

Supplementary Information

Recent Advances in Bismuth Oxyhalide Photocatalysts for Degradation of Organic Pollutants in Wastewater

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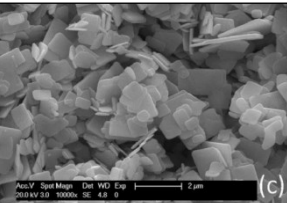
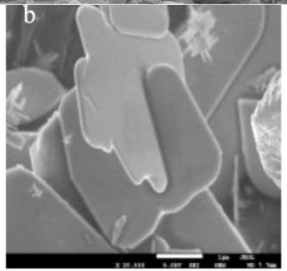
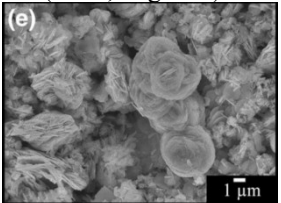
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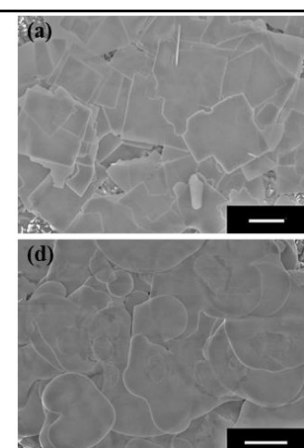
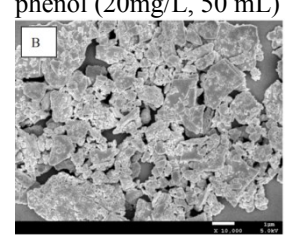
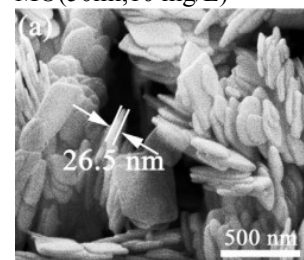
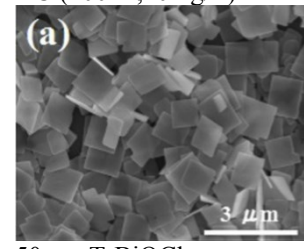
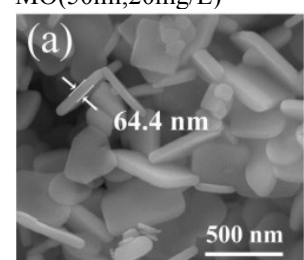
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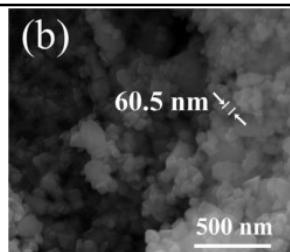
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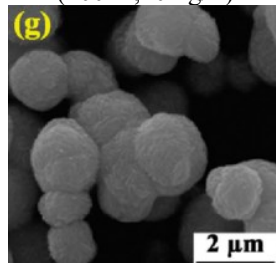
Table S1 Controllable synthesis of BiOX photocatalysts and their photodegradation performance

Material/method	Morphology/Dye/concentration	Light	Degradation performance	Refer
BiOCl hydrothermal method; Bi(NO ₃) ₃ ·5H ₂ O, ultra-water, NaCl, NaOH, pH=2/7/10, 160°C 24h		UV lamp	BiOCl-10>BiOCl-7>BiOCl-2 efficiency of oxidation gaseous Hg Degradation rate: Hg 2500s 60%	[3]
BiOBr hydrothermal approach NaBiO ₃ ·2H ₂ O, HNO ₃ , deionised water, 200°C for 24 h		400W halogen lamp	K(pH=9)=0.037	[4]
BiOBr hydrothermal Method; Bi(NO ₃) ₃ ·5H ₂ O, NaBr, water pH=2-10, 180°C for 20h	0.02g BiOBr CIP(40ml, 5mg L ⁻¹) 	Xe lamp	BiOBr-8>BiOBr-6>BiOBr-4>BiOBr- 10>BiOBr-2. Degradation rate: RhB 45min 99%	[5]
	0.2g BiOBr RhB (200ml, 1×10 ⁻⁵ M)			

