A Z-scheme magnetic recyclable Ag/AgBr@$CoFe_2O_4$ photocatalyst with enhanced photocatalytic performance for pollutant elimination and antibacteria

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Method

1. Characterization

The powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 diffractometer using Cu-Kα radiation (λ = 1.5418 Å) operated in the 2θ range of 10 – 80° at a scanning rate of 7°/min. Scanning electron microscope (SEM) images were obtained on a field emission microscope (JEOL JWSM-7001F) which was equipped with an energy-dispersive X-ray spectroscope (EDS) and operated at an acceleration voltage of 10 kV. The X-ray photoelectron spectroscopy (XPS) spectra were measured on an ESCALab MKII X-ray photo-electron spectrometer with Mg Kα radiation and the spectra were calibrated to the C 1s peak at 284.6 eV. The ultraviolet-visible (UV-vis) diffuse reflectance spectra were carried out by a UV-3600Plus UV–vis spectrophotometer (Shimadzu Corporation, Japan) in solid state with $BaSO_4$ as a reference (before the UV-vis absorption spectra test, 0.03 g samples and 0.07 g $BaSO_4$ were homogenized by grounding in an agate mortar). The magnetic properties of the samples were monitored by a vibrating sample magnetometer (VSM) (Quantum Design Corporation, USA) under a maximum applied field of ± 2 T. Photocurrent measurements were performed on an electrochemical workstation (CHI 660B, Chenhua Instrument Company, Shanghai, China). The photoluminescence (PL) intensity of the prepared samples were collected on a Varian Cary Eclipse spectrometer.

Table S1. Material input mass and ratio.

sample	Mass of raw material(g)			$m(CoFe_2O_4)/m(AgNO_3)$[a]
	$AgNO_3$	$CoFe_2O_4$	NaBr	
Ag/AgBr	0.4	0	0.2422	0%
10% Ag/AgBr@$CoFe_2O_4$	0.4	0.004	0.2422	10%
15% Ag/AgBr@$CoFe_2O_4$	0.4	0.006	0.2422	15%
20% Ag/AgBr@$CoFe_2O_4$	0.4	0.008	0.2422	20%

a. the weight ratio of $CoFe_2O_4$ to $AgNO_3$

Table S2. Ag/AgBr-based photocatalysts for pollutant degradation.

Photocatalysts	**Pollutants**	**Degradation efficiency**	**Disinfection activity**	**Magnetic recovery**	**Reaction Conditions**
AgBr@Ag@TiO_2[1]	benzyl alcohol (BA)	91%, 8h	-	-	300 W, Xe lamp, λ> 420 nm
Ag/AgBr/Bi_5O_7I[2]	Rhodamine B (RhB)	98%, 1h	-	-	500 W, Xe lamp, λ> 420 nm
Ag-AgX/RGOs (X = Cl,Br,I)[3]	Escherichia coli K-12	-	10^7, 8 min	-	15W, Twelve fluorescent tubes, full wavelength
Ag/AgBr/$ZnFe_2O_4$[4]	Rhodamine B (RhB)	98%, 5h	-	Yes	500 W, metal halide lamp, λ> 420 nm
Fe_3O_4@SiO_2@Ag/AgBr[5]	Acid Orange 7	93%, 1 h	-	Yes	300 W, Xe lamp, λ> 400 nm
γ-Fe_2O_3@SiO_2@AgBr:Ag[6]	Acid Orange 7	93.1%, 20 min	-	Yes	500 W Xe lamp, λ> 400 nm
ZnO/AgBr/Fe_3O_4/Ag_3VO_4[7]	Rhodamine B (RhB)	98%, 105 min	-	Yes	50 W, LED source
Ag/AgBr@Fe_2O_3[8]	bisphenol A (BPA)	69.0%, 3h	10^5, 13 min	Yes	300 W, Xe lamp, λ> 420 nm
Fe_2O_3–AgBr cloth[9]	parachlorophenol (4-CP)	52.8%, 2h	-	Yes	300 W, Xe lamp, λ> 400 nm
This work	bisphenol A (BPA)	73.9%, 2h	10^7, 20 min	Yes	300 W, Xe lamp, λ> 420 nm

