Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Construction of Z-scheme g-C_3N_4/NBGO/$BiVO_4$ heterostructure with visible-light-driven photocatalytic degradation of tetracycline：Efficiency, reaction pathway and mechanism

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Synthesis of Three-dimensional graphene-like biochar from orange peel (GBO)

Firstly, the crushed orange peel (passing through 200 mesh sieve) was carbonized at 400 °C for 2 h with the protection of N_2 to produce orange peel biochar (OPB-400). Then the carbonized orange peel was mixed with K_2CO_3 with a mass ratio of 2:1 and calcined at 900 °C for 2 h in the atmosphere of nitrogen. After cooling to room temperature, the samples were washed with deionized water until the pH was neutral. And the samples were then dried at 60 °C for 24 h. The as-prepared samples were named as GBO-900. For comparison, a modification temperature of 800°C, noted as GBO-800, was also prepared.

Then 320 mg of GBO-900 was dispersed in 120 mL of deionized water, and 348 μL of hydrazine hydrate was added. After gentle sonication and stirring treatment. After gentle sonication and stirring treatment, the above solution was transferred to a 200 mL stainless steel autoclave lined with Teflon and kept at 180 °C for 18 h. The black product was collected, washed three times each with water and ethanol, and then dried at 80 °C for 6 h to obtain nitrogen-doped graphene-like (NGBO).

Synthesis of $BiVO_4$

In the conventional synthesis method, 0.02 mol $Bi(NO_3)_3 \cdot 5H_2O$ and 0.02 mol NH_4VO_3 were dissolved in 40 mL nitric acid (2 M) to form solution A and 20 mL NaOH solution (2 M) to form solution B, respectively. The solution B was then added drop by drop to solution A under vigorous stirring to obtain a stable suspension. The resulting suspension was transferred to a 100 mL stainless steel autoclave lined with Teflon. The reaction was maintained at 180 °C for 12 h. Finally, it was washed three times with alternating deionized water and ethanol and then dried at 60 °C to obtain the yellow powder of $BiVO_4$.

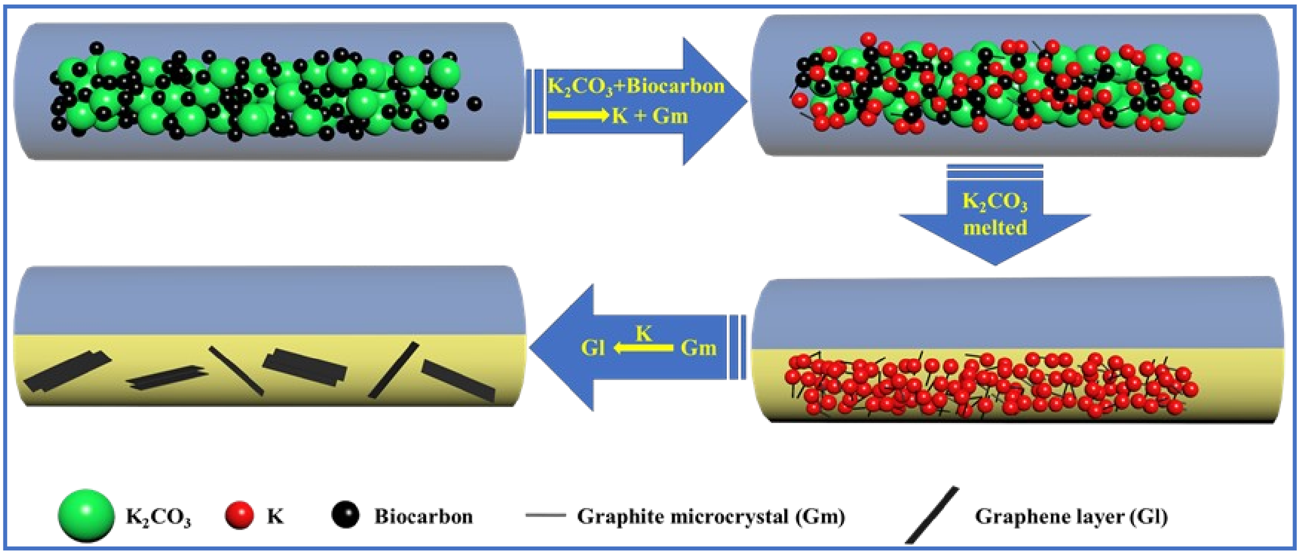


Fig. S1. GBO material preparation flow chart.