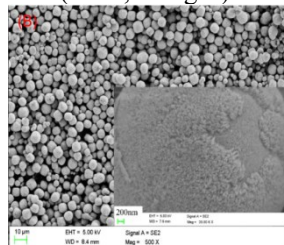
<p>BiOBr-1 2 3 4 hydrothermal method; Bi(NO₃)₃·5H₂O, CTAB, NaOH(adjust pH=7 5 3 2)170°C for 17h (a) BiOBr-squareBiOBr-1 (b) BiOBr-circle BiOBr-4</p>		<p>300W Xe lamp</p>	<p>Degradation rate RhB MO phenol BiOBr-circle>BiOBr-square> N doped P25 Degradation rate: RhB 30min 100%</p>	<p>[6]</p>
<p>BiOI hydrothermal approach; Bi(NO₃)₃·5H₂O, KI, F127, glacial acetic acid; 180°C 24h and 300° 2h</p>		<p>500W Xe lamp</p>	<p>F127-BiOI>BiOI KF127-BiOI=0.229 kBiOI=0.108</p>	<p>[7]</p>
<p>BiOCl hydrothermal method; Bi(NO₃)₃·5H₂O, dulcitol, KCl, HNO₃/ KOH adjusted pH=4/6/8/10 160°C 24h</p>		<p>visible light</p>	<p>BiOCl-4>BiOCl-6>BiOCl-8>BiOCl- 10 Degradation rate: RhB 6 min more than 98% Degradation rate: TC-HCl 90 min 60%</p>	<p>[8]</p>
<p>BiOCl hydrothermal route; Bi(NO₃)₃·5H₂O, HNO₃, C-PAM, Sodium Citrate, 0.3g NaOH, 150°C4h</p>		<p>300W mercury lamp</p>	<p>BiOCl-150°>BiOCl-180°>BiOCl-120° BiOCl-12h>BiOCl-4h>BiOCl- 2h>BiOCl-1h BiOCl(1.2gNaOH)>BiOCl(0.9gNaOH)>BiOCl(0.6gNaOH)>BiOCl(0.3gNaO H)>BiOCl(0gNaOH) BiOCl>P25 K=0.0655</p>	<p>[9]</p>
<p>BiOCl hydrothermal route ; BOC-1 BOC-2 BOC-3 BOC-4 Bi(NO₃)₃·5H₂O, deionized water, Xylitol(0.1g,0.3g,0.5g,1.0g),KCl, KOH,160°C24h (a)BOC-1 (b)BOC-4</p>		<p>visible light</p>	<p>BOC-1>BOC-3>BOC-1>BOC-2> BOC-4 Degradation rate: RhB 20min 98%</p>	<p>[10]</p>



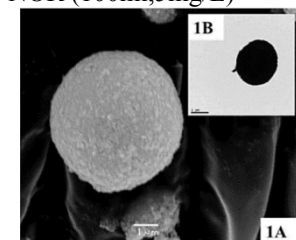
50 mg BiOCl
RhB(100ml,20mg/L)



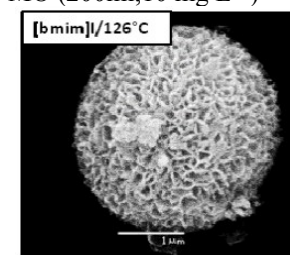
40 mg BiOCl
CBZ(50ml,2.5mg/L)



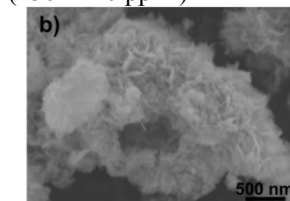
50 mg BiOCl
NOR (100ml,5mg/L)



0.08g BiOBr
MO (200ml,10 mg L⁻¹)



0.025 g BiOI
gallic acid solution
(250ml 20 ppm)



100 mg BiOI
RhB(20 mg L⁻¹)

BiOCl
ethylene glycolmediated solvothermal
method;
BiOCl-1/5/10/15
Bi(NO₃)₃·5H₂O,KCl(1/5/10/15),ethyl
ene glycol,160°C 12h

BiOCl-120/140/160/180;
one-stepsolvothermal method;
Bi(NO₃)₃,ethyleneglycol,HCl;
120/140/160/180°C 24h
BiOCl-140-400;
BiOCl-140,400°C 2h

