Supplementary Material (ESI) for New Journal of Chemistry

The Increased Photoremoval Performance of Boron Carbon Nitride-Pyromellitic Dianhydride Composite for Tetracycline and Cr(VI) by Itself to Change the pH of Solution

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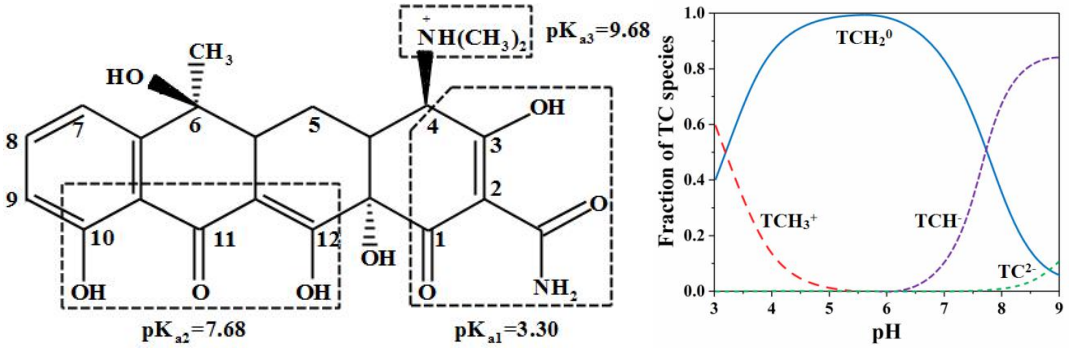


(a) (b)

Fig. S1. (a) The structure of tetracycline (TC), the dotted areas represent the structural moieties associated with the three acidic dissociation constants (pK_a); (b) speciation distributions of TC in different pH values.

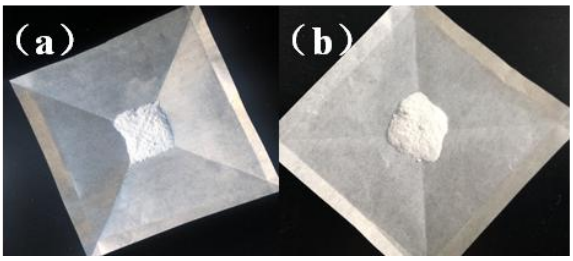


Fig. S2. (a) the image of BCN; (b) the image of PA.

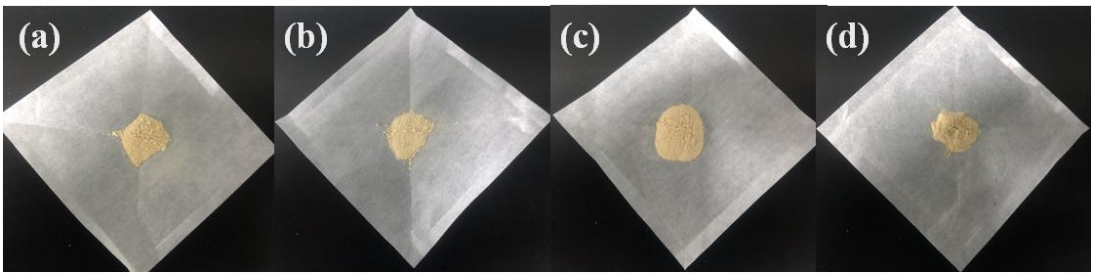


Fig. S3. (a) the image of BCNPA1; (b) the image of BCNPA2; (c) the image of BCNPA3; (d) the image of BCNPA4.

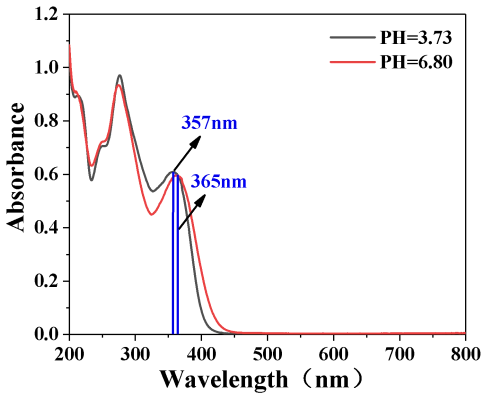


Fig. S4. The UV spectra of TC solution at different pH values

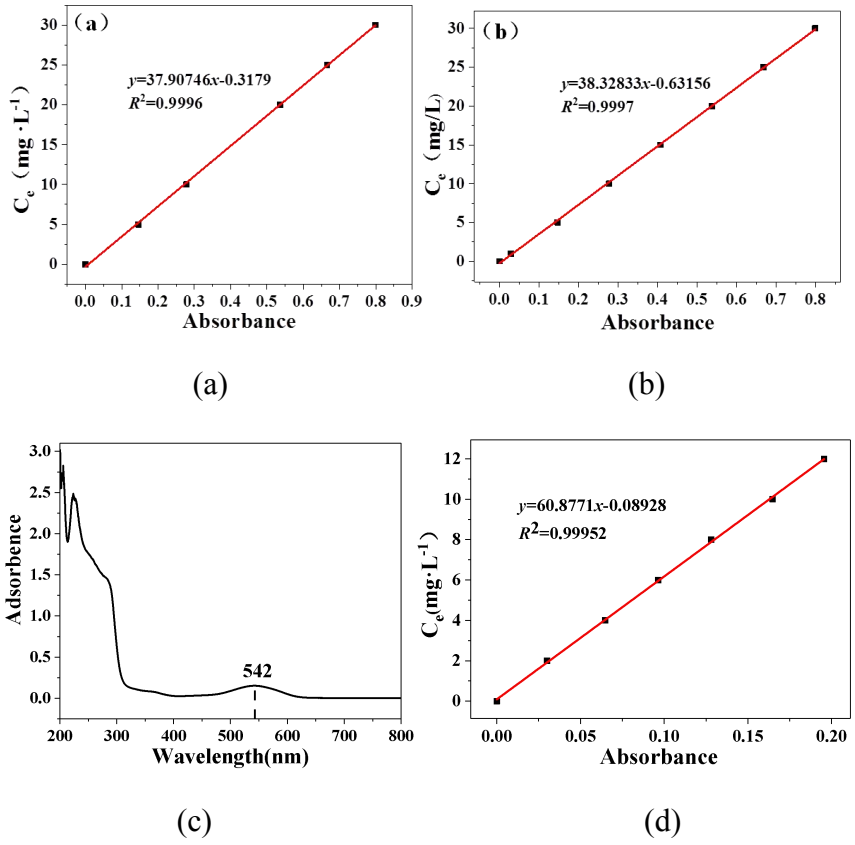


Fig. S5. (a) the standard curve of TC at pH 6.80; (b) the standard curve of TC at pH 3.80; (c) The UV spectra of Cr(VI) solution; (d) the standard curve of Cr(VI).

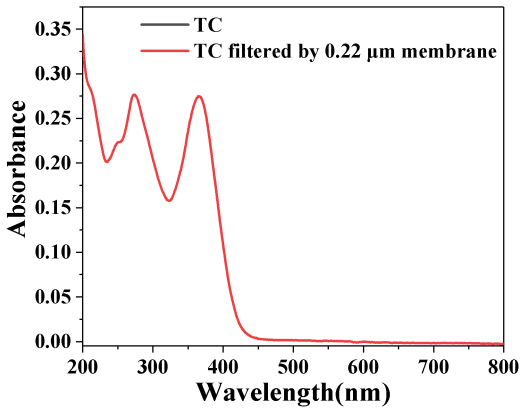


Fig. S6. The UV spectra of TC solution before and after filtration by 0.22 μm membrane.

