Constructing highly catalytic oxidation over BiOBr-based hierarchical microspheres: Importance of redox potential of doped cations

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ABSTRACT

In this work, we prepared BiOBr-based hierarchical microspheres by a simple solvothermal method. The phase structure, morphology and optical properties of catalysts were well characterized by XRD, FESEM, FTIR, UV-DR spectra, XPS valence band and BET surface area analysis. Among the Vis/catalyst/H2O2 system, Cu-BiOBr is found to be the most effective for rhodamine b degradation while Fe-BiOBr exhibits the highest catalytic activity for the mineralization of 2-chlorophenol. Hydroxyl radicals generation rate and H2O2 decomposition rate follow: Fe-BiOBr > BiOBr > Zn-BiOBr > Ni-BiOBr > Ag-BiOBr > Cu-BiOBr, and Cu-BiOBr > Fe-BiOBr > BiOBr > Zn-BiOBr > Ni-BiOBr > Ag-BiOBr, respectively. The catalytic mechanisms under Vis/catalyst/H2O2 systems are proposed and compared, as following: (1) for BiOBr/Zn-BiOBr/Ni-BiOBr/Ag-BiOBr, the activation of H2O2 by photoelectrons to generate hydroxyl radical; (2) for Fe-BiOBr, the reaction of Fe(II) or photoelectrons with H2O2 to produce hydroxyl radical, and Fe(III) is reduced by photoelectrons to Fe(II); (3) for Cu-BiOBr, the activation of H2O2 by photoelectrons to generate hydroxyl radical that probably oxides Cu(II) to Cu(III), and the reaction of Cu(I) with H2O2 to generate Cu(III). The trapping experiments display that holes and hydroxyl radicals (or Cu(II))/ have dominant roles.

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1. Introduction

Nowadays, the removal of organic contaminants from industrial wastewater has attracted increasing interest. Stable organic dye and chlorophenols molecules are prominent in their contribution towards water pollution. Large amounts of wastewater containing dyes are generated from textile dyeing industries. These dyes and pigments not only give colour to water but also inhibit biological treatment processes [1–3]. Chlorophenols are widely used as raw materials or intermediates in chemical industries such as the production of pesticides, synthetic resins, and pharmaceuticals [4–6]. Due to their potential carcinogenic and mutagenic activity, they can bring a potential negative impact on the environment, particularly damaging livers’ physiological processes. Various techniques are adopted to remove these contaminants, including adsorption, coagulation, electrochemical oxidation, semiconductor photocatalysis, degradation by strong oxidizing agents etc [7–10]. Among these techniques, semiconductor photocatalysis has been great attention in this area due to its attractive features such as environmentally friendly and readily available materials, ease of operation as well as efficient degradation.

Recently, BiOBr has been widely concerned because of outstanding optical and electrical properties. It has a tetragonal matlockite structure, a layer structure characterized by [Bi2O2] slabs interleaved by double slabs of Br atoms [11]. The band gap of BiOBr is round 2.7 eV [12], which can adsorb parts of visible light (Vis) and has high recombination chance of holes and photoelectrons. Researchers have devoted intensive efforts to find out some methods that reduce their recombination opportunity and increase the visible light adsorption range, for instance, various hierarchical nanostructures [13], halogen-mixing solid solutions [14], semiconductor coupling [15,16] and metal doping [17,18]. The modified BiOBr photocatalyst showed the high photocatalytic activity for methylene blue [19,20], while lower catalytic performance for those resistant pollutants (i.e., 2-chlorophenol and bisphenol A).

Fenton-like reaction system is also proven to be an efficient system for the mineralization of organic pollutants in wastewater. Li et al. reported that FeOx/NiOx/SBA-15 showed the highest Fenton-like catalytic activity for acid red 73, and nickel played an important role in the catalytic activity [21]. The acetaminophen was completely degraded within 24 h by Cu–Zn–Fe LDH in the Fenton-like reaction as Lu reported [22]. Park et al. found that the fully dispersed PVP-AgNPs exhibited fast degradation kinetics for EE2 in the presence of

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H$_2$O$_2$ [23]. This attributes that low transition metal can react with H$_2$O$_2$, producing the hydroxyl radicals. However, in the Fenton-like reaction, the reduce rate of high-valent metal to low-valent metal by H$_2$O$_2$ is extremely slow [24,25]. Light irradiation can improve the catalytic activity of some semiconductor heterogeneous Fenton catalysts [26–29]. The decomposition rate of H$_2$O$_2$ becomes one of the crucial factors on the photocatalytic degradation efficiency [30]. Thus, the development of transition metal modified BiOBr with enhanced Vis-light-driven activity is of high interest.

