Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Surfactant Free Fabrication and Improved Charge Carrier Separation Induced Enhanced Photocatalytic Activity of {00} Facet Exposed Unique Octagonal BiOCl Nanosheets

Zeeshan Haider, Jin You Zheng and Young Soo Kang*

Korea Center for Artificial Photosynthesis and Department of Chemistry,
Sogang University, Seoul 121-742, Republic of Korea

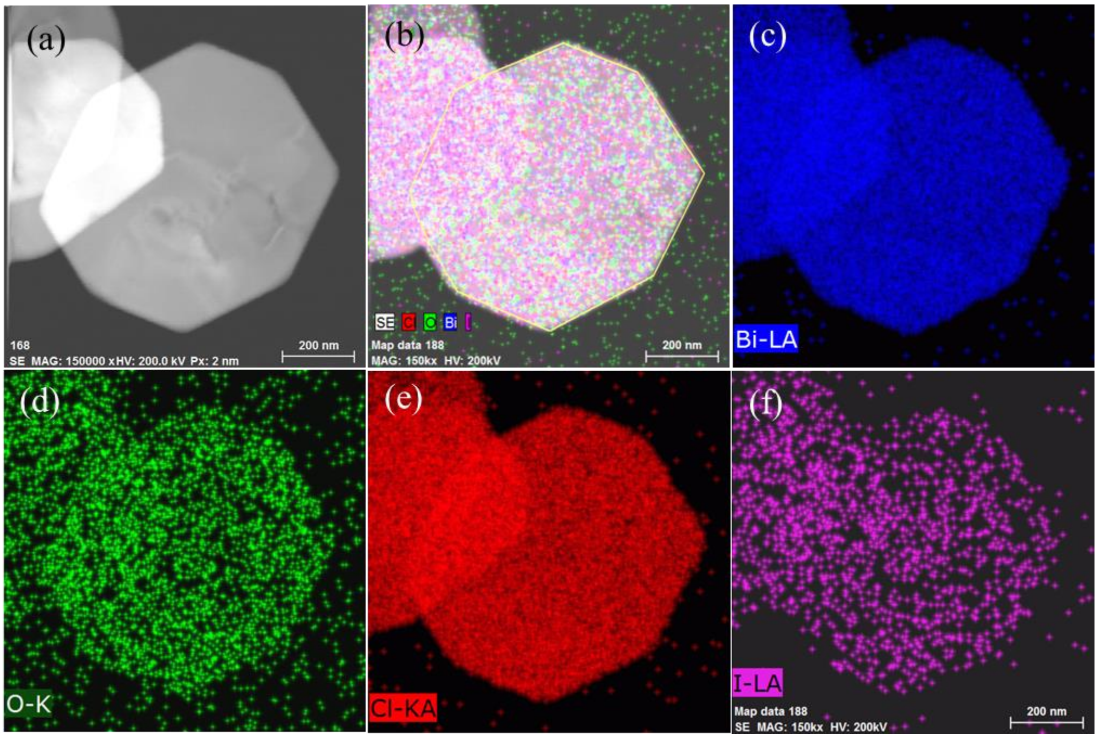
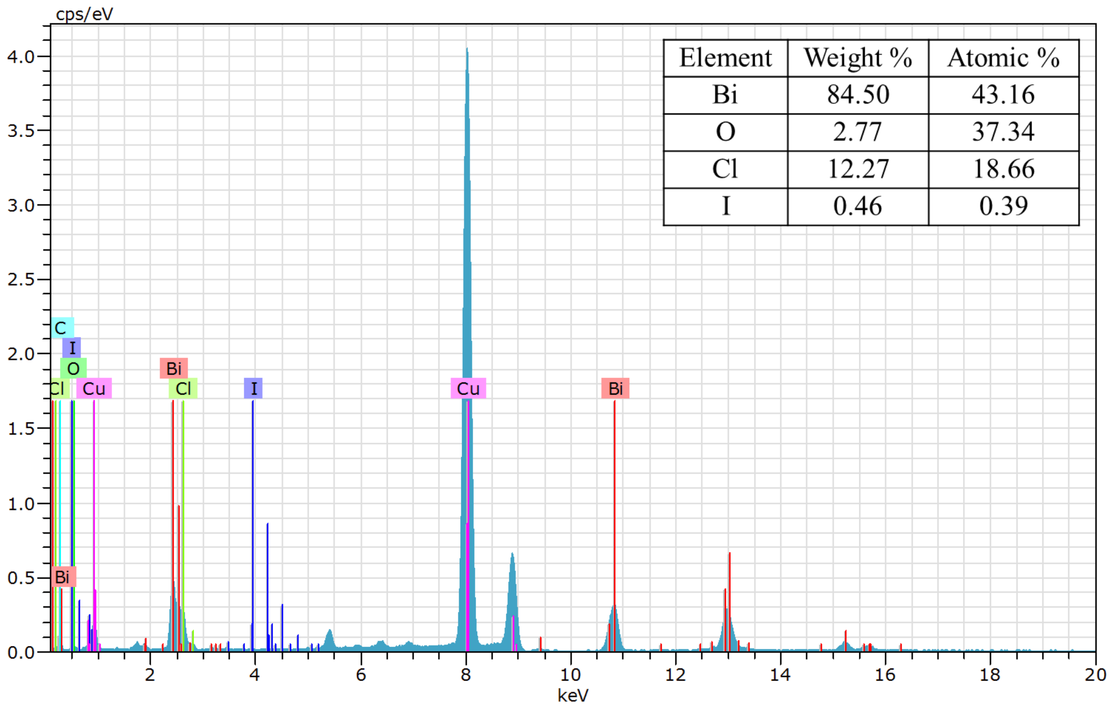