BiOBr microspheres
solvothermal synthesis;
Bi(NO₃)₃·5H₂O ,KBr,ethylene glycol;
145°C18h

BiOI
solvothermal method;
Bi(NO₃)₃·5H₂O ,KI ,ethylene
glycol;120-216.6°C12-24.5h,
Bi(NO₃)₃·5H₂O , ionic liquid 1- 5
butyl-3-metilimidazolium
iodide,ethylene glycol;120-
216.6°C12-24.5h

BiOI:hollow flower
solvothermal method;
Bi(NO₃)₃·5H₂O ,KI ,ethylene glycol;
160°C24h

300W
xenon lamp

BiOCl-10>BiOCl-5>BiOCl-
15>BiOCl-1
Degradation rate:
CBZ 180min 70%

[11]

300W
xenon lamp

BiOCl-140>BiOCl-120>BiOCl-
160>BiOCl-180>BiOCl-140-400
Degradation rate:
NOR 120min 57.8%

[12]

12W
xenon lamp

BiOBr>BiOBr(with HA_c)
BiOBr(pH=2)>BiOBr(pH=other)
Degradation rate:
MO 60min 97%

[13]

12W
xenon lamp

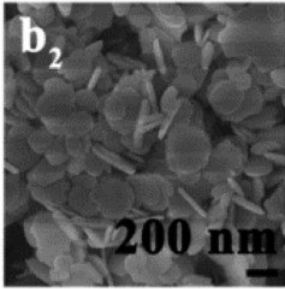
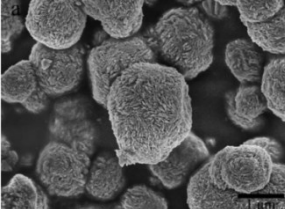
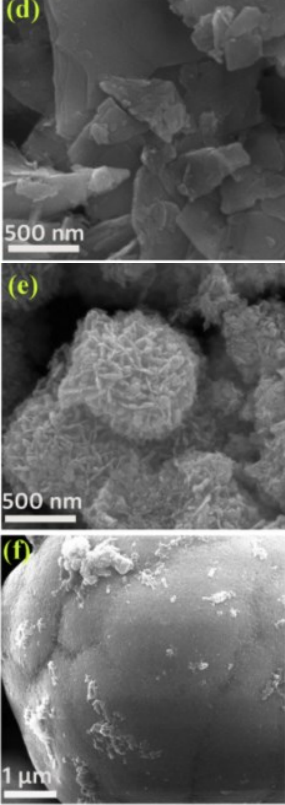
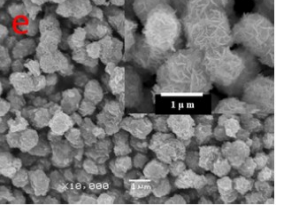
[bmim]I>KI(126°18h)>other
Degradation rate:
gallic acid 60 min 61%

