Electronic Supplementary Information (ESI)

An intimate coupling of Bi_2WO_6/CN heterojunction and biodegradation for the degradation and mineralization of atrazine in water

Text S1. Preparation of CN and Bi_2WO_6/CN

Synthesis of carbon nitride (CN)

A facile method with heating urea directly was used to gain light yellow CN powder. In a typical synthesis procedure, 10 g urea was put in an alumina crucible with a cap, and then it was transferred into a muffle furnace and heated to 550 ℃ for 4 h with a ramp rate of 2.5 ℃/min. After that, the bulk CN was ground and calcined at 500 ℃ for 2 h with a heating rate of 2.5 ℃/min to carry out the deammoniation treatment.

Synthesis of Bi_2WO_6/CN heterojunction

The heterojunction Bi_2WO_6/ CN was prepared via a hydrothermal method. Briefly, glacial acetic acid was used to dissolve 2 mmol $Bi(NO_3)_3 \cdot 5H_2O$ to form clear solution. In the same time, CN and 1 mmol $Na_2WO_4 \cdot 2H_2O$ were added into 30 mL of distilled water and stirred 3 h to gain suspension. Then, the $Na_2WO_4 \cdot 2H_2O$ solution was quickly added to the above suspension and the mixture solution was retained for another 5 h upon continuous stirring. Subsequently, the pH value of the mixed solution was adjusted to pH 8 via NaOH solution (2M), and then it was transferred to 100 mL Teflon-lined autoclave holding 160 ℃ for 20 h. Finally, the product was washed three times via deionized water and dried at 60 ℃ for 10 h.

Text S2. Characterization

The microstructure of ICPB carriers and the morphology of Bi_2WO_6, CN and Bi_2WO_6/CN were obtained by JEOL 7500F scanning electron microscopy (SEM) with a voltage of 2 kV. Electron spin resonance (ESR) spectra were detected by a Bruker E-500 spectrometer. The X-ray diffraction (XRD) patterns were used to acquire the information of crystallography and detected on a D8 ADVANCED X-ray diffractometer with Cu Kα radiation (λ = 0.154 nm). UV-Vis diffuse reflection spectroscopy (DRS) spectrum was obtained via Hitachi UV-3900 spectrophotometer

with $BaSO_4$ as reference. Thermo ESCALAB 250Xi using Al Kα (1486.6 eV) as the X-ray source was applied to measure the X-ray photoelectron spectra (XPS) analysis. Mott-Schotty curves were investigated on CHI 660E electrochemical analyzer (CH Instruments, shanghai).

Text S3. Photocatalytic activity test

100 mg of powder sample and 100 ml of atrazine solution (20.0 mg/L) were putted in the above reactor, followed by stirring for 30 min in dark to reach the adsorption-desorption equilibrium and reaction solution was maintained in room temperature via circulating water during the whole process. After the light was turned on, the mixed solution was taken at 2 h, 4 h, 6 h and 8 h. The photocatalytic activity were detected with HPLC. All samples solutions were filtered by 0.2 μm PVDF membrane filter before analysis and the concentrations of atrazine were detected through HITACHI Primaide HPLC system.

The ·OH and $\cdot O_2^-$ in the photocatalytic reaction of Bi_2WO_6/CN heterojunction were also investigated by the degradation of atrazine. 100 mg Bi_2WO_6/CN powder was dispersed in 100 mlatrazien solution (20.0 mg/L) with continuous stirring, and reactor was kept in room temperature via circulating water. The TBA(0.1 mmol/L), NaC_2O_4(0.5 mmol/L), p-benzoquinone(0.5 mmol/L) and Fe(Ⅱ)-EDTA(0.1 mmol/L) were respectively added to the above solution. The TBA can scavenged ·OH, p-benzoquinone for the scavenging of $\cdot O_2^-$, NaC_2O_4 for the quenching of h^+ and Fe(II)-EDTA was used for scavenging H_2O_2. Prior to the light irradiation, the mixed solution was stirred for 30 min to achieve adsorption equilibrium under dark condition. After that, 300 W Xenon Lamp simulating the solar light was used as the excitation light. After that, supernatants without photocatalytic powder were collected every 1 h from the reactor and filtered by 0.2 μm PVDF membrane filter. In addition, ESR spectroscopy with 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin trapping agent was applied to detect the production of $\cdot O_2^-$ and ·OH.