The specific objective of this work was to evaluate the Vis-light-catalytic activity of transition metal modified BiOBr system for rhodamine (RhB) and 2-chlorophenol (2-CP) degradation with coupling heterogeneous Fenton-like oxidation. Herein, the M (Ag/Ni/Cu/Fe/Zn) modified BiOBr catalyst was prepared by a solvothermal method and characterized by XRD, FESEM, XPS valence band, UV–vis absorption spectroscopy and N$_2$ adsorption-desorption. The possible mechanism for organic contaminants degradation by metal modified BiOBr were proposed and explained by EPR technology. H$_2$O$_2$ consumption and hydroxyl radical measurement experiments. The difference of oxidation process among Vis/modified BiOBr/H$_2$O$_2$ systems was also elucidated by XPS valence band analysis for the first time.

2. Experimental section

2.1. Preparation of catalysts

The 1% M-doped BiOBr sample was prepared by a solvothermal method, as following: 3 mmol Bi(NO$_3$)$_3$·5H$_2$O and M(NO$_3$)$_x$ with a M/Bi molar ratio of 0.03 were dissolved in 30 ml ethylene glycol containing 3 ml acetic acid under magnetic stirring for 30 min. The resultant solution was added to 30 ml ethylene glycol with 3 mmol CTAB under vigorous stirring for 30 min. Next, the mixture was transferred to a 100 ml of Teflon autoclave and kept for 12 h at 433 K. After being cooled to room temperature, the obtained precipitate was separated centrifugally and washed with ethanol and ultrapure water. Finally, the sample was freeze-dried under vacuum. The resultant products were denoted as M-BiOBr, where M referred to Ag, Cu, Fe, Zn, and Ni.

2.2. Characterization

The phase structures of pure and modified BiOBr photocatalysts were analyzed using an X-ray diffractometer (X’Pert PRO MPD, PANalytical) with a 2° of 5–90° at 40 kV and 40 mA using Cu K$_\alpha$ as the irradiation source ($\lambda = 1.5406$Å). The morphologies of the as-prepared products were measured by field emission scanning electron microscope (FESEM) (SU-8020, Hitachi Limited). The UV–vis diffuse reflectance spectra (UV–vis DRS) of the samples were recorded on a UV–vis spectrometer (UV-3600, Shimadzu) with an integrating sphere using BaSO$_4$ as the reference. The Brunauer-Emmett-Teller (BET) specific surface area was measured using a full automatic analyzer (ASAP2020HD88, Micromeritics Instrument Corp.). The XPS valence band was analyzed via the X-ray photoelectron spectroscopy with Al-K X-ray irradiation (ESCALAB 250Xi, Thermo Fisher Scientific).

2.3. Catalytic activity evaluation

The catalytic activities of M-doped BiOBr systems were studied by examining the visible light Fenton-like oxidation of 2-CP and RhB. A 300 W Xe lamp with a 400 nm cut-off filter was used as a visible light, and the vertical distance between lamp and liquid level was 15 cm. In a typical experiment, 50 mg of catalyst was mixed with 100 ml of 20 mg/L 2-CP solution. Prior to illumination and injection of 5 mM H$_2$O$_2$, the suspension was magnetically stirred in the dark for 30 min to ensure the establishment of adsorption–desorption equilibrium. After visible light catalytic reaction, 1 ml reacting solution was withdrawn at selected time intervals, and then centrifuged to remove the photocatalysts.

2.4. Analytical methods

The concentration of RhB was determined from the absorbance at the wavelength of 554 nm by an UV–visible spectrophotometer (UV-2990, Shimadzu, Japan). The analysis of 2-CP concentration was carried out via HPLC-UV (Thermo Fisher Ultimate 3000, USA) at 276 nm using a mixture of 65/35 (acetoniitrile/H$_2$PO$_4$ solution ($pH = 3$), volume percentage) as the mobile phase and 1 ml/min of flow rate. The total organic carbon (TOC) of the solution was analyzed using a TOC–VCPH analyzer (Shimadzu). The concentrations of hydroxyl radical and H$_2$O$_2$ were spectrophotometrically determined by deoxyribose method [31] and titanium potassium oxalate method [6]. Electron paramagnetic resonance (EPR) spectra were obtained on an EPR spectrometer (Bruker A300-10/12) using 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin-trapping agent.

