.3</td>
<td>(Mills et al., 1996)</td>
</tr>
<tr>
<td>Pseudo-BM/TiO₂</td>
<td>UV/385</td>
<td>0.2</td>
<td>200</td>
<td>7.0</td>
<td>4.1–9.2</td>
<td>(Noguchi et al., 2003)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>UV/385</td>
<td>0.5</td>
<td>128</td>
<td>1.5–13.5</td>
<td>6.2</td>
<td>(Zhang et al., 2010b)</td>
</tr>
<tr>
<td>CB/BeMoO₄</td>
<td>Vis (&gt;420)</td>
<td>0.83</td>
<td>30</td>
<td>7.0</td>
<td>3.4–10.0</td>
<td>(Zha et al., 2011)</td>
</tr>
<tr>
<td>RGO/TiO₂</td>
<td>UV/254</td>
<td>0.1</td>
<td>10,000</td>
<td>5.1–9.2</td>
<td>9.4–21.0</td>
<td>(Huang et al., 2014)</td>
</tr>
<tr>
<td>Ag@RGO@BiVO₄</td>
<td>Vis (&gt;420)</td>
<td>0.5</td>
<td>150</td>
<td>3.0–11.0</td>
<td>15–117</td>
<td>In this study</td>
</tr>
</tbody>
</table>

### Table 3

The c-potentials and bromate reduction efficiency of Ag@BiVO₄@RGO composite at different initial pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>c-potential (mV)</th>
<th>Bromate reduction efficiencyb (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>3.24</td>
<td>56.7%</td>
</tr>
<tr>
<td>5</td>
<td>−15.32</td>
<td>81.5%</td>
</tr>
<tr>
<td>7</td>
<td>−25.48</td>
<td>99.1%</td>
</tr>
<tr>
<td>9</td>
<td>−37.25</td>
<td>38.4%</td>
</tr>
<tr>
<td>11</td>
<td>−46.32</td>
<td>16.3%</td>
</tr>
</tbody>
</table>

**Note:**
- The pH was pre-adjusted with 0.1 mol/L H₂SO₄ and 0.1 mol/L NaOH.
- Reaction conditions: initial BrO₃⁻ concentration 150 µg/L, catalyst dosage 0.5 g/L, reaction time 2 h, pH 7.0, reaction temperature 25 °C, light intensity 100 mW cm² (λ > 420 nm, 300 W Xe lamp).
pure BiVO₄ sample, the residual concentration of BrO₃⁻ in de-ionized water (43 µg/L) was obviously lower than that in tap water (67 µg/L) after photocatalytic reduction. Based on the concrete composition in tap water (Table 4), it could be deduced that the competitive anions such as NO₃⁻, NO₂⁻ might consume photo-generated electrons, therefore BrO₃⁻ reduction was hampered. On the other hand, natural organic matters (NOMs) in tap water could also impact the transporting or transferring of electrons between reduced graphene oxide and BiVO₄ (Huang et al., 2014). The dissolved organic matters (DOMs) were absorbed by RGO prior to BrO₃⁻ ions, resulting in less electrons in the photocatalytic system. Thus an adequate pre-treatment should be added for better reduction efficiency of BrO₃⁻.

### 3.7. The photocatalytic stability of Ag@BiVO₄@RGO

The photo-stability was a critical property for photocatalyst in practical application. Fig. 3A depicted the typical time course for BrO₃⁻ reduction by Ag@BiVO₄@RGO composite at four consecutive runs. After each run, the catalyst was washed by de-ionized water and ethanol, and retested in the fresh BrO₃⁻ (150 µg/L) under the same experimental conditions as previously mentioned. It could be noticed that there were no significant loss for the reduction ability of BrO₃⁻ during the cycles, suggesting that Ag@BiVO₄@RGO composite possessed high photo-stability in repeated use.

### 3.8. Proposed photo-reduction mechanism in BrO₃⁻ removal

For better understanding the enhancement of photocatalytic activity as well as the detailed degradation process by Ag@BiVO₄@RGO composite, it is pivotal and necessary to discuss the intrinsic reaction mechanism. Enhanced production of photo-generated electrons and separation of electron-hole pairs were proposed responsible for superior photo-reduction property, and a series of characterization methods (ESR, PL, PC and EIS) were adopted to ascertain our speculation.

The previous study had confirmed that electrons preferred to react with S₂O₅²⁻ other than BrO₃⁻ (Zhao et al., 2011), thus the introduction of K₂S₂O₈ was a marker to analyze the major species in the reduction process. To determine the role of electron in the photo-reduction process, K₂S₂O₈ was employed and added into the solution with the catalyst. The test results in Fig. 3B were in good consistence with the hypothesis, the efficiency of BrO₃⁻ removal significantly decreased with the addition of K₂S₂O₈. Along with the increasing amount of the quencher, the photo-reduction process was hindered to a greater extent, and almost restrained with 8 mmol K₂S₂O₈. (only 2.1% of BrO₃⁻ was reduced). It could be recognized that electrons should be responsible for the reduction of BrO₃⁻ ions.