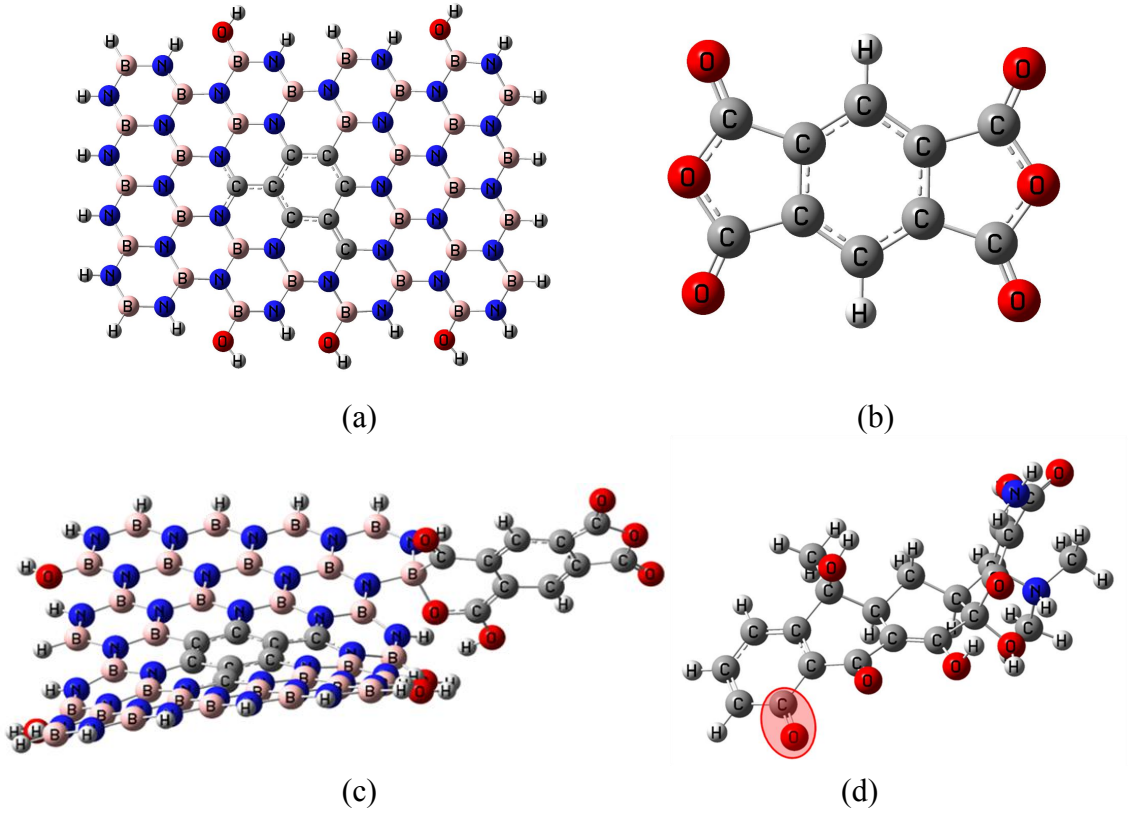
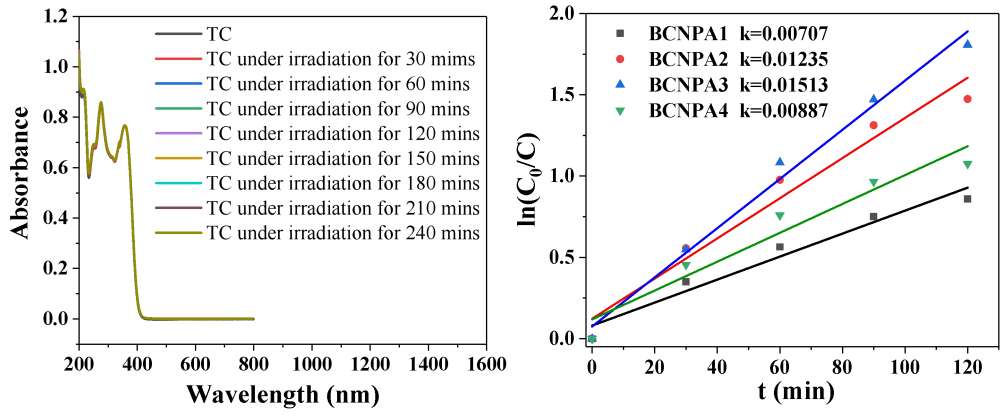
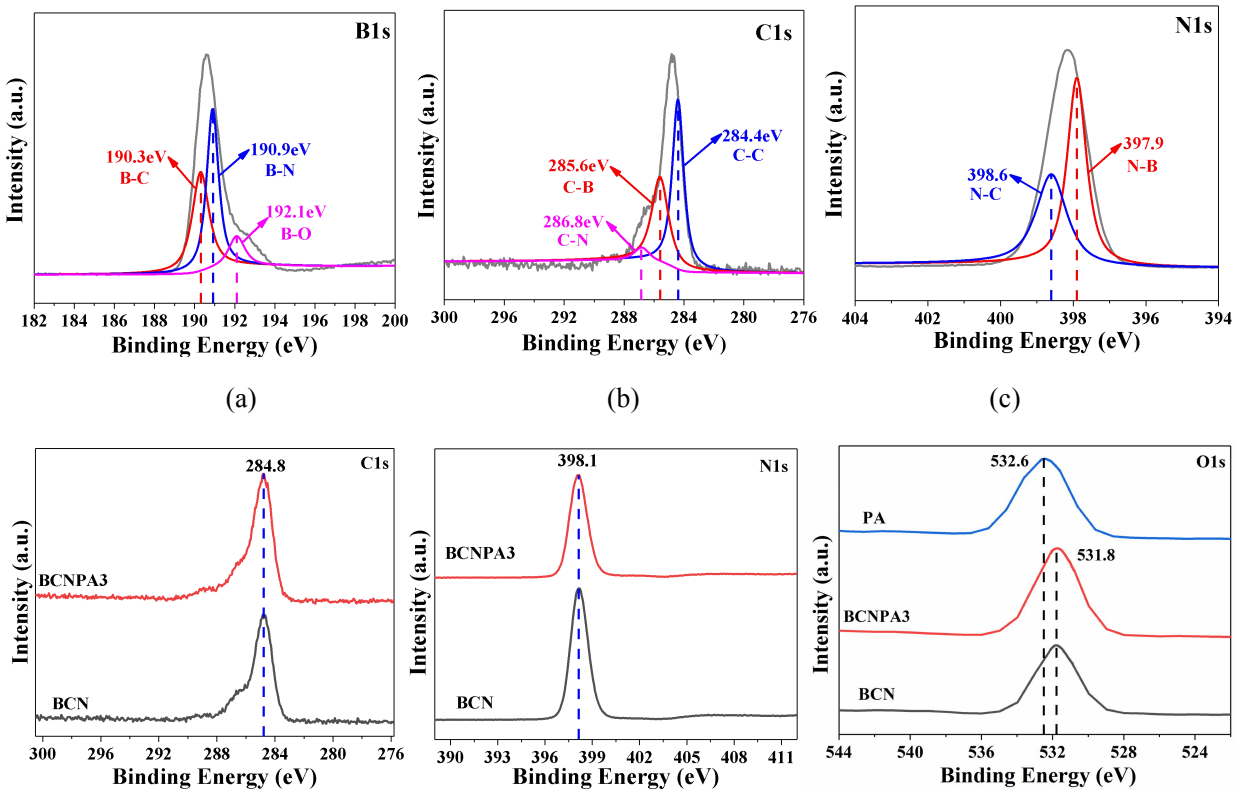


Fig. S7. (a) the optimized molecular structure of BCN model; (b) the molecular structure of PA model; (c) the optimized molecular structure of BCNPA3 model; (d) the molecular structure of the neutral TC, in which a proton is lost from the O atom (please see the red colour circle).