Fig. 1. XRD pattern of pure and modified BiOBr samples (insert: diffraction peak position of {110} in the range from 28 to 34°).
Fig. 2. Magnified-FESEM images of M-doped BiOBr (insert: FESEM images).

3. Results and discussion

3.1. Comparisons of characterization of products

The power XRD patterns of pure BiOBr and the modified systems are shown in Fig. 1. Sharp intense peaks account for the high crystalline nature of the prepared BiOBr systems. The characteristic peaks of BiOBr are observed at 2θ values that 11.0°, 25.1°, 31.7°, 32.3°, 39.4°, 46.3°, and 57.2° correspond to the crystal face {001}, {101}, {102}, {110}, {112}, {200} and {203}, respectively. These data are compared with standard BiOBr (JCPDS card no. 09-0393), which shows the formation of pure phase BiOBr with tetragonal structure. The patterns reveal that except Fe doped and Ag doped BiOBr, other systems show no extra peaks when compared to pure BiOBr sample. The Bi crystal phase in the Fe-BiOBr sample, which is indexed to the rhombohedral phase of Bi (JCPDS card no.00-044-1246), is detected; silver cubic crystal phase (JCPDS card no. 01-089-3722) is detected in the Ag-BiOBr. As Zheng reported [32], Bi3+ is reduced into metal nanoparticles by ethylene glycol. In Table 1, the redox potential of metal ions follows: $\text{Ag}^{+}/\text{Ag} > \text{Fe}^{3+}/\text{Fe}^{2+} > \text{Bi}^{3+}/\text{Bi} > \text{Cu}^{2+}/\text{Cu}^{+} > \text{Ni}^{2+}/\text{Ni} > \text{Zn}^{2+}/\text{Zn}$ (Table S1). The Fe(III) and Cu(II) ions can be also reduced into low
The scanning electron micrographs of BiOBr based systems are shown in Fig. 2. The average particle size of all the supported systems like microsphere is estimated to be 3–5 μm. From the images it can be seen clearly that the exterior surfaces of Ni-BiOBr and Zn-BiOBr microspheres are comprised of many wheat-like nanoparticles like that of BiOBr, but Ag-BiOBr, Fe-BiOBr and Cu-BiOBr microspheres were formed of many nanosheets packed together. Compared with pure BiOBr, Zn- and Ni-BiOBr, significant amount of porosity also is obvious for Ag-, Fe- and Cu-BiOBr from the SEM images. The specific surface area and porosity of pure BiOBr and modified BiOBr systems is shown in Fig. 3. The isotherms belong to type IV with a distinct hysteresis loop observed in the range of 0.5–1.0 p/p0, which is characteristic of mesoporous materials. According to the IUPAC recommendations [33], the above hysteresis loops can be categorized as type H3 loops, which are reported for materials comprised of aggregates (loose assemblages) of platelike particles forming slitlike pores. The BET specific areas of products are calculated from N2 adsorption–desorption isotherms (Fig. 3a). After the addition of metal ions, in Fig. 3b, the pore sizes, pore volumes and surface areas of BiOBr are changed, which is listed in Table 1. For example, the average mesopores of Ag-BiOBr and Cu-BiOBr are obviously increased from 7.94 nm to 12.34 nm and 11.74 nm, respectively, which are determined by using the Brunauer–Emmett–Teller (BET) method. However, the surface area of Ag-BiOBr is decreased from 17.65 m²/g to 6.62 m²/g; those are increased to 28.48 m²/g and 37.18 m²/g for Cu-BiOBr and Fe-BiOBr, respectively.

The Fourier transform infrared (FTIR) spectra are shown in Fig. 4. Two broad peaks centered at 3500 cm⁻¹ and 1603 cm⁻¹ can be observed in BiOBr, which correspond to the stretching of O–H and flexural vibrations of the O–H in free water. The peaks within the wavenumber range of 1000–1500 cm⁻¹ should be attributed to the Bi-Br bond in BiOBr[34]. For example, the absorption peaks at 1479 cm⁻¹ and 1051 cm⁻¹ may be assigned as the asymmetry and symmetric stretching vibration peaks of Bi-Br bond in BiOBr structure, respectively. The adsorption peaks below 1000 cm⁻¹ is assigned to the Bi-O bond symmetric stretching vibration [35]. For modified BiOBr samples, all the characteristic vibration bonds are almost no changed.