Figure S1(A): TEM image (a), diffused elemental mapping (b), elemental mapping of bismuth (c), oxygen (d), chlorine (e) and iodine (f).



Element	Weight %	Atomic %
Bi	84.50	43.16
O	2.77	37.34
Cl	12.27	18.66
I	0.46	0.39

Figure S1 (B): EDX spectrum and elemental compositions of {001} BiOCl NS.

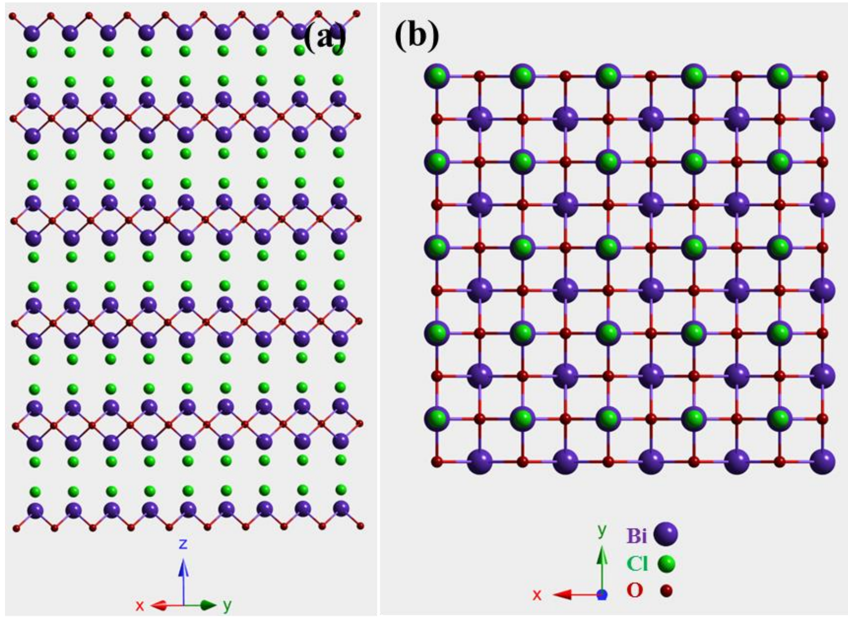
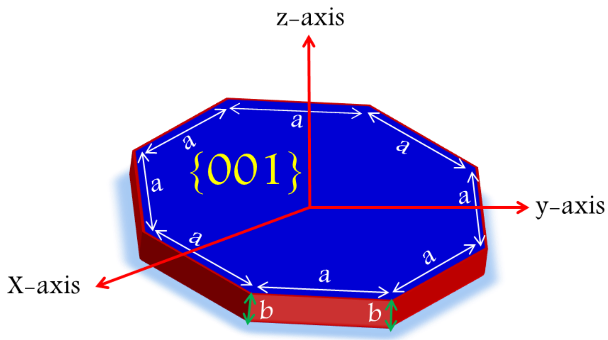


Figure S2: Crystal model (a) and c-axis view of {001} BiOCl NS.

Procedure for calculations of percentage exposure of {001} facet

(a): {001} BiOCl NS

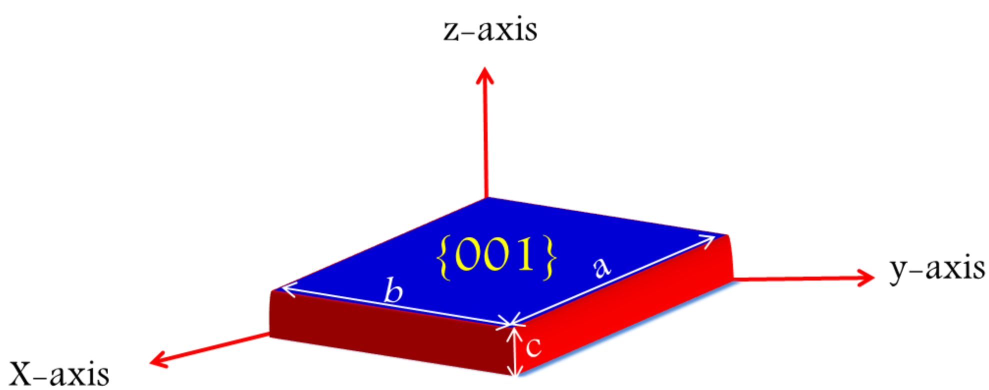


Area of {001} facet, $A = 2(1 + 2\sqrt{2})\, a^2$

Area of side facets, $B = ab$

Percentage of {001} facet = $\{2A/(2A + 8ab)\}$ X 100

(b): Pristine BiOCl



Percentage of {001} facet = $\{2ab/2(ab + ac + bc)\}$ X 100

Figure S3: Geometrical models for calculating percentage exposure of {001} crystal facet of (a): {001} BiOCl NS and (b): Pristine BiOCl.