Text S4 Experimental setup

Atrazine degradation was carried out in the PCBBR with a working volume of 540

mL, and the schematic was shown in Fig. 8. The draft section of reactor was a plexiglass with a diameter of 40 mm and a height of 130 mm, and its bottom was mounted an aeration disc diffuser with a diameter of 40 mm. The annular section was an annular quartz tube, which has an inner diameter of 70 mm and a total height of 180 mm. The liquid mixture flowed down via annular quartz tube to be recycled into the draft tube section. Air was provided to the internal loop of the reactor via 35 W aeration pump (SOBO, Weifang, China), producing an aeration rate of 480 g O_2/ (g atrazine · h). 300 W Xe Lamp simulating the solar light was used as light source and all the experiments were proceeded at room temperature.

Text S5 Analytical procedures

HPLC system with a 4.6Ø250 mm, 5-μm Eclipse Plus C18 column. The mobile phase consisted of deionized water (50%) and acetonitrile (50%), and the flow rate was 1.0 mL/min. The column temperature was held constant at 30 ℃. 10.0 μL sample was injected into the column and the eluate was analyzed with a fluorescence detector at 215 nm.

To further analyzed the degradation products of atrazine in ICPB system, the UPLC-MS system (Agilent 1290 Infinity, USA) equipped with an ACQUITY UPLC BEH C18 column (100Ø2.1 mm, 1.7 μm) was used. The LC-MS was operated in the full scan mode. The injection volume was 10 μL.The mobile phase was a mixture of 50% (v/v) acetonitrile and 50% deionized water (v/v), and it was applied at a flow rate of 0.2 mL/min. MS was performed using ESI in positive-ion mode The scanning mass range was from 50 to 300 m/z.