(a) (b)

Fig. S8. (a) the UV-vis spectra of TC at different time scales under visible light irradiation for 180mins. The time scales are 30 mins, 60 mins, 90 mins, 120 mins, 150 mins, 180 mins, 210 mins and 240 mins, respectively; (b) the kinetic curves data of TC photo-removal by different BCNPA composites under visible light irradiation.



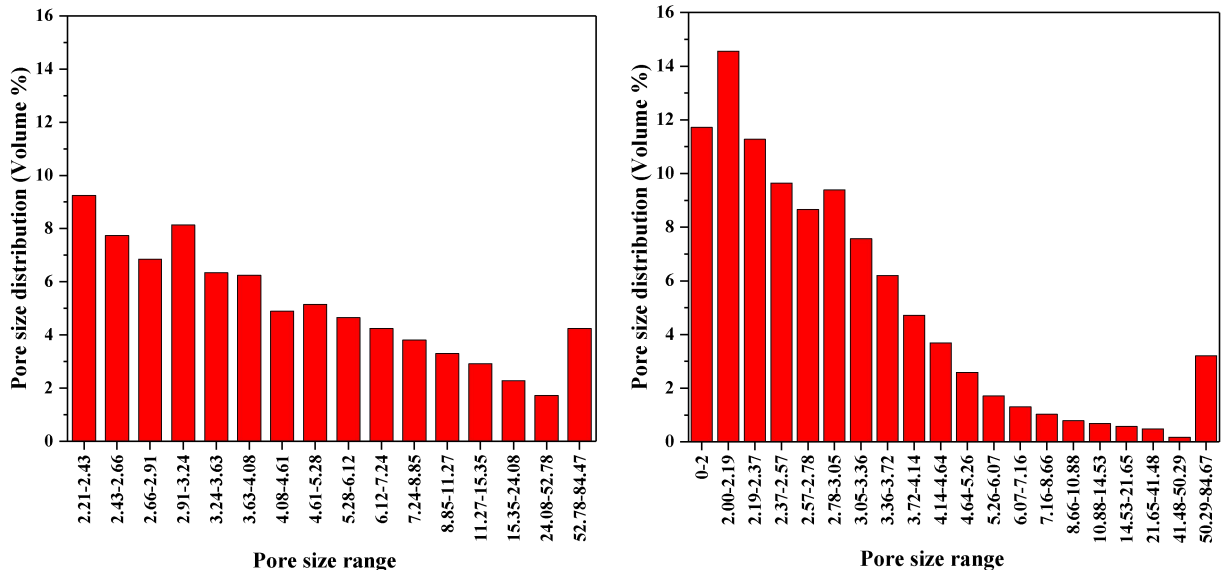
(a) (b) (c)

(d) (e) (f)

Fig. S9. (a) the B1s spectra of BCN; (b) the C1 spectra of BCN; (c) the N1s spectra of BCN; (d) the C1s spectra of BCN and BCNPA3; (e) the N1s spectra of BCN and BCNPA3; (f) the O1s spectra of PA , BCN and BCNPA3.

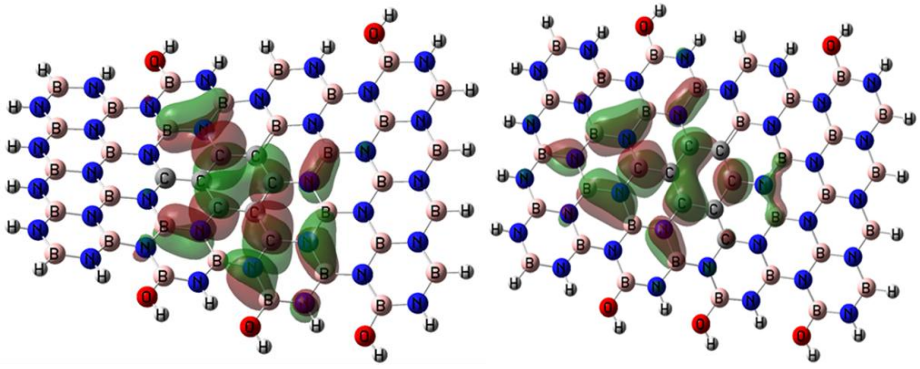
Table S1 the BET area values and pore size distribution results of BCN and BCNPA3

Sample	BET area ($m^2 \cdot g^{-1}$)	Adsorption average pore size (nm)	Pore size ⩽2 nm (%)	2 < Pore size ⩽50 nm (%)	Pore size >50 nm
BCN	18.708	6.372	5.29	90.47	4.24
BCNPA3	28.611	3.276	11.72	85.07	3.21



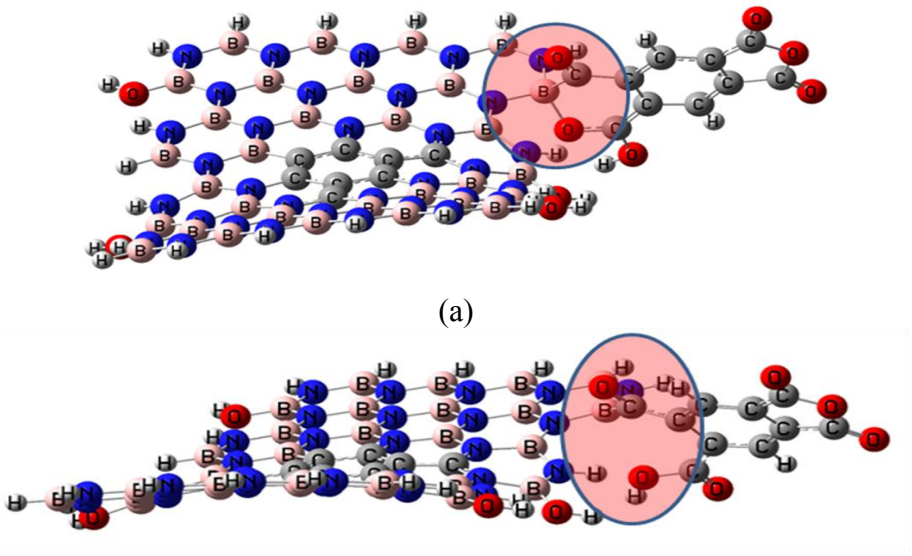
(a) (b)

Fig. S10. (a) the pore size distribution of BCN; (b) the pore size distribution of BCNPA3.



(a) (b)

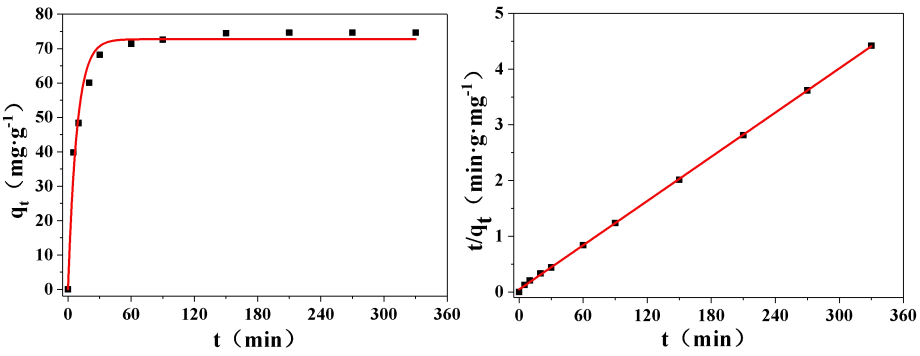
Fig. S11. (a) HOMO orbital of BCN model; (b) LUMO orbital of BCN model.



(a)

(b)

Fig. S12. (a) the optimized molecular structure of BCNPA3 model; (b) the optimized molecular structure of BCNPA3a model.