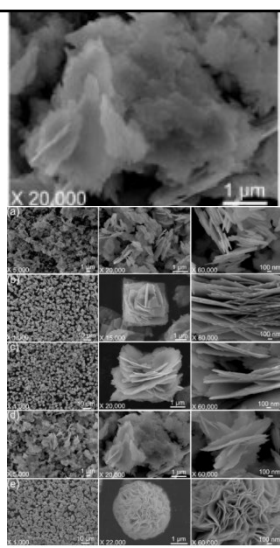
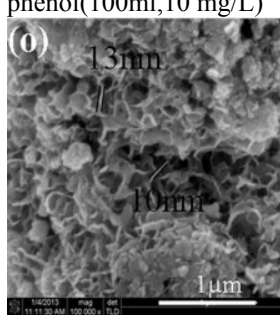
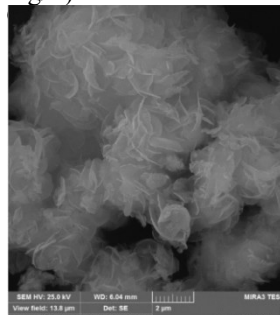
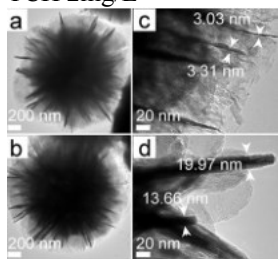
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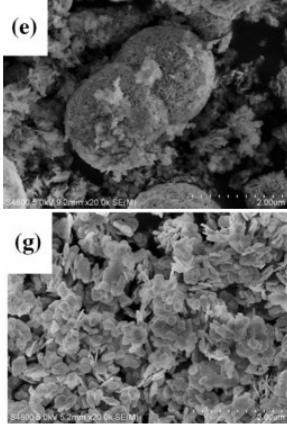
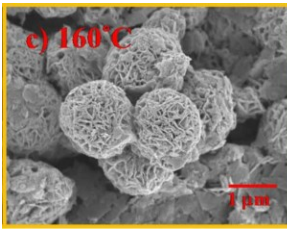
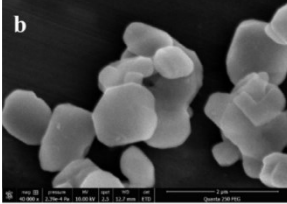
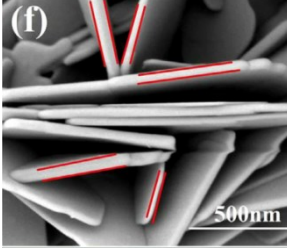
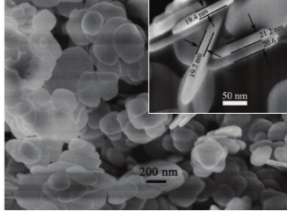
350W
Xe arclamp

hollow flowerBiOI>bulk BiOI
Degradation rate :
60min 99.6% RhB

[15]

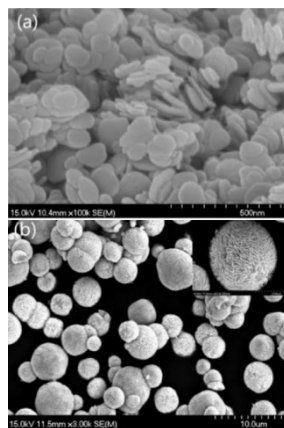
<p>BiOBr_xI_{1-x} solvothermal method; Bi(NO₃)₃·5H₂O, NH₄Br, NH₄I, ethylene glycol; 160 °C for 12 h</p>		<p>350W Xe arc lamp</p>	<p>BiOBr_xI_{1-x}(x=0.8)>BiOBr_xI_{1-x}(x=0.5) >BiOBr_xI_{1-x}(x=1)>BiOBr_xI_{1-x}(x=0.2) >BiOBr_xI_{1-x}(x=0)>P25 Degradation rate: RhB 90min 99%</p>	<p>[16]</p>
<p>BiOCl solvothermal modification method; OV-BOC Bi(NO₃)₃·5H₂O, NaCl, EG, 160 °C, 16 h BOC Bi(NO₃)₃·5H₂O, NaCl, EtOH, 160 °C, 16h</p>		<p>300W xenon lamp</p>	<p>OV-BOC+H₂O₂>OV-BOC>BOC >H₂O₂</p>	<p>[17]</p>
<p>BiOCl alcohol mediated solvothermal method; Bi(NO₃)₃·5H₂O, KCl, 1-ethanol/ 2-ethylene glycol/3-glycerol; 160 °C, 12h (d)BiOCl-1 (e)BiOCl-2 (f)BiOCl-3</p>		<p>350W xenon lamp</p>	<p>BiOCl-2>BiOCl-3>BiOCl-1 K=0.0118</p>	<p>[18]</p>
<p>BiOBr solvothermal route; Bi(NO₃)₃·5H₂O, KBr, deionized water (ETH, ISO, EG, GLY) 140 °C 16h</p>		<p>300W Xenon lamp</p>	<p>BiOBr(GLY)>BiOBr(EG)>BiOBr(ISO) >BiOBr(E)>BiOBr(W) Degradation rate : brilliant blue K-NR 120min 90.9%</p>	<p>[19]</p>
<p>0.2g BiOBr Brilliantblue K-NR (100ml, 30 mg L⁻¹)</p>				