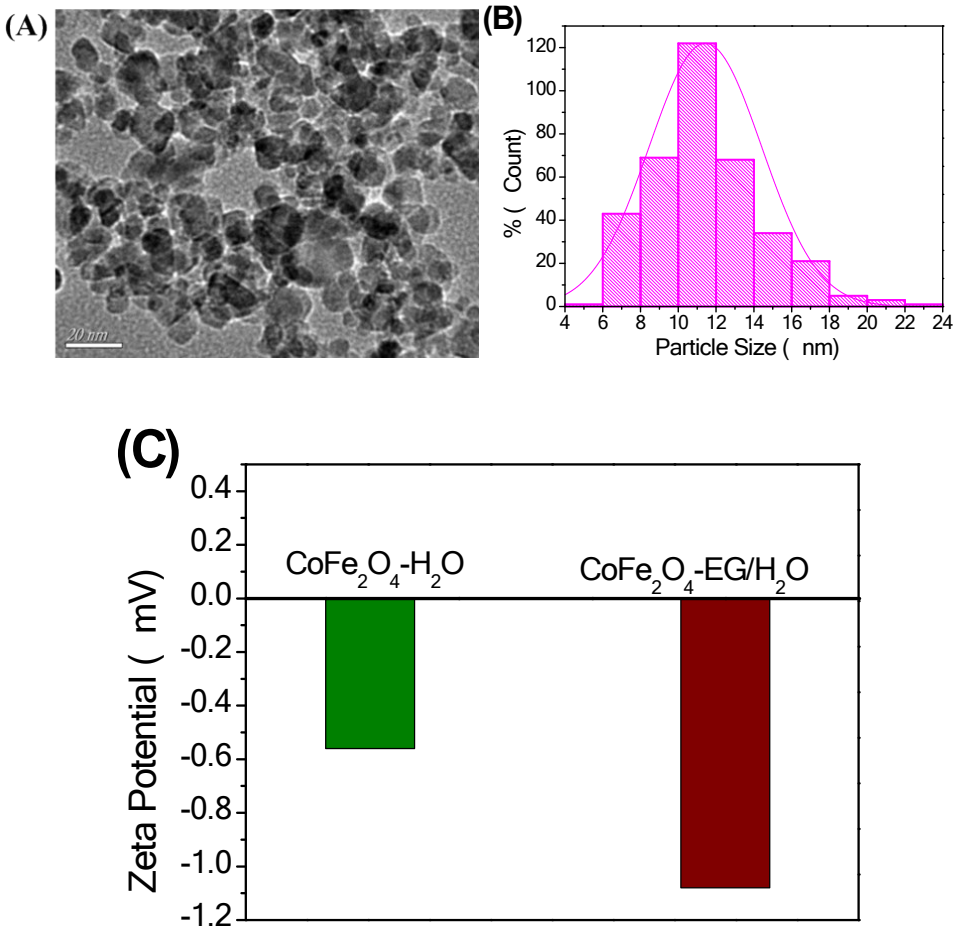
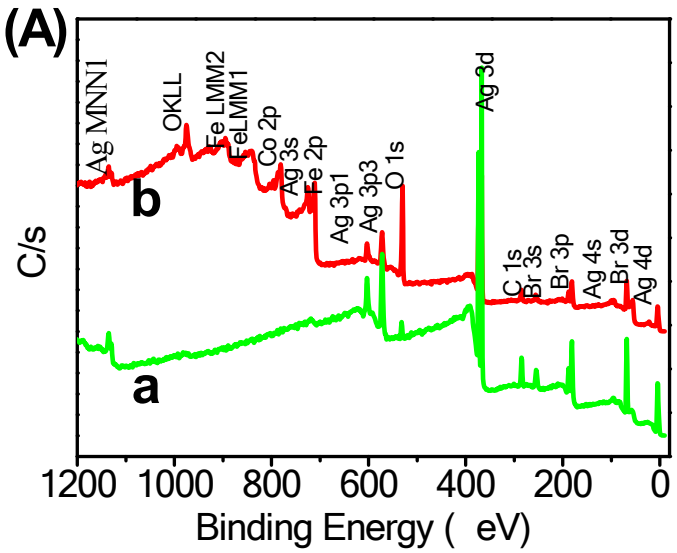


Fig. S1. (A) TEM image of $CoFe_2O_4$ NPs; (B) size distribution histogram with Gaussian-fitting curve of the as-prepared $CoFe_2O_4$ NPs; (C) The Zeta potential of $CoFe_2O_4$ in different solution.



