Fe\textsuperscript{II}/Fe\textsuperscript{III} Doped Bi/BiOBr Hierarchical Microspheres as a Highly Efficient Catalyst for Degradation of Organic Contaminants at Neutral pH: The Role of Visible Light and H\textsubscript{2}O\textsubscript{2}

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A novel Fe\textsuperscript{II}/Fe\textsuperscript{III} doped Bi/BiOBr (FBB) visible-light, Fenton-like catalyst was successfully synthesized by using the solvothermal method. The morphological and structural features of FBB were analyzed by XRD, field emission (FE)-SEM, TEM, Brunauer–Emmett–Teller (BET), and X-ray photoelectron spectroscopy (XPS) techniques. The results revealed that the presence of Fe could promote the growth of Bi metal nanoparticles, and increase the specific surface areas of FBB. Rhodamine B (RhB) photodegradation experiments indicated that FBB with the Fe/Bi molar ratio (0.2–0.3) exhibited higher photocatalytic activities. In the photo-Fenton-like reaction, the degradation efficiency of bisphenol A (BPA) over FBB-25 was increased to 100% within 30 min whereas it was 3% and 12% in the Fenton-like and photocatalytic reactions. Moreover, 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), and 2,4,6-trichlorophenol (2,4,6-TCPP) were completely degraded within 30 min over FBB-25. The presence of visible light can promote the rapid reaction rate between Fe\textsuperscript{II} and Fe\textsuperscript{III} over FBB with H\textsubscript{2}O\textsubscript{2} producing more hydroxyl radicals (\textsuperscript{\textbullet}OH) and more holes. The radical scavenger experiments demonstrated that holes and hydroxyl radicals (\textsuperscript{\textbullet}OH) were the main active species. FBB-25 is still stable after five cycles. Therefore, FBB-25 has great potential in wastewater treatment.

Introduction

For several decades, chlorophenols (CPs) and bisphenol A (BPA), known as ubiquitous environmental contaminants, have been widely present in nature. CPs have been widely used as common raw materials or intermediates in chemical industries\textsuperscript{[1–3]} including the production of pesticides, synthetic resins, and pharmaceuticals. BPA is mainly used to manufacture polycarbonate plastic and epoxy resins.\textsuperscript{[4, 5]} Owing to their potential carcinogenic and mutagenic activities, they can negatively affect the environment and damage the physiological processes in the liver. BPA and CPs (i.e., 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCPP)) have been listed as priority toxic pollutants by the US Environmental Protection Agency (EPA).\textsuperscript{[6, 7]}

Traditional wastewater treatment methods for CPs and BPA, including biodegradation,\textsuperscript{[8]} physical adsorption,\textsuperscript{[9]} and chemical treatment processes,\textsuperscript{[10]} are difficult to satisfy humanities requirements for water quality. As an emerging alternative technology, advanced oxidation processes (AOPs) are efficient enough to remove organic wastewater pollutants. Because strong oxidizing radical species generated by AOPs can completely degrade organic pollutants into non-toxic products such as CO\textsubscript{2}, H\textsubscript{2}O, and inorganic salts. Among the AOPs, the hydroxyl radical (\textsuperscript{\textbullet}OH) is an environmentally friendly active species from Fenton-like processes [Eq. (1)–(5)].\textsuperscript{[11, 12]} In the \textsuperscript{\textbullet}OH formation process, Fe\textsuperscript{III} is a vital factor to aid in the activation of hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), where Fe\textsuperscript{II} and Fe\textsuperscript{III} mean the Fe\textsuperscript{II}/Fe\textsuperscript{III} species in solid or solution phase. In general, the reaction rate of Fe\textsuperscript{II} with H\textsubscript{2}O\textsubscript{2} [Eq. (1)] is several orders of magnitude higher than that reaction rate [Eq. (2)],\textsuperscript{[13]} and thus the reduction of Fe\textsuperscript{II} to Fe\textsuperscript{III} [Eq. (2)] becomes the rate-limiting step, leading to a lower activity.

\begin{equation}
\begin{align*}
\text{Fe}^{\text{II}} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{\text{III}} + \text{OH} + \text{OH}^- \\
\text{Fe}^{\text{III}} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{\text{II}} + \text{O}_2 + \text{H}^+ \\
\text{OH} + \text{H}_2\text{O}_2 & \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \\
\text{Fe}^{\text{II}} + \text{O}_2/\text{HO}_2^- & \rightarrow \text{Fe}^{\text{III}} + \text{O}_2 \\
\text{Fe}^{\text{II}} + \text{O}_2/\text{HO}_2^- & \rightarrow \text{Fe}^{\text{III}} + \text{H}_2\text{O} \\
\text{H}_2\text{O}_2 + \text{e} & \rightarrow \text{OH} + \text{OH}^- 
\end{align*}
\end{equation}

