

Supplementary Material for

Catalytic degradation of tetracycline hydrochloride using surface nitrogen-rich activated carbon based on polyaniline

Text S1 Chemicals and reagents

All chemicals were of high-purity reagent grade and used without further purification. Aniline was purchased from Tianjin Jin dong tian zheng Precision Chemical Reagent Factory. Tetracycline hydrochloride (TC), oxytetracycline hydrochloride (OTC) and L-histidine were obtained from Shanghai Aladdin Biochemical Co., Ltd. Chlortetracycline Hydrochloride (CTC) were purchased from Shanghai Macklin Biochemical Co., Ltd. Sodium persulfate (PS, $\text{Na}_2\text{S}_2\text{O}_8$), $(\text{NH}_4)_2\text{S}_2\text{O}_8$, Tert-butyl alcohol (TBA), methanol (MeOH), 1, 4-benzoquinone (BQ), phenol, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ and NaNO_3 , were obtained from Chengdu Kelong Chemical Reagent CO., Ltd. Hydrochloric acid (HCl), NaCl and NaHCO_3 were purchased from Chongqing Chuandong chemical (Group) Co., Ltd. Commercial activated carbon was obtained from Chengdu Organic Chemicals CO., Ltd. All other chemicals are analytical reagents.

Text S2 Characterization

In order to analyze the crystalline shape, morphology and surface elemental states of the resulting materials, we conducted a series of analyses on the two groups of experimental materials with the best TC degradation (3.0PANI@AC and 3.0PANI-AC) and partially characterized the carbon materials with different amounts of nitrogen doping under in-situ doping in order to illustrate the advantages of in-situ doping in nitrogen doping methods, and some of the means of characterization are as follows .

The texture properties of samples were recorded by N₂ adsorption/desorption isotherms at 77 K measured on a 3H-2000PM2 instrument (Beijing Beishide Instrument Technology CO., Ltd., China), Specific surface area (S_{BET}) of NMC was measured by Brunauer-Emmett-Teller (BET) model. Pore size distribution, mean pore size (DBJH) and mesopore volume (V_{meso}) were determined by the Barrett-Joyner-Halenda (BJH) method, and the amount of adsorbed N₂ at $P/P_0 = 0.99$ was used as the total pore volume (V_{total}), all samples were degassed at 160 °C for 4 h. The morphology analyses of the samples were studied by field emission scanning electron microscopy (SEM, Zeiss, Sigma 300, Germany). TEM combined with elemental mapping analysis were determined by Bruker Esprit (Super X FEI Talos-S). The surface morphology of samples (SEM) were investigated by scanning electron microscopy (SEM, Sigma500, Zeiss, Germany). The surface morphology of the samples was further confirmed by atomic force microscopy (AFM, Hitachi, E-SPEED, Japan). Fourier transform infrared spectra (FTIR) of samples were determined using Tensor 27, Bruker Optics. Raman scattering patterns were performed using LabRAM HR 800, Jobin Yvon. X-ray diffraction (XRD) analysis were carried out on a D8 Advance X-ray Diffractometer (Bruker, Germany) using Cu- K α radiation with λ at 1.5418 Å under the accelerating voltage of 40 kV and current of 40 mA. The chemical composition states on the surface of samples were investigated using X-ray photoelectron spectroscopy (XPS) (Escalab 250Xi, Thermo Fisher Scientific) with monochromatic Al-K α X-rays at a photon energy of 1486.7 eV. All spectra are calibrated to yield a primary C 1s component at 284.5 eV with the Shirley background. The radical species were detected by an electron paramagnetic resonance spectrometer (EMX plus, Bruker, Germany). Electrochemical

impedance spectra (EIS) measurement was conducted using a CHI 660D electrochemical workstation and a standard three-electrode electrochemical cell with an Hg/HgO reference electrode, a graphite piece counter electrode and an obtained catalyst modified Ni foam working electrode. Elements (C, N, O) in bulk phase were determined by element analyzer (Vario EL cube, elementar, Germany). The pyrolysis of the samples were measured by STA 409PC (Netzsch, Germany).