DMPO spin-trapping technology was introduced to further investigate the role of electrons in the photo-reduction process of BrO₃⁻ removal over Ag@BiVO₄@RGO composite. As depicted in Fig. 4A, the characteristic peak of DMPO-•O₂ adduct was observed for pure BiVO₄ and Ag@BiVO₄@RGO composite under visible light irradiation, but the characteristic peak did not find at dark condition. Thus, the •O₂ was proven to be generated in the photocatalytic process. The peak intensity of the DMPO-•O₂ adduct for Ag@BiVO₄@RGO composite was much higher than that of pure BiVO₄, suggesting that Ag@BiVO₄@RGO promoted the production of electrons. Furthermore, in order to exclude the adverse effect of •O₂ for BrO₃⁻ reduction, parallel experiments were carried out under air and N₂ atmosphere, respectively (Fig. S7, Supplementary information). It could be seen that the reduction process was promoted under N₂ atmosphere, due to the inhibition role for the production of oxidation species •O₂. It had been suggested that 2,2,6,6-Tetramethylpiperidinooxy (TEMPO) could also be used as a spin label for indirect detecting the electrons generated among photocatalytic process. The ESR spectra of TEMPO aqueous solution all displayed two stable signal peaks with catalysts or without catalysts before irradiation. In this study, the same signal intensities were achieved for the as-prepared samples at dark condition. After 4 min of visible-light irradiation, the signal intensity for Ag@BiVO₄@RGO was much lower than that of pure BiVO₄ (Fig. 4B), indicating that more electrons were produced in the presence of Ag@BiVO₄@RGO and revealed with a better photo-reduction performance (He et al., 2014; Zhang et al., 2005). The above-mentioned results validated that more photo-induced electrons were

### Table 4

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
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<tr>
<td>DO</td>
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</tr>
<tr>
<td>COD (mg/L)</td>
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<td>Sulfate (mg/L)</td>
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<tr>
<td>NH₄-N (mg N/L)</td>
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</tr>
<tr>
<td>Nitrate (mg N/L)</td>
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</tr>
<tr>
<td>Nitrite (mg N/L)</td>
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</tr>
<tr>
<td>Bromide (µg/L)</td>
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</tr>
<tr>
<td>Bromate (µg/L)</td>
<td>0.5 ± 3.82%</td>
</tr>
</tbody>
</table>

Fig. 3. Photo-reduction of BrO₃⁻ at four successive cycles (A) and effect of K₂S₂O₈ (B) on the reduction of BrO₃⁻ by Ag@BiVO₄@RGO composite under visible light irradiation. (Experimental conditions: initial BrO₃⁻ concentration 150 µg/L, catalyst dosage 0.5 g/L, reaction time 2 h, pH 7.0, reaction temperature 25 °C, light intensity 100 mW cm⁻² (λ > 420 nm, 300 W Xe lamp)).
The PL emission intensity is an indicative of electron-hole separation efficiency, which is often used to explore the charge carrier trapping, migration and transfer (Wang et al., 2016). As seen in Fig. 5A, Ag@BiVO4@RGO composite exhibited the lowest PL intensity in comparison with pure BiVO4, Ag@BiVO4 and RGO@BiVO4, which implied that the recombination of electron-hole pairs was restricted effectively for the co-effect of metallic Ag and reduced graphene oxide.

To obtain the transient photo-response of pure BiVO4, Ag@BiVO4, RGO@BiVO4 and Ag@BiVO4@RGO, photocurrent density were measured under illumination with several cycles of 20 s intervals light on or off in 0.5 M Na2SO4 solution. Larger photocurrent indicated a higher electrons and holes separation efficiency (Wang et al., 2016). As illustrated in Fig. 5B, it was worth noticing that the photo-current density of Ag@BiVO4@RGO composite electrode (2.68 μA cm⁻²) was 3.7 times higher than that of pure BiVO4 (0.72 μA cm⁻²), 2.5 times of Ag@BiVO4 (1.08 μA cm⁻²) and 1.6 times of RGO@BiVO4 (1.64 μA cm⁻²). The results demonstrated that metallic Ag and RGO co-modified BiVO4 possessed higher separation efficiency of photo-generated electron-hole pairs and a lower recombination rate of charge carriers. The superior photo-electric reproducibility of Ag@BiVO4@RGO will greatly exploit its potential application in other fields, such as photodector, solar cell and so on.

