Electronic Supplementary Information

ZnO@ZIF-8 core-shell heterostructures with improved photocatalytic activity

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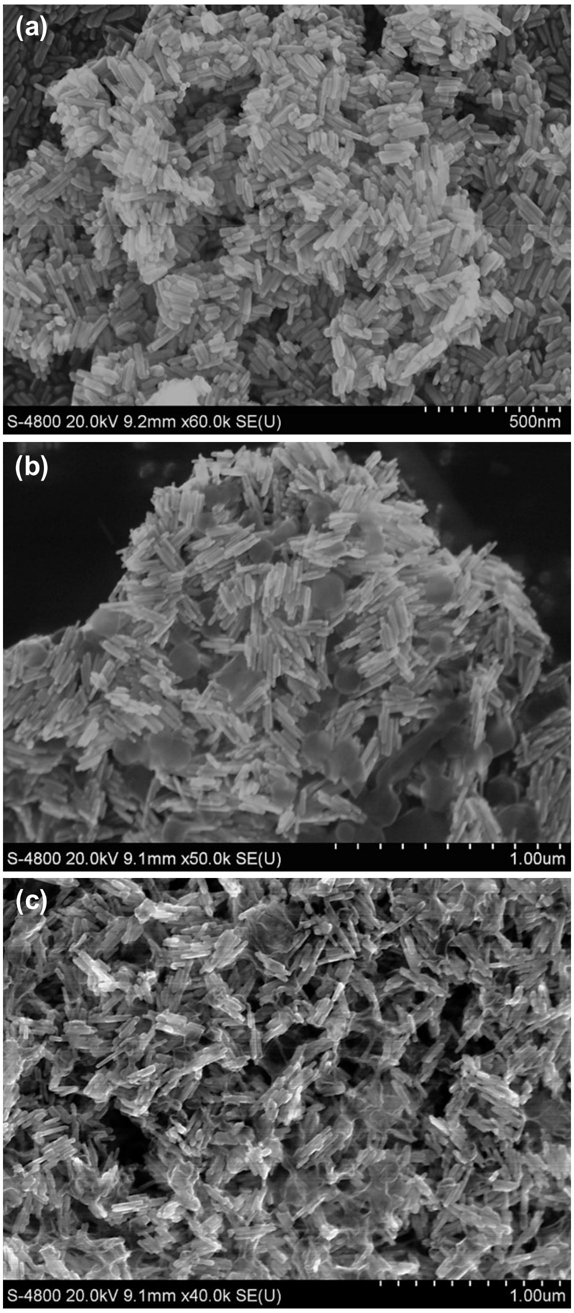

Fig. S1 (a) SEM image of ZnO@ZIF-8 with a concentration of 2 mg/mL. (b) SEM image of ZnO@ZIF-8 with a concentration of 5 mg/mL. (c) SEM image of ZnO@ZIF-8 with a concentration of 10 mg/mL.

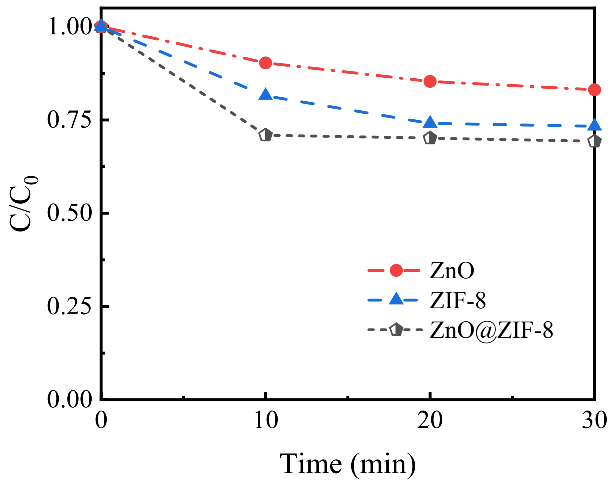

Fig. S2 Dark adsorption experiments of ZnO, ZIF-8, and ZnO@ZIF-8 for MB. The as-prepared nanoparticles (50 mg) were mixed with 50 mL 1.0 × 10^{-5} mol/L MB solution (3.19 mg/L) under magnetic stirring for 30 min in darkness to uniformly disperse the photocatalyst powder. 1 mL of the liquid part was collected from the mixed solution every 10 min with a syringe and filtered using a microporous membrane (0.22 μm).