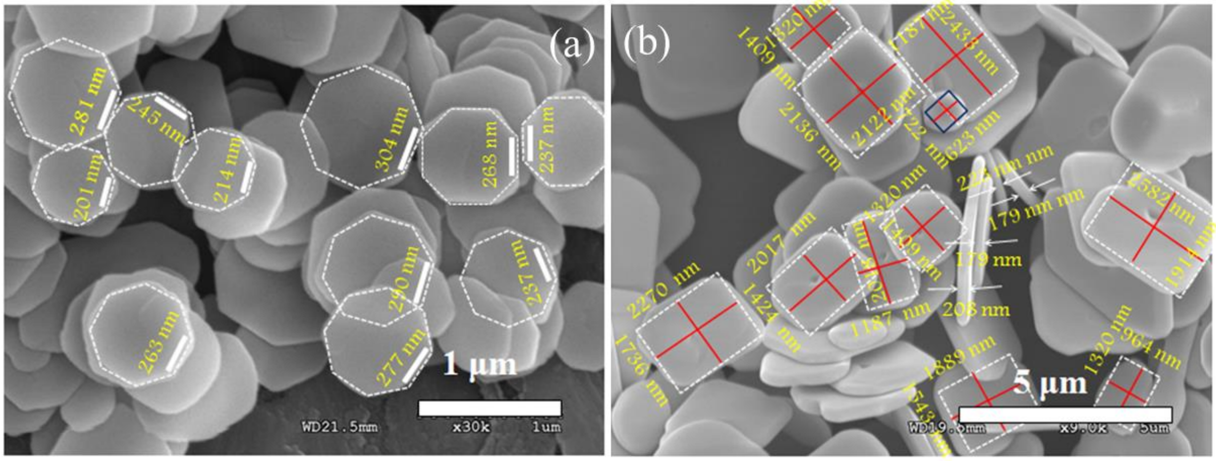


Figure S4: SEM images of (a) {001} BiOCl NS and (b) pristine BiOCl referred for calculating percentage exposure of {001} facet.

