Supporting Information

Effect of in situ Fe(II)/Fe(III)-doping on the visible light-Fenton-like catalytic activity of Bi/BiOBr hierarchical microspheres

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Additional Experiments

Synthesis of 0.2-F(III)BB sample

3 mmol $Bi(NO_3)_3 \cdot 5H_2O$, and 0.6 mmol $FeCl_3 \cdot 6H_2O$ were dissolved in 30 ml ethylene glycol containing 3 ml acetic acid under magnetic stirring for 30 min. 3 mmol of KBr was dissolved in 30 ml ethylene glycol, and the resultant solution was added fast to the above mentioned $Bi(NO_3)_3$ solution with vigorous stirring for 30 min. Next, the mixture was transferred to a 100 ml Teflon autoclave, followed by solvothermal treatment at 433 K for 12 h. After naturally cooling to room temperature, the obtained sample was separated by centrifugation and washed with absolute ethanol and deionized water several times. Finally, the samples were freeze-dried under vacuum. The resultant products were denoted as 0.2-F(III)BB.

Preparation of 0.2-FBB after HCl treatment

50 mg of 0.2-FBB was put into 10 ml HCl solution (pH = 1). After being stirred for 2 h, the product was centrifuged and washed to neutral pH to carry out the following experiments.

The photogradation test of RhB with 0.2-FBB after HCl (pH = 1) treatment was the same with that with 0.2-FBB.

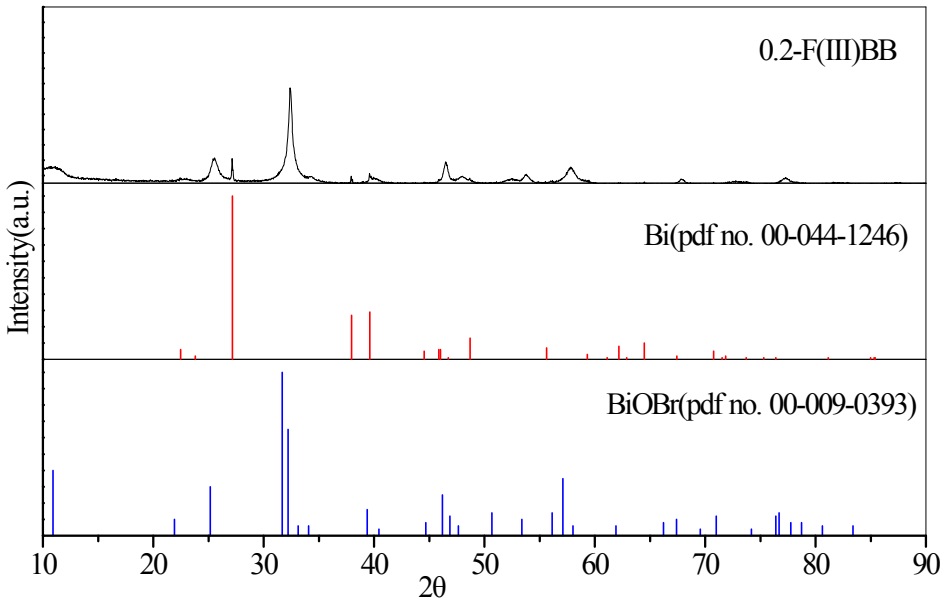

Figure S1. XRD patterns of 0.2-F(III)BB

In the XRD pattern of 0.2-F(III)BB (Figure S1), both the characteristic peaks of Bi and BiOBr can be observed, which was consistent with the XRD pattern of 0.2-FBB(Figure.1). This indicates that the reduction of Bi^{3+} to Bi^{0} should be caused by Fe^{2+}. In addition, the oxidation-reduce redox (0.77 eV) of Fe^{3+}/Fe^{2+} is far higher than that (0.31 eV) of Bi^{3+}/ Bi^{0}. In Figure1, the peaks intensities of Bi crystal phase in Fe doped Bi/BiOBr samples were increased with the increase of Fe content. This shows that the presence of Fe (II) can contribute to transformation of amorphous to crystal for Bi metal nanoparticles. Therefore, the amorphous Bi metal nanoparticles could be existed in the BiOBr that was prepared by the solvothermal method (seen in experimental section). This result is agreed with the XPS fitting results (Figure 5c).