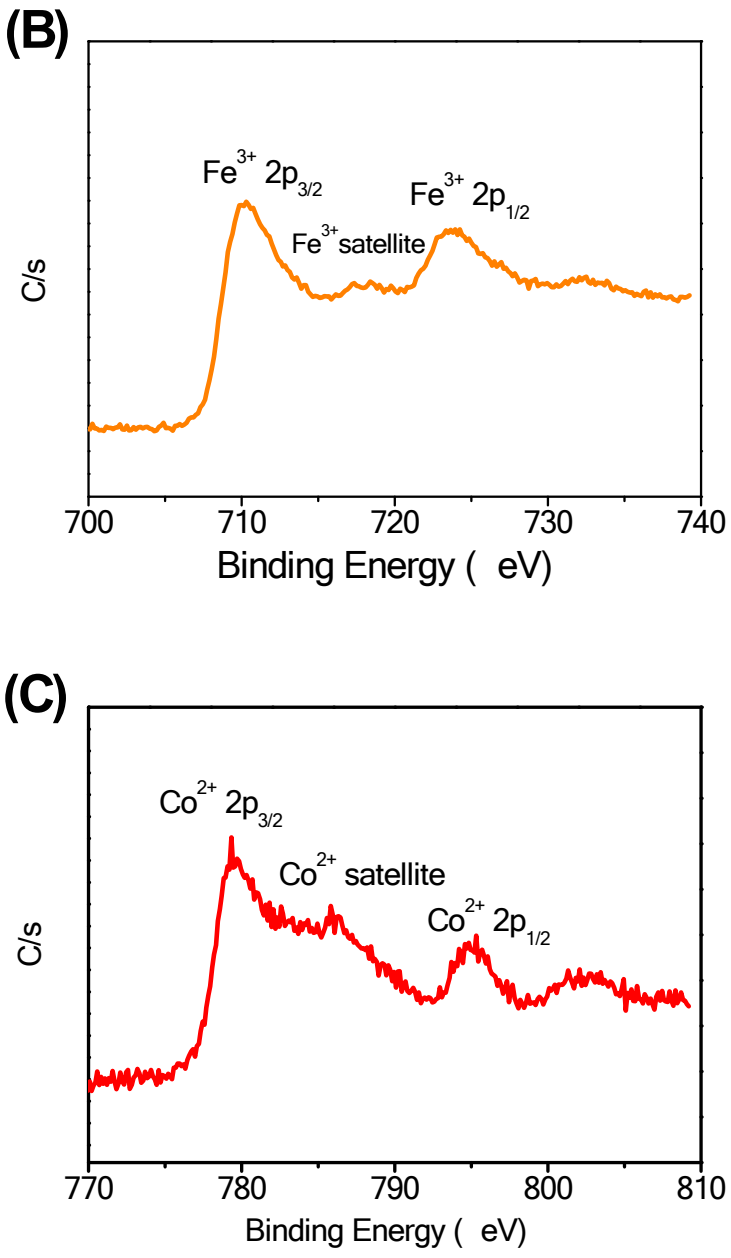
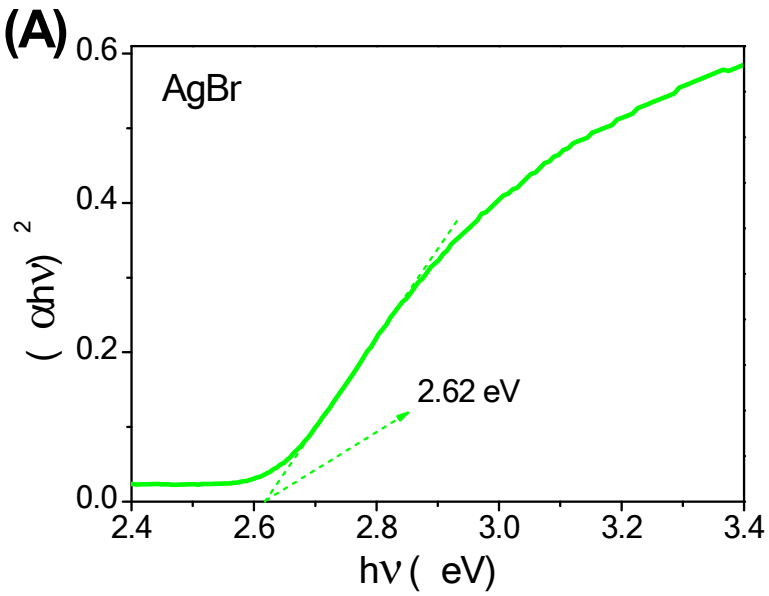


Fig. S2. (A) XPS survey spectra of (a) Ag/AgBr and (b) 15% Ag/AgBr@$CoFe_2O_4$ composite. XPS spectra of the as-prepared photocatalysts: (B) Fe 2p and (C) Co 2p of 15% Ag/AgBr@$CoFe_2O_4$ composite.