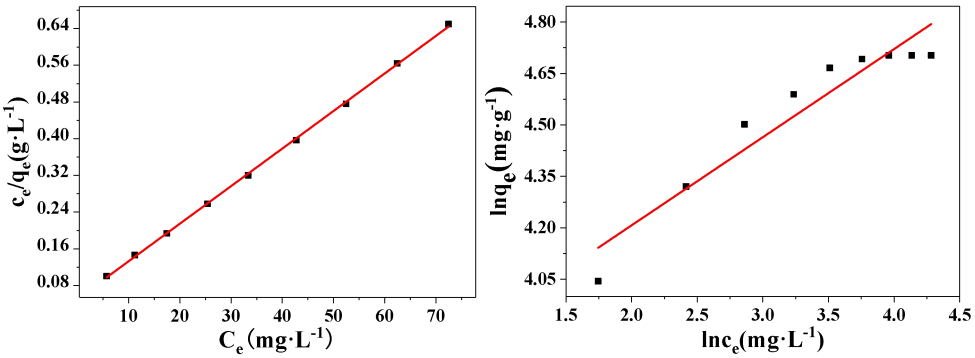


(a) (b)

Fig. S13. (a) The pseudo-first-order kinetic adsorption of TC by BCNPA3; (b) the pseudo-second-order kinetic adsorption of TC by BCNPA3.

Table S2 Pseudo-first-order, pseudo-second-order kinetic parameters for the adsorption of TC by BCNPA3

$q_{e,exp}$	Pseudo-first-order			Pseudo-second-order		
(mg·g^{-1})	k_1 (min^{-1})	$q_{e,cal}$ (mg·g^{-1})	R^2	k_2 (g·mg^{-1}·min^{-1})	$q_{e,cal}$ (mg·g^{-1})	R^2
74.66	0.1190	72.73	0.9763	0.0037	75.64	0.9994



(a) (b)

Fig. S14. (a) the Langmuir isotherm adsorption curve of TC by BCNPA3; (b) the Freundlich isotherm adsorption curve of TC by BCNPA3.

Table S3 The Langmuir and Freundlich isotherm model parameters for the adsorption of TC by BCNPA3.

The Langmuir model			The Freundlich model		
Q_m (mg·g^{-1})	K_L (L·mg^{-1}))	R^2	K_F (mg/g(1/mg)$^{1/n}$)	n	R^2
122.1001	0.14	0.9996	40.19	3.89	0.9124

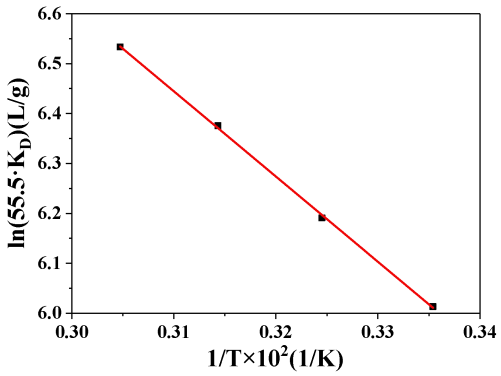


Fig. S15. The thermodynamic fitting curve

Table S4 The list of thermodynamic parameters

T (℃)	Δ G°(kJ·mol^{-1})	Δ H° (kJ·mol^{-1})	Δ S° (kJ·mol^{-1})
25	-341.40	14.19	97.58
35	-492.07		
45	-651.54		
55	-816.03		

Table S5 The relationship between specific surface area and adsorption capacity of adsorbents

Adsorbents	BET ($m^2 \cdot g^{-1}$)	Adsorption quantity ($mg \cdot g^{-1}$)	Adsorption quantity per unit specific surface area ($mg \cdot m^{-2}$)
BCNPA1	27.805	68.64	2.469
BCNPA2	27.867	69.58	2.497
BCNPA3	28.611	74.66	2.609
BCNPA4	27.706	69.07	2.493

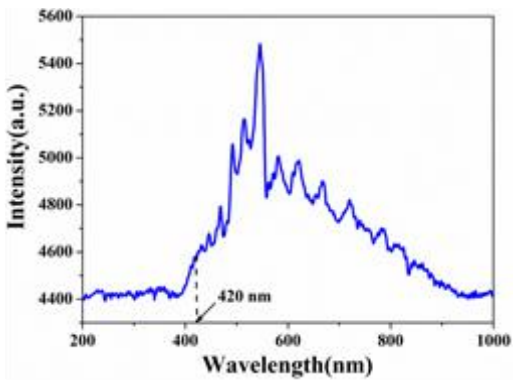
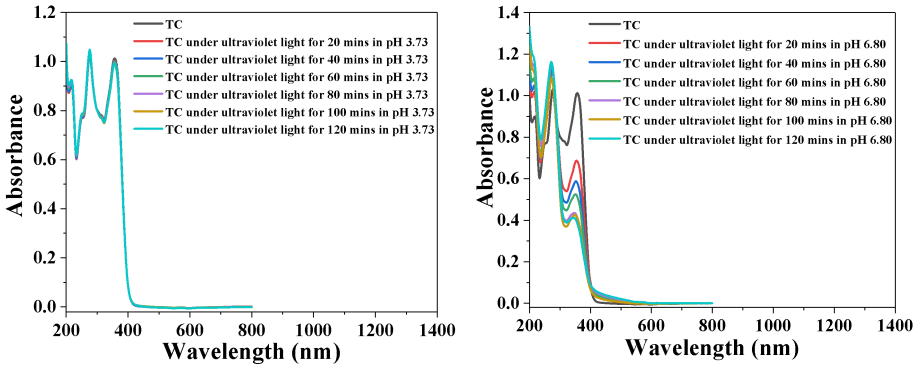
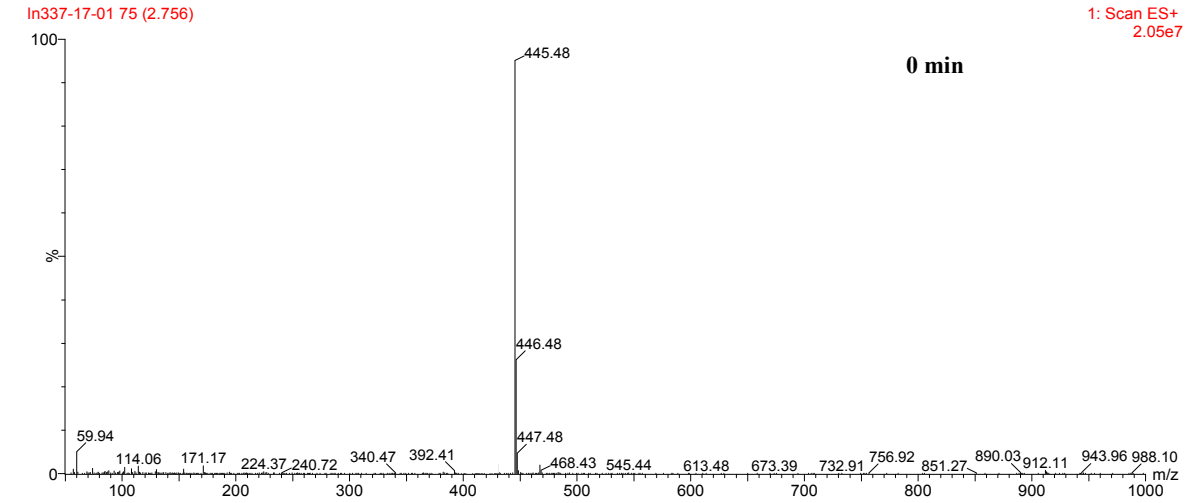


Fig. S16. The light spectrum of visible light source that used in the photo-removal experiments of TC by BCNPA3 under visible light irradiation. A 420 nm filter is used during whole irradiation process.