The optical properties of the as-prepared samples were investigated. Fig. 5a shows the diffuse reflectance spectra. It can be seen that the absorption edges of Fe-BiOBr and Cu-BiOBr have the red shift, while the same result can be not found in the Ag-BiOBr, Zn-

![Fig. 3. N2 adsorption-desorption isotherms (a) and pore size distribution (b) of pure BiOBr and modified BiOBr samples.](image)

![Fig. 4. FTIR spectra of pure BiOBr and modified BiOBr microspheres.](image)

| Samples         | Eg (eV) | Ev (eV) | Eb (eV) | Surface area (m²/g) | Pore size (nm) | Pore volume (cm³/g) |
|-----------------|---------|---------|---------|---------------------|----------------|---------------------|
| BiOBr           | 2.50    | 2.10    | -0.40   | 17.65               | 7.94           | 0.035               |
| Ag-BiOBr        | 2.50    | 2.04    | -0.46   | 6.62                | 12.34          | 0.020               |
| Cu-BiOBr        | 2.11    | 2.14    | 0.03    | 28.48               | 11.74          | 0.084               |
| Zn-BiOBr        | 2.52    | 2.10    | -0.42   | 22.64               | 8.41           | 0.048               |
| Ni-BiOBr        | 2.50    | 1.78    | -0.72   | 20.35               | 7.58           | 0.039               |
| Fe-BiOBr        | 1.56    | 1.88    | 0.32    | 37.18               | 5.91           | 0.055               |

valences while Ni(II) and Zn(II) cannot be reduced due to negative oxidation-reduction potential values. A observed notation is that the peak at 31.7° obviously disappears for Fe doped BiOBr and Cu doped BiOBr samples. This attributes that the differences among the ionic radius result into the changes of the lattice parameters.
BiOBr and Ni-BiOBr like pure BiOBr. As crystalline semiconductor, the optical absorption near the band edge follows the equation [36]:

\[ \alpha h \nu = A (h \nu - E_g)^n \]  

(1)

where \( \alpha \), \( h \nu \), \( E_g \), \( A \) and \( n \) are the absorption coefficient, light frequency, band gap energy, a constant, and the transition constant, respectively. Among them, \( n \) is determined by the type of optical transition of the semiconductor, and the value of \( n \) is 4 for BiOBr. The band gap energy (\( E_g \) value) of BiOBr could be estimated from a plot of \( (\alpha h \nu)^{1/2} \) versus photon energy \( (h \nu) \). As shown in Fig. 5b, the band energy gap of pure BiOBr, Ag-BiOBr, Zn-BiOBr, Ni-BiOBr, Cu-BiOBr and Fe-BiOBr are estimated to be 2.50 eV, 2.52 eV, 2.52 eV, 2.50 eV, 2.11 eV and 1.56 eV. This indicates the high absorption in wider visible light region for Fe-BiOBr and Cu-BiOBr. The density of states (DOS) of the valence band of BiOBr and modified BiOBr samples were measured using valence band XPS, as shown in Fig. 6. The edges of the maximum energy of the BiOBr, Zn-BiOBr, Ag-BiOBr, Cu-BiOBr, Fe-BiOBr and Ni-BiOBr are estimated to be about 2.10 eV, 2.10 eV, 2.04 eV, 2.14 eV, 1.88 eV, and 1.78 eV, respectively. As shown in Table 2, the \( E_g \) values of BiOBr, Zn-BiOBr, Ag-BiOBr, Cu-BiOBr, Fe-BiOBr and Ni-BiOBr are 2.50 eV, 2.52 eV, 2.50 eV, 2.11 eV, 1.56 eV and 2.50 eV, respectively. Based on the experimental formula: \( E_{VB} - E_{CB} = E_g \), the conduction band minimum would occur approximately at −0.40 eV, −0.42 eV, −0.46 eV, 0.03 eV, 0.32 eV and −0.72 eV, respectively.