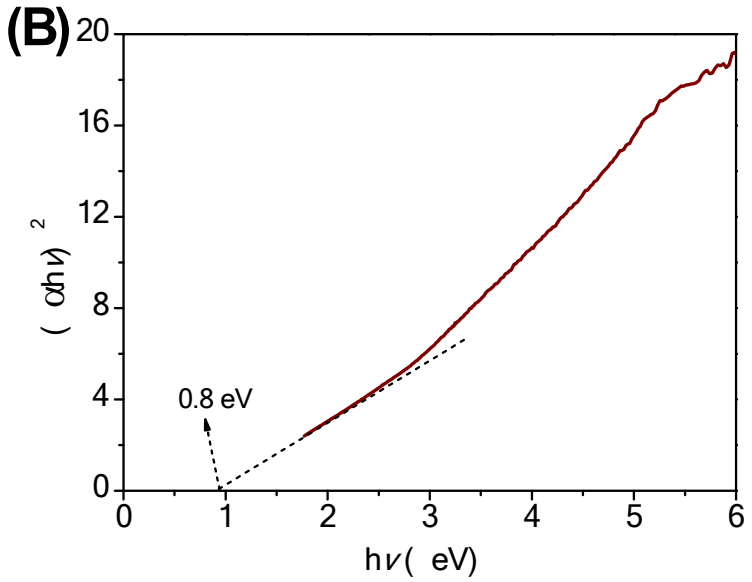
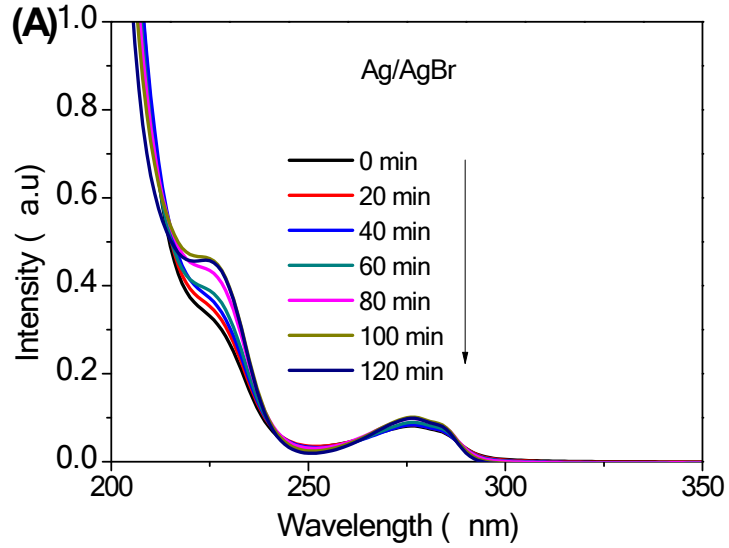
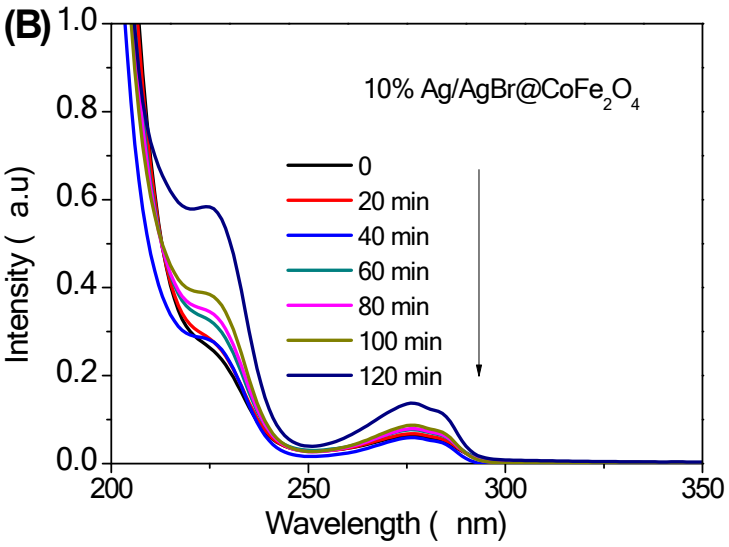
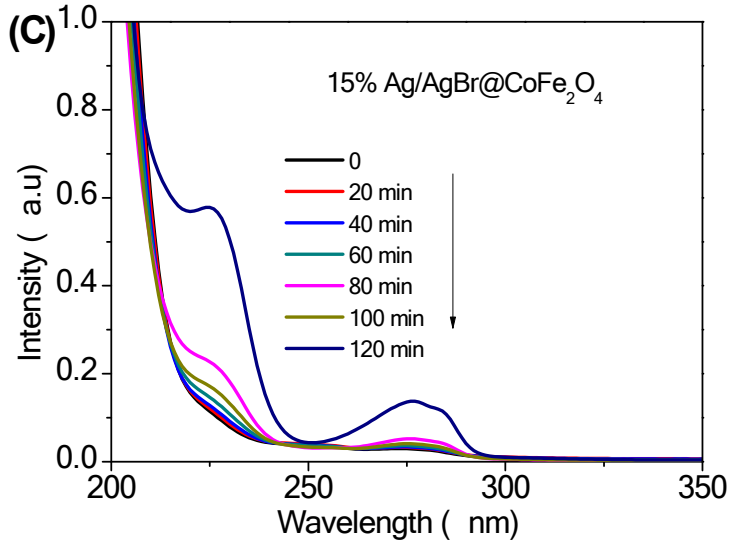
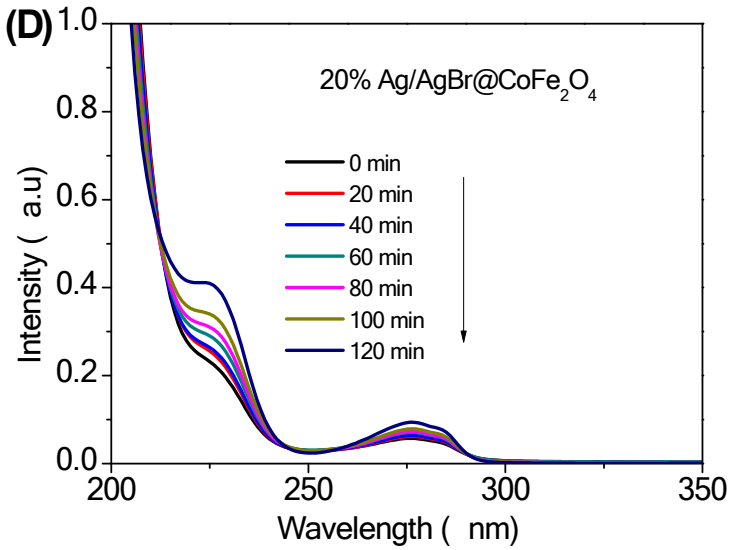