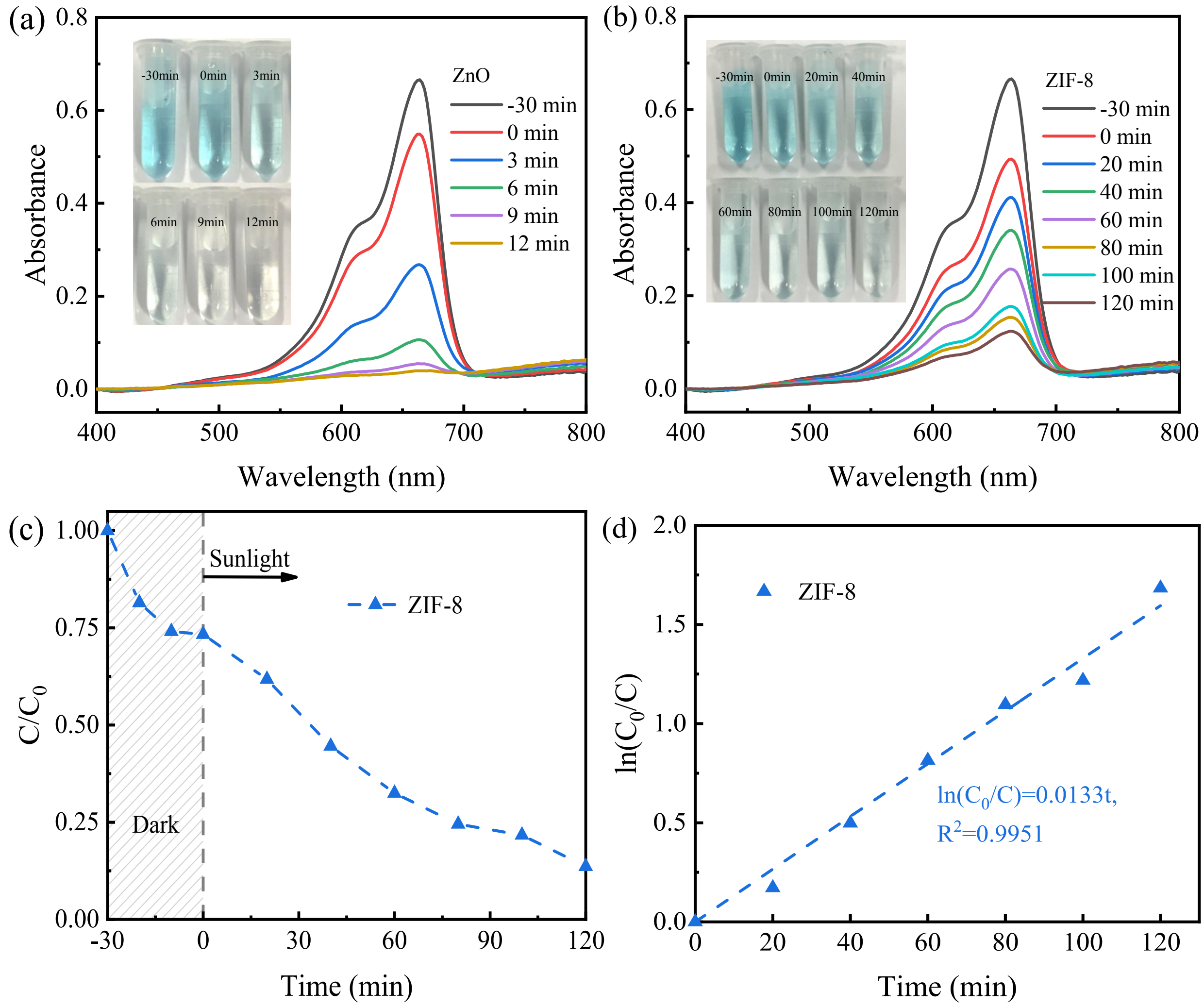

Fig. S3 Time-dependent UV–Vis absorption spectra for the MB degradation using (a) ZnO photocatalyst and (b) ZIF-8 photocatalyst. (Inset a and b: photographs of color change of photodegradation reaction solution). (c) Photocatalytic degradation of MB in aqueous solution using ZIF-8 photocatalyst. (d) Plots of $\ln(C_0/C)$ vs reaction time for the MB photocatalytic degradation using ZIF-8 photocatalyst. 50 mg of photocatalyst was added to 50 mL of 1.0×10^{-5} M dye aqueous solution.