With the aid of light irradiation, some heterogeneous Fenton catalysts can show higher catalytic activities.\textsuperscript{[14–16]} The electron is excited by light from the semiconductor, leaving...
more holes in the valence band. Then, the photoinduced electrons react with $\text{H}_2\text{O}_2$ to generate more $\text{OH}$ radicals [Eq. (6)] or promote the reduction of $\text{Fe}^{2+}$ to $\text{Fe}^0$. These active species can further oxidize organic contaminants $^{[17–19]}$. Many semiconductors have been reported to remove contaminants under light radiation, such as $\text{TiO}_2$ $^{[20,21]}$, $\text{CdS}$ $^{[22,23]}$, $\text{ZnO}$ $^{[24]}$ and $\text{BiOX}$ $(X = \text{Cl}, \text{Br}, \text{I})$ $^{[25,26]}$. However, $\text{BiOBr}$ has been most extensively investigated because it can capture solar energy from the visible-light region. Zhang et al. prepared the 3D microspherical $\text{BiOBr}$ by an ethylene glycol-assisted solvothermal method, and investigated the effect of morphology on the photocatalytic performance $^{[27]}$. Cheng et al. reported that a $\text{Ag}/\text{AgBr}/\text{BiOBr}$ hybrid exhibited superior visible-light-driven photocatalytic performance in the degradation of organic dye compared with N-doped P25 $^{[28]}$. Xiong et al. showed that more exposed $\{110\}$ facets could enhance the photocatalytic activity of $\text{BiOBr}$ under visible light $^{[29]}$. Although many methods are adopted to improve the photocatalytic activity of $\text{BiOBr}$, these improvements are not efficient for CPs and BPA degradation.

To better degrade CPs and BPA, $\text{H}_2\text{O}_2$ is introduced to enhance the photocatalytic performance. In this work, a $\text{Fe}^{2+}/\text{Fe}^{3+}$ doped Bi/$\text{BiOBr}$ (FBB) visible-light, Fenton-like catalyst was prepared by the ethylene glycol-assisted solvothermal method. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), UV/Vis diffuse reflectance spectroscopy (DRS), and Brunauer–Emmett–Teller (BET) specific surface area determinations were carried out to characterize the structural properties of FBB. BPA and CPs were selected to evaluate the photo-Fenton-like catalytic activity of $\text{Fe}^{2+}/\text{Fe}^{3+}$ doped Bi/$\text{BiOBr}$ hierarchical microspheres. The results showed that FBB exhibited excellent catalytic performance in the visible-light-driven, Fenton-like reaction. This was attributed to the presence of $\text{H}_2\text{O}_2$, which increased the multiple transformation rate of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ over FBB under visible-light irradiation.

Results and Discussion

Phase structure and morphological structure

Figure 1 shows the XRD patterns of the as-prepared samples. The diffraction peaks of $\text{BiOBr}$ are perfectly indexed as a tetragonal $\text{BiOBr}$ phase (JCPDS-ICDD Card No. 00-009-0393). After the addition of Fe to the precursors, the diffraction position of the $\{110\}$ plane shifts slightly towards a higher $2\theta$ value with the increase of Fe/Bi ratio (see in the inset image in Figure 1), and other peaks exhibit similar behaviors. This confirms that the incorporation of Fe ions into the $\text{BiOBr}$ matrix by replacing $\text{Bi}^{3+}$ lattice sites results in changes of the lattice parameters $^{[30]}$. In addition, the rhombohedral phase of Bi (JCPDS-ICDD Card No. 00-044-1246) is observed in the samples. The intensity of the diffraction peaks of Bi metal phase is intensified with the addition of Fe $^0$, indicating that the addition of Fe $^0$ improves the crystallinity of the rhombohedral Bi phase in the samples.

The morphological structures of the as-prepared samples were examined by FESEM and TEM. Figure 2 displays the magnified images of FESEM and TEM, as well as FESEM mapping. The pure $\text{BiOBr}$ sample (Figure 2a, $a_1$ and $b_1$) consists of many flower-like hierarchical microspheres ($\sim 5 \mu\text{m}$) self-assembled in nanosheets. The FBB-25 microspheres (Figure 2b, $b_2$) with a decreased diameter of around $3 \mu\text{m}$ are self-assembled in nanosheets and are looser. Figure S1 (see the Supporting Information) shows that the nanosheets and pore diameters become bigger when the Fe/Bi molar ratio is increased from 0.15 to 0.35, and this result was caused by the incorporation of Fe into the $\text{BiOBr}$ matrix. The morphological structure of the sample was further analyzed by TEM. As shown in Figure 2b, the FBB-25 sample consists of hierarchical microspheres that have solid centers, which present much thinner edges for the
single nanosheet compared with BiOBr (Figure 2a). Figure S2 (in the Supporting Information) exhibits the energy-dispersive X-ray (EDX) spectra of one point of a microsphere (Figure 2b), and the result indicates that the Bi/Br atomic ratio in FBB-25 is 1.0, which is higher than that of BiOBr (0.76). This fact implies that elemental Bi particles are deposited on FBB-25, which is consistent with the XRD and XPS results (see Table S1 in the Supporting Information). The EDX mapping of a microsphere in FBB-25 (Figure 2b) suggests that the Fe, Br, O, and Bi elements are distributed uniformly in FBB-25.