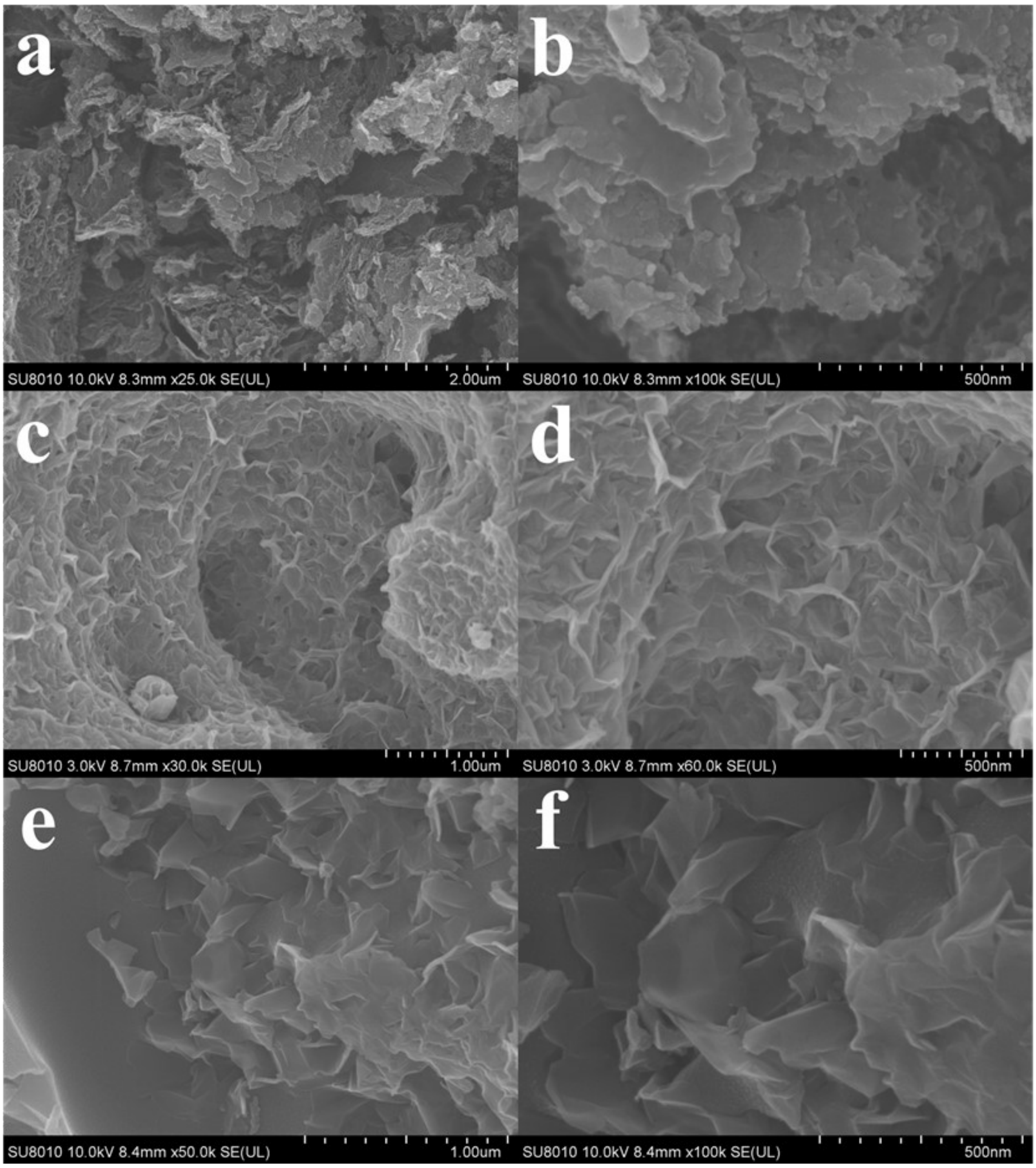


Fig. S2. (a-b) SEM of OPB-400; (c-d) SEM of GBO-800; (e-f) SEM of GBO-900.

SEM of OPB-400, GBO-800 and GBO-900 were shown in Fig.S2. A condensed surface of OPB-400 was observed with covered with some extracts (Fig.S2. a-b). After the activation of K_2CO_3, more porous structures were formed on the surface of biochar, where some nanosheets are anchored in GBO-800 (Fig.S2. (c-d)). When the temperature was increased to 900 °C, the porous three-dimensional architecture with high amounts of interconnected nanosheets was formed in the GBO-900 (Fig.S2. (e-f)).

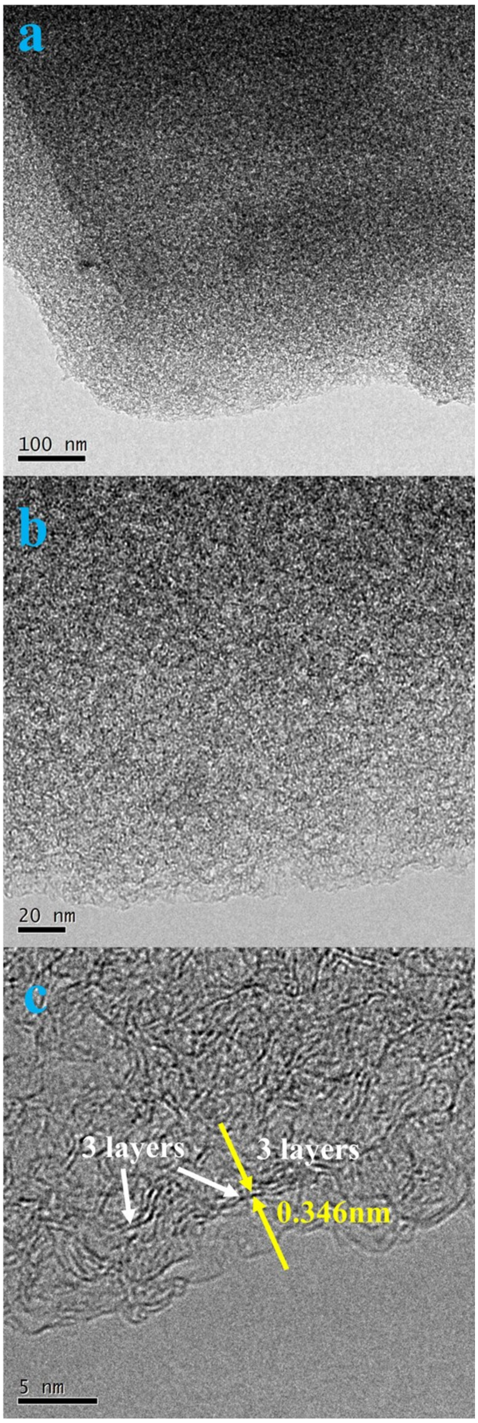


Fig. S3. (a) TEM image of GBO-900 (100 nm), (b) TEM image of GBO (20 nm), (c) TEM image of GBO (5 nm) and (d) Raman spectra of OPP-400 and GBO-900.