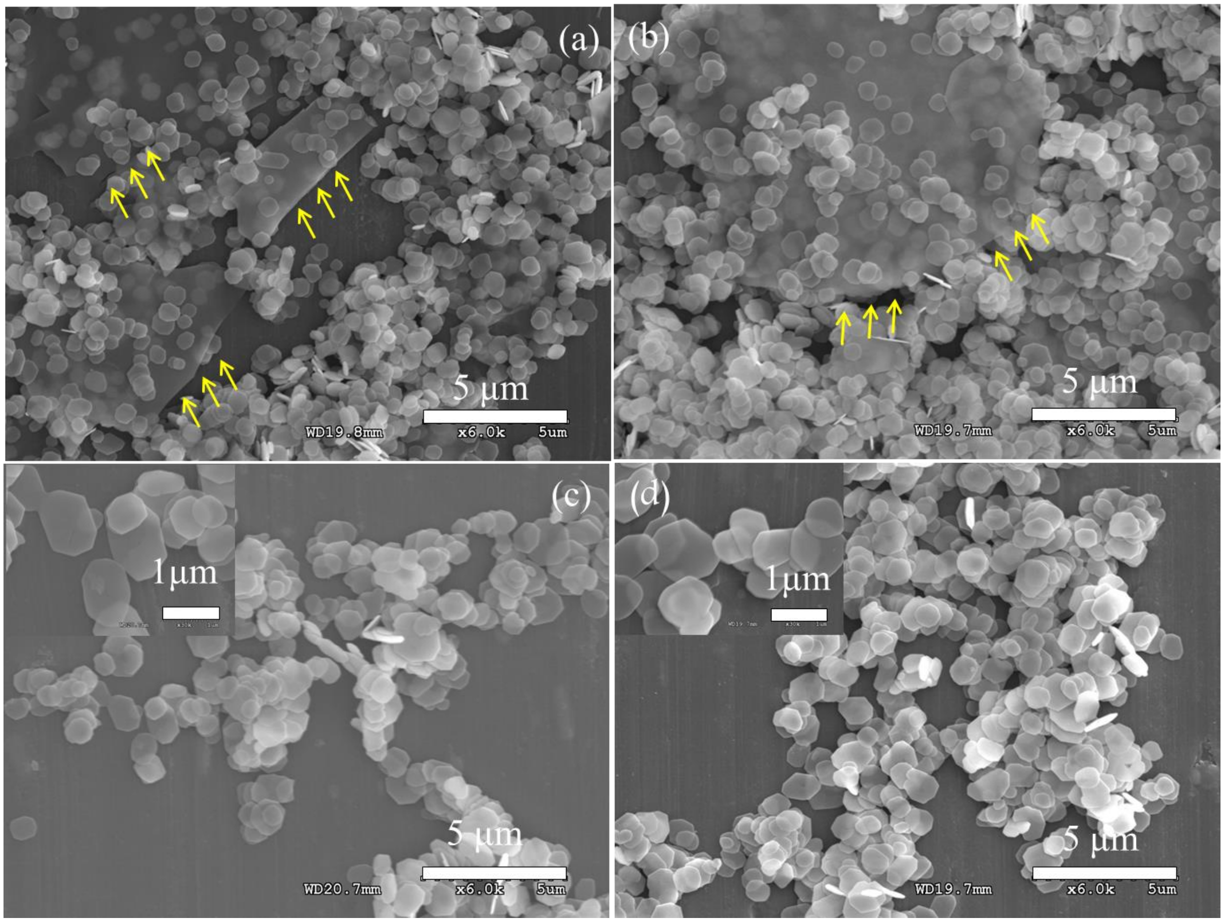


Figure S5: SEM images of {001} BiOCl NS prepared under varying amount of solvent ratio of ethanol/DI water, (a) 6/9, (b) 4/11, (c) 2/13 and (d) 1/14 ml.

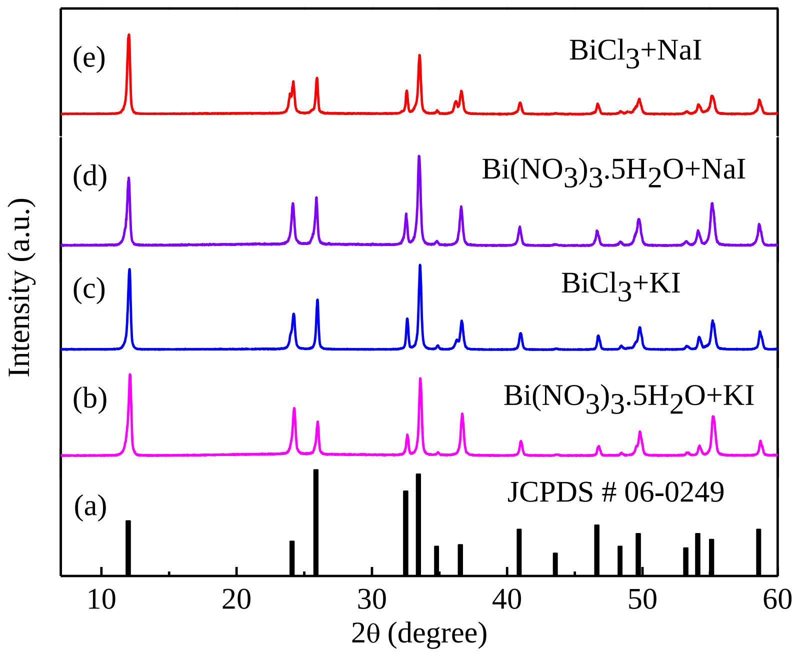


Figure S6: XRD patterns, standard BiOCl (a) and product with different Bi and I precursors, $Bi(NO_3)_35H_2O$+KI (b), $BiCl_3$+KI (c), $Bi(NO_3)_3$ $5H_2O$+NaI (d) and $BiCl_3$+ NaI (e).