3.2. Catalytic activity of BiOBr and modified BiOBr

3.2.1. Rhodamine degradation

The catalytic activity of pure BiOBr and modified BiOBr samples were evaluated by the degradation of RhB in solution under different systems. All the experiments were performed under neutral pH conditions and room temperature. The temporal changes in the concentration of RhB were monitored by examining the variation in maximal absorption in UV–vis at 554 nm. Before illumination, all experiments were stirred in the dark for 30 min to achieve absorption–desorption equilibrium. For comparison, a
blank experiment was executed. In the absence of catalysts, there is no degradation for RhB (not shown). In Fig. 7, the pseudo-first-order reaction constants (k) of RhB degradation by BiOBr, Zn-BiOBr, Cu-BiOBr, Ag-BiOBr, Fe-BiOBr and Ni-BiOBr in Vis/catalyst/H2O2 system are 0.048 min⁻¹, 0.069 min⁻¹, 0.10 min⁻¹, 0.035 min⁻¹, 0.039 min⁻¹, and 0.052 min⁻¹; those in the Vis-catalytic reactions are 0.060 min⁻¹, 0.056 min⁻¹, 0.052 min⁻¹, 0.033 min⁻¹, 0.01 min⁻¹, 0.047 min⁻¹, respectively. By comparisons, H2O2 can increase the Vis-catalytic activities of metal doped BiOBr, especially for Fe-BiOBr and Cu-BiOBr. For instance, RhB degradation efficiencies within 20 min under the Vis/catalyst system, are 77.5%, 77.4%, 79.0%, 56.8%, 24.1%, 72.1% for BiOBr, Zn-BiOBr, Cu-BiOBr, Ag-BiOBr, Fe-BiOBr and Ni-BiOBr (Fig. S1a), while, in the Vis/catalyst/H2O2 system, those are 70.6%, 83.5%, 95.3%, 54.5%, 58.7% and 74.3%, respectively (Fig. S1b).

3.3.2. Oxidation of 2-chlorophenol

To exclude the organic contaminant adsorption in Vis/catalyst/H2O2 system, we further studied the degradation of 2-CP by pure and modified BiOBr. The results show that 2-CP is almost adsorbed on the catalyst after 30 min dark reaction (Fig. S2), and not degraded in the blank experiment. The results in Fig. S2 show that 2-CP degradation and TOC removal efficiencies by BiOBr, Zn-BiOBr, Cu-BiOBr, Ag-BiOBr, Fe-BiOBr and Ni-BiOBr within 60 min under Vis/catalyst/H2O2 system are 57.3%, 45.8%, 75.3%, 56.3%, 99.4%, 49.2% and 48.4%, 43.8%, 43.3%, 69.7%, 35.8%. In Fig. 8, the pseudo-first-order rate constants of 2-CP degradation and TOC removal by BiOBr, Zn-BiOBr, Cu-BiOBr, Ag-BiOBr, Fe-BiOBr and Ni-BiOBr are 0.012 min⁻¹, 0.023 min⁻¹, 0.015 min⁻¹, 0.041 min⁻¹, 0.014 min⁻¹ and 0.0092 min⁻¹, 0.0073 min⁻¹, 0.0081 min⁻¹, 0.0077 min⁻¹, 0.016 min⁻¹, 0.0064 min⁻¹. Compared with photocatalytic reaction (Fig. S2 and Fig. 8), H2O2 can increase the catalytic activities for 2-CP degradation. Especially, Fe-BiOBr and Cu-BiOBr show the better catalytic activities for 2-CP degradation. For Cu-BiOBr, the mineralization degree of 2-CP is lowest among catalysts, which it is attributed that the Cl atom in 2-CP is reduced by superoxide radicals instead of 2-CP mineralization [37].

In the presence of visible light, the holes and electrons can be generated by the band gap radiation of pure and modified BiOBr photocatalysts (Eq. (2)). The holes could degrade RhB and 2-CP by direct oxidation or formation of *OH via the reaction with surface H2O molecule (Eq. (3)) [38]. Meanwhile, the superoxide radicals (O2⁻•−) might be formed via the capture of the electrons by O2 [39]. However, it is still difficult for the rapid separation of holes and photoelectrons to efficiently utilize them, decreasing the photocatalytic activity in the Vis/catalyst system. When with vis-light and H2O2, the photoelectrons are captured by H2O2 (E°(H2O2/H2O)=0.38 V vs. NHE) to produce the hydroxyl radicals instead of oxygen trapping (E°(O2/H2O)=−0.33 V vs. NHE) (Eqs. (4) and (5)) [40]. In addition, H2O2 can be also activated by the regenerated metal (i.e., Fe(II) or Cu(I)), which could be formed from the reaction of Fe(III) or Cu(II) with photoelectrons [41]. Thus, the separation efficiency of holes and photoelectrons is improved and more hydroxyl radicals are continuously regenerated to degrade RhB and 2-CP.

\[
\text{BiOBr} + \text{hv} \rightarrow h^+ + e^-
\]

\[
h^+ + \text{H}_2\text{O} \rightarrow \cdot \text{OH} + \text{OH}^-
\]