Text S3 Analytical methods

The concentration of tetracycline hydrochlorides (TC), oxytetracycline hydrochloride (OTC) and chlortetracycline hydrochloride (CTC) were determined using UV-1100 spectrophotometer (Mapada, Shanghai) at 365 nm, 353 nm and 364 nm, respectively. Chemical oxygen demand (COD) was determined by Hach DR1010 COD analyzer with sealed catalytic digestion colorimetry (HJ/T, 399-2007). The degradation products of TC were detected using UPLC-MS (Waters, 4500QTRAP) in positive electrospray ionization mode (ESI+) equipped with a C18 column (Atlantis, 100Å, 3 μm, 4.6 mm × 150 mm, pH 3-7, maximum pressure 6000 psi). The mobile phase consists of (A) MeOH / acetonitrile = 1/2 (v/v) and (B) 0.1% formic acid, and the flow rate was 0.3 mL/min. The gradient elution scheme was as follows: 20% A at 0-1 min; 20%-70% A at 1-3 min; 70% A at 3-7 min; 70%-20% A at 7-8 min; 20% A at 8-10 min. The injection volume was 2 μL. Instrumental condition were as follows: cone voltage 3 V, capillary voltage 3 KV, sheath gas flow rate 800 L/h (400 °C). The mass spectra were recorded the m/z range of 0 - 1000. The UV detector wavelength range from 200-800 nm. DMPO was used to capture HO·, and TEMP was used to capture ¹O₂. In an experiment to examine the effect of different inorganic ions on catalyst activation of PS degradation of TC. Aqueous solutions of sodium chloride (NaCl), sodium nitrate (NaNO₃), sodium bicarbonate (NaHCO₃), and disodium hydrogen phosphate (Na₂HPO₄ · 12H₂O) at different concentrations were added to the TC solution, respectively, and then PS and catalyst were added to initiate the reaction, and the TC degradation efficiency was determined after 60 min of reaction. The solution degrading TC without the above ions was used as a blank.

Table S1 Textural properties of samples.

Samples	S_{BET} (m^2g^{-1})	V_{total} (cm^3g^{-1})	V_{meso} (cm^3g^{-1})	$V_{\text{meso}}/V_{\text{total}}$	D_{BJH} (nm)
0.5PANI@AC900	669.8	0.391	0.122	0.31	3.70
1.0PANI@AC900	497.5	0.322	0.135	0.42	4.29
2.0PANI@AC900	332.0	0.283	0.184	0.65	5.73
3.0PANI@AC900	324.7	0.265	0.167	0.63	6.81
3.0PANI@AC800	252.0	0.240	0.164	0.68	7.53
3.0PANI@AC700	229.0	0.226	0.156	0.69	6.92
3.0PANI@AC900- U(ads)	230.6	0.190	0.109	0.57	5.09
3.0PANI@AC900-U	288.1	0.227	0.138	0.61	5.26
3.0PANI-AC900	821.8	0.560	0.234	0.42	5.33
3.0PANI-AC900(ads)	583.9	0.428	0.203	0.47	5.82
3.0PANI-AC900-U	659.7	0.433	0.202	0.47	5.36

Table S2 Relative surface concentrations of oxygen species obtained by fitting the O 1s XPS spectra.

Samples	O 1s			
	O-1	O-2	O-3	O-4
AC900	1.22	1.89	3.00	0.61
PANI900	1.70	1.31	1.14	0.35
3.0PANI-AC900	1.21	1.47	1.47	0.39
3.0PANI@AC900	1.20	1.69	2.05	0.36

Table S3 Elemental composition of the surface of samples determined by XPS (C

+ O + N = 100 at.%).