<p>BiOBr solvothermal approach; $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, CTAB, ethanol, 150°C 24h (a)BiOBr-EtOH, (b)BiOBr-EG, (c)BiOBr-TB, (d)BiOBr-BA (e)BiOBr-ME</p>	 <p>0.025g BiOBr RhB (100ml, 10 mg L⁻¹) 0.1g BiOBr phenol(100ml, 10 mg/L)</p>	<p>300W Xenon lamp</p> <p>BiOBr(BA)>BiOBr(ME)>BiOBr(TB) >BiOBr(EtOH)>BiOBr(EG)>BiOBr (W)</p> <p>Degradation rate: RhB K=0.148 Degradation rate: Phenol 3h almost 20%</p> <p>[20]</p>
<p>BiOI hydrothermal or solvothermal method; $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, KI, H₂O, ETH, EG, GLY; 160°C, 12 h</p>	 <p>40 mg BiOI As(III)solution(80 mL 5 mg/L)</p>	<p>300W Xe lamp</p> <p>GLY>EG>ETH Degradation rate: As(III) 40 min 96.6%</p> <p>[21]</p>
<p>BiOI hydrolysis method (BiOI-H) solvothermal method (BiOI-ST); BiOI-ST: $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, KI , ethylene glycol distilled water; 180°C 12h</p>	 <p>0.68g/L BiOI TCH 2mg/L</p>	<p>1000W tungsten halogen lamp</p> <p>BiOI-ST>BiOI-H Degradation rate: TCH: 101.5 min 100%</p> <p>[22]</p>
<p>BiOCl-1 solvothermal process $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, PEG 10000, PEG 400, NaCl, 180°C 24h BiOCl-2 $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, CTAB, PEG 400, NaCl , 180°C 15h BiOCl $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, mannitol solution, NaCl, 160°C 3h (a)BiOCl-1 (b)BiOCl-2</p>	 <p>50 mg BiOCl BPA aqueous (50ml, 1×10^{-5} M)</p>	<p>300W Hg arc lamp</p> <p>BiOCl-1>BiOCl-2 Degradation rate: BPA 6h 96% Degradation rate: TOC 13h 96%</p> <p>[23]</p>

<p>BiOCl facile solvothermal method; $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, KCl, methanol ,desired volume fractions of water (0, 5, 10, and 15%)120°C12h BOC-1 BOC-2 BOC-3 BOC-4 (e)BOC-1 (g)BOC-3</p>		<p>300W xenon lamp</p>	<p>BOC-3>BOC-1>BOC-2>BOC-4 Degradation rate: MO 50min almost 100% Degradation rate: RhB 40min almost 100%</p>	<p>[24]</p>
<p>BiOX microwave-assisted solvothermal method; $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, KX, EG, EtOH, PEG, m icrowave 450W(10 20 30 60min)(120 140 160°C)pH (3, 5, 7, and 9) BiOAxB1-x KAB</p>		<p>350W xenon light</p>	<p>hydrogen evolution rate BiOI Ph=7>Ph=5>Ph=9>Ph=3 Ph=7(1,316.9 $\mu\text{mol h}^{-1}\text{g}^{-1}$) catalyst dosage 0.2g/L>other 1316.9 $\mu\text{mol h}^{-1}\text{g}^{-1}$ Catalyst type BiOI>BiOBr, BiOCl</p>	<p>[25]</p>
<p>BiOCl hydrolysis method; $\text{NaBiO}_3 \cdot 2\text{H}_2\text{O}$, deionized water, HCl,</p>		<p>500W xenon lamp</p>	<p>BiOI>BiOAxB1-x BiOCl(400mg/L)>BiOCl(300mg/L)> BiOCl(200mg/L)>BiOCl(100mg/L)> BiOCl(50mg/L) Degradation rate:BiOCl(300mg/L) ATL 60min 90% BiOCl(pH=5.2)>BiOCl(pH=6)>BiOCl (pH=7)>BiOCl(pH=8.7)>BiOCl(pH=8)</p>	<p>[26]</p>
<p>BiOCl hydrolytic method; bismuth nitrate, HCl, Sodium carbonate, pH=2</p>		<p>UV Irradiation (254nm, 10 W)</p>	<p>BiOCl>In₂O₃>P25 defluorination efficiency : 24h, 59.3%</p>	<p>[27]</p>
<p>BiOCl hydrolysis method; NaCl, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, ethanol, NaCl , 90°C 3h</p>		<p>500W xenon lamp</p>	<p>RhB> MO > MB . Degradation rate: MB 30min 94%</p>	<p>[28]</p>