(a) (b)

Fig. S17. (a) UV-visible spectra of TC photodegradation under ultraviolet light irradiation at pH 3.73 (concentration: 30 $mg \cdot L^{-1}$, volume: 100 mL); (b) UV-visible spectra of TC photodegradation under ultraviolet light irradiation at pH 6.80 (concentration: 30 $mg \cdot L^{-1}$, volume: 100 mL).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392.41
468.43
545.44
613.48
673.39
732.91
756.92
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500
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800
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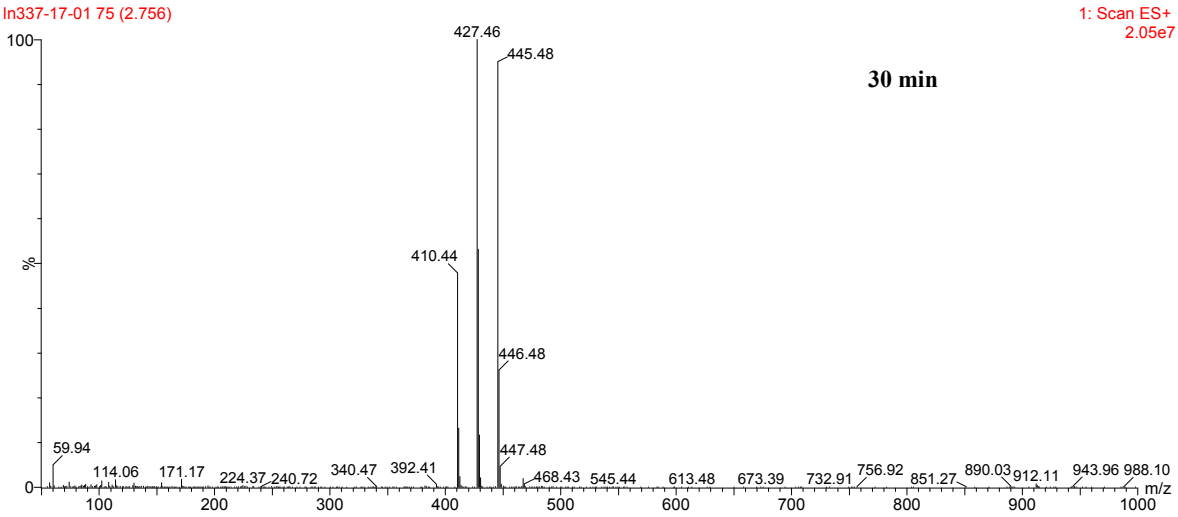
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673.39
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756.92
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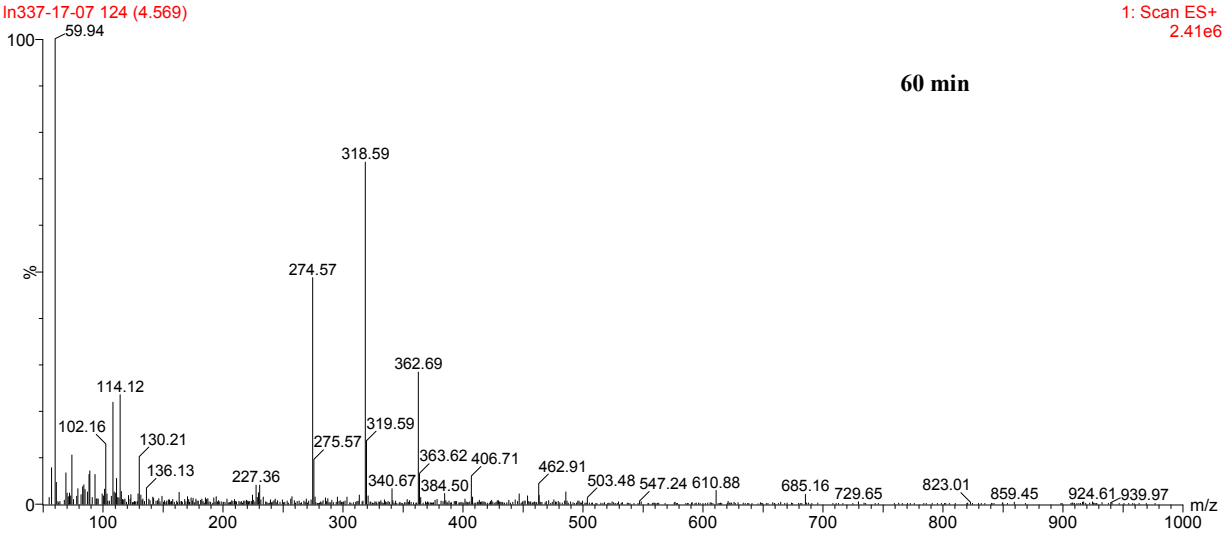
m/z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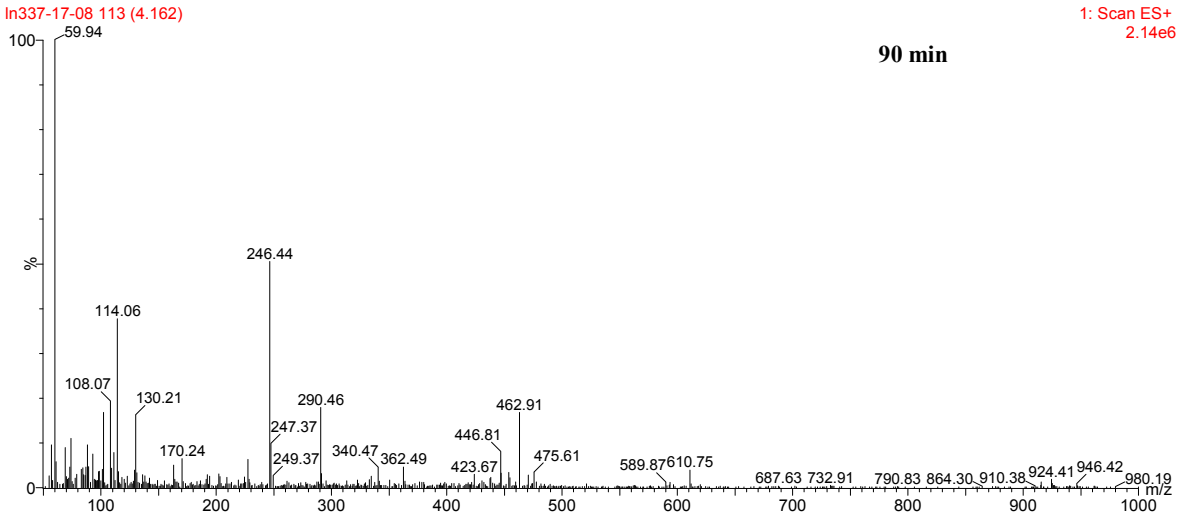
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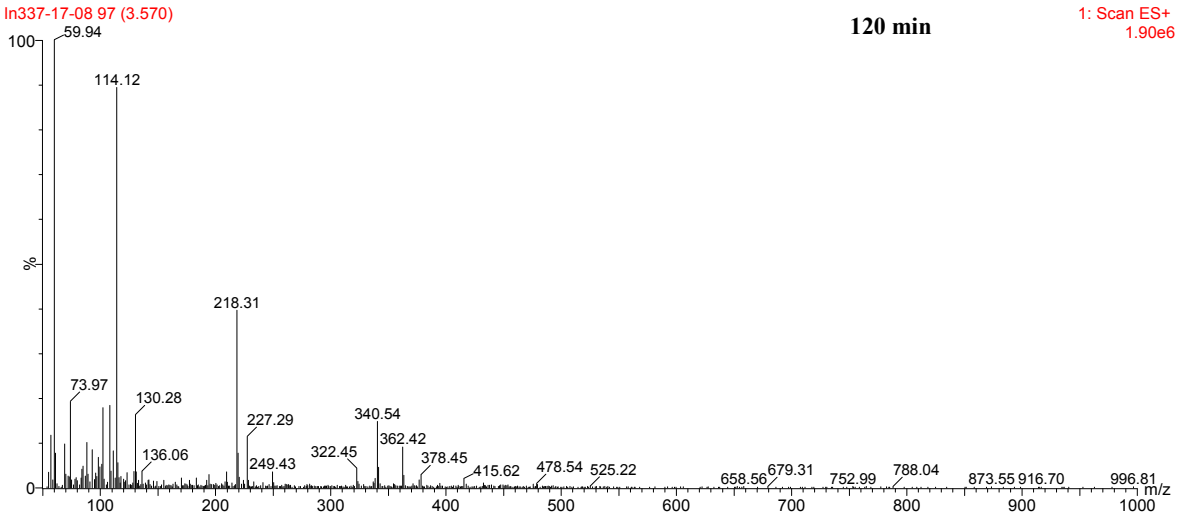
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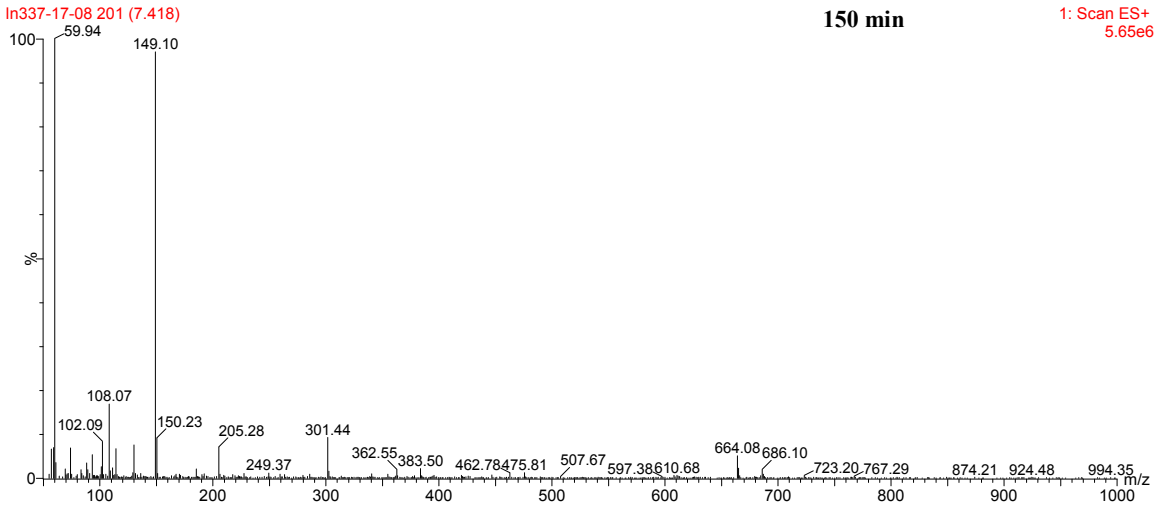
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462.78
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597.38
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664.08
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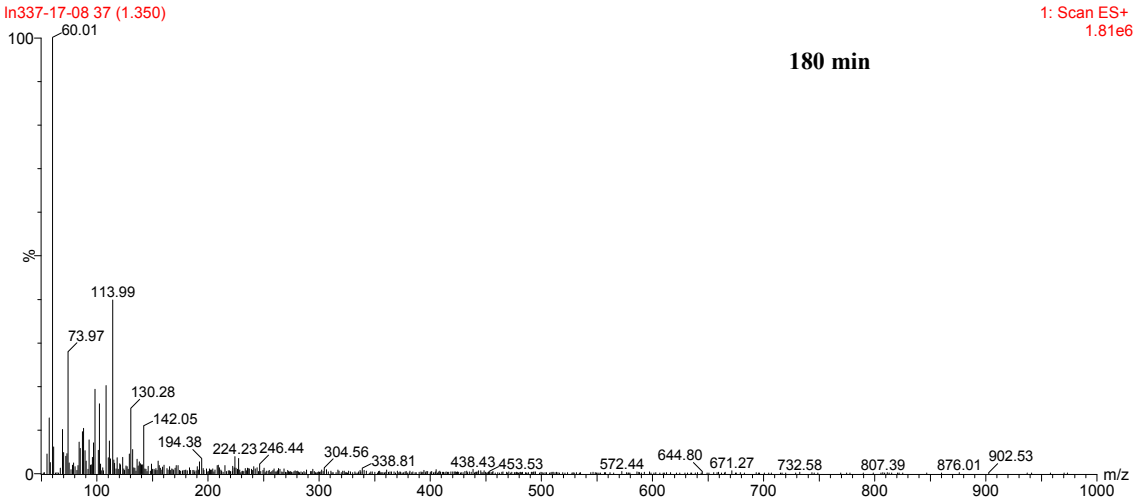


