

Supporting Information:

A highly efficient photoelectrochemical sensor for detection of chlorpyrifos based on 2D/2D β -Bi₂O₃/g-C₃N₄ heterojunctions

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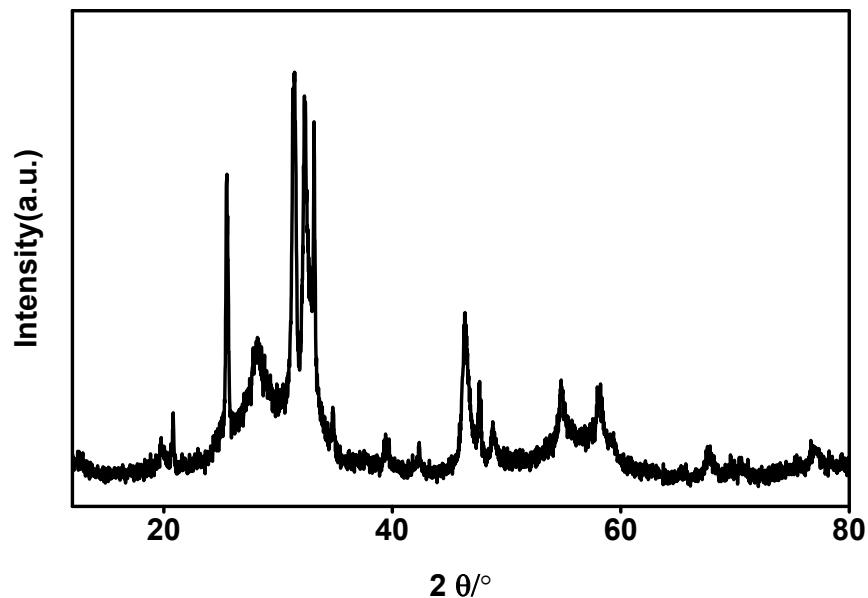


Fig.S1 XRD pattern of the product without the addition of I^- ions.

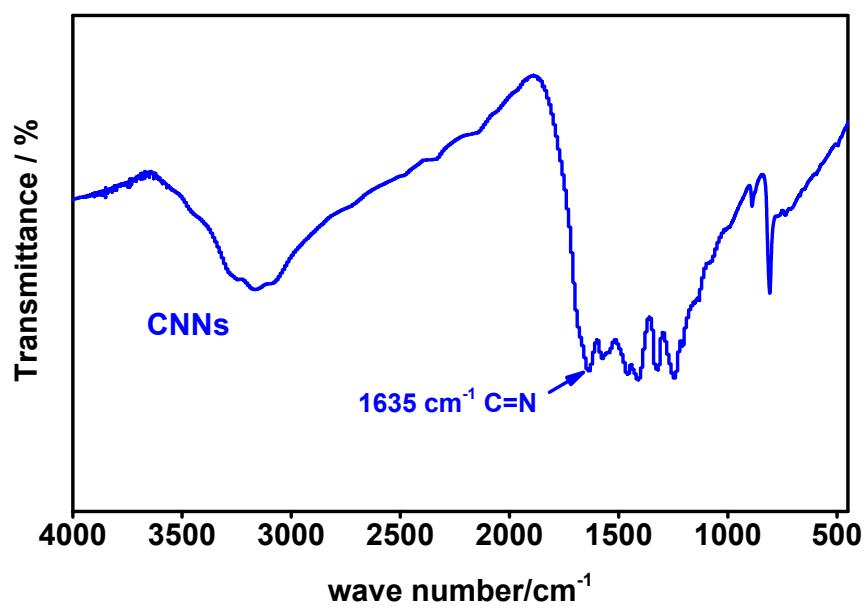


Fig.S2 FT-IR spectra of CNNs.