Shown in Figure 3a are the N$_2$ adsorption–desorption isotherms of BiOBr and FBB. The distinct hysteresis loops are observed at 0.5–1.0 p/p$_0$ from the isotherms, which belong to type IV, indicating a characteristic mesoporous material. According to the IUPAC recommendations,[31] the above hysteresis loops can be categorized as type H3 loops, which are defined as materials made up of plate-like particles. The mesopore sizes and specific areas of the products were determined by using the Barrett–Joyner–Halenda (BJH) and Brunauer–Emmett–Teller (BET) methods, respectively, as shown in Figure 3b. After the addition of Fe$^3+$, the pore size, pore volume, and surface specific area of the FBB sample are clearly increased, which is listed in Table S2 (in the Supporting Information). For example, the BET surface areas and pore sizes of BiOBr, FBB-15, FBB-20, FBB-25, FBB-30, and FBB-35 are determined to be 20.37, 30.72, 44.82, 62.97, 55.64, 58.44 m$^2$g$^{-1}$ and 6.57, 7.39, 8.89, 8.24, 8.62, 8.36 nm, respectively. The replacing of Bi$^{3+}$ lattice sites by Fe ions results in these increased physical parameter values.

Chemical composition by XPS and light adsorption

The surface chemical compositions of the BiOBr and FBB-25 sample were investigated by XPS (Figure 4A). Figure S3 (in the Supporting Information) shows the survey spectra of BiOBr and FBB-25, indicating that BiOBr and FBB-25 consist of Bi, O, Br and Bi, O, Br, Fe, including trace C. Figure 4A–a shows the high-resolution XPS spectra for Bi 4f. The two strong peaks at binding energies around 159 eV and 165 eV can be ascribed to Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$, respectively. For FBB-25 (or BiOBr), the peak at 159 eV can be fitted into two peaks of 158.3 eV (158.0 eV) and 159.5 eV (159.6 eV), which are assigned to metallic Bi$^0$ and Bi$^{3+}$ in BiOBr.[32] The concentrations of Bi on the surface of BiOBr and FBB-25 are determined to be 5% and 10%, respectively, as shown in Table S3 (in the Supporting Information). In Figure 4A–b, the O 1s peak centered at 531 eV can be assigned to three peaks of 530.4 eV (530.4 eV), 531.8 eV (531.4 eV), and 533.2 eV (532.9 eV), which are attributed to Bi–O bonds in BiOBr, hydroxyl groups on the surface, and oxygen deficient regions, respectively.[33] The addition of Fe can increase the oxygen deficiency from 6% to 9% (see Table S3 in the Supporting Information). Figure 4A–c shows the Br 3d peaks at 68.7 eV (68.6 eV) and 69.7 eV (69.7 eV), which correspond to Br 3d$_{5/2}$ and Br 3d$_{3/2}$. The Fe 2p peaks at 711 eV and 723 eV are ascribed to Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ (Figure 4A–d). The peak at 711 eV can be fitted to 710.3 eV and 712 eV, which are ascribed to Fe$^{2+}$ and Fe$^{3+}$,[34] where the molar ratio of Fe$^{2+}$/Fe$^{3+}$ is 0.5:0.05. In Table S1 (in the Supporting Information), the Bi/O atomic ratio in FBB-25 is 0.54, which is higher than that of BiOBr (0.69). This indicates that Bi particles are deposited on FBB-25, and the oxygen deficiency is increased.

The UV/Vis diffuse reflectance spectra of the BiOBr and FBB samples were further investigated and are shown in Figure 4B–a, where it is found that the adsorption edge is around 430 nm for BiOBr. However, the adsorption edge of Fe$^3$/Fe$^{2+}$ doped Bi/BiOBr appears shifted remarkably towards higher wavelengths with the addition of Fe. This suggests that the transition of impurity energy levels can enhance the adsorption of visible light. According to the classical formula [Eq. (7)],[35] the band gaps ($E_g$) of BiOBr and FBB can be calculated, as shown in Table S2 (in the Supporting Information).

$$A(hv-E_g)^{1/2} = a hv \tag{7}$$

In Equation (7), $A$, $h$, $a$, $v$, and $E_g$ represent a constant, Planck’s constant, the absorption coefficient, frequency of incident photon, and band gap energy, respectively. The $v$ value is directly determined by the optical transition types of semiconductors, such as the $v$ value of 4 for BiOBr.[36] The band gaps of BiOBr and FBB-25 are calculated to be 2.52 eV and 1.61 eV, respectively (Figure 4B–b).