MO/MB(40ml,10mg/L)

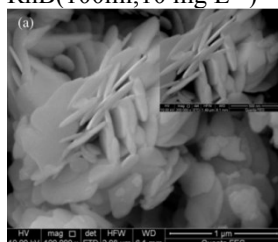
BiOBr-1 a
 hydrolysis process;
 $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, KBr, EG, deionised water
 BiOBr-2 b
 solvothermal synthesis;
 $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, KBr, EG, 160°C, 10h



300W xenon lamp
 UV irradiation:
 RhB 120min 97%
 BiOBr-1>P25>BiOBr-2
 vis-light irradiation:
 BiOBr-1>BiOBr-2>P25 [29]

0.02g BiOBr
 RhB(100ml, 10 mg L⁻¹)

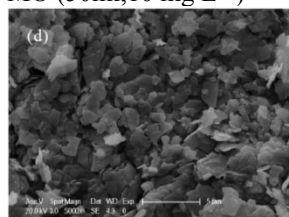
BiOBr
 hydrolysis or alcoholysis method;
 BiBr_3 , water(H₂O), ethanol, isopropyl alcohol, room temperature, magnetic stirring 20°C 40°C 60°C



350W Xenon lamp
 BiOBr-60(IPA)>BiOBr(H₂O)>BiOBr(EtOH) [30]
 Degradation rate :
 BiOBr(IPA)
 MO 75min 98.9%
 BiOBr(H₂O)
 MO 75min 91.3%

0.03g BiOBr
 MO (50ml, 10 mg L⁻¹)

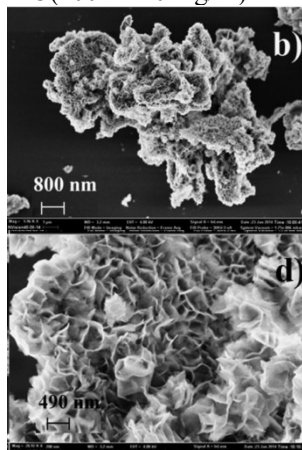
BiOI
 hydrolysis method;
 $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, KI, deionized water:
 10-50ml, room temperature.



300W Xe arc lamp
 BiOI-40>BiOI-50>BiOI-30>BiOI-20 >BiOI-10 [31]
 Degradation rate:
 MO 120 min 71.4%

0.05 g BiOI
 MO(100 ml 10 mg/L)

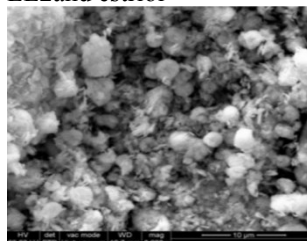
BiOX(Cl/I) BiOCl /BiOI
 hydrolysis method
 NaBiO_3 , ethanol, DI water, HCl/HI
 (b)BiOCl
 (d)BiOI



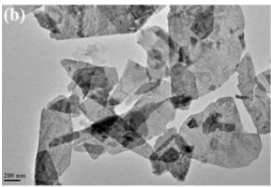
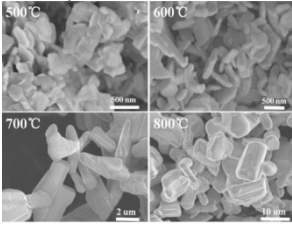
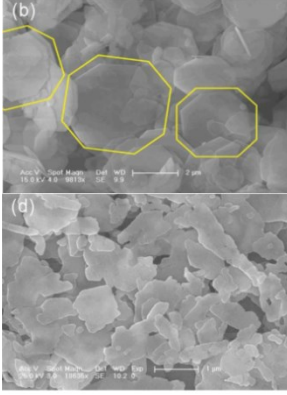
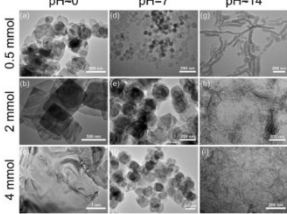
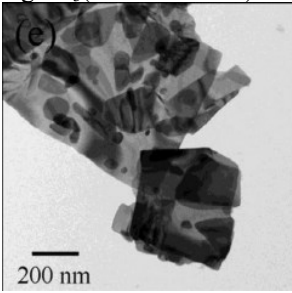
four 128W/m² 254nm bulbs
 Degradation rate: BiOI>BiOCl>TiO₂ EE2 30min 100% [32]
 Degradation rate: BiOCl>BiOI>TiO₂ estriol 30min 100%