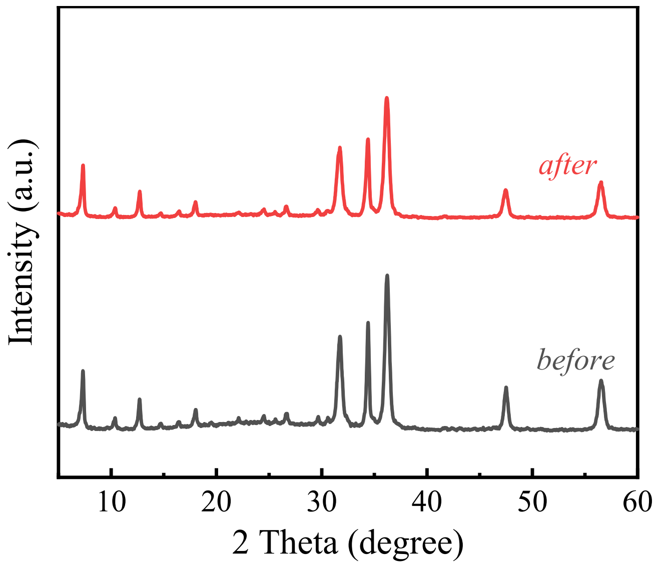

Fig. S4 XRD patterns of the ZnO@ZIF-8 after the cyclic experiment

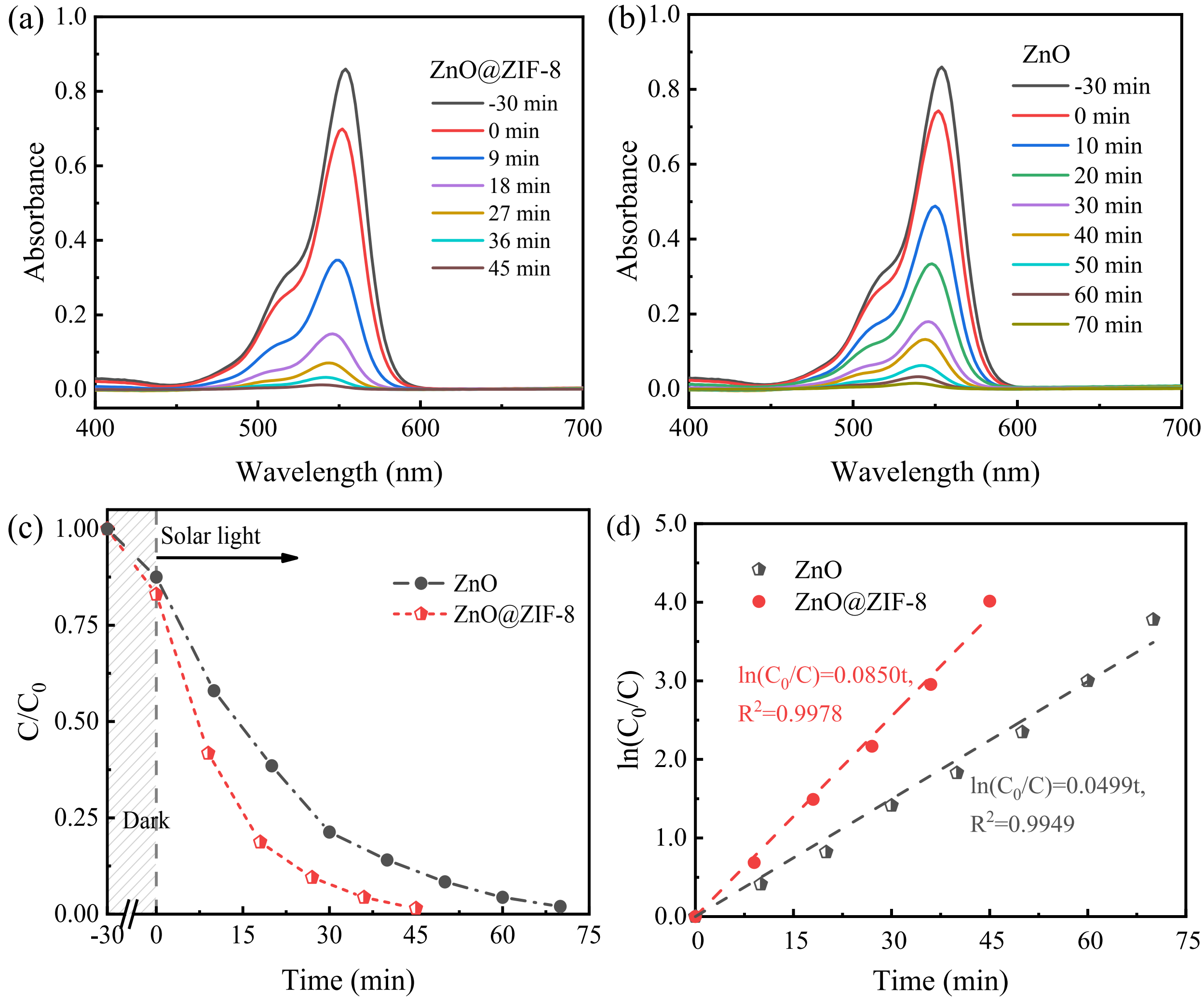

Fig. S5 Time-dependent UV–Vis absorption spectra for the Rhodamine B (RhB) degradation using ZnO@ZIF-8 (a) and (b) ZnO photocatalyst. (c) Photocatalytic degradation of RhB in aqueous solution using different photocatalyst nanoparticles. (d) Plots of $\ln(C_0/C)$ vs reaction time for the RhB photocatalytic degradation using various photocatalyst nanoparticles. 50 mg of photocatalyst was added to 50 mL of 1.0×10^{-5} M dye aqueous solution.

The position of the valence band (VB) and the conduction band (CB) can be calculated according to the following formulas:

$$E_{VB}=X-E^{e}+0.5E_{g} \quad (1)$$

$$E_{CB}=E_{VB}-E_{g} \quad (2)$$

where E_{VB} is the band edge of the VB, E_{CB} is the band edge of the CB, X is the electronegativity average of the atoms, and E^{e} is the energy of the free electrons at the hydrogen level (about 4.5 eV).[1] The bandgap values derived from these spectra were 3.12 and 3.17 eV for the ZnO and ZnO@ZIF-8 nanorods, respectively (Fig. S6b). Since the X value of ZnO is 5.79,[2] the VB and CB of ZnO are calculated to be 2.85 eV and -0.27 eV combined with the above formula. The measured VB of ZIF-8 is reported as 1.60 eV, [3] thus, the CB edge position of ZIF-8 can be calculated as -3.40 eV. In addition, the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of MB were -0.94 eV and 0.92 eV, respectively.[4]