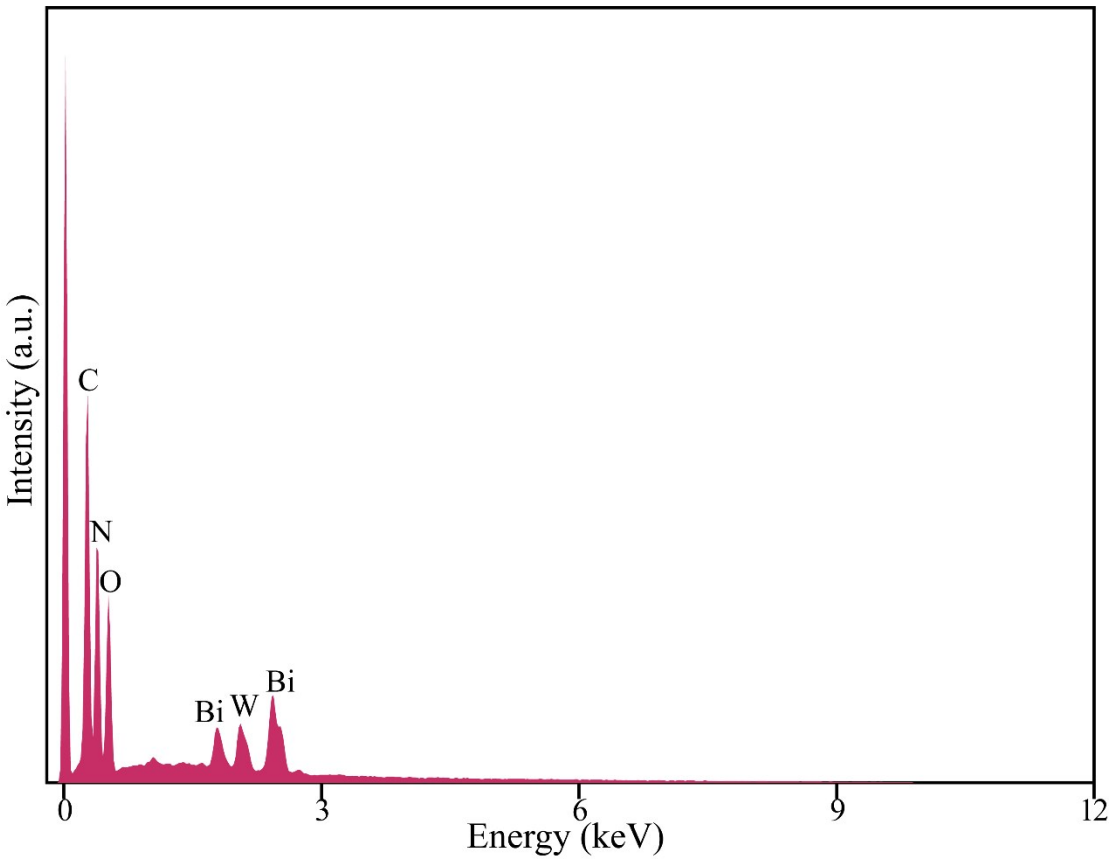

Fig. S1. EDX spectrum of Bi_2WO_6/g-C_3N_4 samples.

Fig. S2. Photograph of polyurethane sponge carrier used in this study.