3.3. Catalytic oxidation analysis

3.3.1. Hydroxyl radicals and H2O2 consumption

Considering the generation of hydroxyl radicals in Vis/catalyst/H2O2 system, 2-deoxy-d-ribose, which can easily react with *OH to produce the malondialdehyde that reacts with 2-thiobarbituric acid, was employed to measure the hydroxyl radicals concentration [31]. Fig. 9a displays the change of *OH concentration under various systems. It is seen that *OH concentration increases with irradiation time, because of H2O2 decomposition (Eq. (2)) and Fenton-like reaction (Eq. (8)). As shown in Fig. 9b, the *OH generation rate constants by BiOBr, Zn-BiOBr, Ni-BiOBr, Ag-BiOBr, Fe-BiOBr and Cu-BiOBr are 0.079 uM/min, 0.068 uM/min, 0.065 uM/min, 0.044 uM/min, 0.23 uM/min and 0.023 uM/min, respectively. Among reaction systems, large amounts of *OH can be generated under Vis/Fc-BiOBr/H2O2 system due to reaction of Fe(II) with H2O2 (Eq. (8)), while less under Vis/Cu-BiOBr/H2O2 system probably because of the formation of Cu(III) by Cu(I) reacting with H2O2 (Eq. (9)) [42].

\[
\text{Fe(II)} + \text{H}_2\text{O} \rightarrow \text{Fe(III)} + \cdot \text{OH} + \text{OH}^-
\]

\[
\text{Cu(I)} + \text{H}_2\text{O} \rightarrow \text{Cu(II)} + 2\text{OH}^-
\]

\[
\text{Cu(II)} + \text{H}_2\text{O} \rightarrow \text{Cu(III)} + \text{H}^+ + \cdot \text{OH}
\]

To understand well this reaction process, H2O2 consumption was measured using the potassium titanium (IV) oxalate spectrophotometric method [6]. Fig. 9c exhibits the change of H2O2 concentration versus reaction time. Within 30 min, H2O2 decomposition efficiencies for BiOBr, Fe-BiOBr, Cu-BiOBr, Ag-BiOBr, Zn-BiOBr and Ni-BiOBr are 18.9%, 60.8%, 91.3%, 4.6%, 16.5% and 14.4%. The H2O2 consumption rate constants, fitted by pseudo-first-order kinetics model, are 0.0084 min⁻¹, 0.0084 min⁻¹, 0.0072 min⁻¹, 0.0031 min⁻¹, 0.034 min⁻¹ and 0.060 min⁻¹ for BiOBr, Zn-BiOBr, Ni-BiOBr, Ag-BiOBr, Fe-BiOBr and Cu-BiOBr (Fig. 9d). By comparisons of Vis/catalyst/H2O2 system, Fe-BiOBr and Cu-BiOBr can rapidly react with H2O2. Interestingly, large amount of H2O2 is consumed by Cu-BiOBr to produce other active specie instead of hydroxyl radicals.

3.3.2. EPR spectroscopy

The EPR technique with DMPO as a spin-trapping agent was used to further identify the production of *OH in Vis/pure and modified BiOBr/H2O2 systems within 20 min (Fig. 10). The results
display that all the systems, Vis/Cu-BiOBr/H\textsubscript{2}O\textsubscript{2} system, exhibit the signal of DMPO – •OH spin adduct, 1:2:2:1 quartet lines with hyperfine constants of $a_{N} = a_{H} = 15.0$ G [43]. Meanwhile, the signal intensity of the Vis/Fe-BiOBr/H\textsubscript{2}O\textsubscript{2} system is much higher than that of other systems. The stronger signal of DMPO – •O\textsubscript{2} – spin adduct with six characteristic peaks is observed under Vis/Cu-BiOBr/H\textsubscript{2}O\textsubscript{2} system [44], which is mainly attributed to reaction of Cu(II) with H\textsubscript{2}O\textsubscript{2}(k=460 M\textsuperscript{-1}s\textsuperscript{-1}) (Eq. (10)) [37]. This indicates that the catalytic mechanism on the Vis/Cu-BiOBr/H\textsubscript{2}O\textsubscript{2} system is significantly different from those on Vis/other modified BiOBr and pure BiOBr/H\textsubscript{2}O\textsubscript{2} systems.