Fig. S18. LC-MS chromatogram of TC transformation intermediates in TC solution at different reaction time.

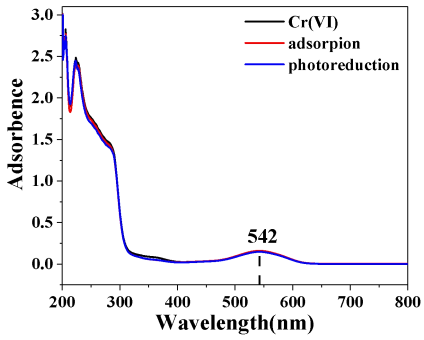
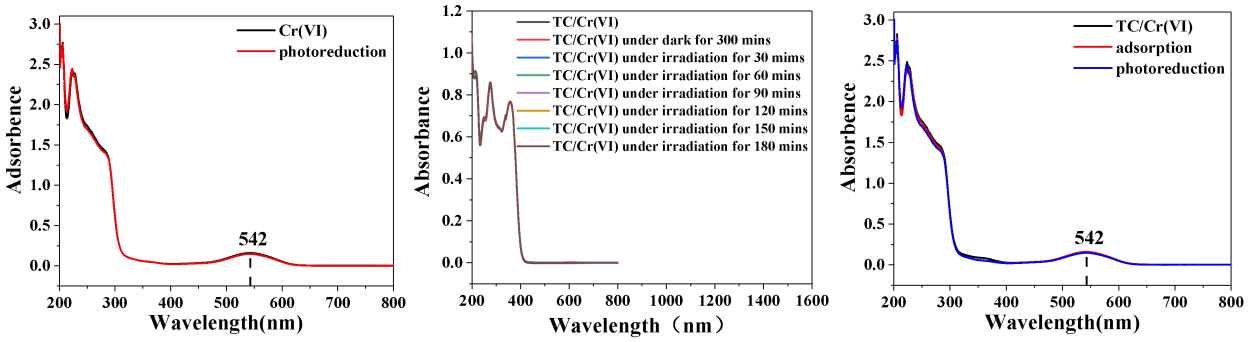


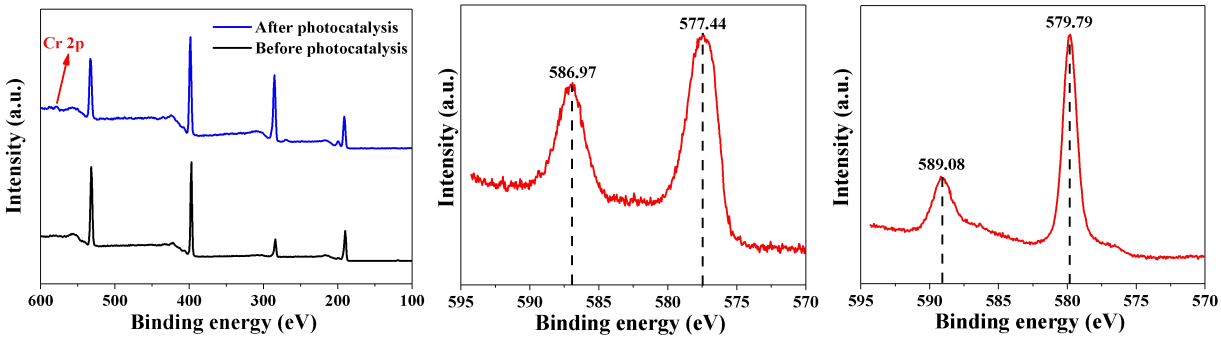
Fig. S19. The UV-visible spectra of single Cr(VI) solution after adsorption for 300 minutes and photoreduction under visible light irradiation for 180 minutes by BCNPA3.