The morphological structure of GBO-900 was shown in Fig.S3. (a-c). The TEM images showed the formation of graphene-like nanostructure in orange peel-based biochar. Fig. S3c showed typical sheets composed of three layers of graphene with a graphite lattice spacing of approximately 0.346 nm (Fig. S3c).

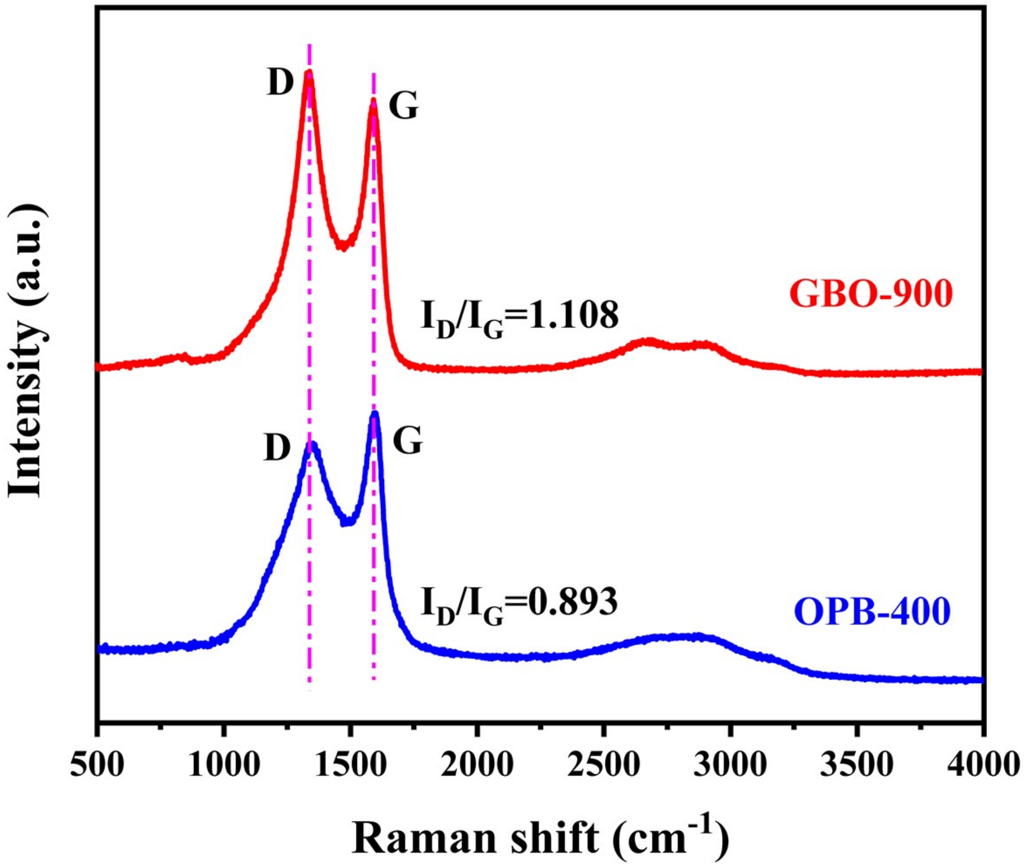
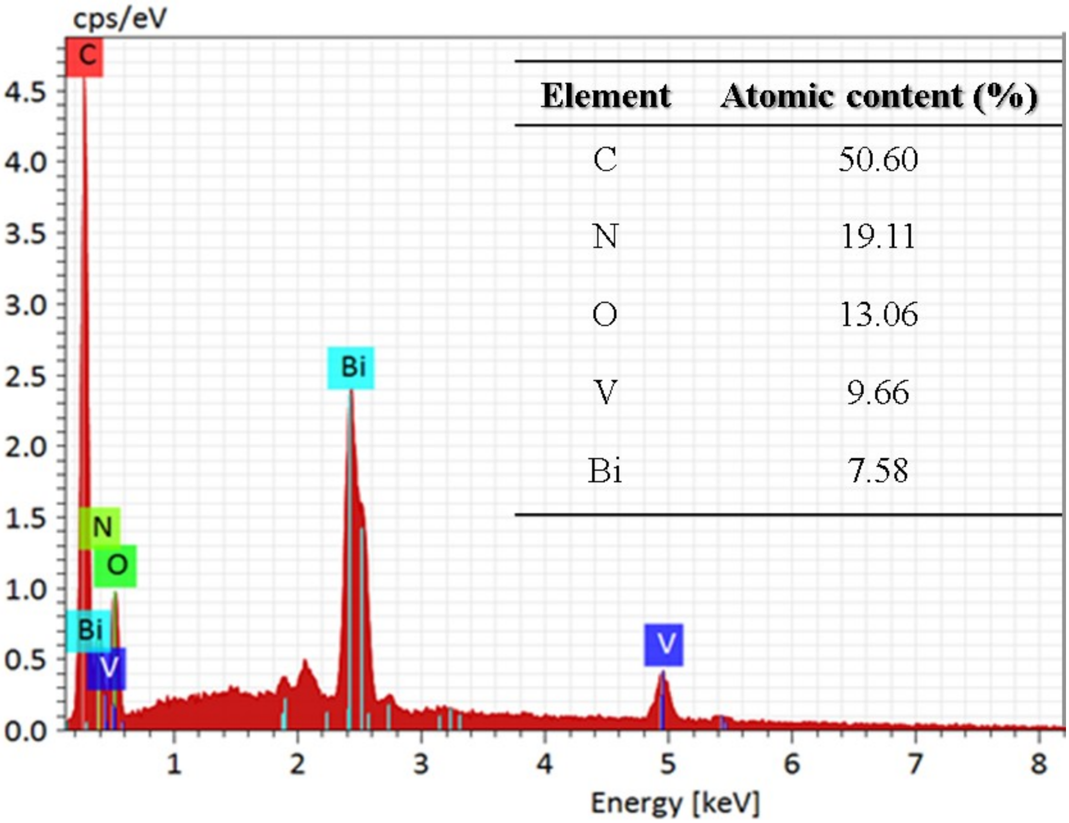


