

## Supplementary data for

### Engineering Z-scheme TiO<sub>2</sub>-OV-BiOCl *via* oxygen vacancy for photocatalytic degradation of imidacloprid

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The calculation of intensity-average lifetime of samples:

In this work, the time-resolved photoluminescence (TRPL) decay spectra was applied to study the effective transfer of photo-generated electrons intuitively. As shown in Fig. 5(d), all of the TRPL spectra is consistent with a multi-exponential decay process. And their decay dynamics can be obtained through fitting to a biexponential function [1,2]:

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1)$$

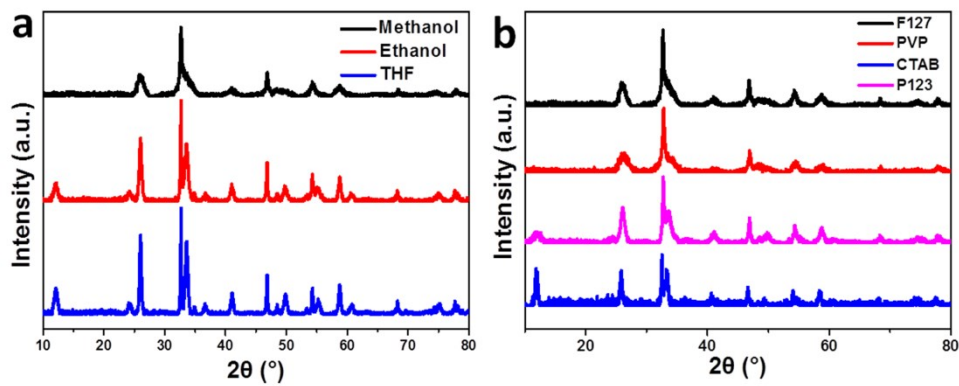
where  $I(t)$  indicates the PL intensity,  $A_1$  and  $A_2$  are used to represent the amplitude (or weighting factors). the  $\tau_1$  and  $\tau_2$  represent the corresponding lifetime. The average lifetime ( $\tau_m$ ) is often used to evaluate carrier separation efficiency of photogenerated charges, and the  $\tau_m$  was calculated according to the following equation:

$$\tau_m = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2) \quad (2)$$

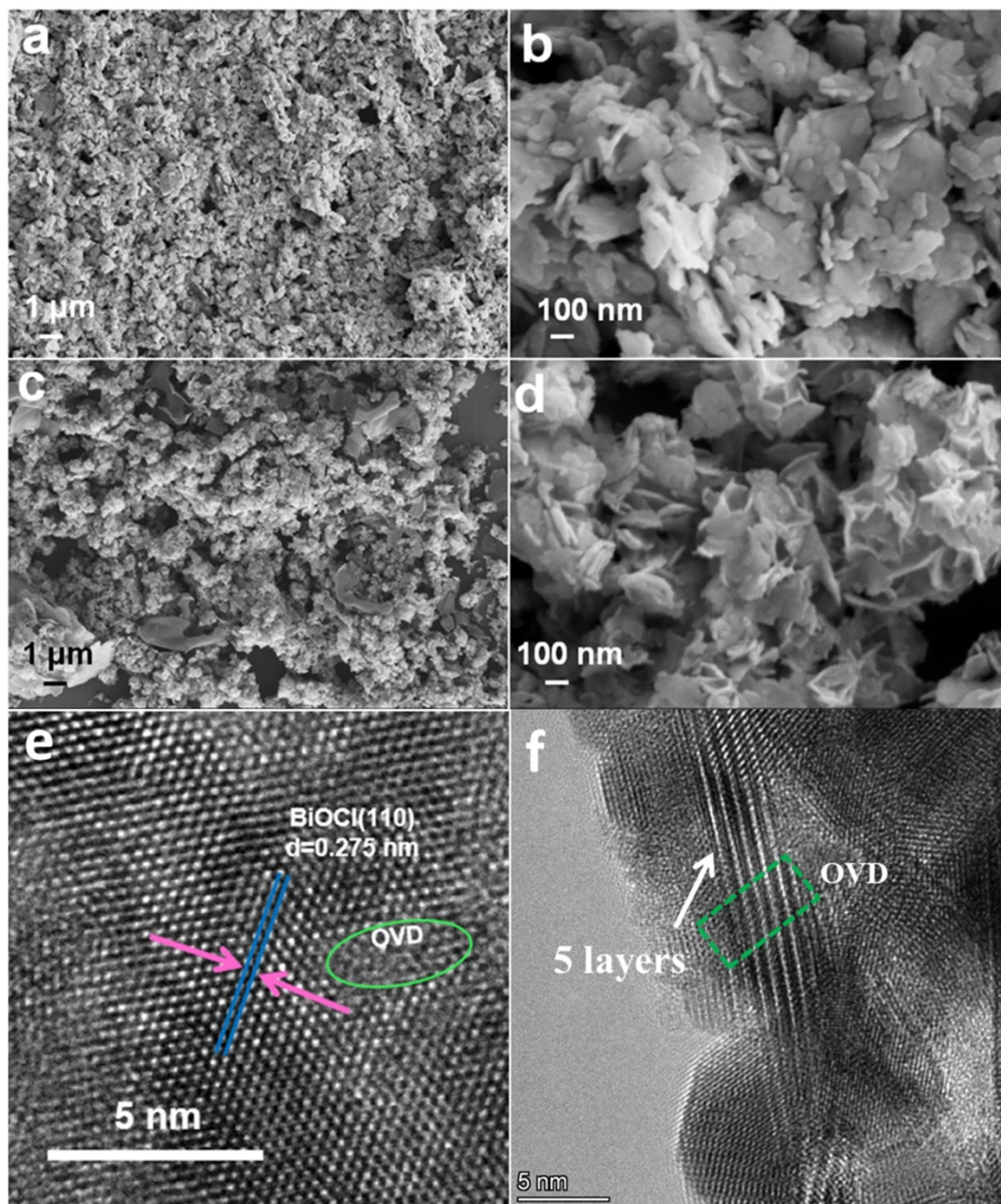
The short lifetime component ( $\tau_m$ ) stems from the nonradiative recombination of the  $\tau_1$  photogenerated electrons with the surface defects. And, the long lifetime component ( $\tau_2$ ) is derived from the interband recombination of the free-excitons [3]. The experimental decay profiles of  $\text{TiO}_2\text{-OV-BiOCl}$  samples are listed in Table. S1. For  $\text{TiO}_2\text{-OV-BiOCl}$ , the two exponential constants ( $\tau_1$  and  $\tau_2$ ) are 2.207 ns and 2.261 ns, which are longer than that of  $\text{TiO}_2/\text{BiOCl}$  ( $\tau_1 = 3.779$  ns and  $\tau_2 = 8.059$  ns) and  $\text{BiOCl}$  ( $\tau_1 = 2.207$  ns and  $\tau_2 = 0.245$  ns). Therefore,  $\text{TiO}_2\text{-OV-BiOCl}$  possess a longer average lifetime ( $\tau_m = 5.83$  ns) than that of  $\text{TiO}_2/\text{BiOCl}$  ( $\tau_m = 4.76$  ns) and  $\text{BiOCl}$  ( $\tau_m = 4.33$  ns).

Sample	$A_1$	$\tau_1$ (ns)	$A_2$	$\tau_2$ (ns)	$\tau_{ave}$ (ns)
TiO <sub>2</sub> -OV-BiOCl	0.6348	5.978	0.276	2.261	5.83
TiO <sub>2</sub> /BiOCl	0.624	3.799	0.803	8.050	4.76
BiOCl	0.363	2.207	0.276	6.245	4.33

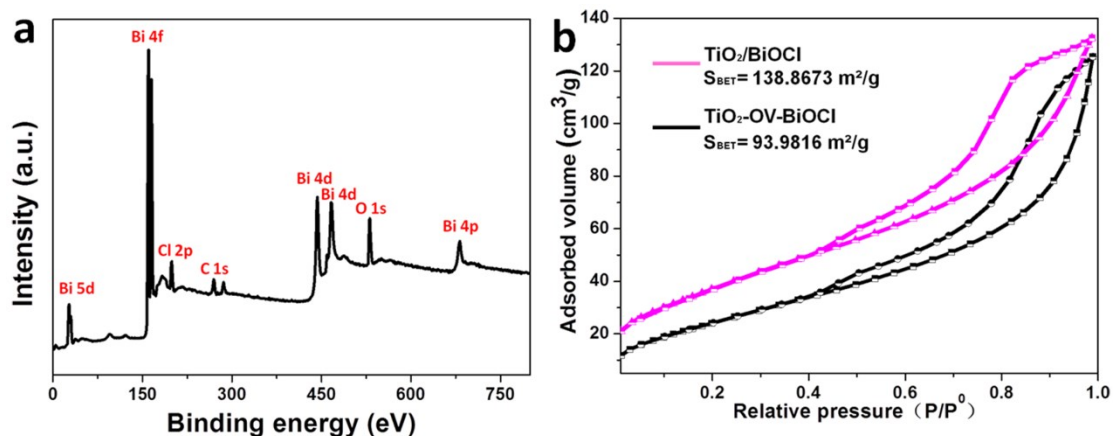
**Table S1.** The fitted parameters of the TRPL decay profiles.