(a) (b) (c)

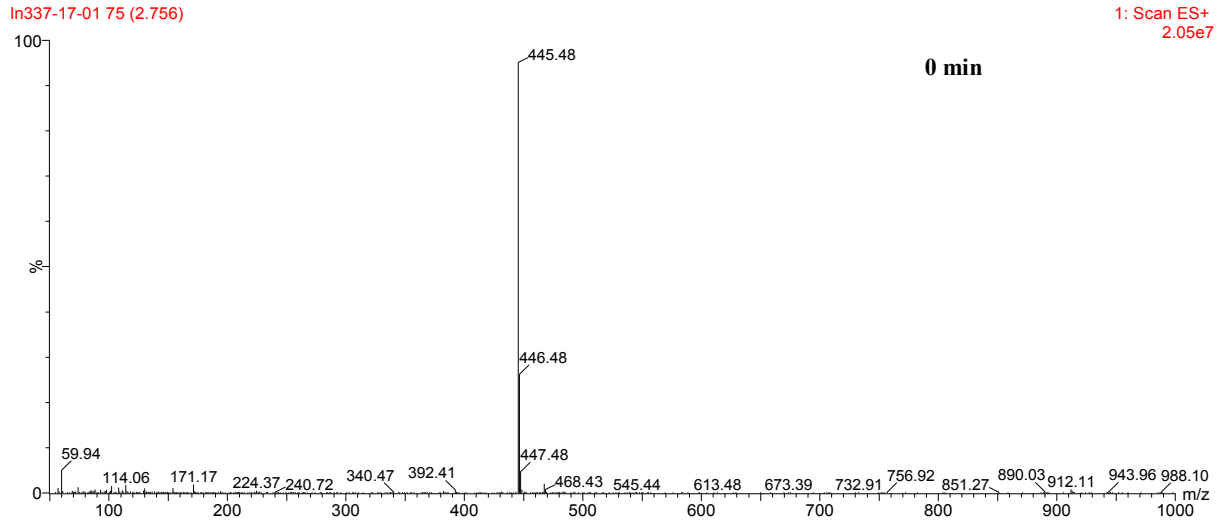
Fig. S20. (a) UV-visible spectra of Cr(VI) under visible light irradiation for 180 mins via diphenylcarbazide spectrophotometric method (Cr(VI) concentration: 10 mg·L^{-1}, volume: 100mL, photodegradation time: 180 minutes); (b) The UV-visible spectra of TC adsorption and

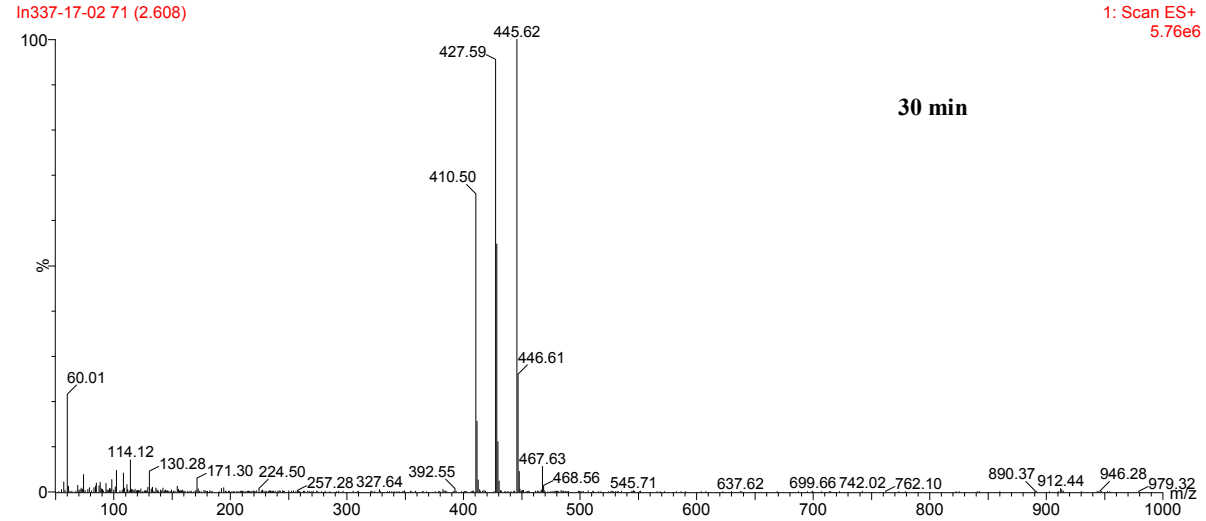
photodegradation for TC/Cr(VI) system under visible light irradiation (TC/Cr(VI) concentration: 30/10 mg·L^{-1}, volume: 100mL, adsorption time: 300 minutes, photodegradation time: 180 minutes); (c) UV-visible spectra of Cr(VI) adsorption and photoreduciton for TC/Cr(VI) system under visible light irradiation via diphenylcarbazide spectrophotometric method (TC/Cr(VI) concentration: 30/10 mg·L^{-1}, volume: 100mL, adsorption time: 360 minutes, photoreduction time: 180 minutes).



(a) (b) (c)

Fig. S21. (a) XPS spectra of BCNPA3 before and after simultaneous photocatalytic redox conversion of TC and Cr(VI) system; (b) High-resolution XPS spectrum of standard Cr(III) samples($CrCl_3 \cdot 6H_2O$); (c) High-resolution XPS spectrum of standard Cr(VI) samples($K_2Cr_2O_7$).