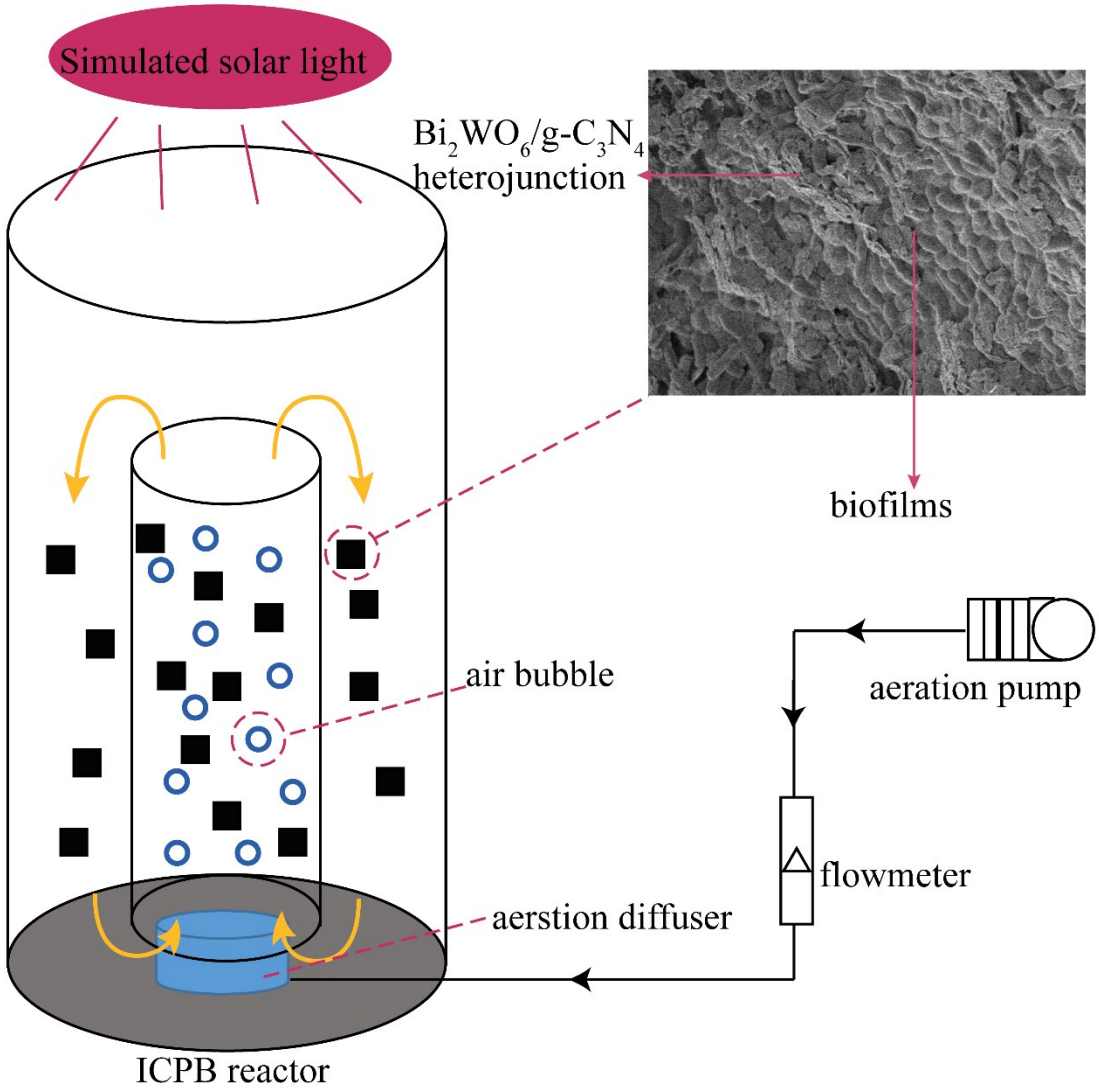

Fig. S3. Schematic diagram of photocatalytic circulating-bed biofilm reactor.

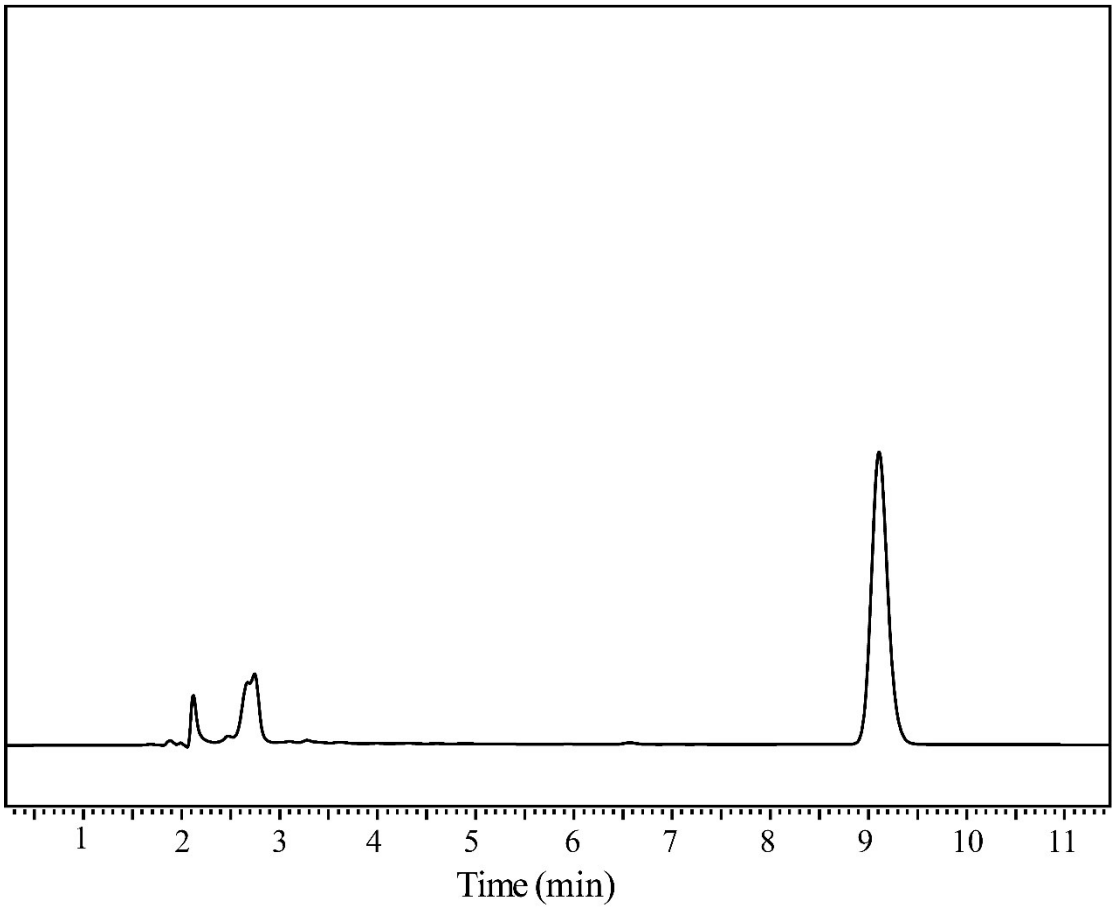

Fig. S4. HPLC chromatogram of atrazine solution.