Catalytic activity: Photodegradation of RhB

The photocatalytic activities of the obtained samples were evaluated by RhB degradation with an initial concentration of 20 mg L$^{-1}$ (see Figure S4 in the Supporting Information). Clear-
ly, RhB photodegradation efficiency is negligible with the absence of photocatalysts. In the adsorption–desorption equilibrium, FBB-25 exhibits the highest adsorption capacity (around 21 mg g⁻¹). After 30 min irradiation, RhB degradation efficiencies of 71.8 %, 53.6 %, 71.4 %, 78.7 %, and 62.8 % are achieved for BiOBr, FBB-15, FBB-20, FBB-25, FBB-30, and FBB-35, respectively, indicating that the Fe/Bi molar ratios of 0.2–0.3 exhibit higher photocatalytic activities for RhB degradation.

Considering the chemical composition in the FBB samples, H₂O₂ is introduced to activate the photocatalytic sites, generating hydroxyl radicals to efficiently degrade organic contaminants. The degradation efficiencies of BPA and CPs were chosen to evaluate the photo-Fenton-like catalytic performance of FBB-25.

**Catalytic oxidation of BPA in the visible-light/catalyst/H₂O₂ system**

Figure 5 shows the change of BPA concentration (C/C₀) versus reaction time for FBB-25 under different conditions. In the dark or under visible light, there is almost no BPA degradation efficiency, and around 15 % of BPA degradation is achieved in the Fenton-like reaction. However, 20 mg L⁻¹ BPA is completely degraded within 30 min in the presence of 5 mM H₂O₂ and visible light, implying that the combination of visible light and H₂O₂ has a significant role in the BPA degradation efficiency. The H₂O₂ degradation rate in the Fenton-like reaction is far lower than that in the visible-light-driven Fenton-like reaction (Figure S5 in the Supporting Information). This is because visible light can increase a propagating reaction between Fe²⁺ and Fe³⁺ under H₂O₂ [Eqs. (1), (8)–(9)].¹⁰

The H₂O₂ initial concentration is a key parameter in the visible-light-driven Fenton-like reaction. Hence, the degradation of 20 mg L⁻¹ BPA with FBB-25 was initially conducted to evaluate the effect of H₂O₂ concentration. Figure 6a and b show the change of BPA concentration or total organic carbon (TOC) removal efficiency versus irradiation time under different H₂O₂ concentrations. The results show that the BPA degradation rate and TOC removal efficiency are increased with increasing H₂O₂ concentration. The TOC removal efficiencies with 1 mM, 5 mM, 10 mM, and 20 mM of H₂O₂ are 35.0 %, 57.2 %, 83.4 %, and 77.5 % at 120 min. With more than 10 mM of H₂O₂ initial concentration, the BPA degradation rate constant and TOC removal rate constant almost remained stable (Figure 6c and Figure S6 in the Supporting Information). This indicates that 10 mM H₂O₂ is the optimized value for BPA degradation. In the oxidation of BPA, most of the TOC was removed in the formation of CO₂ and H₂O, and little was left, including some low-molecular-weight organic acids (i.e., acetic acid, oxalate, and propanedioic acid),¹⁷ which agreed with the decrease of pH (from 7.0 to 5.5).
Catalytic degradation of chlorophenols in the visible-light/catalyst/H\textsubscript{2}O\textsubscript{2} system

Visible-light-driven Fenton-like catalytic oxidation of chlorophenols (2-CP, 4-CP, 2,4-DCP, and 2,4,6-TCP) degradation were carried out over FBB-25. Figure 7a and b shows the results of chlorophenols degradation and TOC removal. As seen from Figure 7a and b, the degradation efficiencies of 2-CP, 4-CP, 2,4-DCP, and 2,4,6-TCP at 30 min irradiation are almost 100%, whereas the TOC removal efficiencies are 39.2%, 79.8%, 73.3%, and 47.9%, respectively. The extent of chlorophenols degradation and TOC removal follows the order of 4-CP > 2,4-DCP > 2,4,6-TCP (Figure 7c), which is a distinct difference from previous reports. Benitez and co-workers suggested that the order of oxidation rate was 4-CP > 2,4-DCP > 2,4,6-TCP for both UV radiation and Fenton’s reagent and 2,4,6-TCP > 2,4-DCP > 4-CP for ozonation.\[38, 40\] Tang and Huang also reported the same order of 2-CP > 2,4-DCP > 2,4,6-TCP by Fenton’s reagent.\[39\] In general, the hydroxyl radicals react faster with chlorophenols with lower number of chlorine atoms, which indicates that the visible-light-driven Fenton-like catalytic oxidation mechanism of chlorophenols by FBB-25 is different from the Fenton’s reagent oxidation process.