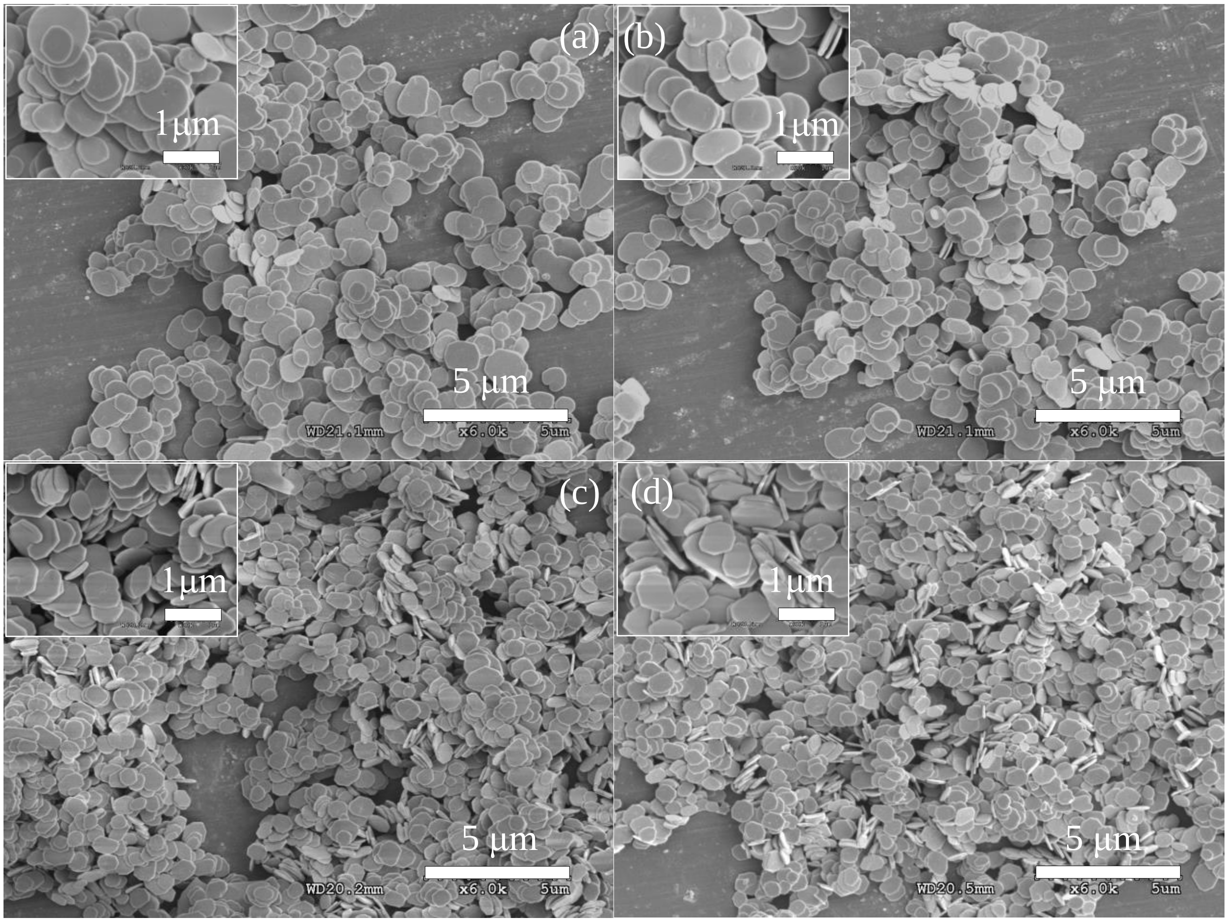


Figure S7: SEM images of products with different Bi and I precursors, $Bi(NO_3)_3$**.**$5H_2O$+KI (a)**,** $Bi(NO_3)_3$**.**$5H_2O$+NaI (b), $BiCl_3$+KI (c) and $BiCl_3$+ NaI (d).

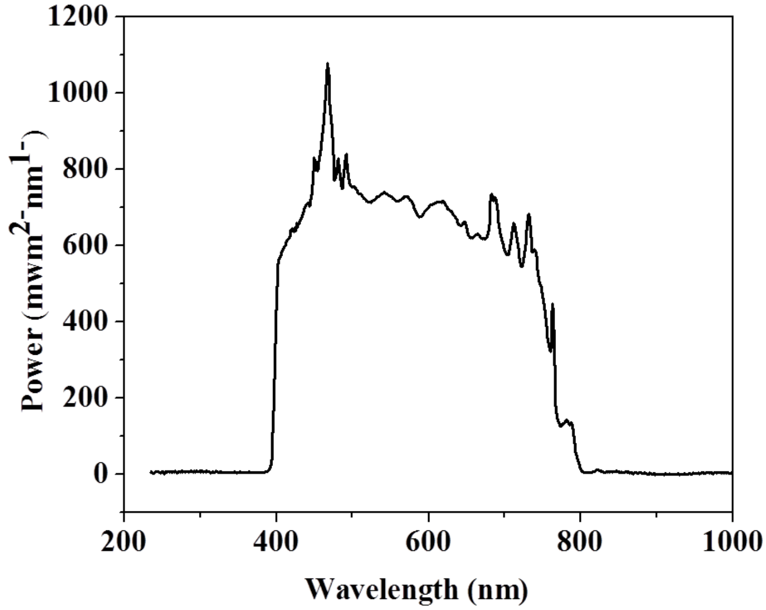


Figure S8: Output irradiance spectrum of Xenon lamp Max-302, Asahi spectra, equipped with visible mirror module and 400 nm long pass optical filter. Distance between collimating lens and photoreactor was adjusted 20 cm, irradiation area was 2.6 cm × 2.6 cm.

