

Supporting Information

Graphitic Carbon Nitride-BiVO₄ Heterojunctions: Simple Hydrothermal Synthesis and High Photocatalytic Performances

Yanlong Tian, Binbin Chang, Zhichong Yang, Baocheng Zhou, Fengna Xi and Xiaoping Dong*

Department of Chemistry, School of Sciences, Zhejiang Sci-Tech University, 928 Second Avenue, Xiasha Higher Education Zone, Hangzhou, China.

Fax: 86-571-86843653; Tel: 86-571-86843228;

Email: xpdong@zstu.edu.cn

Synthesis of mechanically mixed $0.7\text{C}_3\text{N}_4\text{-}0.3\text{BiVO}_4$ sample: Mechanically mixed $0.7\text{C}_3\text{N}_4\text{-}0.3\text{BiVO}_4$ sample was prepared by finely grinding 0.7 g of C_3N_4 with 0.3 g of BiVO_4 .

Synthesis of $0.7\text{C}_3\text{N}_4\text{-}0.3\text{TiO}_2$ heterojunction: $0.7\text{C}_3\text{N}_4\text{-}0.3\text{TiO}_2$ heterojunction was synthesized by a mixing-heating method^[1]. A mixture of C_3N_4 (0.7 g) and P25 TiO_2 (0.3 g) was finely ground and then calcined at 400 °C for 1 h. After cooling to the room temperature, the resultant product was collected and crushed to a powder for further use.

Synthesis of $0.7\text{TiO}_2\text{-}0.3\text{BiVO}_4$ heterojunction: $0.7\text{TiO}_2\text{-}0.3\text{BiVO}_4$ heterojunction was obtained by a hydrothermal method. In a typical synthesis, a mixture of P25 TiO_2 (0.7 g) and NH_4VO_3 (0.1083 g) were added into 30 mL of deionized water, followed by vigorous stirring 2 h to obtain a uniform suspension. Meanwhile, a stoichiometric amount of $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ solid (0.4492 g) was dissolved in glacial acetic acid to form a clear solution. After that, the suspension and the solution were mixed together and stirred for another 2 h at room temperature. Then NaOH solution was added dropwise into this mixed solution until pH 8 was obtained. Subsequently, the mixture was transferred into an autoclave with an inner Teflon lining and maintained at 180 °C for 24 h. The obtained $0.7\text{TiO}_2\text{-}0.3\text{BiVO}_4$ heterojunction in the autoclave was collected by filtration, washed several times with deionized water, dried at 60 °C for 12 h, and finally ground for further use.

Synthesis of N-modified TiO_2 photocatalyst: N-modified TiO_2 photocatalyst was prepared by means of solid-state reaction method using urea as a nitrogen source^[2]. P25 TiO_2 (1.0 g) was finely milled with urea (2.0 g) and the mixture was heated at 400 °C for 2 h. After cooling to the room temperature, the N-modified TiO_2 photocatalyst was obtained.

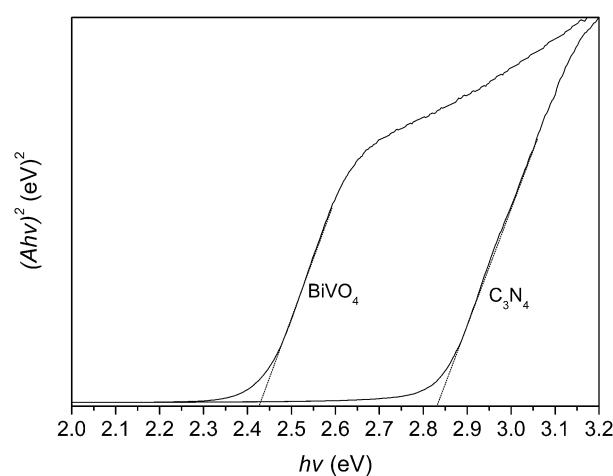


Figure S1. Plots of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) of C_3N_4 and BiVO_4 .