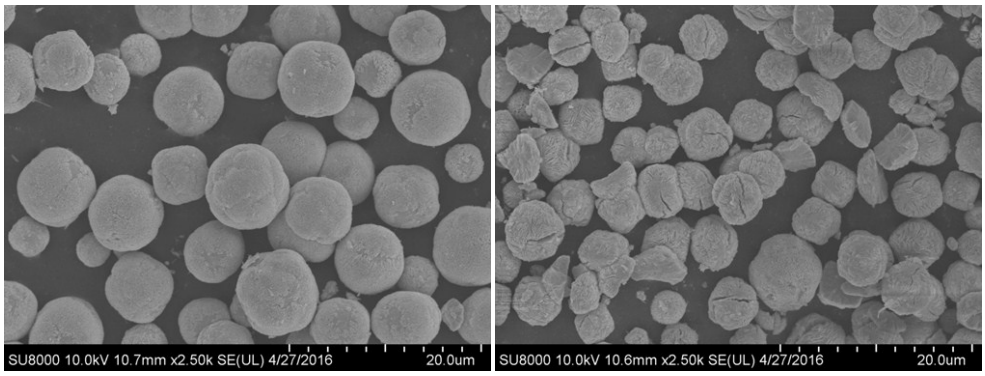

Figure S2. Magnified images of BiOBr(left) and 0.05-FBB(right)

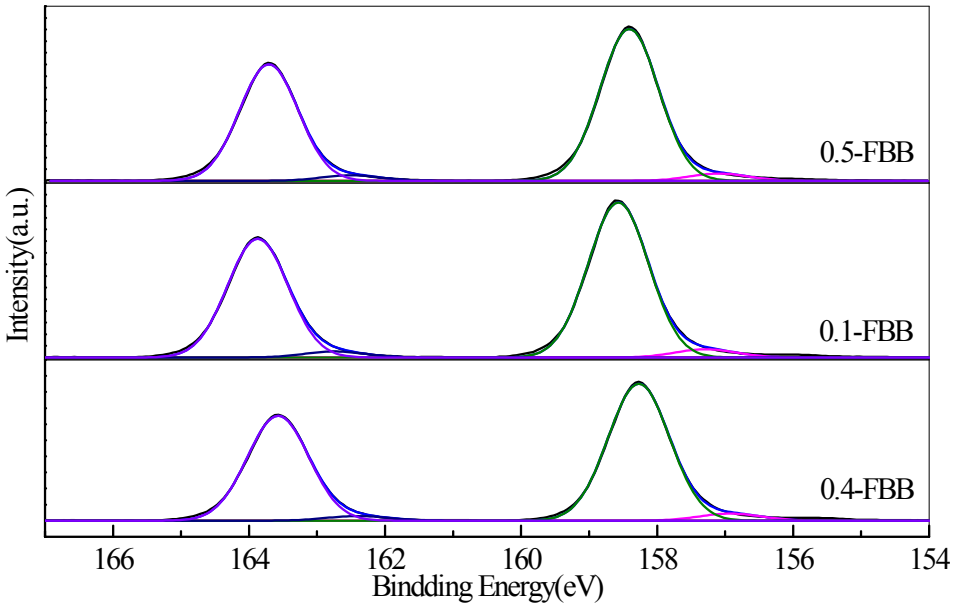

Figure S3 High-resolution spectrum of the XPS Bi 4f in 0.05-FBB, 0.1-FBB and 0.4-FBB samples