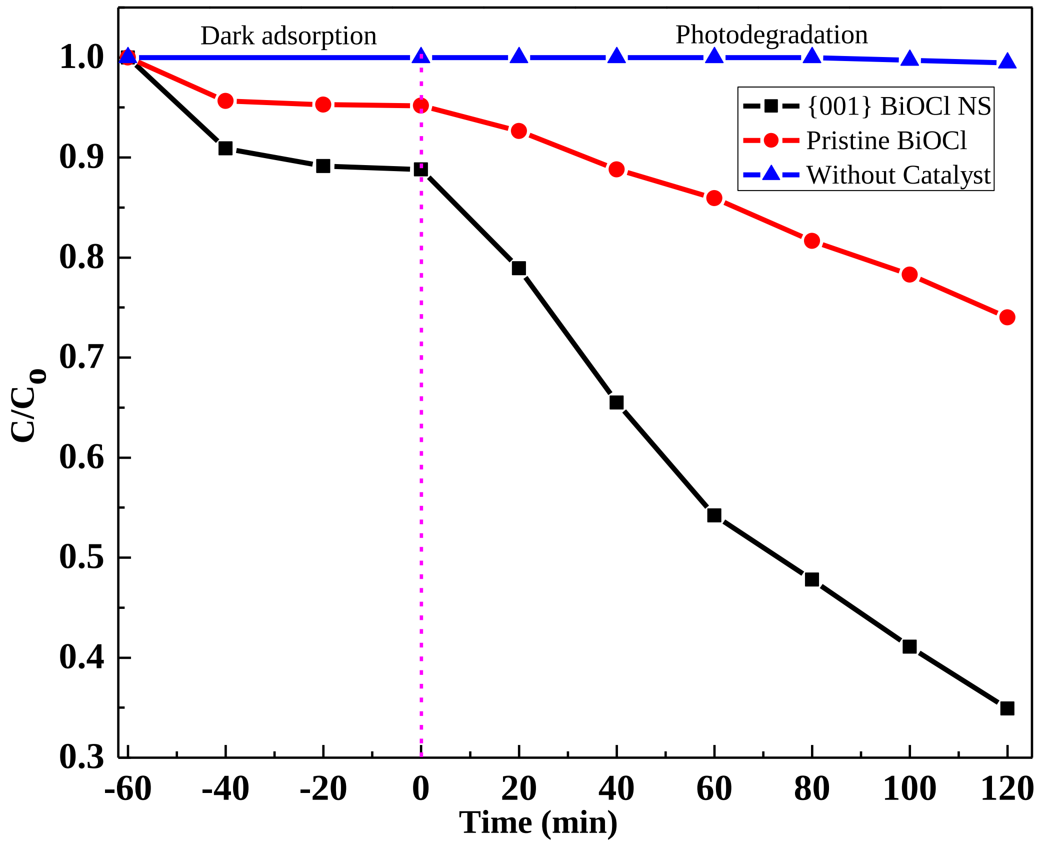


Figure S9: Adsorption and photodegradation curves of RhB versus time under dark and visible light illumination (λ > 400 nm).

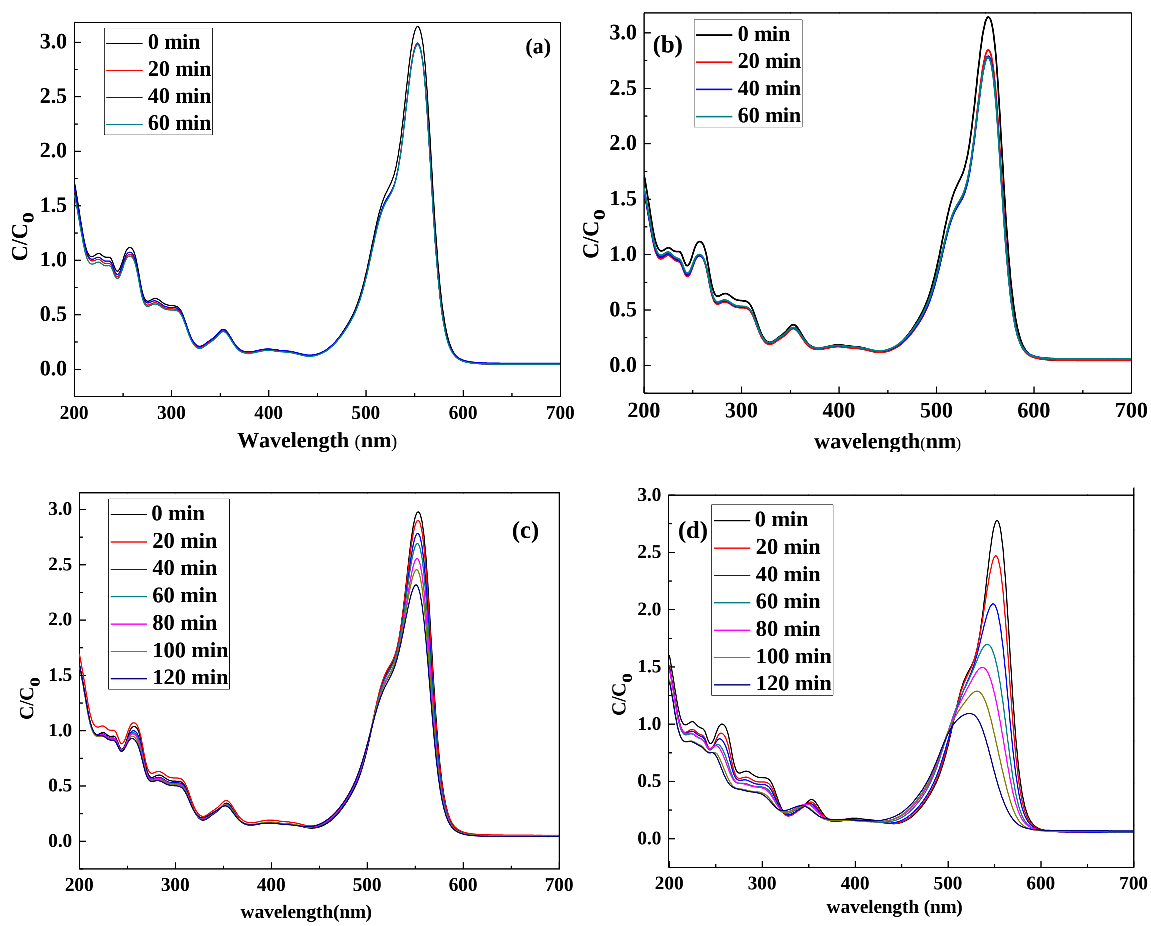


Figure S10: UV-Visible absorption spectra of RhB after dark adsorption (a), after photodegradation (b) by pristine BiOCl; dark adsorption (c) and after photodegradation (d) by {001} BiOCl NS.