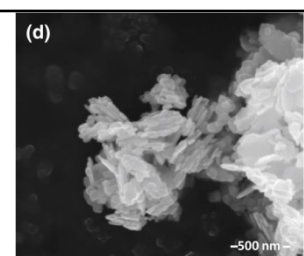
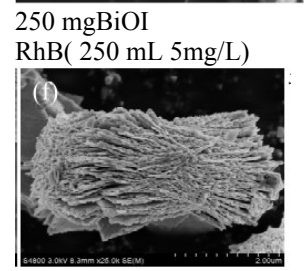
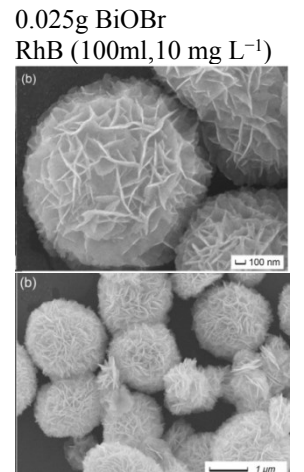
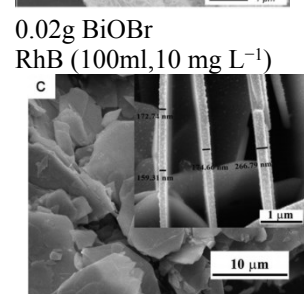
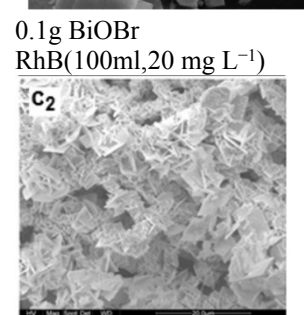
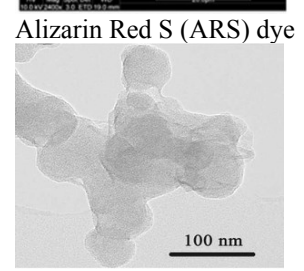
BiOX(500mg/L)
 EE2and estriol

BiOX
 facile co-precipitation method,
 $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, NaBr solution,
 stirre 24 h
 low-temperature solution route,
 facile chemical etching method