In this study, the transfer and migration processes of the photo-generated electron-hole pairs were revealed by electrochemical impedance spectra (EIS). The arc radius on the EIS Nyquist plot has been used to investigate the reaction rate occurring at the surface of the as-prepared working electrodes (Li et al., 2015; Wang et al.,...
As depicted in Fig. 5C, the diameter of arc radius of pure BiVO₄, Ag@BiVO₄, BiVO₄@RGO and Ag@BiVO₄@RGO appeared a trend of diminishing under visible light irradiation. The Nyquist arc radius diameter of Ag@BiVO₄@RGO was the minimum, demonstrating that the reaction rate on the electrode surface was the fastest and the electrode resistance was the smallest, so the separation efficiency of photo-generated electrons and holes over Ag@BiVO₄@RGO composite was the highest. Meanwhile, Ag@BiVO₄@RGO exhibited a smaller diameter under visible light than in the darkness (Fig. 5D), which should be attributed to the generation of photo-excited carriers under visible light condition.

On the basis of the results described above, the possible mechanism for BrO₃⁻ reduction by Ag@BiVO₄@RGO composite was proposed and illustrated in Fig. 6. Metallic Ag played an important role in two aspects, electron donor and electron mediator, under visible light irradiation. Ag nanoparticles could absorb the incident photons and produced electrons and holes attributable to the surface plasmon resonance (SPR) induced electronic field (Sun et al., 2016; Li et al., 2015). The photo-generated electrons from Ag particles could be transformed to the conduction band of BiVO₄, resulting in electron-deficient Ag and a lower recombination rate of photo-generated electrons and holes. In addition, metallic Ag was served as an electron mediator in the reduction procedure. The electrons on the CB of BiVO₄ could be quickly transferred to the conduction band of RGO with the help of Ag transporter. Through such way, photo-generated electrons were effectively formed and transported in whole reduction process, presenting as superior electron-hole pairs separation efficiency and enhancement in photocatalytic activity. Owing to the large surface area and electron storage, more BrO₃⁻ could be absorbed on the surface of RGO and the accumulated electrons could commendably react with the target electron acceptor Br₂. Furthermore, a small amount of Ag might be switched into Ag⁺, then free Ag⁺ in the system which combined with the product Br⁻ and emerged as AgBr. The photo-reduction performance could be enhanced ascribed to the forming heterojunction between AgBr and BiVO₄ with higher electron-hole pairs separation. Generally speaking, noble Ag functioned as electron donor coupling with electron mediator, leading to plentiful electrons formed and facilitating the charge transfer process simultaneously. The reduced graphene oxide worked as an effective platform for BrO₃⁻ absorption and provided enough electrons for BrO₃⁻ reduction. Consequently, in the presence of metallic Ag and RGO, co-modified BiVO₄ could acquire excellent production, transportation and mobility of electrons, revealing highly improved photo-reduction performance for BrO₃⁻ removal.

4. Conclusions

In this study, novel visible-light photocatalyst of Ag@BiVO₄@RGO was fabricated by a facile chemical and photo-deposition process. The coupling effects of metallic Ag and RGO prompted a satisfying photocatalytic activity over modified BiVO₄, realizing the high charge-separation efficiency as well as long-term stability. The corresponding photocatalytic performance was evaluated by photo-reduction of BrO₃⁻ under visible light irradiation. After 90 min, 99.1% of BrO₃⁻ was removed by Ag@BiVO₄@RGO composite with catalyst dosage 0.5 g/L and pH 7.0, which was 8.1, 4.4 and 2.6 times higher than those of BiVO₄, Ag@BiVO₄, RGO@BiVO₄, respectively. Substantial improvement of photo-generated electrons production and electron-hole pairs separation was verified by ESR, PL, PC and EIS measurements. The introduction of metallic Ag played a crucial role in electron generation as well as RGO acted as an electron accepter and enhanced the adsorption of target pollutant. Compared with the reduction process in de-ionized water, there was a significant loss for BrO₃⁻ removal by Ag@BiVO₄@RGO composite in tap water originated from Xiang River. The competitive anions consumed the electrons and other natural organic matters adsorption on the surface of RGO, resulting in lower BrO₃⁻ reduction efficiency. New insight into metallic Ag and RGO co-modified BiVO₄ for BrO₃⁻ reduction under visible light illumination may provide a more comprehensive potential for other disinfection byproducts removal in drinking water. Possible applications in other fields, such as photodector, solar cell and so on, owing to its superior photoelectric properties of Ag@BiVO₄@RGO composite.

Acknowledgments

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Appendix A. Supplementary information

Supplementary information related to this article can be found at http://dx.doi.org/10.1016/j.watres.2016.06.006.