Fig. S3. $(\alpha h\nu)^2$ vs. $(h\nu)$ plots of (A) AgBr and (B) $CoFe_2O_4$.


(A)
Ag/AgBr
0 min
20 min
40 min
60 min
80 min
100 min
120 min
Intensity (a.u)
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
200
250
300
350


(B)
10% Ag/AgBr@CoFe2O4
0
20 min
40 min
60 min
80 min
100 min
120 min
Intensity (a.u)
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
200
250
300
350


(C)
15% Ag/AgBr@CoFe2O4
0
20 min
40 min
60 min
80 min
100 min
120 min
Intensity (a.u)
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
200
250
300
350


(D)
20% Ag/AgBr@CoFe2O4
0 min
20 min
40 min
60 min
80 min
100 min
120 min
Intensity (a.u)
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
200
250
300
350

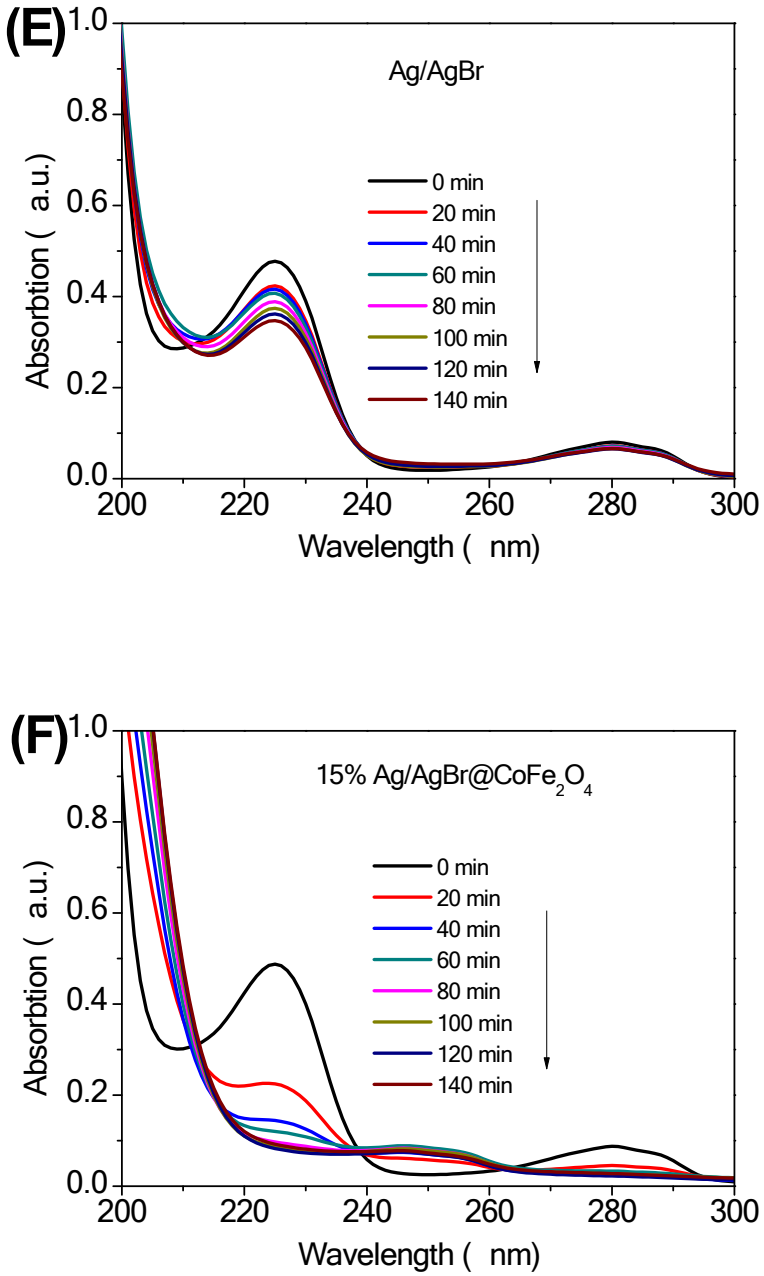


Fig. S4 The evolution of the absorption spectra of BPA (A, B, C, D) and 4-CP (E, F) over time in the presence of Ag/AgBr and Ag/AgBr@$CoFe_2O_4$ composites with different $CoFe_2O_4$ content.