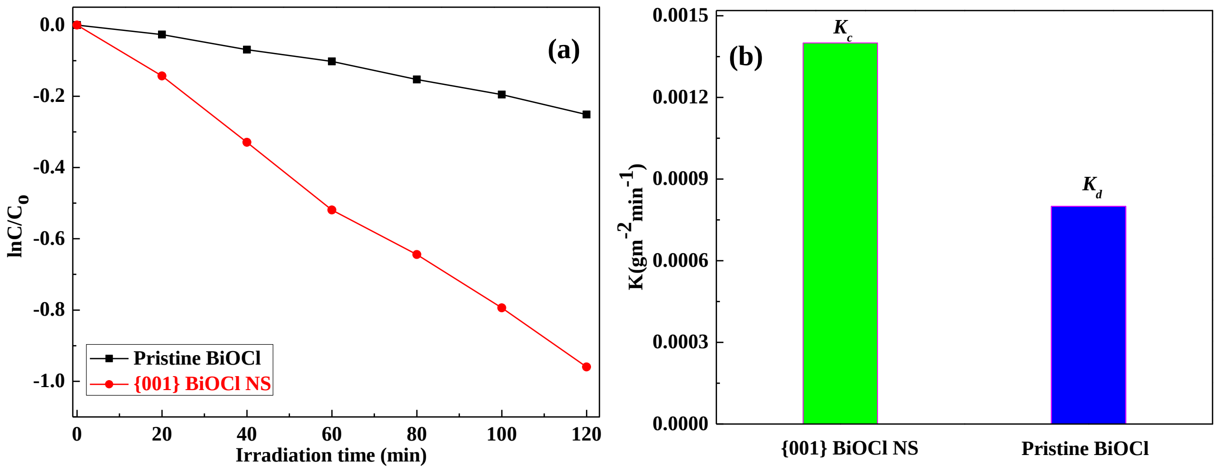


Figure S11: Plots of (a) ln(C/C_o) versus irradiation time and (b) rate of reaction for photodegradation of RhB normalized to BET surface area of pristine BiOCl and {001} BiOCl NS.

Figure S12: Procedure for calculation of photonic efficiency, PE (φ)

Photonic efficiency for photodegradation of RhB (φ) as a function of irradiation time in term of moles can be expressed as follow,[1]

$$\varphi(\%) = \frac{degradation\ rate\ of\ RhB\ (mole/sec)}{moles\ of\ incident\ photons\ (mole/sec)} \times 100$$

PE can also be expressed by following relation.[2]

$$\varphi(\%) = \frac{d[x]/dt}{d[hv]/dt} \times 100$$

In above expression, $d[x]/dt$ photodegradation rate of RhB (mole/sec), whereas $d[hv]/dt$ represent incident photons (moles/sec) on the sample. Moles of incident photons can be obtained by dividing total energy of incident photons with energy of single photon and Avogadro's number, N_A = 6.02 * 10^{23} mol^{-1}.[3]

$$moles\ of\ photons = \frac{E_{total}}{N_A\, E_{photon}}$$

Energy of single photon at a given wavelength is calculated from following equation, using planks constant, h = 6.26*10^{-34} JS and speed of light, c = 3*10^8 m/s.[3]

$$E_{photon} = \frac{hc}{\lambda}$$

For monochromatic source of radiation moles of incident photons can be calculated from following expression.[3]

$$moles\ of\ photons = \frac{E_{total}}{N_A E_{photon}} = \frac{PSt\lambda_{inc.}}{N_A hc}$$

In above expression, *S* is the irradiation area (m^2), *t* is illumination time (sec) and *P* is the power density of incident light.[3] However when incident light is composed of wide range of wavelengths, moles of incident photons can be calculated by integrating over spectral window using following expression.[4]

$$moles\ of\ photons = \frac{E_{total}}{N_A E_{photon}} = \frac{St}{N_A}\int_{\lambda 1}^{\lambda 2} \frac{P_\lambda \lambda d\lambda}{hc}$$

Spectral width from 400 to 600 nm was chosen for the calculation of φ, hence integration was performed in the mentioned range of wavelength. The overall expression for the calculation of PE can be expressed as follow.

$$\varphi(\%) = \frac{n_{RhB}/dt}{\left(\frac{St}{N_A}\int_{\lambda\ 400\ \mathrm{nm}}^{\lambda\ 600\ \mathrm{nm}} \frac{P_\lambda \lambda d\lambda}{hc}\right)/dt} \times 100$$