### 3.3.3. Quenching tests

By comparisons of these catalytic systems, we find that Cu-BiOBr system shows larger difference in catalytic efficiency and free radicals than other systems. To further understand the roles of active species for 2-CP degradation, holes and hydroxyl radicals trapping experiments in Vis/Fe-BiOBr/H\textsubscript{2}O\textsubscript{2} and Vis/Cu-BiOBr/H\textsubscript{2}O\textsubscript{2} systems were employed. The triethanolamine (TEOA) and iso-propanol (IPA) were used as holes and •OH radical (or Cu (III)) scavengers [40,45–47]. As depicted in Fig. 11, in the absence of scavengers, 2-CP degradation rate constants and efficiencies within 60 min by Cu-BiOBr and Fe-BiOBr are 0.023 min\textsuperscript{-1}, 75.3%, and 0.041 min\textsuperscript{-1}, 99.4%, respectively. When 10 mM TEOA was separately added to Cu-BiOBr and Fe-BiOBr reaction systems, the degradation rate declined to 0.006 min\textsuperscript{-1} and 0.003 min\textsuperscript{-1}, and led to a 60% and 85% drop in degradation efficiency, indicating the vital role of holes for 2-CP degradation. The addition of 10 mM IPA inhibited the 2-CP degradation efficiency decreasing from 75.3% to 39.8% (i.e., reducing by 35.5%) and 99.4% to 56.1% (i.e., reducing by 43.3%) (Eq. (11)). This suggests that hydroxyl radicals and Cu(III) also play an important role in 2-CP degradation, which was reported by Waite et al. [48].

\begin{equation}
\text{Cu (III)} + \text{IPA} \rightarrow \text{Cu (II)} + \text{IPA}.
\end{equation}
3.3.4. Redox potential

The conduction band (CB) and valence band (VB) potentials of pure and modified BiOBr were analyzed by XPS valence band. It is clearly seen that Zn and Ag doping has slight influence on the energy band of BiOBr while Fe, Ni and Cu doping can significantly affect them. In additionally, the band edges usually move with pH. The potentials of VB and CB can be calculated using the following equation [Eq. (12)] [49, 50]:

\[
E = E^0 - 0.05915 \times \text{pH}
\]  

In the above equation, \(E^0\) is the flat band potential of catalyst at pH 0. When pH is 7.0, the corresponding potentials of VB and CB are obtained in Fig. 12. The VB potential of catalyst at pH 7.0 is lower than the oxidation potential of \(\cdot \text{OH}\)/H\(_2\)O (2.68 V vs. NHE) [51–53], suggesting that the photogenerated holes cannot oxide H\(_2\)O to \(\cdot \text{OH}\).

On the other hand, the potential difference between CB of catalysts and O\(_2\)/O\(_2\)\(\text{•}^+\) (\(\Delta E = 0.48–0.80\) V vs. NHE) is small compared with the difference between the CB potential of catalyst and oxidation potential of H\(_2\)O\(\text{•}^+\)/OH \(\Delta E = 1.19–1.51\) V vs. NHE), suggesting that the photoelectrons would likely reduce H\(_2\)O instead of O\(_2\) in aqueous. The CB potentials of catalysts are almost lower than the redox potential of metal oxides under neutral condition \(E(\text{Fe}_2\text{O}_3/\text{FeO}) = -0.85\) V vs. NHE; \(E(\text{Ni(OH)}_2/\text{Ni}) = -0.31\) V vs. NHE; \(E(\text{Ag}_2\text{O}/\text{Ag}) = 0.75\) V vs. NHE; \(E(\text{Fe}_2\text{O}_3/\text{FeO}) = -0.02\) V vs. NHE; \(E(\text{CuO}(\text{Cu}_2\text{O}) = 0.34\) V vs. NHE) (Table S2), which is calculated by the nernst equation. This indicates that the photoelectrons can be also captured by doped metal ions in the lattice or surface.
3.4. Possible mechanism