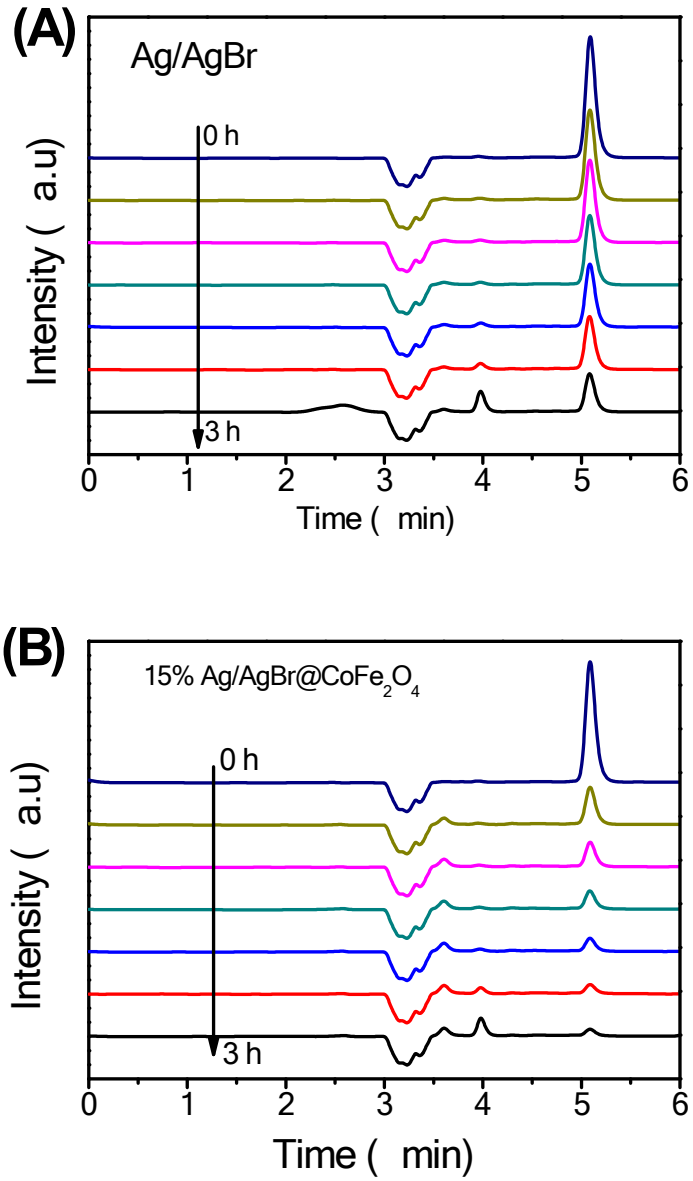


Fig. S5. The HPLC of the BPA degraded solution in the presence of (A) Ag/AgBr and (B) 15% Ag/AgBr@$CoFe_2O_4$ composites after irradiation for 120 min.

Without photocatalysts, the HPLC pattern of BPA solution shows a strong characteristic peak at 5.08 min. In the present of photocatalysts the characteristic peak of BPA was disappeared after irradiating for 120 min, confirming that BPA was decomposed.

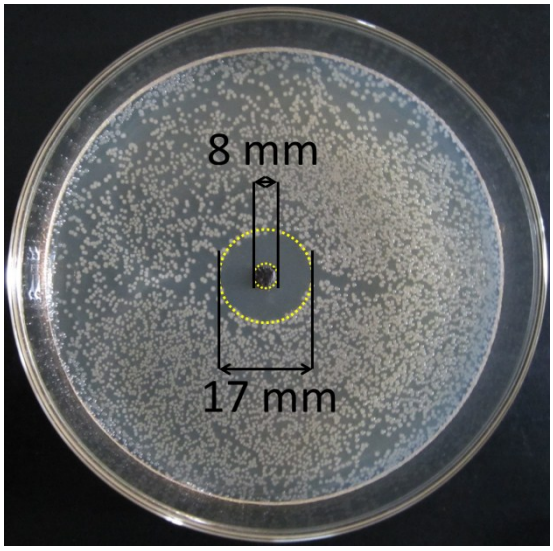


Fig. S6 The representative inhibition zone of 15% Ag/AgBr@$CoFe_2O_4$ disks against E. coli after 16 h incubation in the dark.