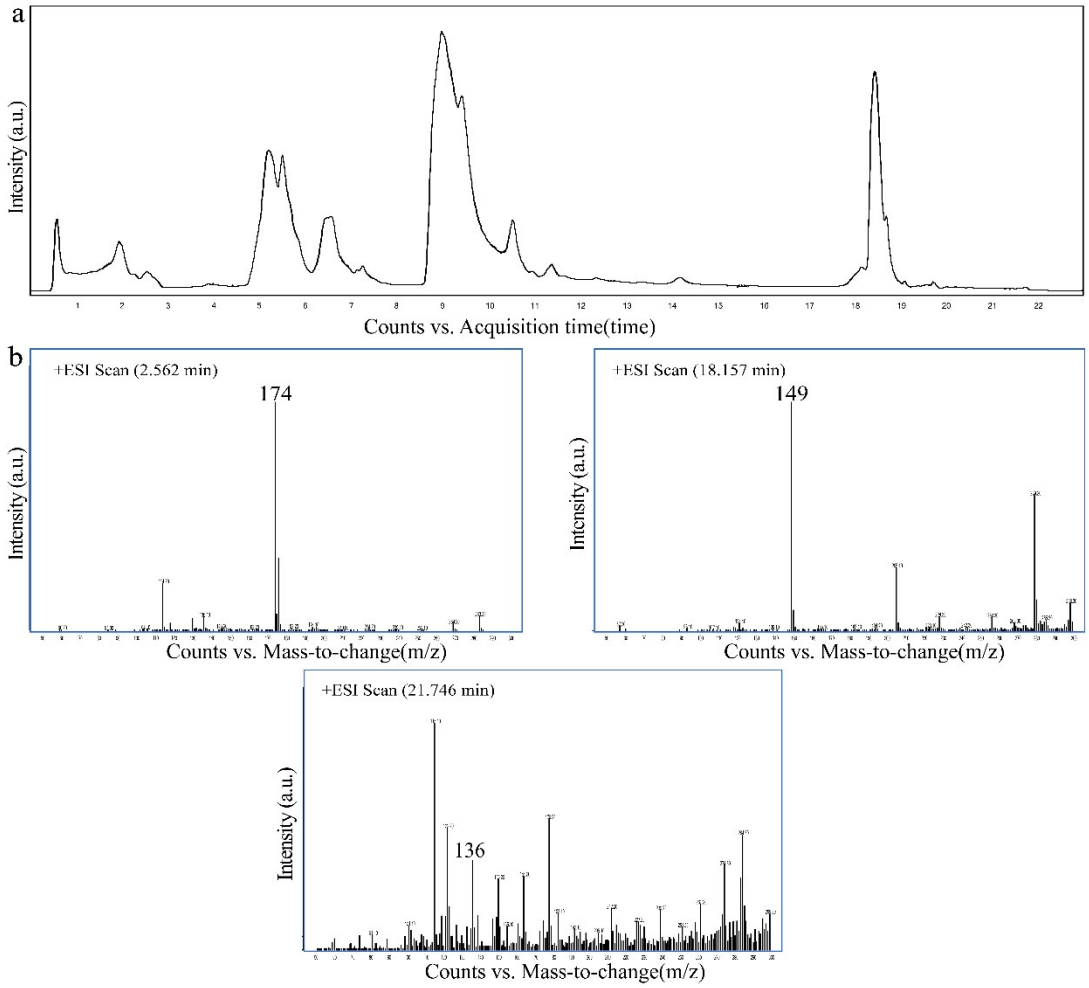

Fig. S5. Mass spectra of atrazine and intermediates with photocatalytic.