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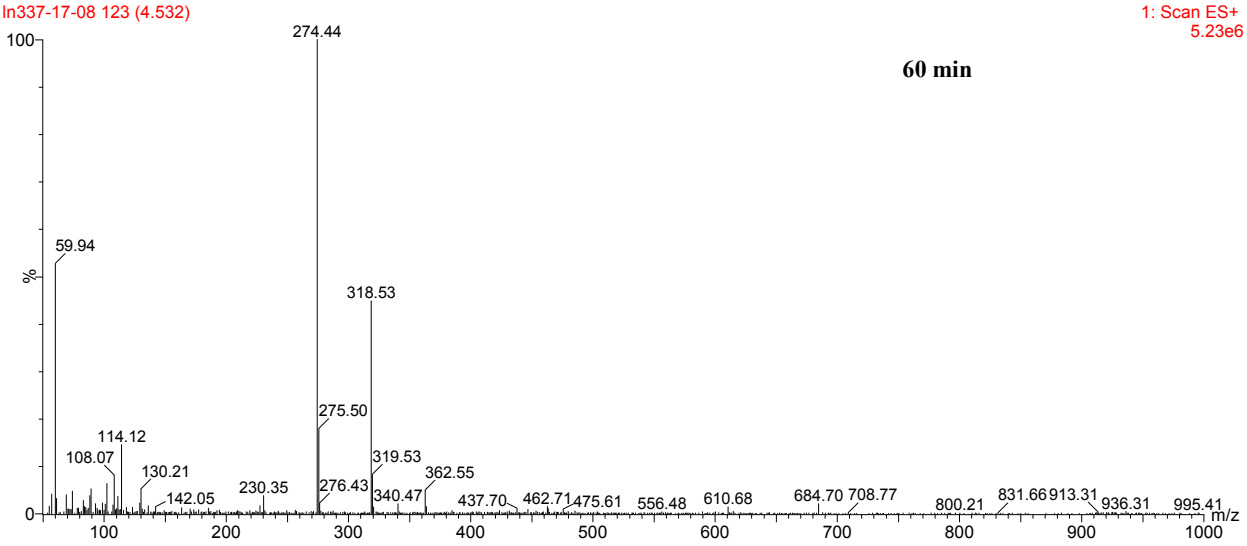
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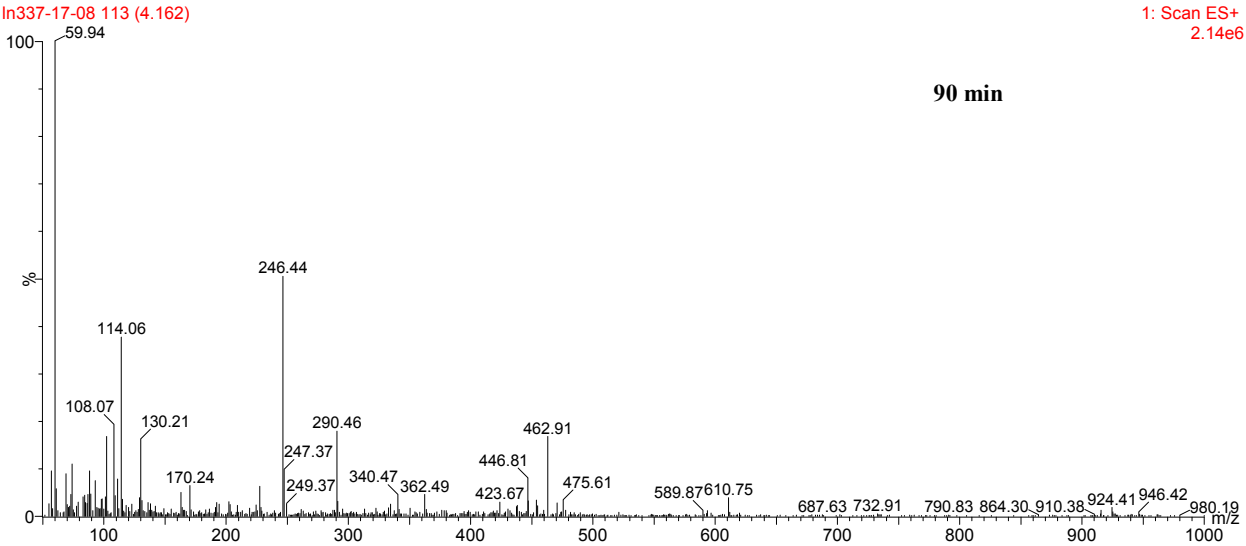
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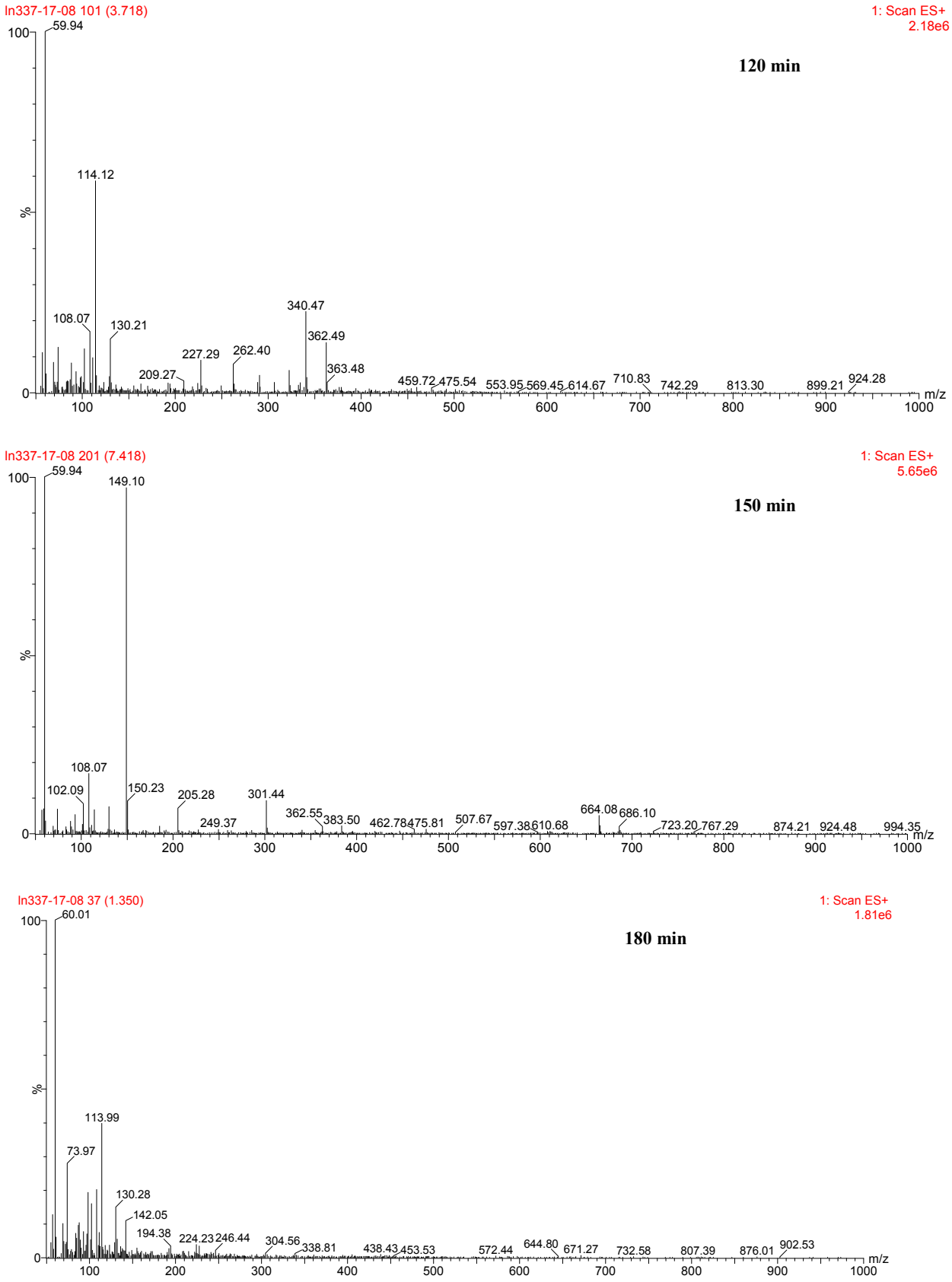

Fig. S22. LC-MS chromatogram of TC transformation intermediates in TC/Cr(VI) solution at different reaction time.

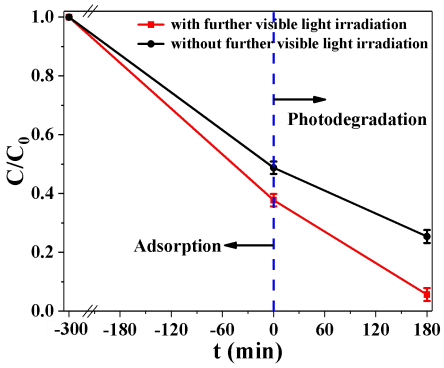

Fig. S23. The test for why BCNPA3 need a further irradiation treatment after the adsorption and photodegradation experiment (dosage: 25 mg, TC/Cr(VI) concentration: 30/10 mg·L^{-1}, volume: 100 mL).