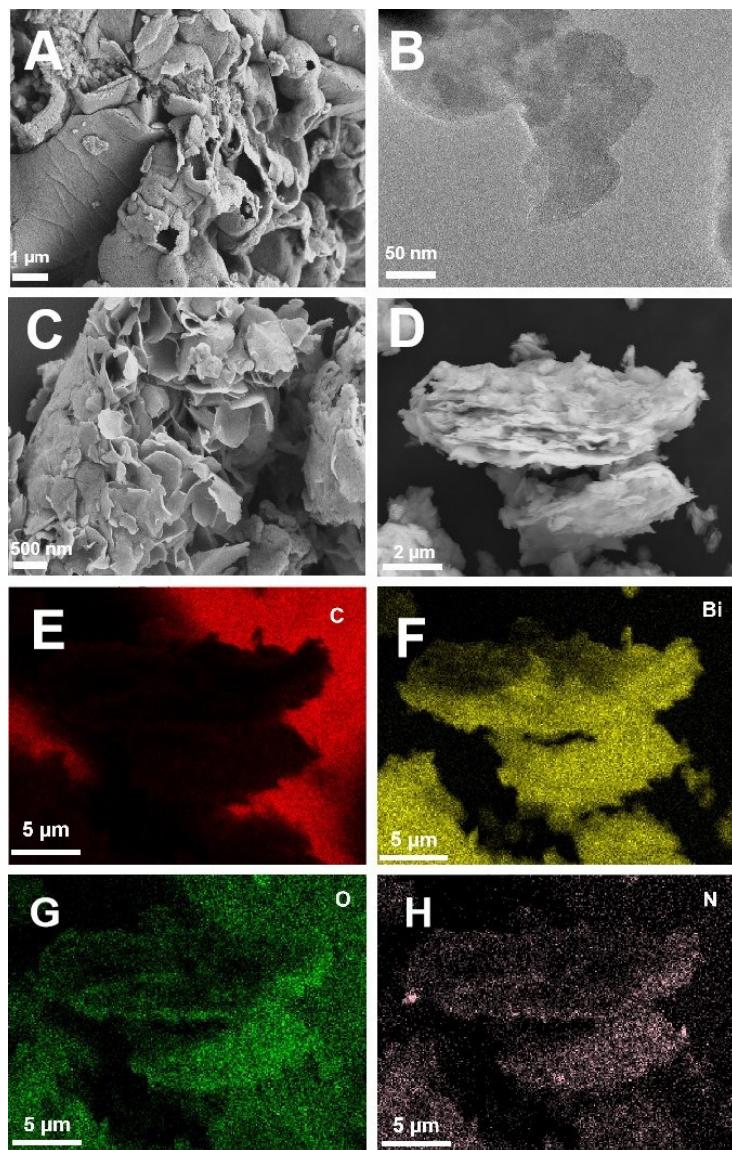


Fig.S3 SEM images of CNNs (A), β -Bi₂O₃ (C) and TEM images of CNNs 2% (B). Elemental EDX mapping images of β -Bi₂O₃/CNNs composites (D-H).

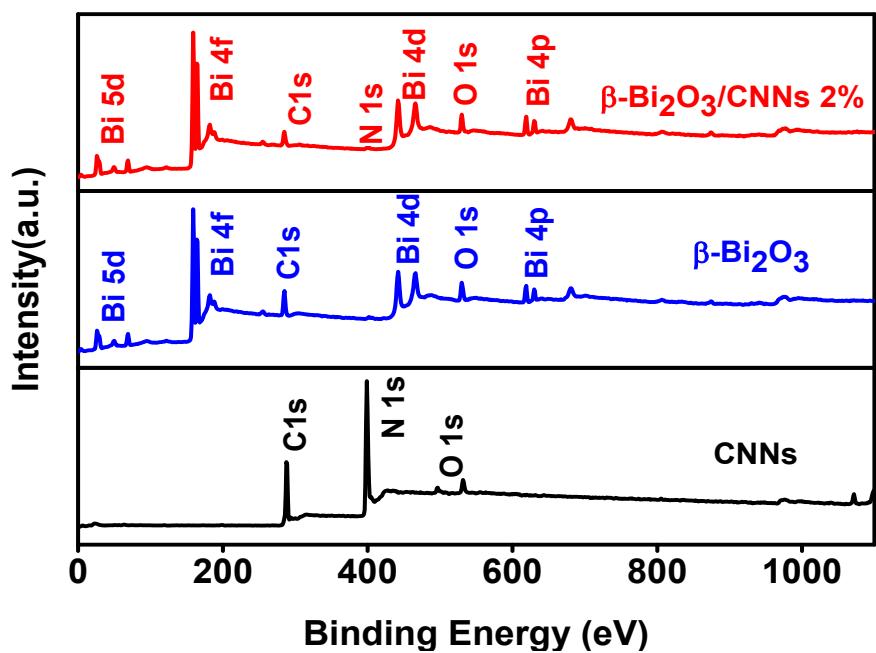


Fig. S4 The wide scan XPS survey spectra of CNNs , β -Bi₂O₃ , β -Bi₂O₃/CNNs 2%.