Fig.S4. Raman spectra of OPP-400 and GBO-900

Raman spectroscopy is a non-destructive, fast and effective method to provide structural information of different carbonaceous materials while identifying them.[1] Raman spectra of OPP-400 and GBO-900 were shown in Fig. S4. The characteristic peaks of the D and G bands correspond to imperfect carbon structures. The D band is produced by the breathing modes of sp^2 atoms in rings, being usually very intense in amorphous carbon samples. The G band, on the other hand, originates from the bond stretching of all paired sp^2 atoms in the ring and chain.[2] I_D/I_G can reflect the degree of defects and graphitization in carbon materials.[3-5] The I_D/I_G value of the OPP-400 was 0.893, while the I_D/I_G value of the GBO-900 was 1.108. The I_D/I_G value increased from 0.893 to 1.108 indicated that more defects were generated during the activation of K_2CO_3.[6-8] Therefore, the results of Raman mapping showed that the method used in this experiment can effectively prepare graphene-like materials with high purity.



Element	Atomic content (%)
C	50.60
N	19.11
O	13.06
V	9.66
Bi	7.58

Fig.S5. The EDS of CN/NGBO/BV.

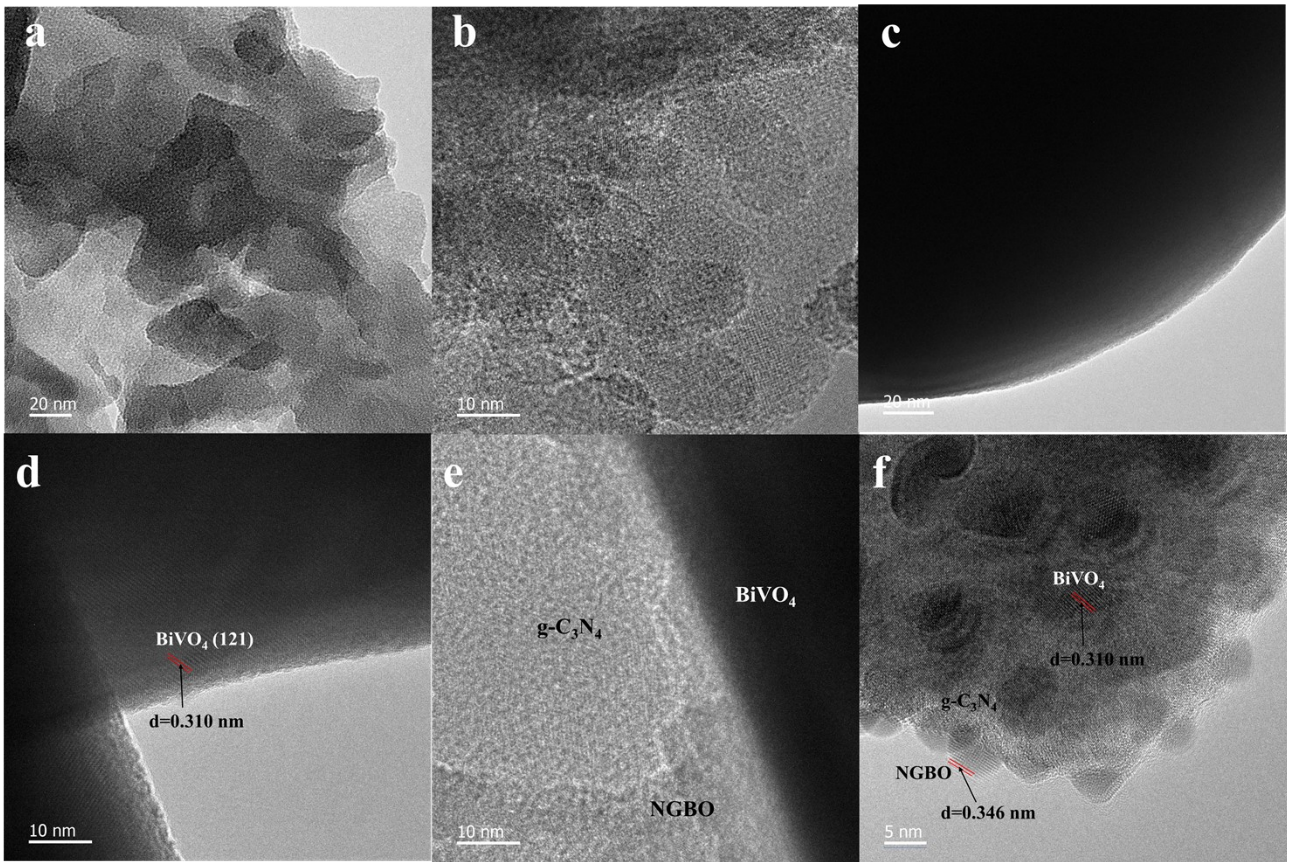


Fig. S6.TEM images of (a) g-C_3N_4, (c) $BiVO_4$ and (e) CN/NGBO/BV. HRTEM images of (b) g-C_3N_4, (d) $BiVO_4$ and (f) CN/NGBO/BV.