The zone of inhibition test was carried out to identify the antibacterial activities of the prepared photocatalysts in dark. In a typical procedure, a bit of the as-prepared powder photocatalysts were placed on the nutrient agar medium that has been inoculated with 100 µL (1 *10^3 cfu/mL) of the prepared Escherichia coli (E. coli) bacteria suspension. Then the plates were incubated at 37℃ for 16 h in dark. In Fig. S5, it is clearly that the 15 % Ag/AgBr@$CoFe_2O_4$ composite has a clear inhibition zone of about 17 mm against E. coli. Indicating the 15 % Ag/AgBr@$CoFe_2O_4$ composite has a good antibacterial ability in the dark.

3.8. Photoluminescence analysis

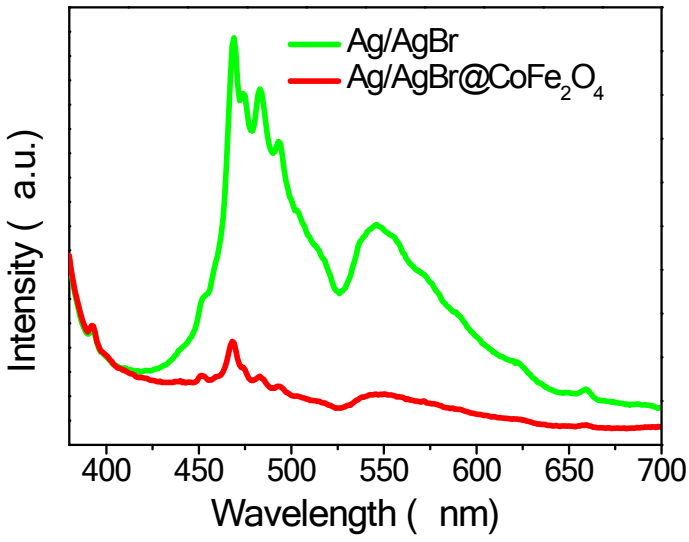


Fig. S7 PL spectra of Ag/AgBr and Ag/AgBr@$CoFe_2O_4$ composites.

Photoluminescence (PL) spectra measurement is another method that can reveal the information of the separation and recombination of photo-induced charge carriers.[10] Therefore, PL spectra of the as-prepared Ag/AgBr and Ag/AgBr@$CoFe_2O_4$ composites were carried out to confirm the charge transfer, migration and recombination processes in photocatalysts. As shown in Fig. S6, the PL spectra of Ag/AgBr composites show the similar peaks center position with that of pure Ag/AgBr, but an evidently decrease in the peak intensity were observed as the $CoFe_2O_4$ were loaded on the surface of Ag/AgBr particles. Indicating the introduction of $CoFe_2O_4$ NPs enables effective suppression of the detrimental electron−hole recombination. PL results verified the enhanced separation rate of electron−hole pairs by coupling the $CoFe_2O_4$ on the surface of Ag/AgBr and that may enhance the photocatalytic performance.

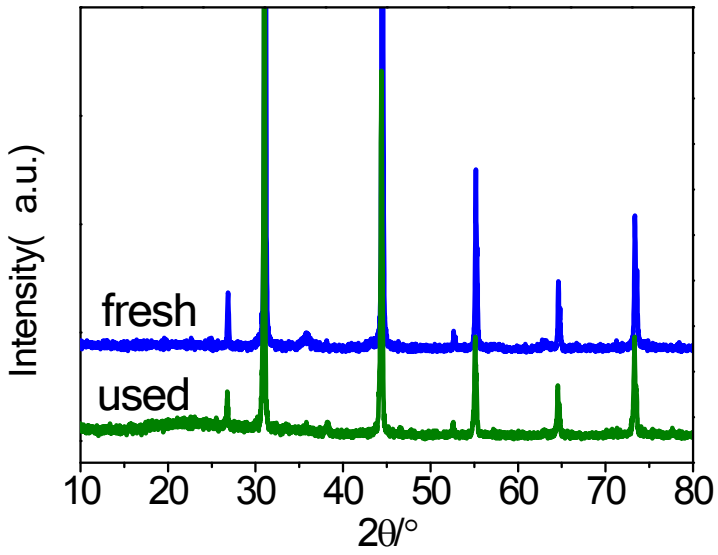


Fig. S8. The XRD patterns of 15% Ag/AgBr@$CoFe_2O_4$ before and after photocatalysis.