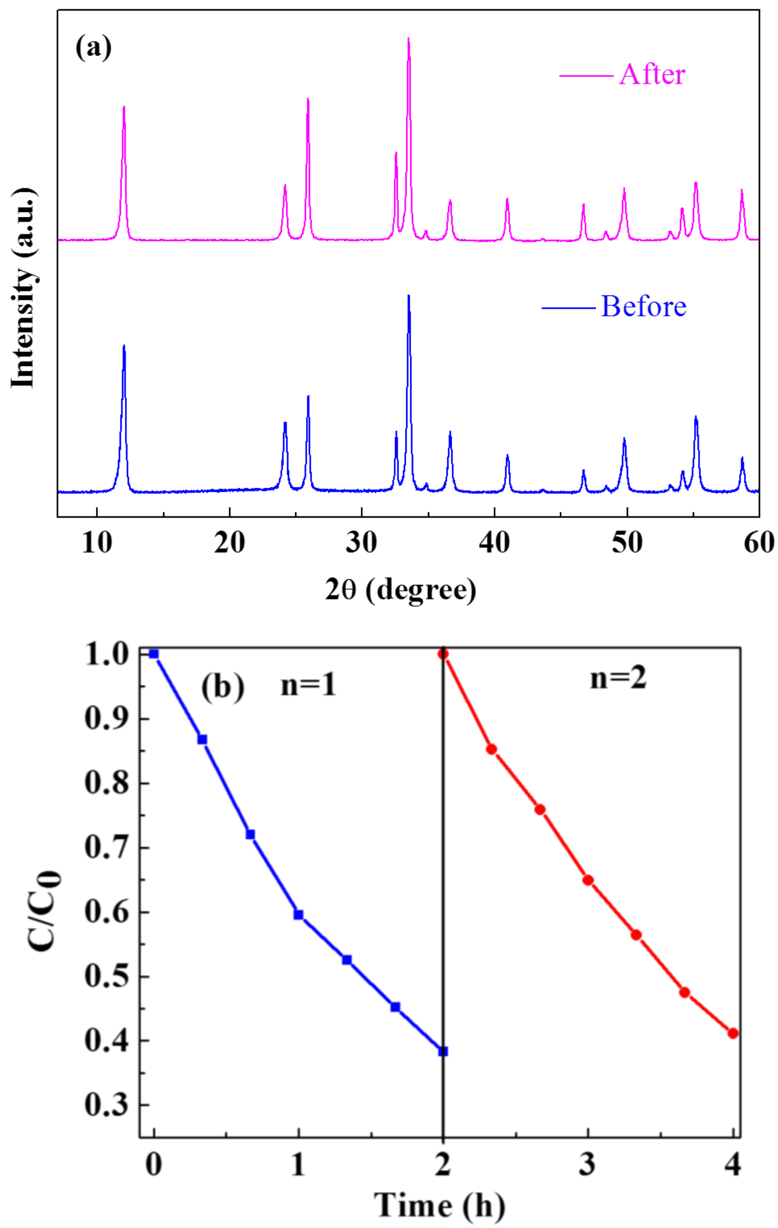


Figure S13: XRD patterns before and after photodegradation (a) and (b) recycling test for photodegradation of RhB by {001} BiOCl NS.

Table S1: Fitting parameters for time resolved PL decay curves.

Sample	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	B_1	B_2	B_3	$\langle\tau\rangle_{amp.}$ (ns)	$\langle\tau\rangle_{int.}$ (ns)	Mean $\langle\tau\rangle_{amp.}$ (ns)	Mean $\langle\tau\rangle_{int.}$ (ns)
{001}BiOCl NS	32.481	0.542	3.836	427.29	9856.28	1752.49	2.16	18.48	1.94	17.24
	30.451	0.458	3.138	216.9	6242.33	1049.03	1.7	16.68		
	29.82	0.497	3.34	329.5	7784.67	1543.99	1.95	16.56		
Pristine BiOCl	1.986	0.544	7.25	915.42	2606.55	104.61	1.1	2.47	1.07	2.52
	2.023	0.504	7.645	1444.16	4437.71	177.63	1.01	2.3		
	1.991	0.533	7.678	1212.36	3872.91	176.3	1.11	2.79		

Table S2: Photonic efficiency (φ) of {001} BiOCl NS for photodegradation of RhB under visible light illumination with long pass filter $\lambda > 400$ nm.

Sample	**Illumination Time (h)**	**[x] of RhB** (mmol)	**d[x]/dt** (mmol*/s)	**dh[v]/dt** (mmol/s)	**φ (%)**
	0	2.505×10^{-3}	-	-	
{001} BiOCl NS	2	1.545×10^{-3}	2.1467×10^{-7}	4.409×10^{-4}	0.0486
Pristine BiOCl	2	5.511×10^{-4}	7.6545×10^{-8}	4.409×10^{-4}	0.0173

* mmol of RhB photodegraded after 2 h of illumination were calculated using Figure S9, considering both direct and indirect photoexcitation.

References

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