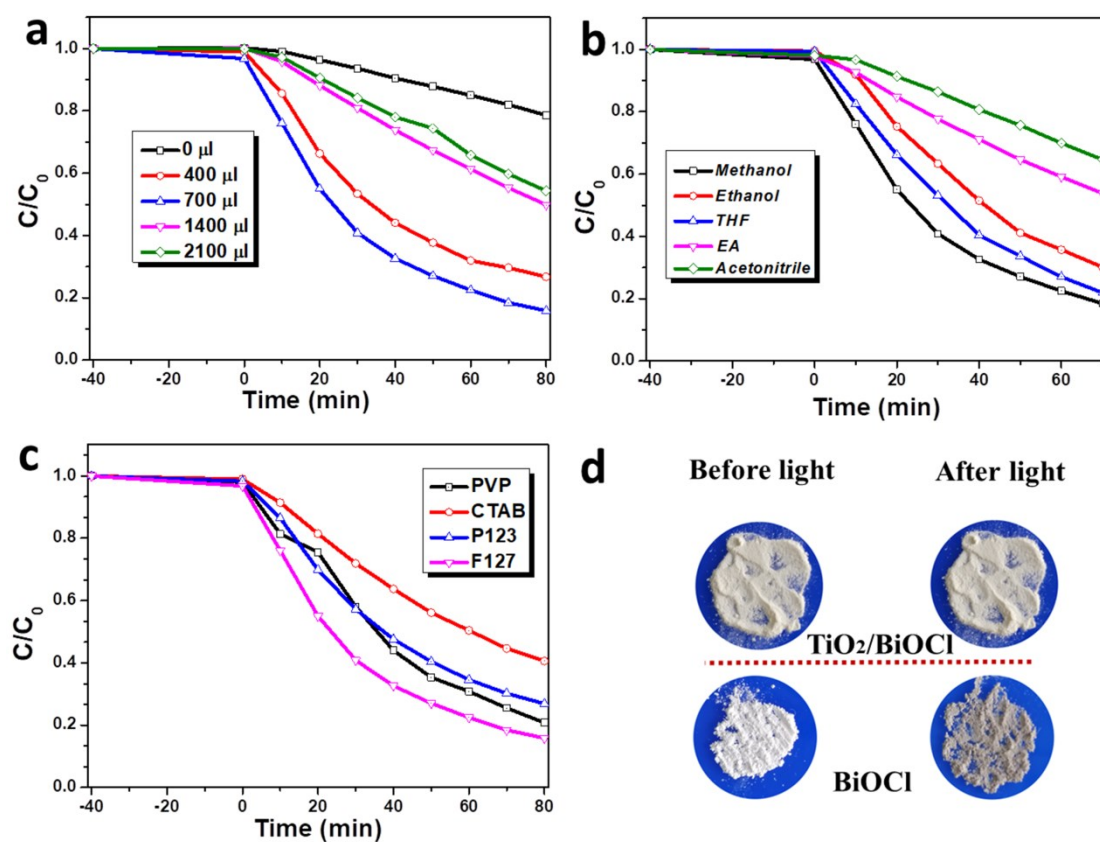
**Fig. S1.** The prepared TiO<sub>2</sub>/BiOCl using F127 as the surfactant in other solvents (a) and in the methanol solvent using other surfactants (b).