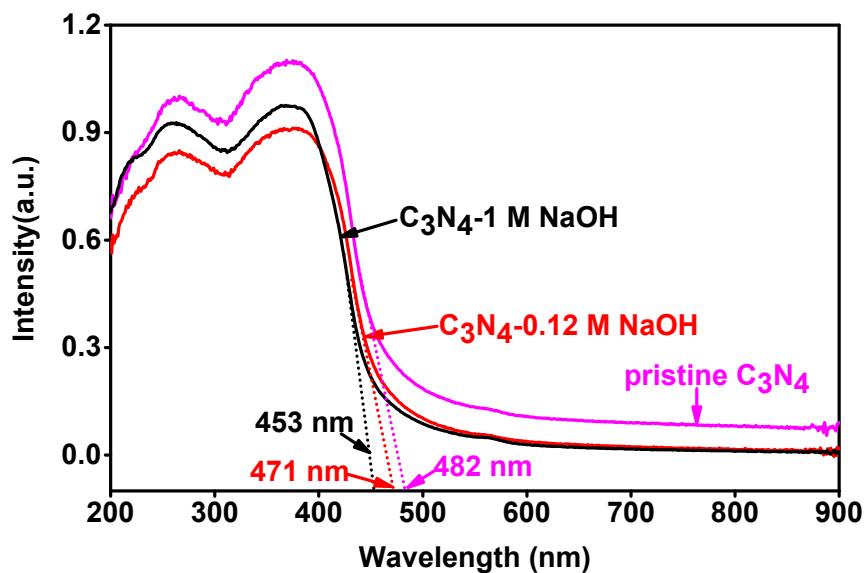


Fig. S5 UV-vis absorption spectra of CNNs obtained after hydrothermal treatment with different concentrations of NaOH.

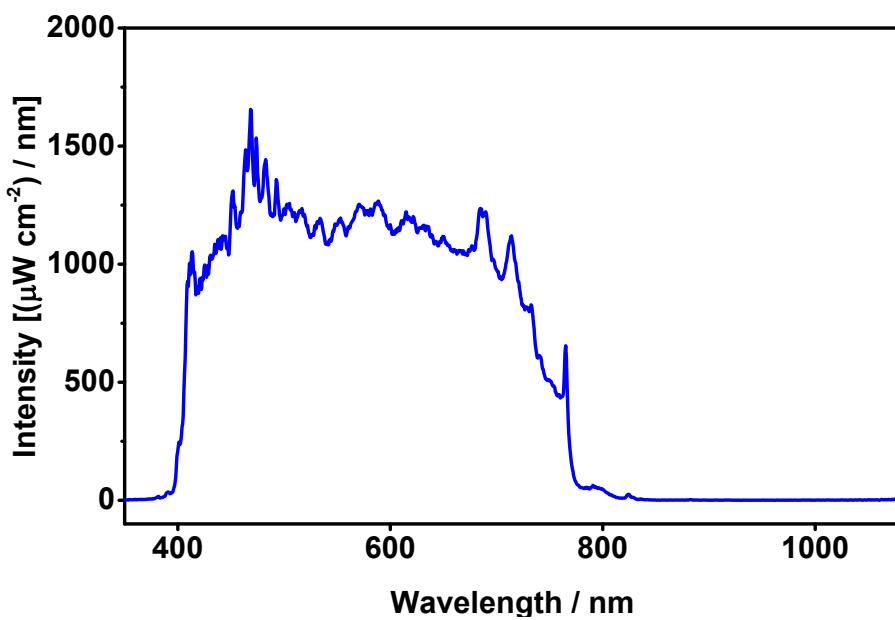
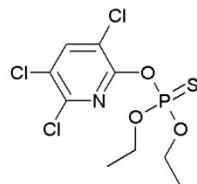
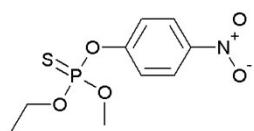


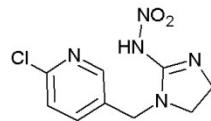
Fig. S6 The intensity spectrum of visible light.



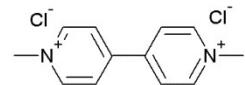
Chlorpyrifos



Parathion methyl



Imidacloprid



Methyl viologen

Fig. S7 Chemical structural formulas of Chlorpyrifos, parathion-methyl, imidacloprid and acetamiprid.