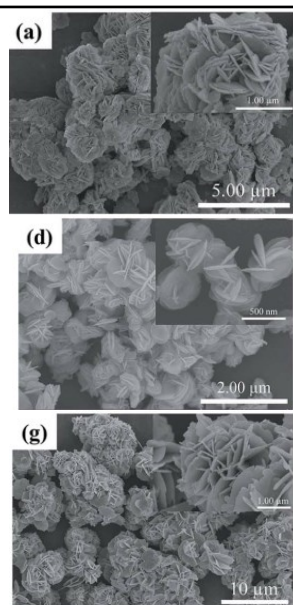


BiOI_{0.5}Br_{0.5}> BiOI>BiOBr [33]
 Degradation rate:
 Lindane 120min 95%

<p>Br-BiOI chemical precipitation route; $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, KI, NaBr, ethylene glycol; room temperature</p>		<p>500W Xe lamp visible light</p>	<p>15% Br-BiOI > 20% Br-BiOI > 10% Br-BiOI > 5% Br-BiOI > BiOI Degradation rate : 15% Br-BiOI ; 2.5h RhB almost 100% 15% Br-BiOI; 10h phenol more than 50%</p>	<p>[34]</p>
<p>$\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ chemical precipitation method; $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, HNO_3, CTAC, NaOH, 400°C-800°C</p>		<p>500W xenon lamp</p>	<p>$\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ > BiOCl > TiO_2/N > Bi_2O_3 Degradation rate: RhB 60min 95%</p>	<p>[35]</p>
<p>BiOCl two-phase reaction; BiOCl-1 octagonal; $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, HCl, deionized water BiOCl-2 $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, KCl, deionized water (b) BiOCl-1 (d) BiOCl-2</p>		<p>500W xenon lamp</p>	<p>BiOCl-1 > BiOCl-2 Degradation rate: MO 80min almost 100%</p>	<p>[36]</p>
<p>BiOX two-phase method; BiOCl/Br-NSS $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, ODE, OA, OLA, N_2, 170°C, KBr/I/Cl, HNO_3, 100°C, 0.5h</p>		<p>300W xenon lamp</p>	<p>BiOBr-acid0.5 > BiOBr-neutral0.5 > BiOBr-acid4 Degradation rate: RhB 50min 96% Degradation rate: MO 120min 39% O_2 evolution BiOBr-acid4 best</p>	<p>[37]</p>
<p>BiOI nanoplates sonochemical method; $\text{Bi}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, NaI, deionized water, NaOH; 35kHz ultrasonic bath at 80°C 5h.</p>		<p>Xe lamp</p>	<p>pH=12 > pH=10 > pH=8 Degradation rate: RhB 180min 81.19%</p>	<p>[38]</p>

<p>BiOI microwave method $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, acetic acid, EDTA, KI, 110°C, 5min</p>		<p>6000K Xenon lamp</p>	<p>B110-40>B130-40>B110-40>B150-40>B110-20>B110-00 Degradation rate: RhB 20min 98.2%</p>	<p>[39]</p>
<p>BiOBr microwave-assisted ionothermal synthesis; $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, HB (OB, HK, CTAB, MI), EG, 1000W, 160°C/400°C 4h</p>		<p>300W Xenon lamp</p>	<p>BiOBr>BiOBr(THB)>BiOBr(BQ)>BiOBr(EDTA)>BiOBr(AgNO_3) Degradation rate : RhB 180min 99.57% TOC 180min 12.24%</p>	<p>[40]</p>
<p>BiOBr porous nanospheres microwave-assisted ionic liquid Synthesis; $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, PVP K30, EG, [C16mim]Br, microwave reactor 160°C 20min BiOBr hollow microspheres(without pvp)</p>		<p>300W Xenon lamp</p>	<p>Porous BiOBr>Hollow BiOBr Degradation rate : RhB 60min almost 100%</p>	<p>[41]</p>
<p>BiOBr combustion method; $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, NH_4Br, urea, nitric acid, deionized water; 300°C</p>		<p>300W xenon lamp</p>	<p>NH_4Br/ $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (3, 4, and 5) BiOBr-5>BiOBr-4>BiOBr-3 Degradation rate : RhB 120min 91.6%</p>	<p>[42]</p>
<p>BiOBr electrospinning and postcalcination BiBr_3 500°C BiBr_3 (as 1%, 2%, 3% and 4%) in polymer (PAN)</p>		<p>150W Xe lamp</p>	<p>BiOBr(X=4)>BiOBr(X=1)>BiOBr(X=3)>BiOBr(X=2)</p>	<p>[43]</p>
<p>BiOBr nanosheets Liquid Phase Exfoliation $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, KBr, formamide,</p>		<p>500W Xenon lamp CO_2 reduction: 200mg BiOBr 300W Xe lamp</p>	<p>monolayered BiOBr>bulk BiOBr Degradation rate: MO 300min 33% CO_2 reduction performance: monolayered BiOBr>bulk BiOBr</p>	<p>[44]</p>

BiOClBiOBr BiOI
solvent-free grinding mechanical
method;
Bi(NO₃)₃·5H₂O, KBr/I/Cl, agate
mortar, ground
for 5 min (0.5/1/2/3/5/10 min)
(a) BiOCl
(d) BiOBr
(g) BiOI



500W
xenon lamp
BiOCl>BiOBr>BiOI

[45]

10 mg photocatalyst
RhB/MB(50 mL 5mg/L)

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