Figure 7d exhibits the degradation of multiple chlorophenols over FBB-25. The results show that the degradation efficiency of every chlorophenol is almost the same (i.e., 100% at 30 min). Compared with single chlorophenol degradation, pseudo-first-order reaction rate constants in the multiple chlorophenols degradation were the same (Figure 7c and d). This implies that the reactive species are not selective.

Half-life times and pseudo-first kinetic constants for the degradation of CPs and BPA over various photocatalysts at neutral conditions are tabulated in Table S4 (in the Supporting Information). The results show that the degradation rate of CPs and BPA was slow when using other photocatalysts, and slower than the Fenton-like reaction. This is attributed to the fact that few active species are produced in those catalytic reactions. It implies that FBB-25 is quite comparable to other catalysts.

Catalytic mechanism of the visible-light/catalyst/H\textsubscript{2}O\textsubscript{2} system

The active species of FBB-25 were investigated by a series of trapping experiments during the visible-light-driven Fenton-like reaction. The degradation of BPA was repeated with 5 mM H\textsubscript{2}O\textsubscript{2} under visible light by adding 1 mM of 1,4-benzoquinone (BQ), 1 mM of isopropanol (IPA), and 10 mM of ammonium oxalate (AO) as a superoxide radical (\textsuperscript{•}\textsuperscript{O}\textsuperscript{2-}) scavenger,\[41\] a hydroxyl...
radical scavenger (OH)\textsuperscript{[42]} and a hole scavenger\textsuperscript{[43]} respectively. As shown in Figure 8a, the removal efficiencies of BPA are inhibited by IPA (\approx 30\%) and AO (\approx 30\%) at 30 min whereas BQ increased the BPA degradation owing to the increased reduction rate of Fe\textsuperscript{III} to Fe\textsuperscript{II}.\textsuperscript{[44]} In addition, the pseudo-first-order rate constants with no scavengers, IPA, AO, and BQ are 0.081 min\textsuperscript{−1}, 0.013 min\textsuperscript{−1}, 0.012 min\textsuperscript{−1}, and 0.12 min\textsuperscript{−1} (Figure 8b), respectively. This indicates that the active species of FBB-25 are mainly holes and OH radicals for BPA degradation in the visible-light-driven Fenton-like reaction.

To further investigate how H\textsubscript{2}O\textsubscript{2} can activate the photocatalytic active sites, H\textsubscript{2}O\textsubscript{2} degradation and surface Fe\textsuperscript{II} concentration over FBB-25 were carried out. As shown in Figure 9, the Fe\textsuperscript{II} concentration on the surface of FBB-25 was increased in the photocatalytic reaction (Eqs. (8) and (9)). In the photo-Fenton-like reaction, the Fe\textsuperscript{II} concentration was increased when H\textsubscript{2}O\textsubscript{2} was completely consumed at 60 min of reaction. This implies that surface Fe\textsuperscript{II} on FBB-25 is reduced to Fe\textsuperscript{II} in the presence of visible light. The OH radical change was observed in the reaction systems (Figure 10). The reaction rate constant (0.205 μM min\textsuperscript{−1}) of OH formation in the photo-Fenton-like reaction is 11-fold higher than that in the Fenton-like reaction (0.019 μM min\textsuperscript{−1}). This indicates that a large amount of Fe\textsuperscript{II} was produced and then oxidized by H\textsubscript{2}O\textsubscript{2} in the photo-Fenton-like reaction [Eqs. (1) and (9)].

\[
\begin{align}
\text{BiOBr} + \text{hv} & \rightarrow \text{h}^{+} + \text{e} \quad (\text{8}) \\
\text{Fe}^{\text{III}} + \text{e} & \rightarrow \text{Fe}^{\text{II}} \quad (\text{9})
\end{align}
\]

To verify the above reaction mechanism, ESR spectroscopy was adopted to track the hydroxyl radical by using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin trapping reagent. The hydroxyl radical, OH characterized by four intensity peaks, was detected in the presence of FBB-25 (Figure 11). During the photo-Fenton-like catalytic reaction, the four peaks’ intensities at 30 min were higher than those at 1 min, whereas their intensities at 30 min were lower than those at 1 min for the
Fenton-like reaction. This indicates that more hydroxyl radicals were produced in the photo-Fenton-like catalytic reaction and confirms the above reaction mechanism.