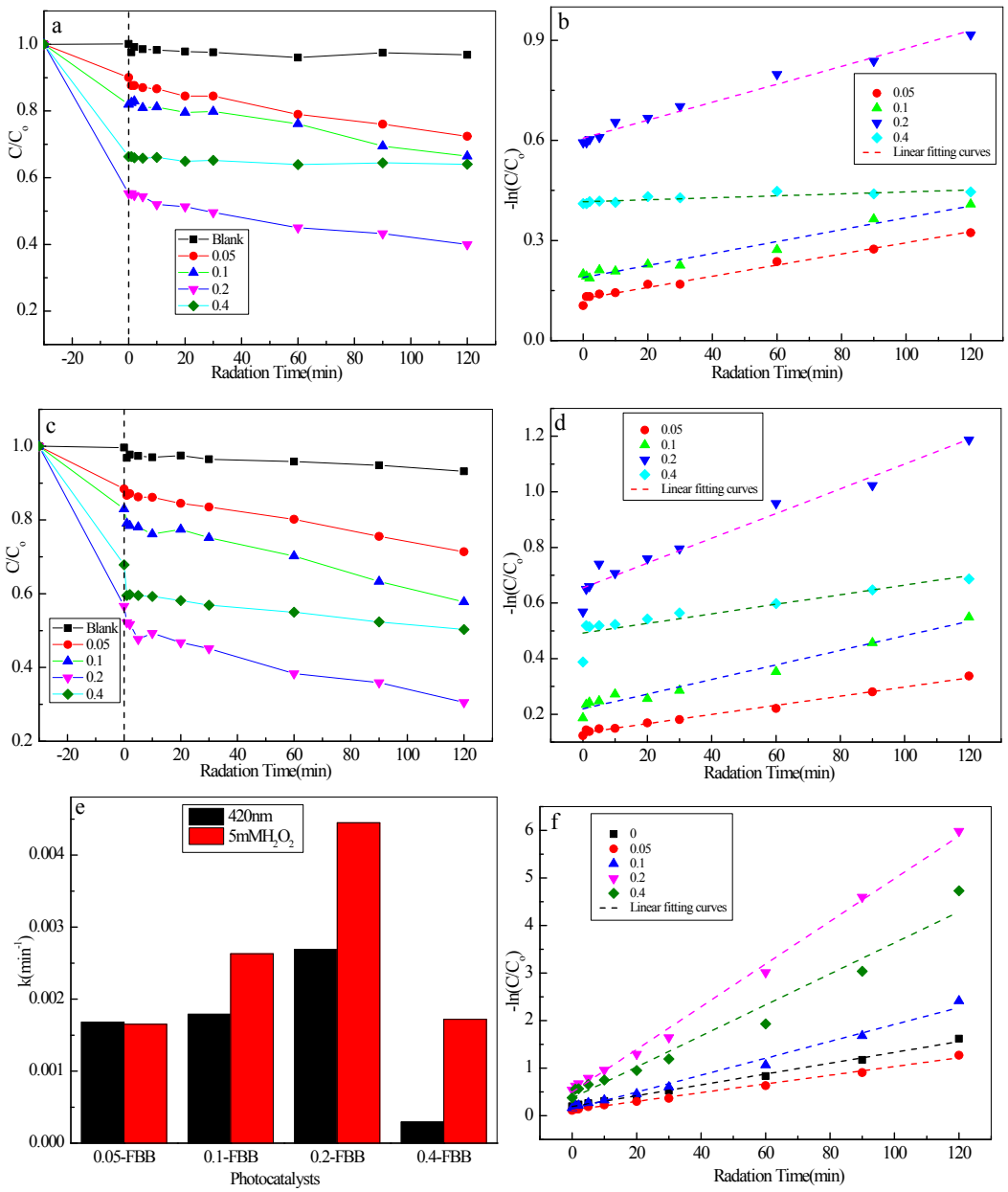

Figure S4 RhB degradation efficiencies as a function of irradiation time by the as-prepared photocatalysts: (a) 420 nm, (c) 5 mM H_2O_2; Pseudo-first-order dynamic fitting curves of RhB degradation on the catayst under different conditions: (b) 420 nm, (d) 5 mM H_2O_2;(f) 5 mM H_2O_2+420 nm; (e)Pseudo-first-order reaction rate constants of RhB under different conditions.