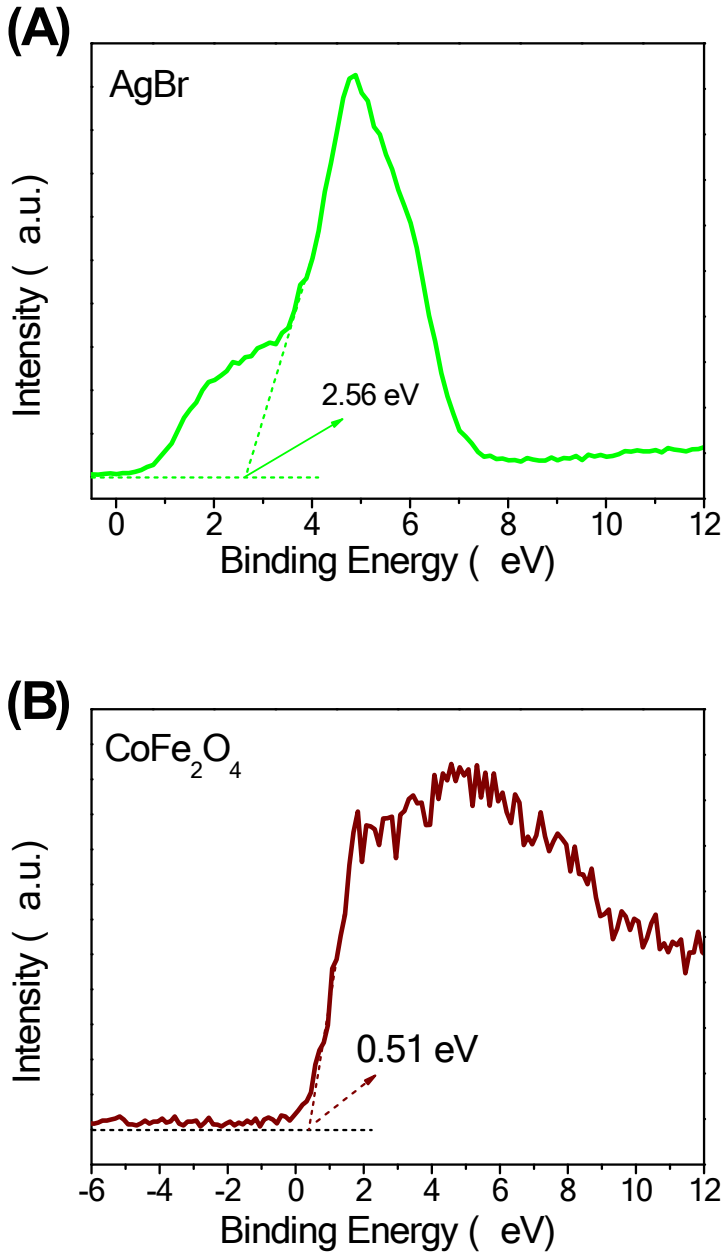


Fig. S9. Valence-band XPS spectra of the (A) Ag/AgBr and (B) $CoFe_2O_4$.

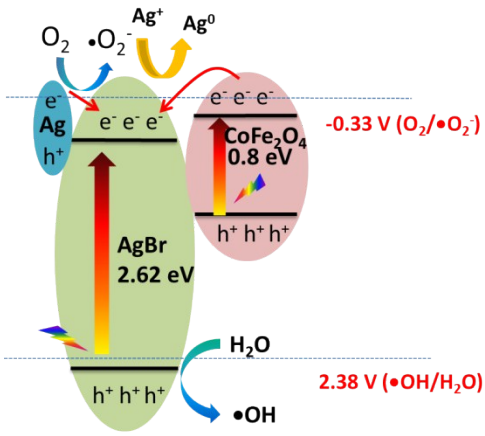


Fig. S10. The hypothesized Type II structure.

Reference

1. P. Zhang, P. Wu, S. Bao, Z. Wang, B. Tian and J. Zhang, *Chem. Eng. J.*, 2016, 306, 1151-1161.
2. Z. Zhao, M. Wang, T. Yang, M. Fang, L. Zhang, H. Zhu, C. Tang and Z. Huang, *J. Mol. Catal. A-Chem.*, 2016, 424, 8-16.
3. D. Xia, T. An, G. Li, W. Wang, H. Zhao and P. K. Wong, *Water Res.*, 2016, 99, 149-161.
4. X. Li, D. Tang, F. Tang, Y. Zhu, C. He, M. Liu, C. Lin and Y. Liu, *Mater. Res. Bull.*, 2014, 56, 125-133.
5. G. Li, K. H. Wong, X. Zhang, C. Hu, J. C. Yu, R. C. Chan and P. K. Wong, *Chemosphere*, 2009, 76, 1185-1191.
6. B. Tian, T. Wang, R. Dong, S. Bao, F. Yang and J. Zhang, *Appl. Catal. B: Environ.*, 2014, 147, 22-28.
7. M. Shekofteh-Gohari and A. Habibi-Yangjeh, *RSC Adv.*, 2016, 6, 2402-2413.
8. S. Huang, Y. Xu, Z. Chen, M. Xie, H. Xu, M. He, H. Li and Q. Zhang, *RSC Adv.*, 2015, 5, 71035-71045.
9. H. Zhao, L. Zhang, X. Gu, S. Li, B. Li, H. Wang, J. Yang and J. Liu, *RSC Adv.*, 2015, 5, 10951-10959.
10. S. Bai, J. Jiang, Q. Zhang and Y. Xiong, *Chem. Soc. Rev.*, 2015, 44, 2893-2939.