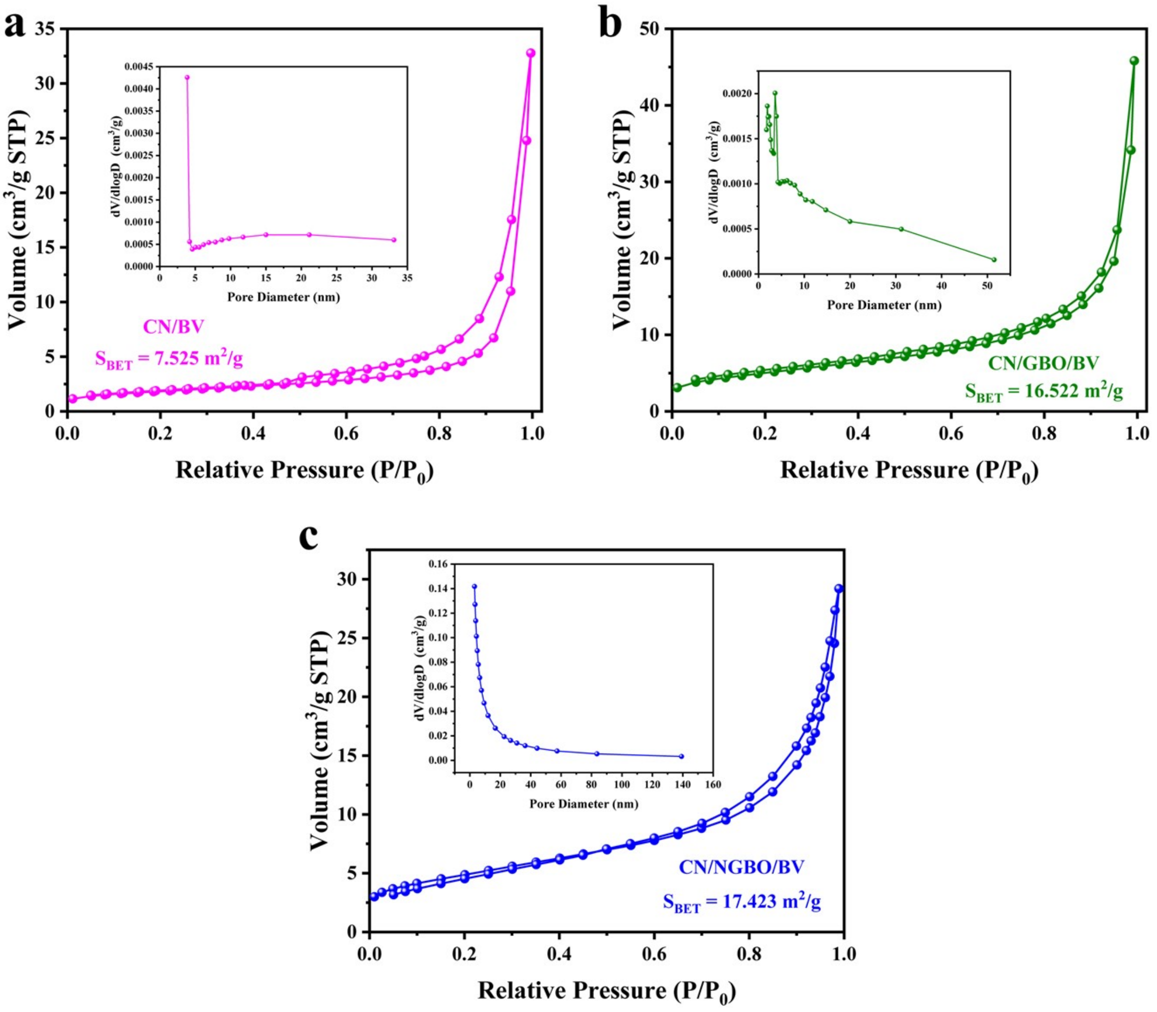


Fig.S7. N_2 adsorption-desorption curves and Pore size distribution of (a)CN /BV, (b)CN/GBO/BV and (c)CN/NGBO/BV.