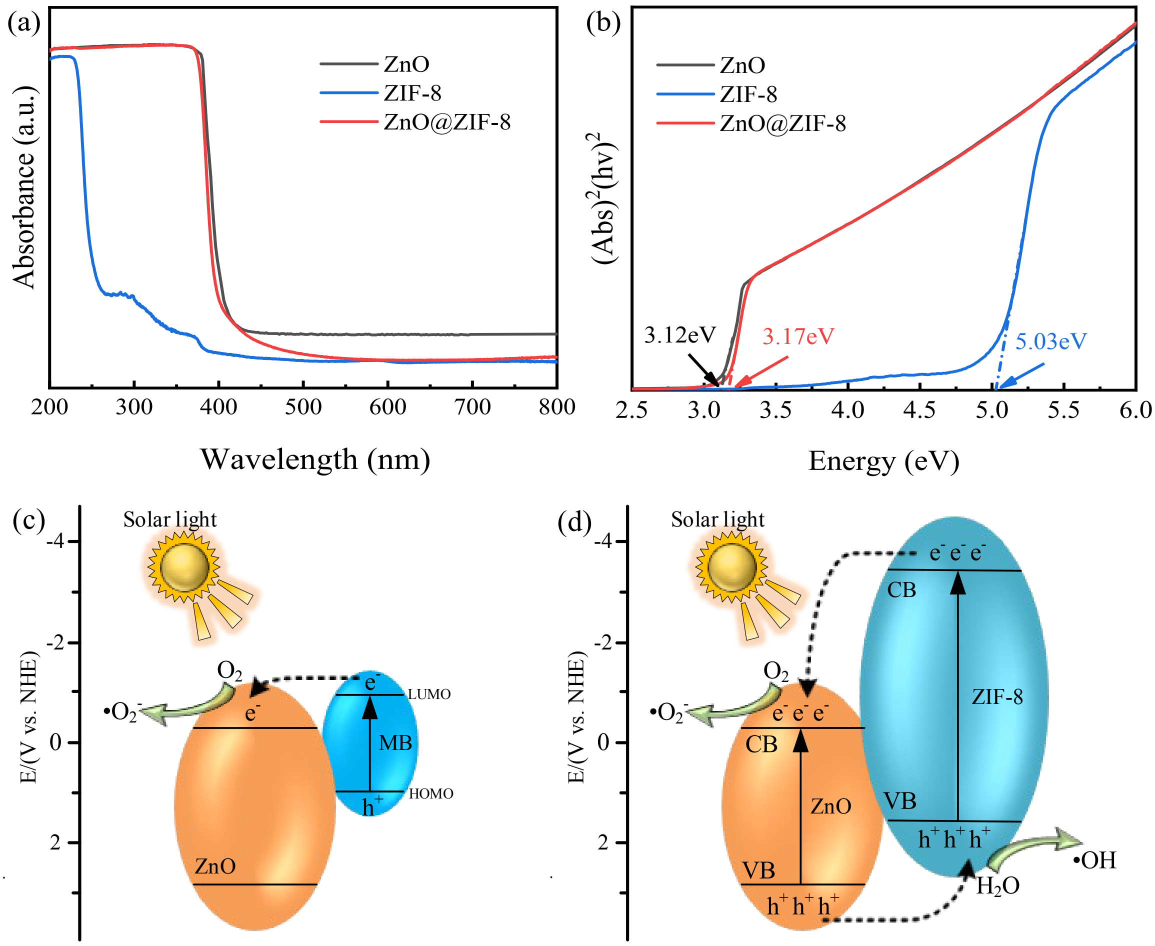

Fig. S6 (a) UV–Vis absorption spectra and (b) band gap measurement of ZnO nanorods, ZIF-8 and ZnO@ZIF-8 heterostructures. (c) Schematic illustration of sensitized MB molecule may transfer electrons to the CB of ZnO. (d) Schematic illustration for the path of photogenerated charge transfer in ZnO@ZIF-8.

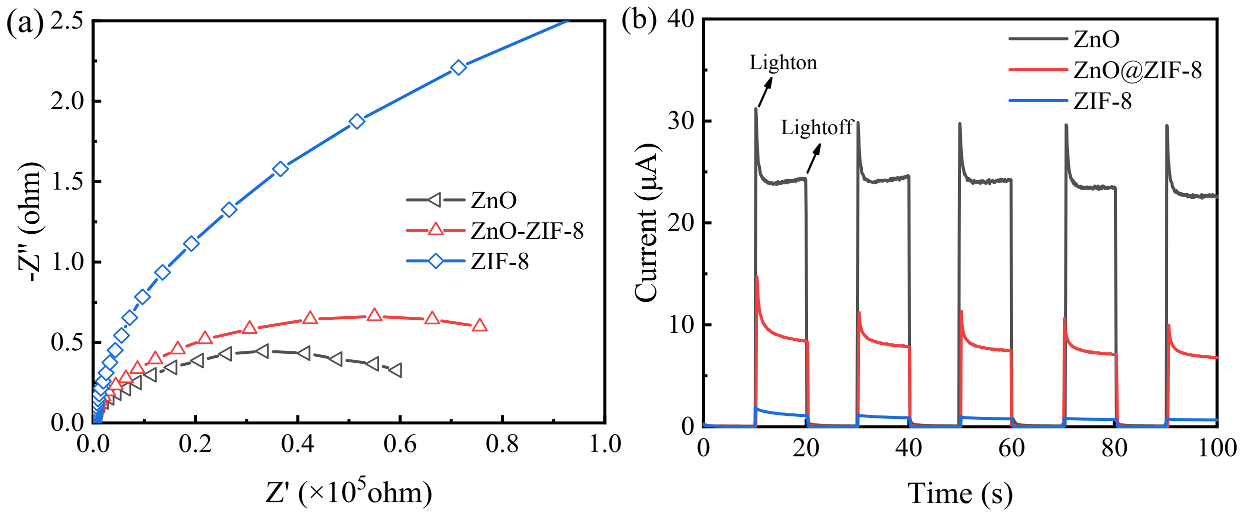

Fig. S7 (a) Electrochemical impedance spectra and (b) Transient photocurrent response curves of ZnO and ZnO@ ZIF-8. In the three-electrode system, the FTO glasses grown with the as-prepared samples with a light area of 1 cm^2 acted as working electrode when working, while a platinum wire and saturated calomel electrode acted as auxiliary electrode and reference electrode, respectively.