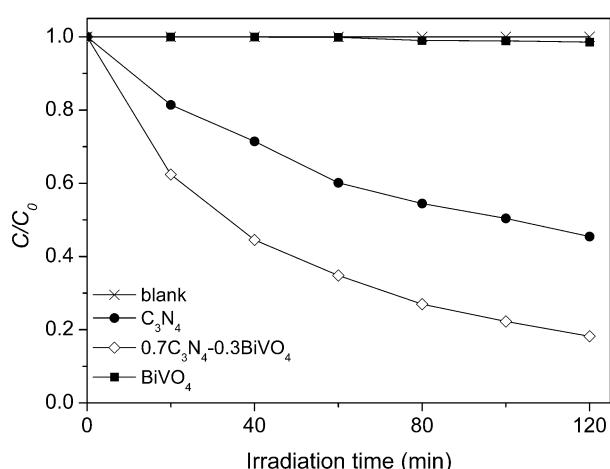


Figure S2. Degradation rates of MO under visible light irradiation without catalyst and in the presence of C_3N_4 , $BiVO_4$, and $0.7C_3N_4-0.3BiVO_4$ heterojunction.

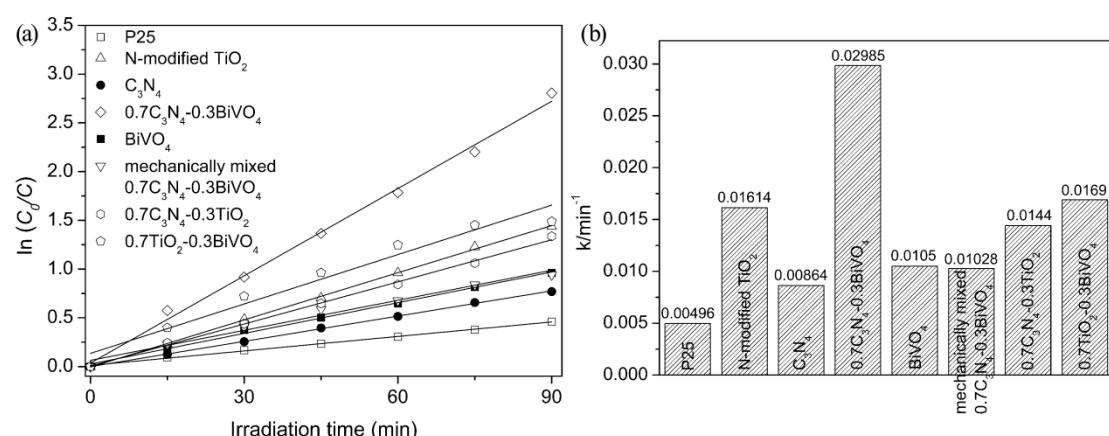


Figure S3. (a) First-order kinetics data for the photodegradation of MB over different catalysts; (b) Value of the rate constant k of the photodegradation of MB over different catalysts.

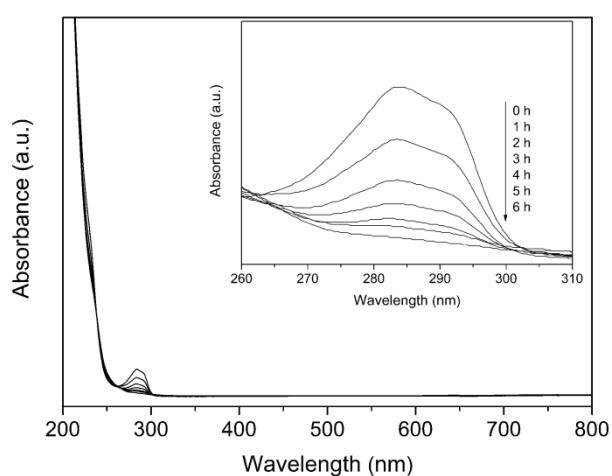


Figure S4. Absorption spectra of 2,4-DCP with irradiation time over 0.7C₃N₄-0.3BiVO₄ heterojunction.

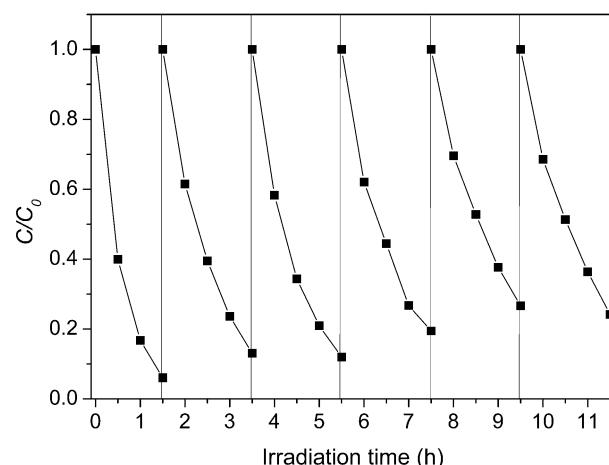


Figure S5. Cycling runs for the photocatalytic degradation of MB over $0.7\text{C}_3\text{N}_4\text{-}0.3\text{BiVO}_4$ heterojunction under visible light irradiation.