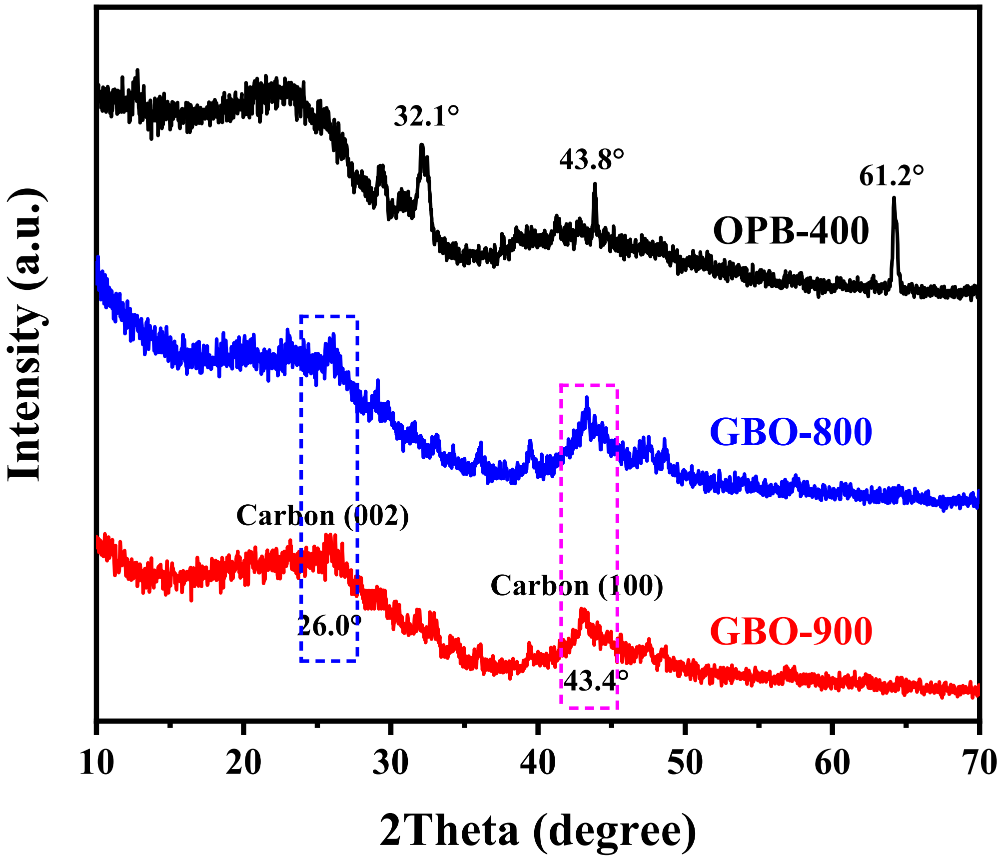


Fig. S8. XRD patterns of OPB-400, GBO-800 and GBO-900.

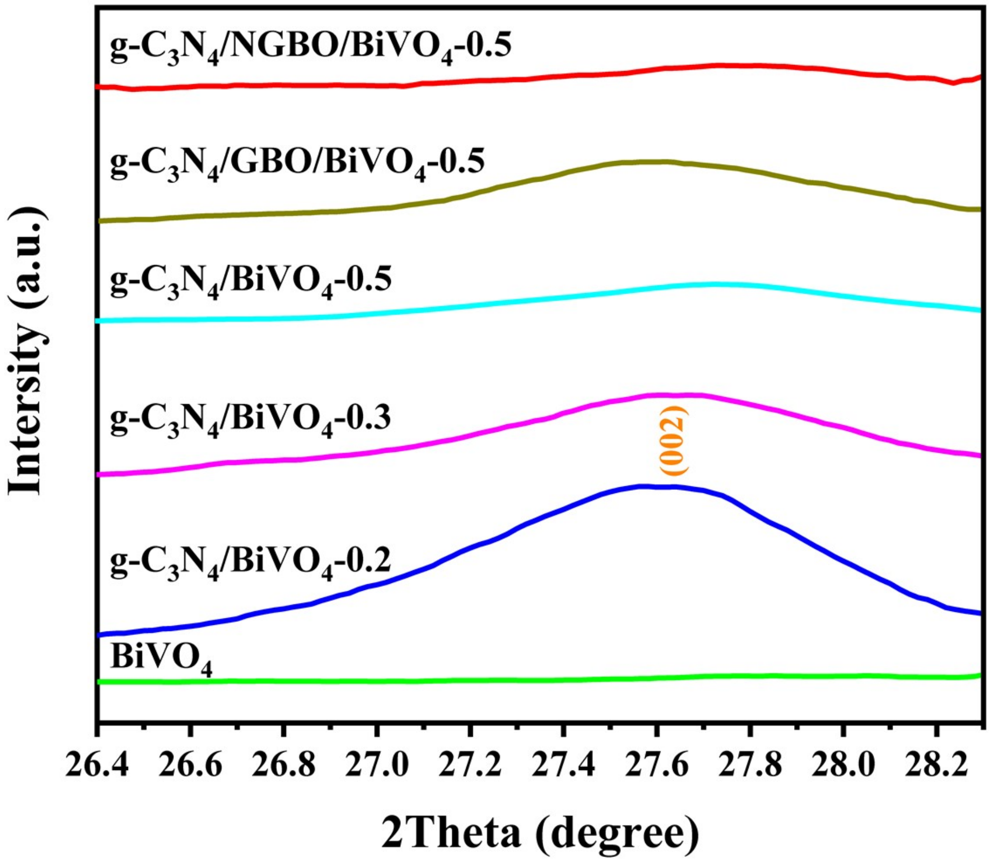


Fig.S9. XRD pattern of the prepared sample in the typical (002) region.