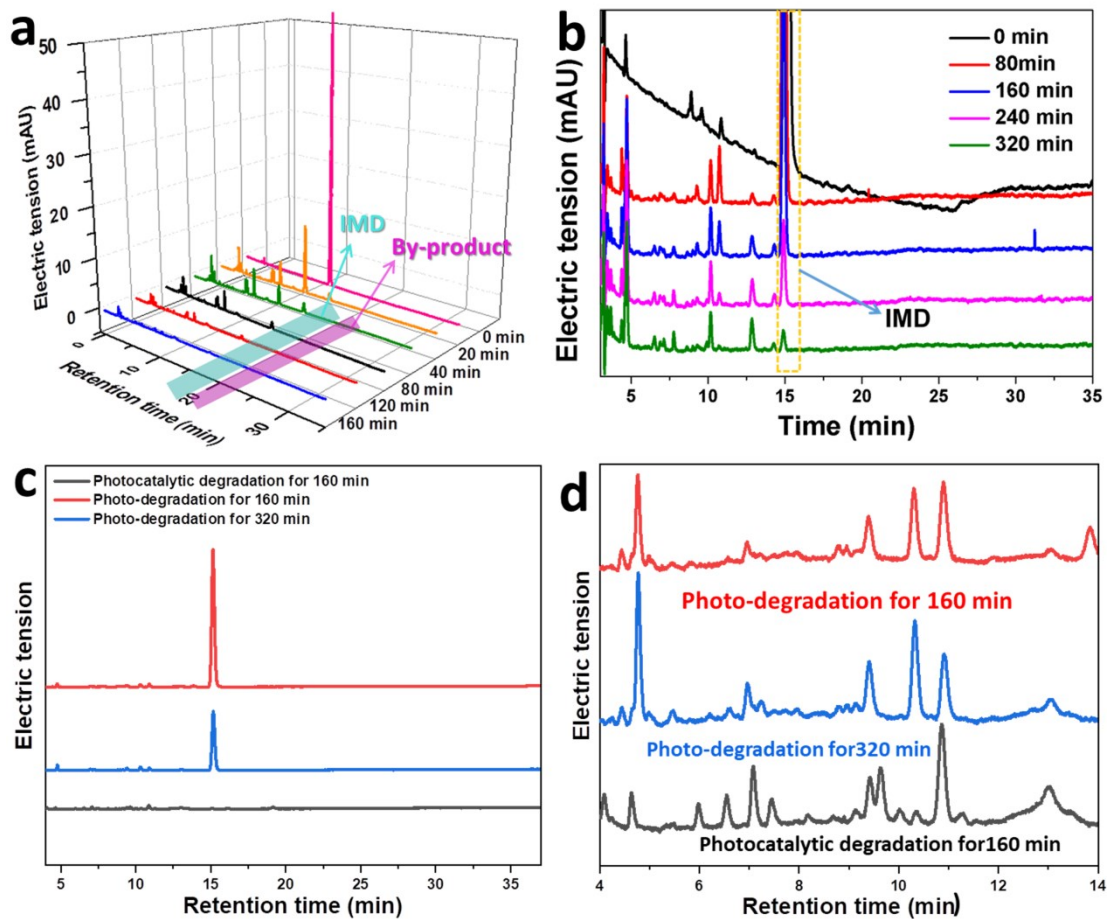
**Fig. S2.** SEM images of  $\text{TiO}_2\text{-OV-BiOCl}$  (a, b) and  $\text{TiO}_2/\text{BiOCl}$  (c, d); HRTEM images of  $\text{TiO}_2\text{-OV-BiOCl}$  (e-f).