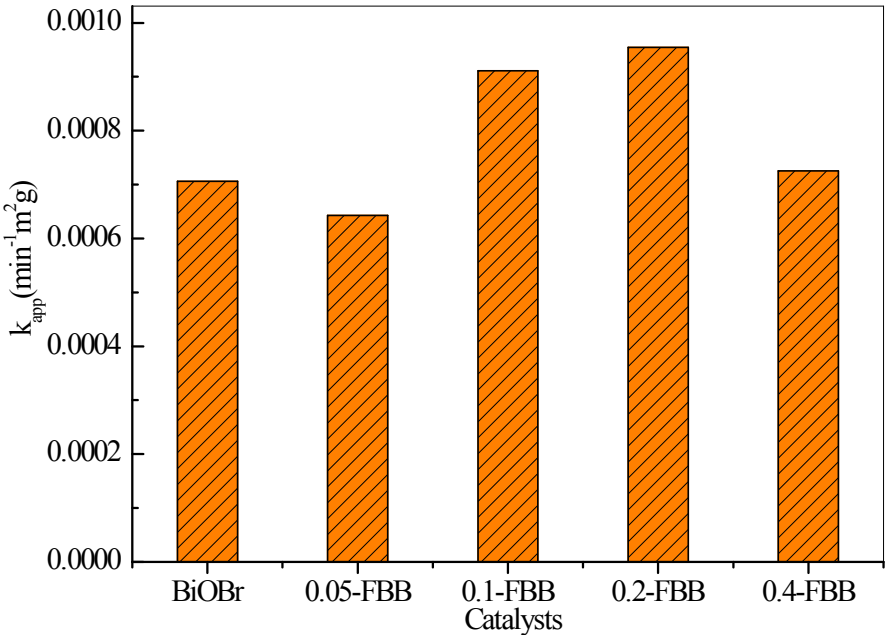

Figure S5 The RhB degradation rate constants by catalysts versus surface area

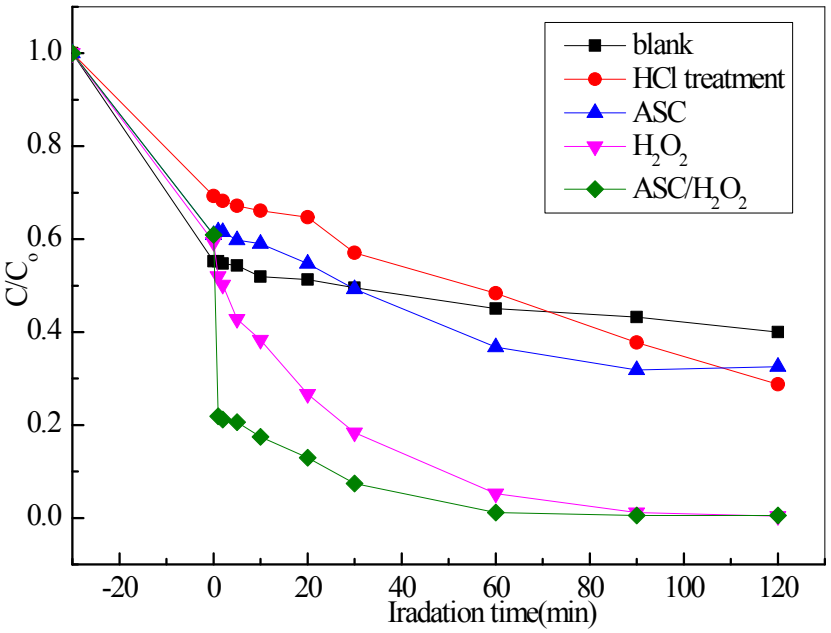

Figure S6 The change of RhB concentration (20 mg/L initial concentration) with 0.2-FBB (0.5 g/L) under visible light at different conditions: a, 0.2-FBB (blank test);b, 0.2-FBB after 0.1 mol/L HCl treatment; c, 0.2-FBB+1 mM ASC; d, 0.2-FBB+5 mM H_2O_2;e, 0.2-FBB+5 mM H_2O_2 + 1 mM ASC

Table. S1a Peak position of the XPS Fe 2p, Bi 4f for BiOBr and Fe doped Bi/BiOBr

Samples	Peak Position(eV)							
	Fe(II)		Fe(III)		Bi(0)		Bi(III)	
	Fe $2p_{3/2}$	Fe $2p_{1/2}$	Fe $2p_{3/2}$	Fe $2p_{1/2}$	Bi $4f_{7/2}$	Bi $4f_{5/2}$	Bi $4f_{7/2}$	Bi $4f_{5/2}$
BB	-	-	-	-	157.2	162.6	158.8	164.1
0.05-FBB	709.7	723.1	711.5	725.1	157.1	162.5	158.4	163.7
0.1-FBB	709.9	723.0	711.5	724.4	157.3	162.7	158.6	163.9
0.2-FBB	709.7	723.0	711.4	724.5	157.1	162.5	158.3	163.6
0.4-FBB	709.6	723.1	711.3	724.7	156.9	162.4	158.3	163.6

Table. S1b Peak position of the XPS O 1s, Br 3d for BiOBr and Fe doped Bi/BiOBr

Samples	Peak Position(eV)				
	O 1s			Br 3d	
	Lattice Oxygen	Surface oxygen	Oxygen deficiency	Br $3d_{7/2}$	Br $3d_{5/2}$
BB	529.5	530.8	532.1	67.9	68.9
0.05-FBB	529.1	530.4	531.7	67.5	68.6
0.1-FBB	529.3	530.6	531.9	67.7	68.7
0.2-FBB	529.0	530.3	531.7	67.5	68.5
0.4-FBB	528.9	530.3	531.6	67.4	68.4

Table. S2 Pseudo-first-order dynamic fitting parameters of RhB on the catalysts under different conditions

Catalysts	420 nm		5 mM H_2O_2		420 nm + 5 mM H_2O_2	
Fe/Bi molar ratio	k(min^{-1})	R^2	k(min^{-1})	R^2	k(min^{-1})	R^2
0	0.01205	0.9864	0.00353	0.9761	0.0114	0.9951
0.05	0.00168	0.9816	0.00165	0.9899	0.00917	0.9940
0.10	0.00179	0.9696	0.00263	0.9638	0.01781	0.9877
0.2	0.00269	0.9764	0.00445	0.9517	0.04488	0.9960
0.4	2.94412E-4	0.7397	0.00172	0.7570	0.03264	0.9672