## **Electronic Supplementary Information (ESI)**

## Facet engineered interface design of NaYF<sub>4</sub>:Yb,Tm upconversion nanocrystals on BiOCl nanoplates for enhanced near-infrared photocatalysis

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**Fig. S1** TEM and HRTEM images of BiOCl nanoplates: (a) TEM image showing the flat surface of nanoplates; (b) TEM image showing the cross section and thickness of the nanoplates; (c) HRTEM image showing the lattice fringes of the flat faces; (d) HRTEM image showing the lattice fringes of side faces.



Fig. S2 TEM images of as-synthesized NaYF<sub>4</sub>:Yb,Tm nanocrystals.



**Fig. S3** TEM images of (a) NaYF<sub>4</sub>:Yb,Tm-(001)BiOCl and (b) NaYF<sub>4</sub>:Yb,Tm-(110)BiOCl with a standing-up BiOCl nanoplate.



Fig. S4 XPS spectra of NaYF<sub>4</sub>:Yb,Tm-(110)BiOCl hybrid structure.



**Fig. S5** XPS spectra of NaYF<sub>4</sub>:Yb,Tm-(001)BiOCl hybrid structure: (a) survey spectrum, (b) Bi4f, (c) O1s, (d) Cl2p, (e) Na1s, (f) F1s, and (g) Yb4d and Tm4d.



**Fig. S6** Absorption spectra of the RhB solution taken at different degradation times using NaYF<sub>4</sub>:Yb,Tm-(001)BiOCl photocatalyst under NIR light irradiation.



**Fig. S7** Absorption spectra of the MB solution taken at different degradation times using NaYF<sub>4</sub>:Yb,Tm-(001)BiOCl photocatalyst under NIR light irradiation.



**Fig. S8** TEM images of (a) NaYF<sub>4</sub>:Yb,Tm-(001)BiOCl and (b) NaYF<sub>4</sub>:Yb,Tm-(110)BiOCl hybrid structures after photocatalytic process.



**Fig. S9** Photocatalytic stability measurement of NaYF<sub>4</sub>:Yb,Tm-(110)BiOCl in the photocatalytic degradation of RhB for three cycles.



**Fig. S10** (a) Absorption spectra of the RhB solution taken at different degradation times using NaYF<sub>4</sub>:Yb,Tm-(110)BiOCl photocatalyst under simulated sunlight irradiation; (b) photocatalytic activities of the BiOCl nanoplates, NaYF<sub>4</sub>:Yb,Tm nanocrystals, NaYF<sub>4</sub>:Yb,Tm-(001)BiOCl and NaYF<sub>4</sub>:Yb,Tm-(110)BiOCl hybrid structures for the degradation of RhB solution under simulated sunlight irradiation.



Fig. S11 Photocatalytic activity of  $NaYF_4$ : Yb, Tm-(001)BiOCl in the presence of different scavengers under NIR light for degradation of the RhB solution.



**Fig. S12** Schematic illustrating the band alignment of (001) and (110) facets in BiOCl nanoplates as well as the spatial charge separation between (001) and (110) facet.



**Fig. S13** (a) TEM image of BiOCl nanosheets with dominant (110) facet; (b,c) TEM and HRTEM images of (110) facet dominant BiOCl nanosheets supported NaYF<sub>4</sub>:Yb,Tm hybrid structure; (d) photocatalytic activities of the as-synthesized (110) facet dominant BiOCl nanosheets supported NaYF<sub>4</sub>:Yb,Tm hybrid structure (NaYF<sub>4</sub>:Yb,Tm-(110)BiOCl NSs) for the degradation of RhB solution under NIR light irradiation with NaYF<sub>4</sub>:Yb,Tm-(001)BiOCl as a reference sample. The (110) dominant BiOCl nanosheets were synthesized according to the previous report.<sup>S1</sup> The NaYF<sub>4</sub>:Yb,Tm nanocrystals were deposited on the flat (110) surface of the BiOCl nanosheets with the same synthetic method as the NaYF<sub>4</sub>:Yb,Tm-(001)BiOCl.



**Fig. S14** (a) Photocatalytic activities of the BiOCl nanoplates, NaYF<sub>4</sub>:Yb,Tm nanocrystals, NaYF<sub>4</sub>:Yb,Tm-(001)BiOCl and NaYF<sub>4</sub>:Yb,Tm-(110)BiOCl hybrid structures in the reduction of Cr(VI) under NIR light irradiation; (b) diagrams of the energy levels and energy/charge transfer in NaYF<sub>4</sub>:Yb,Tm-(001)BiOCl and NaYF<sub>4</sub>:Yb,Tm-(110)BiOCl in the photocatalytic reduction of Cr(VI). In the Cr(VI) reduction reaction, Cr(VI) can only be reduced by photogenerated electrons on the BiOCl(001) facet. As shown in Fig. S14b, though BiOCl(110) facet can absorb more UV emission from NaYF<sub>4</sub>:Yb,Tm nanocrystals in NaYF<sub>4</sub>:Yb,Tm-(110)BiOCl, the migration distance of electrons to the reactive (001) facet is much longer in comparison with that in NaYF<sub>4</sub>:Yb,Tm-(001)BiOCl, resulting in a significant decrease in the advantage.

**Table S1** Loading amounts of of NaYF<sub>4</sub>:Yb,Tm in NaYF<sub>4</sub>:Yb,Tm-(001)BiOCl and NaYF<sub>4</sub>:Yb,Tm-(110)BiOCl samples determined by ICP-MS.

Sample	Tm <sup>3+</sup> :Yb <sup>3+</sup> :Y <sup>3+</sup> :Bi <sup>3+</sup> molar	Loading amount of
	ratio	NaYF <sub>4</sub> :Yb,Tm (wt.%)
NaYF <sub>4</sub> :Yb,Tm-(001)BiOCl	1:42.6:159.4:784.1	17.0
NaYF <sub>4</sub> :Yb,Tm-(110)BiOCl	1:44.8:158.3:803.2	16.8

## References

S1 Z. Cui, L. Mi and D. Zeng, J. Alloy. Compd., 2013, 549, 70.