Based on the above analysis, a mechanism of the photo-Fenton-like catalytic degradation of organic contaminants was proposed: first, the oxidation of $\equiv Fe^\mathit{II}$ to $\equiv Fe^\mathit{III}$ by $H_2O_2$ occurs [Eq. (1)], producing more hydroxyl radicals (‘OH) to oxidize contaminants; second, the reduction of $\equiv Fe^\mathit{III}$ to $\equiv Fe^\mathit{II}$ is promoted by photogenerated electrons [Eq. (2), (9)] from FBB-25 in the presence of visible light; third, the separation efficiency of photogenerated electrons and holes is increased, leaving more holes to degrade organic contaminants.

Stability of the catalyst

To test the stability and reusability of FBB-25 in the photo-Fenton-like catalytic reaction, the catalyst was reused to degrade BPA and 4-CP five times under the same conditions, and the result is shown in Figure 12. The catalytic efficiencies of FBB-25 for BPA and 4-CP were almost up to 100% within 20–30 min after five cycles. The phase structure of FBB-25 after being used in five cycles was further analyzed by XRD (Figure S7 in the Supporting Information), where the characteristic peaks of BiOBr still existed, such as the crystal faces {1 01}, {110}, {2 00}, and {2 03}. In addition, almost no Fe, Bi, or Br was released into solution from FBB-25 (Table S5 in the Supporting Information). It indicates that the FBB-25 is stable during the
photo-Fenton-like catalytic oxidation of the pollutant molecules, and has good potential in future applications.

Conclusions

Fe\(^{II}/\)Fe\(^{III}\) doped Bi/BiOBr hierarchical photocatalysts were successfully synthesized by using a one-step solvothermal method. The presence of Fe\(^{II}/\)Fe\(^{III}\) can promote the growth of Bi metal nanoparticles and increase the surface area of the FBB samples. Compared with previously reported catalysts, FBB-25 shows higher catalytic performance for the degradation of BPA and CPs during the visible-light-driven Fenton-like reaction. This is attributed to the rapid multiple transformation of Fe\(^{III}\) and Fe\(^{II}\) over FBB under visible light and the reaction of H\(_2\)O\(_2\) with Fe\(^{II}\). The radical scavenger experiments demonstrated that holes and hydroxyl radicals (\(\cdot OH\)) were the main active species. After five cycles, the regenerated FBB-25 is still stable.

Experimental Section

Materials

Bismuth nitrate pentahydrate (Bi(NO\(_3\))\(_3\)-5H\(_2\)O, >98%), ferrous chloride tetrahydrate (FeCl\(_2\)-4H\(_2\)O, >99%), potassium bromide (KBr, >98%), rhodamine B (RhB, >95%), ethylene glycol (CH\(_2\)OHCH\(_2\)OH, >98%), acetic acid (CH\(_3\)COOH, >99%), hydrogen peroxide (H\(_2\)O\(_2\), >99%), and 2-thiobarbituric acid (TBA, >98.5%) were obtained from Sinopharm Chemical Reagent Co., Ltd. 2,4,6-Trichlorophenol (2,4,6-TCP, >99.9%), 2-chlorophenol (2-CP, >99.9%), and bisphenol A (BPA, >99%) were purchased from Tokyo Kasei Kogyo Co., Ltd. 2-Deoxy-o-ribose (C\(_9\)H\(_{14}\)O\(_9\), >99%), and trichloroacetic acid (TCP, >99%) were purchased from Alfa Aesar. Ultrapure water (Mill-Q Biocell, 18 M\(_2\)O) was used to prepare the aequous solutions.

Preparation of Fe\(^{II}/\)Fe\(^{III}\) doped Bi/BiOBr

The Fe-doped Bi/BiOBr sample was obtained by a solvothermal method under an Ar atmosphere, as follows: 3 mmol Bi(NO\(_3\))\(_3\)-5H\(_2\)O and FeCl\(_2\)-4H\(_2\)O with different Fe/Bi molar ratios (i.e., 0, 0.15, 0.2, 0.25, 0.3, 0.35) were uniformly mixed in ethylene glycol (30 mL) containing acetic acid (3 mL) under magnetic stirring for 30 min. The resultant solution was added to ethylene glycol (30 mL) with 3 mmol KBr 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 fresh product was separated centrifugally and washed with ethanol and ultrapure water. Finally, the sample was freeze-dried under vacuum. The resultant products were denoted as FBB-x, where x (15, 20, 25, 30, 35) referred to the ratio of Fe to Bi as 0.15, 0.2, 0.25, 0.3, 0.35, respectively. All the operations were done under Ar atmosphere.