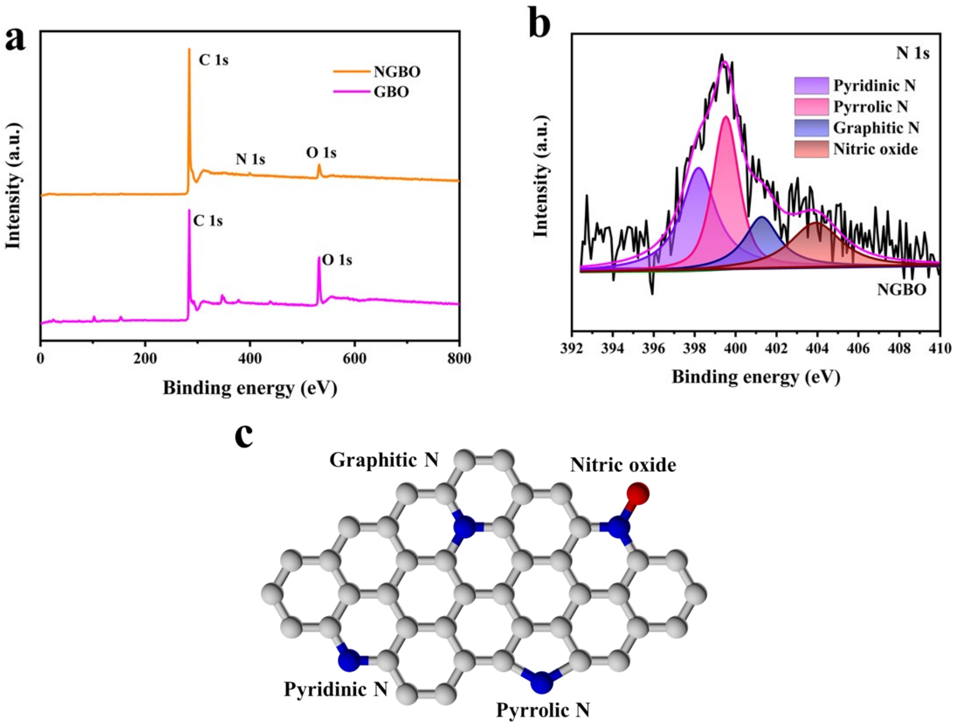


Fig. S10. (a) XPS survey spectra of GBO and NGBO, (b) The XPS N1s spectrum of NGBO and (c) schematic representation of the chemical structure of pyridinic, pyrrolic, and graphitic N species.

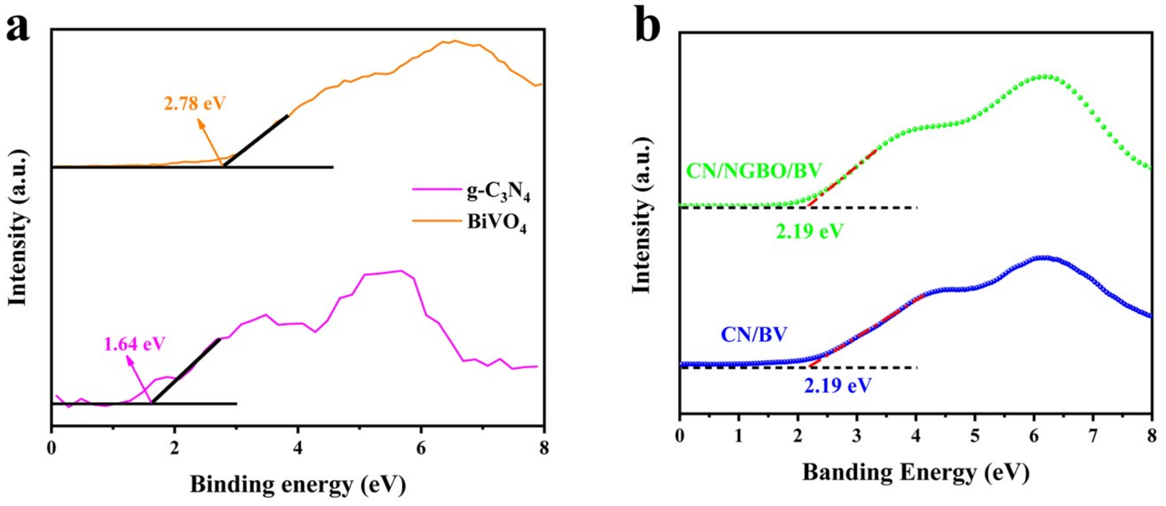


Fig.S11. XPS VBs spectra of (a)g-C_3N_4 and $BiVO_4$, (b) CN/BV and CN/NGBO/BV.

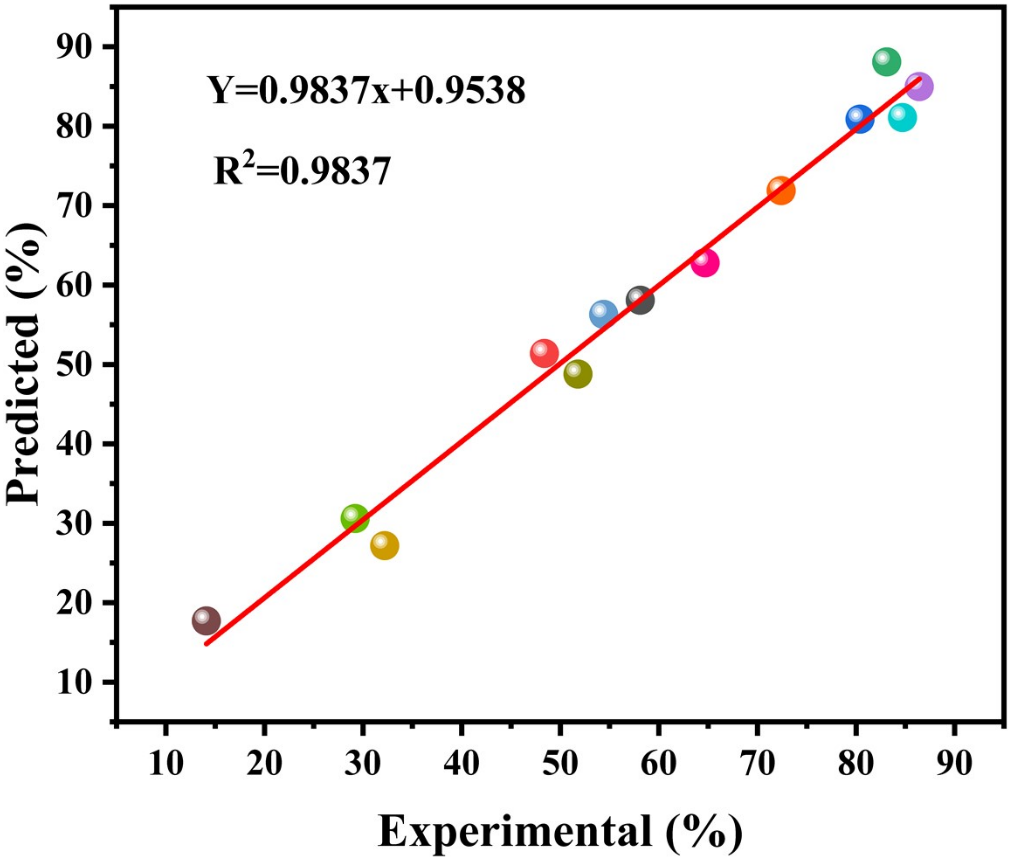


Fig.S12. Correlation of predicted and experimental values of response for TC removal.