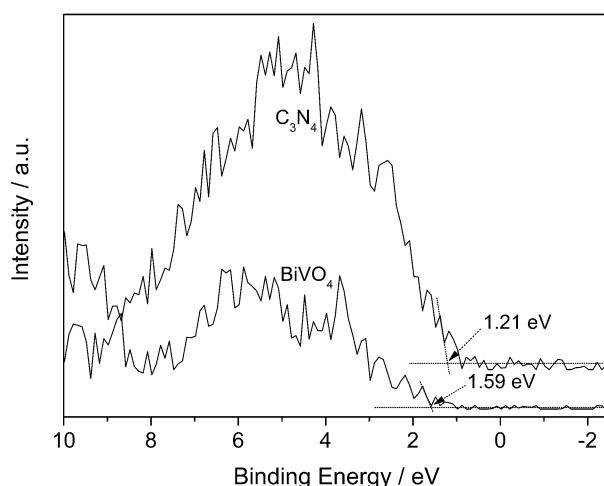


Figure S6. The VBXPS spectra of C_3N_4 and BiVO_4 .

The energy of the VB maximum was estimated by extrapolating the linear part of the low energy edge of the VB to the spectral baseline. Linear extrapolation of the VB edge will provide facile empirical determination of the VB maximum energy. It's worth noting that the zero point of the binding energy scale corresponds to the Fermi Level (E_F)^[3]. Thus, the VB maximum values of C_3N_4 and BiVO_4 were determined to be 1.59 and 1.21 eV relative to E_F , respectively (Figure S2). Given that and the E_F of C_3N_4 and BiVO_4 are different, these VB maximum values must convert into a unified standard. Here, we have chosen the redox potential of the normal hydrogen electrode (NHE) as a unified standard. From the literature, the hydrogen reduction potential $\mu_e(\text{H}^+/\text{H}_2)$ is referred to the vacuum level (E_{vac}) with the value of ~ 4.5 eV^[4-6]. The work functions ($W_s = E_F - E_{vac}$) of C_3N_4 and BiVO_4 are 4.0 and 4.7 eV, respectively^[7,8]. Finally, the VB maximum values (vs. NHE.) of C_3N_4 and BiVO_4 were obtained to be $1.59 - 4.5 + 4.0 = 1.09$ eV, and $1.21 - 4.5 + 4.7 = 1.41$ eV, respectively.

References

- [1] H. Yan and H. Yang, *J. Alloys Compd.*, 2011, **509**, L26.
- [2] D. Mitoraj and H. Kisch, *Angew. Chem. Int. Ed.*, 2008, **47**, 9975.
- [3] D. O. Scanlon, C. W. Dunnill, J. Buckeridge, S. A. Shevlin, A. J. Logsdail, S. M. Woodley, C. R. A. Catlow, M. J. Powell, R. G. Palgrave, I. P. Parkin, G. W. Watson, T. W. Keal, P. Sherwood, A. Walsh and A. A. Sokol, *Nat. Mater.*, 2013, **12**, 798.
- [4] R. Gomer and G. Tryson, *J. Chem. Phys.*, 1977, **66**, 4413.
- [5] S. Trasatti, *J. Electroanal. Chem.*, 1986, **209**, 417.
- [6] F. Yang, V. Kuznetsov, M. Lublow, C. Merschjann, A. Steigert, J. Klaer, A. Thomas and T. Schedel-Niedrig, *J. Mater. Chem. A*, 2013, **1**, 6407.
- [7] F. Yang, M. Lublow, S. Orthmann, C. Merschjann, T. Tyborski, M. Rusu, S. Kubala, A. Thomas, R. Arrigo, M. Havecker and T. Schedel-Niedrig, *ChemSusChem*, 2012, **5**, 1227.
- [8] Y. Q. Liang, T. Tsubota, L. P. A. Mooij and R. V. D. Krol, *J. Phys. Chem. C*, 2011, **115**, 17594.