The photoelectron is transferred from inside to outside in the catalyst, and has large opportunity to reduce the doped metal in the lattice or surface of catalyst. Meanwhile, the photoelectron on the surface of catalyst can react with \( \text{H}_2\text{O}_2 \) to generate the hydroxyl radicals. Low valent metal can participate in the Fenton-like reaction. Based on the transfer pathways of photoelectrons and Fenton-like catalytic activities of metal oxides, the catalytic mechanism of pure BiOBr and metal doped BiOBr in Vis/catalyst/\( \text{H}_2\text{O}_2 \) system is summarized in Fig. 13. The reaction mechanism of Ni-BiOBr, Zn-BiOBr and Ag-BiOBr are similar with that of pure BiOBr (Fig. 13A), as following: under visible light, photocatalysts can be excited to produce the holes and electrons; photoelectrons are captured by \( \text{H}_2\text{O}_2 \) to form hydroxyl radicals, left more holes; Fenton-like catalytic activities from metal oxides (i.e., Bi\( _2\)O\(_3\), ZnO, Ag\(_2\)O and NiO) are much poorer. Compared with the above catalytic mechanisms, the catalytic mechanism of Fe-BiOBr contains strong Fenton-like activity (Fig. 13B): Fe(II) easily react with \( \text{H}_2\text{O}_2 \) to generate hydroxyl radicals and Fe(III); Fe(II) can be reduced by electrons. Among them, the catalytic process of Cu-BiOBr is most complexed (Fig. 13C): first, the photoelectrons, which are formed on Cu-BiOBr in the presence of visible light, are captured by \( \text{H}_2\text{O}_2 \) to generate hydroxyl radical that can more likely oxidize Cu(II) to Cu(III) [40]; secondly, \( \text{H}_2\text{O}_2 \) can react with Cu(I) to produce Cu(II), or Cu(II) is reduced by \( \text{H}_2\text{O}_2 \) to superoxide radicals [41]; thirdly, the reaction of Cu(II) with organic contaminants generate Cu(II) and products. In the Vis/Cu-BiOBr/\( \text{H}_2\text{O}_2 \) system, the formation of Cu(III) appears instead of hydroxyl radicals, which should be attributed to the chemical environment near the Cu atom [54]. In the oxidation process of organic contaminants, holes and hydroxyl radicals (Cu(III)) play the important roles.

3.5. Stability of catalysts

The catalytic stabilities of catalysts were investigated under Vis/catalysts/\( \text{H}_2\text{O}_2 \) systems via a series of cycled experiments (Fig. 14). The results display that the degradation efficiencies of 2-CP via Fe-BiOBr (Cu-BiOBr) within 60 min slightly decrease after 3 cycles, and they almost keep constant via BiOBr (Zn-BiOBr, Ni-BiOBr, and Ag-BiOBr). In addition, the structure of catalysts after used three times were analyzed by XRD (Fig. S3), and the results indicate that the crystal phases of catalysts are almost the same after or before used, such as the crystal face \{101\}, \{110\}, \{200\} and \{203\} in pure BiOBr phase. This implies that pure BiOBr and metal doped BiOBr catalysts exhibit excellent visible-light Fenton-like catalytic stability.

4. Conclusion

Pure BiOBr and transition metal doped BiOBr hierarchical microspheres were prepared, and their catalytic activities were evaluated to the oxidation of 2-CP and RhB in Vis/catalyst/\( \text{H}_2\text{O}_2 \) system. The results display that Cu-BiOBr and Fe-BiOBr present the higher catalytic performance on the degradation of organic contaminants among all the systems. The holes and hydroxyl radicals (or Cu(III)) play the vital role, which is confirmed by active species taping experiments. Based on the EPR technique, hydroxyl radical amount and \( \text{H}_2\text{O}_2 \) decomposition as well as valence band and conduct band potentials of catalysts, the catalytic mechanisms are compared to divide into three catalytic formations: (1) \( \text{H}_2\text{O}_2 \) interacts with electrons to generate hydroxyl radicals, decreasing the recombination opportunity of holes and electrons in Vis/BiOBr (Zn-BiOBr, Ni-BiOBr and Ag-BiOBr)/\( \text{H}_2\text{O}_2 \) systems; (2) the reaction of \( \text{H}_2\text{O}_2 \) with Fe(II) produces hydroxyl radicals, and the reduce of Fe(III) and \( \text{H}_2\text{O}_2 \) generate Fe(II) and hydroxyl radicals in Vis/Fe-BiOBr/\( \text{H}_2\text{O}_2 \) systems, respectively; (3) the reaction of \( \text{H}_2\text{O}_2 \) with Cu(I) (or Cu(II)) generates Cu(III) (or superoxide radicals), and Cu(III) can also be obtained.
by the reaction of Cu(II) with hydroxyl radicals that H$_2$O$_2$ reacts with electrons to generate.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mcat.2017.05.017.

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Fig. 13. Schematic diagram of the catalytic mechanism of pure and modified BiOBr towards organic contaminants: A, Vis/catalysts/H$_2$O$_2$ system (catalyst = BiOBr, Zn-BiOBr, Ni-BiOBr, Ag-BiOBr); B, Vis/Fe-BiOBr/H$_2$O$_2$ system; C, Vis/Cu-BiOBr/H$_2$O$_2$ system.

Fig. 14. 2-CP degradation under Vis/catalyst/H$_2$O$_2$ systems within 60 min after adsorption equilibrium during three times repeated tests ([catalyst] = 0.5 g/L; [2-CP] = 20 mg/L; [H$_2$O$_2$] = 5 mM).
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