Table S1 Photocatalytic degradation performance of the ZnO-based materials

Enhanced method	*Dyes*	*Light source*	m_s *mg/mL*	C_0 mg/L	*t* *min*	*Degradation efficiency /%*	*Ref.*
ZnO	MO	A 15-W UV light-tube (365 nm)	1.25	10	120	100	Tian et al.[5]
Au-doped Au@ZnO	MB	A 300 W Xenon lamp	0.5	16	20	100	Jung et al.[6]
Ag/ZnO nanorods array	MB	A low-pressure fluorescent Hg lamp	/	2	60	49.3	Ren et al.[7]
Fe-doped ZnO nanoflowers	RhB	A high-pressure UV mercury lamp	1	10	180	94	Yi et al.[8]
Eu-doped ZnO	MB, MO	A 300 W Osram Vitalux lamp	1	10	150 60	90 100	Trandafilović et al.[9]
Dy-doped ZnO nanoparticles	AR17	A 100 W visible lamp	1	5	180	67	Khataee et al.[10]
Ce-doped ZnO	DR-23	A 125 W low pressure mercury lamp	0.5	40	70	99.5	Kumar et al.[11]
P-containing ZnO	RhB	A 300 W halogen lamp with a wavelength (λ) >375 nm	0.5	5	180	99	Saffari et al.[12]
S-Doped ZnO	RhB	A halogen lamp (λ > 400 nm)	/	5	90	100	Mirzaeifard et al.[13]
C, N co-doped ZnO	MO	A xenon lamp (380–800 nm, XQ350W	0.5	10	150	99	Zheng et al.[14]
ZnS-modified ZnO	MO	Four UV lamps with a wavelength centered at 254 nm	0.5	10	60	93.7	Yu et al.[15]
CuO/ZnO	MB	Asahi spectra (MAX 303, 500 W, Japan) as light source	1	10	25	96.6	Bharathi et al.[16]
TiO_2/ZnO/rGO	MB, RhB,	A Xenon 300-W lamp solar simulator	0.5	20	180	83.5, 80.3,	Nguyen et al.[17]

	MO						
$ZnO/Ag/Ag_2O$	Phenol	A 300 W Xe arc lamp	1	20	75	95	Feng et al.[18]
$Fe_3O_4@SiO_2@ZnO/CdS$	RhB	A 250 W Xe lamp equipped with a 420 nm cut-off filter	1	7	180	97	Yang et al.[19]
ZnO/polypyrrole composite	DB22	A lamp (Avant, mercury vapor 125W, 280-380nm)	2	50	60	83.6	Ceretta et al.[20]
ZnO@Zeolite A	RhB	An 18 W UV lamp with a maximum emission of about 365 nm	1	10	45	90	Du et al.[21]
ZIF-8	MB	A 500 W Hg lamp	0.5	10	120	82.3	Jing et al.[22]
ZnO@ZIF-8	MB	Solar light	1	3.19	4.5	~100	This work
ZnO-ZIF-8	MO, MB	Eight black fluorescent lamps (Philips TL 15 W/5 BLB)	1	3.27 3.19	70 80	~100 ~100	Tuncel et al.[23]
ZnO@ZIF-8	MB	A 300 W high pressure Hg lamp	1	10 ppm	240	94.1	Yu et al.[24]
ZnO@ZIF-8	Cr(VI)	UVP Pen-Ray mercury lamp (USA) with wavelength of 254 nm	1	20	240	88	Wang et al.[25]

Table S2 Core diameters (ZnO) and shell thicknesses (ZIF-8)) of ZnO@ZIF-8

Ref.	*Morphology*	*Pristine ZnO*	*core diameter*(ZnO)	*shell thickness* (ZIF-8)
This work	Nanorods	18 ± 3 nm in diameter 120 ± 30 nm in length	~16 nm	~3 nm
Yu et al.[24]	Nanoparticles	300 nm	200~250 nm	50~100 nm
Wang et al.[25]	Nanoparticles	/	300~400 nm	~30 nm
Zhan et al.[26]	Nanorods	600 ± 100 nm in diameter 15 ± 5 μm in length	400 ± 25 nm	300 ± 25 nm

Table S3 Band gaps of the ZnO and ZnO@ZIF-8

Ref.	*Morphology*	*Band gap* /eV	
		ZnO	ZnO@ZIF-8
This work	Nanorods	3.12	3.17
Tuncel et al.[23]	Nanoparticles	3.10	3.00
Wang et al.[25]	Nanoparticles	3.27	3.24

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