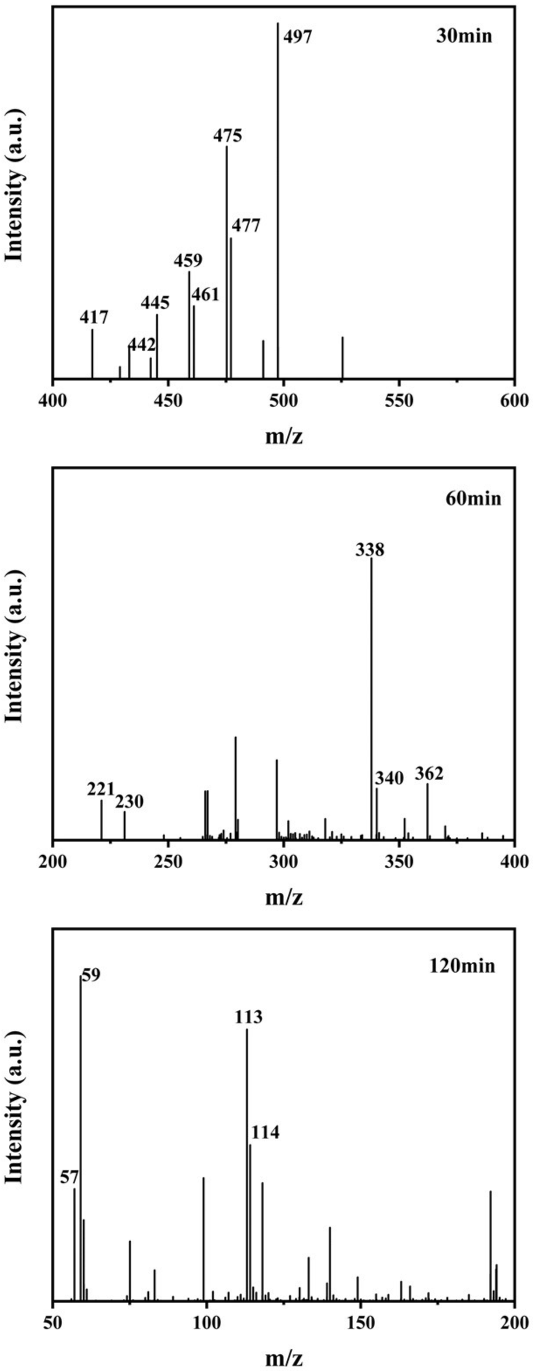


Fig.S13. The spectrum of LC-MS for TC degradation is at different times.

Table S1 Box-Behnken independent variables (coded and uncoded) for optimization of degradation rate of TC.

Factor	Levels		
	-1	0	1
TC concentration (A) mg/L	10	30	50
Catalyst dosage (B) mg	5	22.5	40
Solution pH (C)	4	7	10

Table S2 Experimental data of the BBD.

Run	Independent variables			Degradation rate (%)	
	A	B	C	Experimental	Predicted
1	30	22.5	7	58.1	58.1
2	30	22.5	7	58.1	58.1
3	30	40.0	4	48.4	51.4
4	10	22.5	4	80.4	80.9
5	10	22.5	10	83.1	88.1
6	30	40.0	10	86.4	85.0
7	30	22.5	7	58.1	58.1
8	30	22.5	7	58.1	58.1
9	50	22.5	4	32.2	27.2
10	10	40.0	7	84.7	81.1
11	50	5.0	7	14.1	17.7
12	30	5.0	10	51.8	48.8
13	50	22.5	10	72.4	71.9
14	30	22.5	7	58.1	58.1
15	50	40.0	7	54.4	56.3
16	30	5.0	4	29.2	30.6
17	10	5.0	7	64.7	62.8

Table S3 ANVOA (analysis of variance) for the optimized RSM model.

Source	Sum of Squares	df	Mean Square	F Value	P-Value Prob＞F
Model	6362.09	9	706.90	47.15	＜0.0001
A	2443.00	1	2443.00	162.96	＜0.0001
B	1627.35	1	1627.35	108.55	＜0.0001
C	1339.03	1	1339.03	89.32	＜0.0001
AB	103.02	1	103.02	6.87	0.0343
AC	351.56	1	351.56	23.45	0.0019
BC	59.29	1	59.29	3.95	0.0871
A^2	94.00	1	91.00	6.27	0.0407
B^2	293.57	1	293.57	19.58	0.0031
C^2	74.27	1	74.27	4.95	0.0613
Residual	104.94	7	14.99		
Lack of Fit	104.94	3	34.98		
Pure Error	0.000	4	0.000		
Cor Total	6467.04	16			

Table S4 Calculated value of the CB and VB potentials of g-C_3N_4 and $BiVO_4$.

Sample	E_g (eV)	E_{VB} (eV)	E_{CB} (eV)
g-C_3N_4	2.79	1.625	-1.165
$BiVO_4$	2.42	2.745	0.325

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