Characterization

The XRD patterns of FBB samples were obtained by using an X-ray diffractometer (X’Pert PRO MPD, PANalytical) with a CuK\(_\alpha\) irradiation source (\(\lambda = 1.5406\) A) at 5–90°. The morphological structure and chemical composition of the sample was measured by TEM (H-7500, Hitachi Limited) and FESEM (SU-8020, Hitachi Limited) with the energy-dispersive X-ray spectrometer. XPS was used to analyze the surface chemical compositions and states with AlK\(_\alpha\) X-ray irradiation (ESCALAB 250Xi, Thermo Fisher Scientific, USA). Backgrounds of Shirley and linear type were utilized for peak fitting with C1s calibrated to 284.6 eV for all the spectra. The UV/Vis DRS were obtained by using a UV/Vis spectrometer (UV-3600, Shimadzu, Japan) with an integrating sphere by using BaSO\(_4\) as the reference. The specific surface area was determined by using a full automatic analyzer (ASAP2020HD88, Micromeritics Instrument Corp.).

Catalytic activity

The photo-Fenton-like degradation tests of BPA with FBB-25 were performed to evaluate the catalytic activity of FBB-25, including the Fenton-like and photocatalytic experiments. A 300 W Xe lamp with a 400 nm cut-off filter at 15 A current and 14 V voltage was used as a visible-light source, and the vertical distance between lamp and liquid level was 15 cm. In a typical experiment, 50 mg of photocatalyst was added to 100 mL of 20 mg L\(^{-1}\) BPA solution. Prior to illumination and 5 m\(_3\) H\(_2\)O\(_2\) addition, the suspension was magnetically stirred in the dark for 30 min to achieve the adsorp-
The authors declare no conflict of interest.

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Conflict of interest

The authors declare no conflict of interest.