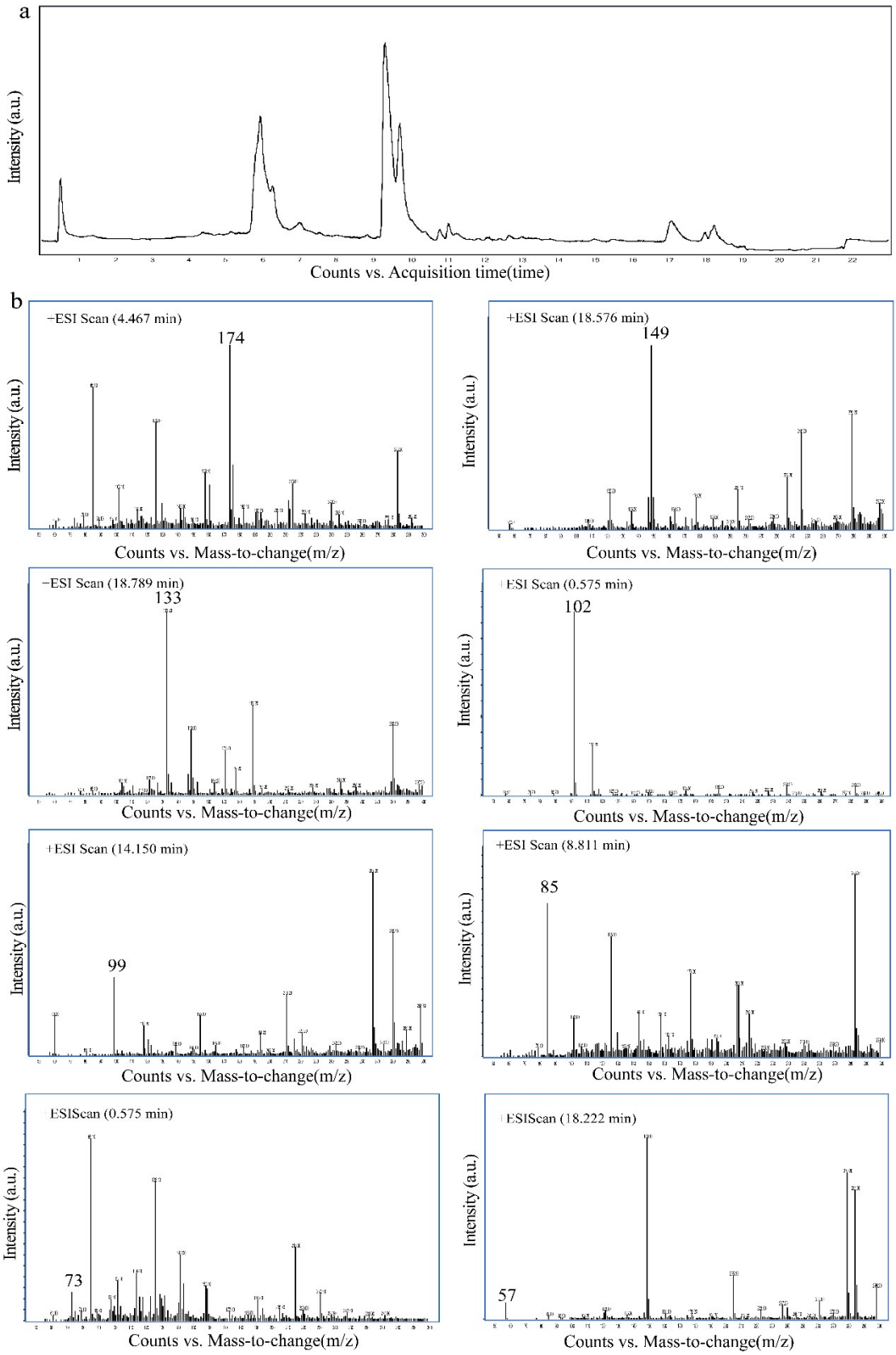

Fig. S6. Mass spectra of atrazine and intermediates with ICPB.