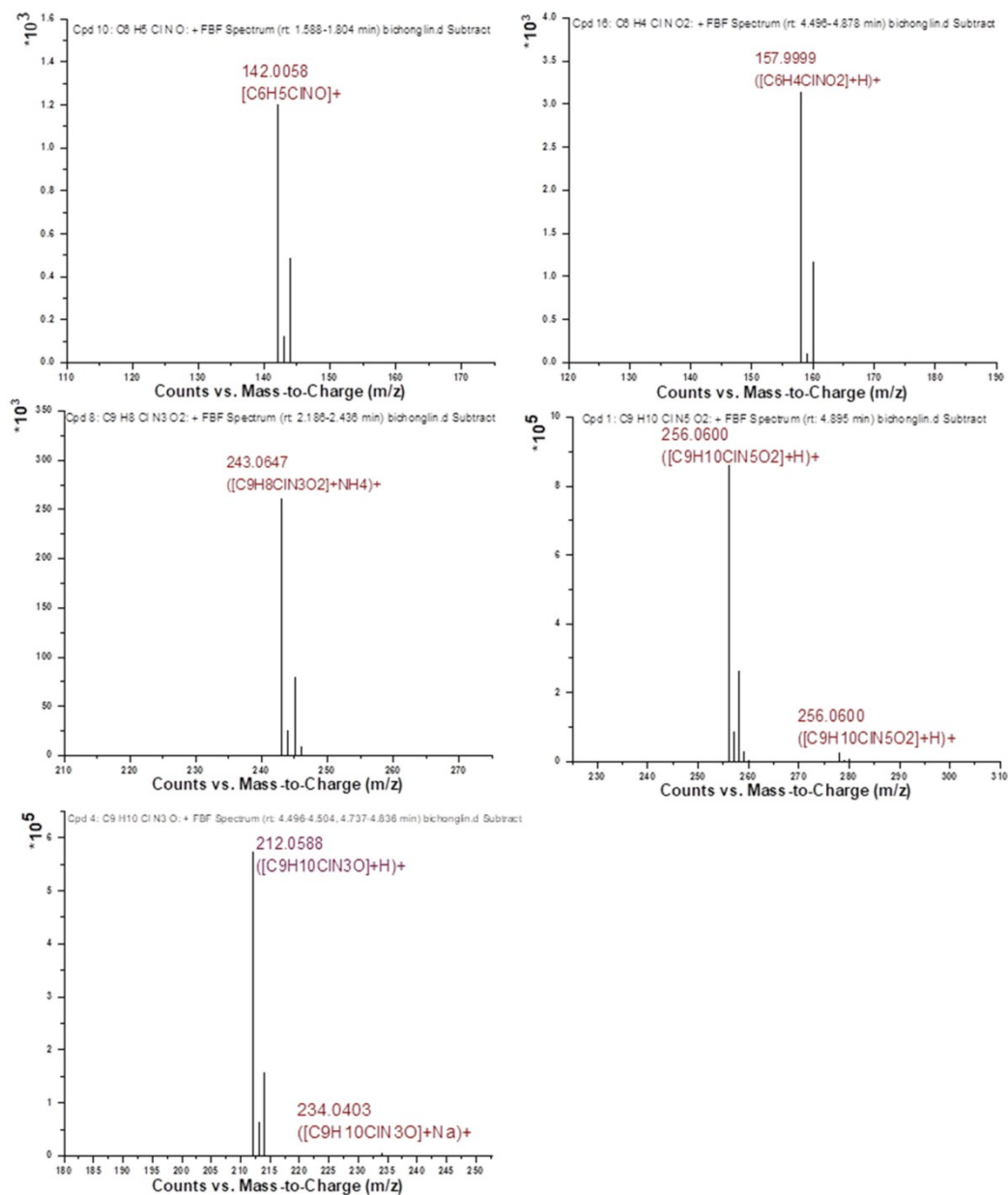
**Fig. S3.** The survey spectra of  $\text{TiO}_2\text{-OV-BiOCl}$  (a); The BET of prepared  $\text{TiO}_2/\text{BiOCl}$  and  $\text{TiO}_2\text{-OV-BiOCl}$  (b).



**Fig. S4.** Photocatalytic degradation of IMD by  $\text{TiO}_2\text{-OV-BiOCl}$  under different the additive amount of titanium trichloride solution (a), solvent systems (b) and types of surfactants (c); The change in colour of  $\text{TiO}_2\text{-OV-BiOCl}$  and  $\text{BiOCl}$  (d) before and after illumination under simulated sunlight.



**Fig. S5.** (a) HPLC graph of IMD and by-products within 35 minutes retention times in IMD undergoing photocatalytic degradation (a) and photo-degradation (b) at varies reaction time; (c) HPLC graph of IMD and by-products (d) undergoing photocatalytic degradation over  $\text{TiO}_2\text{-OV-BiOCl}$  and photo-degradation by simulated sunlight at varies reaction time.



**Fig. S6.** The iron spectra at different retention time of photocatalytic degradation for IMD under irradiation at 40 min.

**Reference:**

[1] L. Zhang, C. Niu, X. Zhao, C. Liang, H. Guo, G. Zeng, *ACS Appl. Mater. Inter.*, 2018, 46 (10) 39723-39734.

[2] H. Gao, R. Cao, X. Xu, S. Zhang, Y. Huang, H. Yang, X. Deng, J. Li, *Appl. Catal. B: Environ.*, 2019, 245 399-409.

[3] X. Wang, C. Liow, A. Bisht, X. Liu, T. C. Sum, X. Chen, S. Li, *Adv. Mater.*, 2015, 27, 2207-2214.