Table S1. Energy band levels of β -Bi₂O₃ and CNNs (E vs. NHE).

Samples	Eg (eV)	E _{CB} (eV)	E _{VB} (eV)
β -Bi ₂ O ₃	2.19	0.827	3.017
CNNs	2.51	-1.093	1.417

Table S2. Calculation of the absorbed photo numbers in each semiconductor.

sample	CNNs	β -Bi ₂ O ₃	β -Bi ₂ O ₃ /CNNs 2%
absorbed photon number	2.68×10^{14}	1.70×10^{16}	1.71×10^{16}
R ^a _p (quanta/cm ² /sec)			

The absorbed photo numbers in each semiconductor was calculated by the following equation:

$$R^a_p = \int_{400}^{800} S \times \alpha \times I$$

Where $S = 0.19$ cm² is the area of the electrode, α is the light absorption and I is the light intensity at each wavelength.¹

Table S3. Comparison of analytical parameters for chlorpyrifos detection in literatures.

Method	Detection limit (ng mL⁻¹)	Linear range (ng mL⁻¹)	references
LC-tandem MS	0.5	0.5-100	2
Surface-enhance-Raman spectra	10	10-50	3
PEC	3.5	70-5600	4
PEC	0.03	0.1-50	5
PEC	0.02	0.05-80	6
PEC	0.03	0.01-80	This work

Table S4. The relative standard deviation of three β -Bi₂O₃-/CNNs 2%-based photoelectrode

photoelectrode	First detection (μ A)	Second detection (μ A)	Third detection (μ A)	Relative standard deviation (%)
β -Bi ₂ O ₃ /CNNs 2%	-1.2	-1.17	-1.21	
β -Bi ₂ O ₃ /CNNs 2%-				
10ng mL ⁻¹	-0.39	-0.303	-0.366	5.56
chlorpyrifos				

Table S5. Determination results of Chlopyrifos in real sample by the PEC method (n = 3).

sample	Added(ng mL ⁻¹)	Detected(ng mL ⁻¹)	Recovery(%)	Relative standard deviation (%)
1	0.05	0.052	104	1.04
2	0.2	0.2	100	1.4
3	1	1.09	109	4.9
4	10	9.8	98	4.4
5	20	20.4	102	5.1

1. M. Liu, X. Qiu, M. Miyauchi and K. Hashimoto, Energy-level matching of Fe(III) ions grafted at surface and doped in bulk for efficient visible-light photocatalysts, *J Am Chem Soc*, 2013, **135**, 10064-10072.
2. P. 47 Salm, P. J. Taylor, D. Roberts and J. de Silva, Liquid chromatography–tandem mass spectrometry method for the simultaneous quantitative determination of the

- organophosphorus pesticides dimethoate, fenthion, diazinon and chlorpyrifos in human blood, *Journal of Chromatography B*, 2009, **877**, 568-574.
- 3. **J. 48 Tang**, W. Chen and H. Ju, Rapid detection of pesticide residues using a silver nanoparticles coated glass bead as nonplanar substrate for SERS sensing, *Sensors and Actuators B: Chemical*, 2019, **287**, 576-583.
 - 4. **H. 49 Li**, J. Li, Q. Xu and X. Hu, Poly(3-hexylthiophene)/TiO₂ nanoparticle-functionalized electrodes for visible light and low potential photoelectrochemical sensing of organophosphorus pesticide chlopyrifos, *Anal Chem*, 2011, **83**, 9681-9686.
 - 5. **Q. 41 Liu**, Y. Yin, N. Hao, J. Qian, L. Li, T. You, H. Mao and K. Wang, Nitrogen functionlized graphene quantum dots/3D bismuth oxyiodine hybrid hollow microspheres as remarkable photoelectrode for photoelectrochemical sensing of chlopyrifos, *Sensors and Actuators B: Chemical*, 2018, **260**, 1034-1042.
 - 6. J. Qian, Z. Yang, C. Wang, K. Wang, Q. Liu, D. Jiang, Y. Yan and K. Wang, One-pot synthesis of BiPO₄ functionalized reduced graphene oxide with enhanced photoelectrochemical performance for selective and sensitive detection of chlorpyrifos, *Journal of Materials Chemistry A*, 2015, **3**, 13671-13678.