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[1] J. Q. Guo, C. H. Wu, S. L. Lv, D. S. Lu, C. Feng, X. J. Qi, W. J. Liang, X. L. Chang, H. Xu, G. Q. Wang, Z. J. Zhou, Environ. Pollut. 2016, 214, 478–484. [2] M. A. Arellano-González, I. González, A. C. Texier, J. Hazard. Mater. 2016, 314, 181–187. [3] F. Xiao, W. T. Li, L. P. Fang, D. S. Wang, J. Hazard. Mater. 2016, 308, 11–20. [4] S. Li, G. S. Zhang, P. Wang, H. S. Zheng, Y. J. Zheng, Chem. Eng. J. 2016, 294, 371–379. [5] X. N. Li, Z. H. Wang, B. Zhang, A. I. Rykov, M. A. Ahmed, J. H. Wang, Appl. Catal. B 2016, 181, 788–799. [6] A. Myridakis, G. Chalkiadaki, M. Fotou, M. Kogevinas, L. Chatzi, E. G. Stephanou, Environ. Sci. Technol. 2016, 50, 932–941. [7] A. Usman, M. Ahmad, Chemosphere 2016, 158, 131–142. [8] M. Pérez, F. Torrades, X. Domènech, J. Peral, Water Res. 2002, 36, 2703–2710. [9] J. Rashid, M. A. Barakat, S. L. Pettit, J. N. Kuhn, Environ. Technol. 2014, 35, 2153–2159. [10] N. Li, C. Descorme, M. Besson, Appl. Catal. B 2007, 71, 262–270. [11] S. J. Hug, O. Leupin, Environ. Sci. Technol. 2003, 37, 2734–2742. [12] W. P. Kwan, B. M. Voelker, Environ. Sci. Technol. 2002, 36, 1467–1476. [13] B. Ensing, F. Buda, E. J. Baerends, J. Phys. Chem. A 2003, 107, 5722–5731. [14] G. K. Zhang, Y. Y. Gao, Y. L. Zhang, Y. D. Guo, Environ. Sci. Technol. 2010, 44, 6384–6389. [15] S. N. Guo, Y. Zhu, Y. Y. Yan, Y. L. Min, J. C. Fan, Q. J. Xu, Appl. Catal. B 2016, 185, 315–321. [16] F. F. Dias, A. A. S. Oliveira, A. P. Arcanjo, F. C. C. Moura, J. G. A. Pacheco, Appl. Catal. B 2016, 186, 136–142. [17] C. F. Zhang, L. G. Oiu, F. Ke, Y. J. Zhu, Y. P. Yuan, G. S. Xu, X. Jiang, J. Mater. Chem. A 2013, 1, 14329–14334. [18] W. J. Liu, F. X. Zeng, H. Jiang, X. S. Zhang, W. W. Li, Environ. Eng. J. 2012, 80, 9–18. [19] W. J. Song, M. M. Cheng, J. H. Ma, W. H. Ma, C. C. Chen, J. C. Zhao, Environ. Sci. Technol. 2006, 40, 4782–4787. [20] B. Erjavec, P. Hudoklin, K. Perc, T. Tišler, M. S. Dolenc, A. Pintar, Appl. Catal. B 2016, 183, 149–158. [21] H. Adamu, P. Dubey, J. A. Anderson, Chem. Eng. J. 2016, 284, 380–388. [22] Y. L. Min, G. Q. He, Q. J. Xu, Y. C. Chen, J. Mater. Chem. A 2014, 2, 2578–2584. [23] F. Q. Zhou, J. C. Fan, Q. J. Xu, Y. L. Min, Appl. Catal. B 2017, 201, 77–83. [24] J. Liu, Z. Y. Hu, Y. Peng, H. W. Huang, Y. Li, M. Wu, X. X. Ke, G. V. Tendeloo, B. L. Su, Appl. Catal. B 2016, 181, 138–145. [25] H. Gaiyem, Y. Sasson, ACS Catal. 2013, 3, 186–191. [26] X. Zhang, Z. H. Ai, F. L. Jia, L. Z. Zhang, J. Phys. Chem. C 2008, 112, 747–753. [27] J. Zhang, F. J. Shi, J. Lin, D. F. Chen, J. M. Gao, Z. X. Huang, X. X. Ding, C. C. Tang, Chem. Mater. 2008, 20, 2937–2941. [28] H. F. Cheng, B. B. Huang, P. Wang, Z. Y. Zhang, Z. Z. Lou, P. J. Wang, X. Y. Qin, X. Y. Zhang, Y. Dai, Chem. Commun. 2011, 47, 7054–7056. [29] X. F. Xiong, Y. L. Ding, Q. Q. Wang, Y. X. Li, Q. Q. Jiang, J. C. Hu, Appl. Catal. B 2016, 188, 283–291. [30] G. L. Huang, Y. F. Zhu, CrystEngComm 2012, 14, 8076–8082. [31] M. Kruk, M. Jaroniec, Chem. Mater. 2001, 13, 3169–3183. [32] D. L. Chen, M. Zhang, Q. J. Lu, J. F. Chen, B. T. Liu, Z. F. Wang, J. Alloys Compd. 2015, 646, 647–654. [33] Y. Yu, C. Y. Cao, H. Liu, P. L. Li, F. F. Wei, Y. Jiang, W. G. Song, J. Mater. Chem. A 2014, 2, 1677–1681. [34] T. Yamashita, P. Hayes, Appl. Surf. Sci. 2008, 254, 2441–2449. [35] S. Shenawi-Khalil, U. Uvarov, S. Fronton, I. Popov, Y. Sasson, J. Phys. Chem. C 2012, 116, 11004–11012. [36] D. Zhang, J. Li, Q. Wang, Q. Wu, J. Mater. Chem. A 2013, 3, 8622–8629. [37] C. Li, X. Z. Li, N. Graham, N. Y. Gao, Water Res. 2008, 42, 109–120. [38] F. J. Benitez, J. Beltran-Heredia, J. L. Acero, F. J. Rubio, Chemosphere 2000, 41, 1271–1277. [39] W. Z. Tang, C. P. Huang, Chemosphere 1996, 33, 1621–1635. [40] L. Z. Zhang, H. Chen, X. F. Zhao, Q. Zhai, D. J. Yin, Y. F. Sun, J. H. Li, Appl. Catal. B 2016, 193, 47–57. [41] J. J. Li, J. B. Zhong, X. Y. He, S. T. Huang, J. Zeng, J. J. He, W. L. Shi, Appl. Surf. Sci. 2013, 284, 527–532.
[42] L. Ismail, A. Rifai, C. Ferronato, L. Fine, F. Jaber, J. M. Chevelon, Appl. Catal. B 2016, 185, 88–99.
[43] X. M. Zhang, G. B. Ji, Y. S. Liu, X. G. Zhou, Y. Zhu, D. N. Shi, P. Zhang, X. Z. Cao, B. Y. Wang, Phys. Chem. Chem. Phys. 2015, 17, 8078–8086.
[44] R. Chen, J. J. Pignatello, Environ. Sci. Technol. 1997, 31, 2399–2406.
[45] D. He, J. X. Ma, R. N. Collins, T. D. Waite, Environ. Sci. Technol. 2016, 50, 3820–3828.
[46] R. M. Sellers, Analyst 1980, 105, 950–954.

[47] J. A. Buege, S. D. Aust, Methods Enzymol. 1978, 52, 302–310.
[48] J. Bolobajev, M. Trapidio, A. Goi, Appl. Catal. B 2016, 187, 75–82.

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