Samples	C	O	N	N 1s			
				N-py	N-pyr	N-g	N-Ox
0.5PANI@AC900	91.53	6.69	1.79	0.51	0.25	0.73	0.30
1.0PANI@AC900	90.27	6.90	2.83	0.60	0.38	1.25	0.60
2.0PANI@AC900	90.63	5.31	4.06	1.02	0.45	1.73	0.85
3.0PANI@AC900	90.54	5.30	4.16	1.03	0.36	1.97	0.79
3.0PANI@AC800	89.34	4.90	5.77	1.82	0.62	2.46	0.86
3.0PANI@AC700	87.98	5.50	6.52	2.01	1.11	2.78	0.63

Table S4 Elemental composition of the surface of samples determined by XPS

(N-py + N-pyr + N-g + N-Ox = 100 %).

Samples	N-py	N-pyr	N-g	N-Ox
3.0PANI@AC900	30.80	16.94	42.54	9.71
3.0PANI@AC800	31.65	10.73	42.63	14.99
3.0PANI@AC700	24.79	8.74	47.38	19.08

Table S5 Relative surface concentrations of oxygen species obtained by fitting the O 1s XPS spectra.

Samples	O 1s			
	O-1	O-2	O-3	O-4
0.5PANI@AC900	1.31	2.03	2.81	0.54
1.0PANI@AC900	1.52	2.01	2.84	0.53
2.0PANI@AC900	1.30	1.47	1.99	0.55
3.0PANI@AC900	1.20	1.69	2.05	0.36
3.0PANI@AC800	1.33	1.58	1.57	0.41
3.0PANI@AC700	1.28	1.35	2.15	0.72

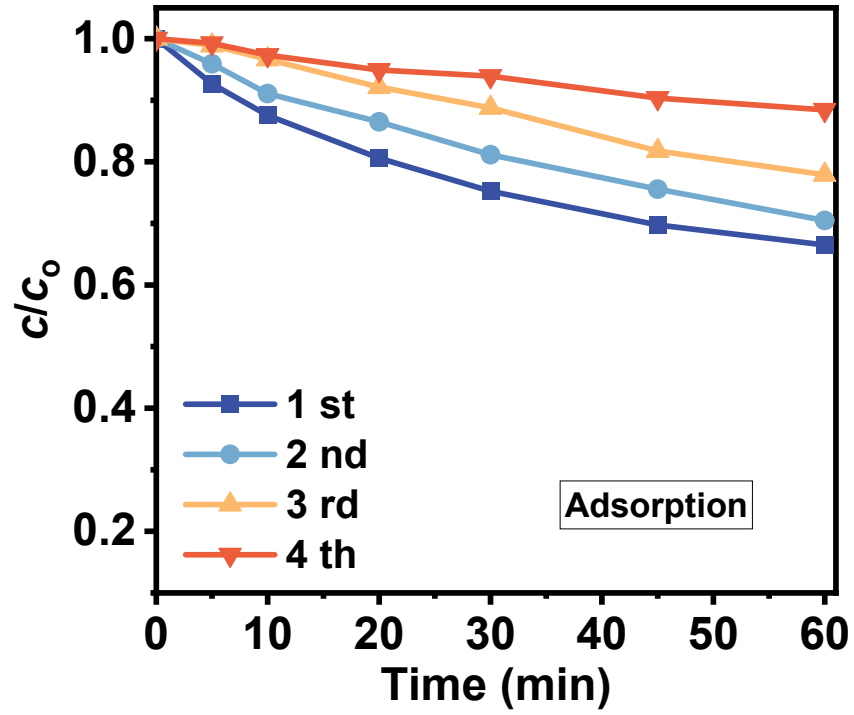


Fig. S1. the corresponding adsorption of 3.0PANI-AC900 under suitable experiment conditions: 25 °C, $c_0 = 25$ mg/L, $c_{cat.} = 0.4$ g/L.

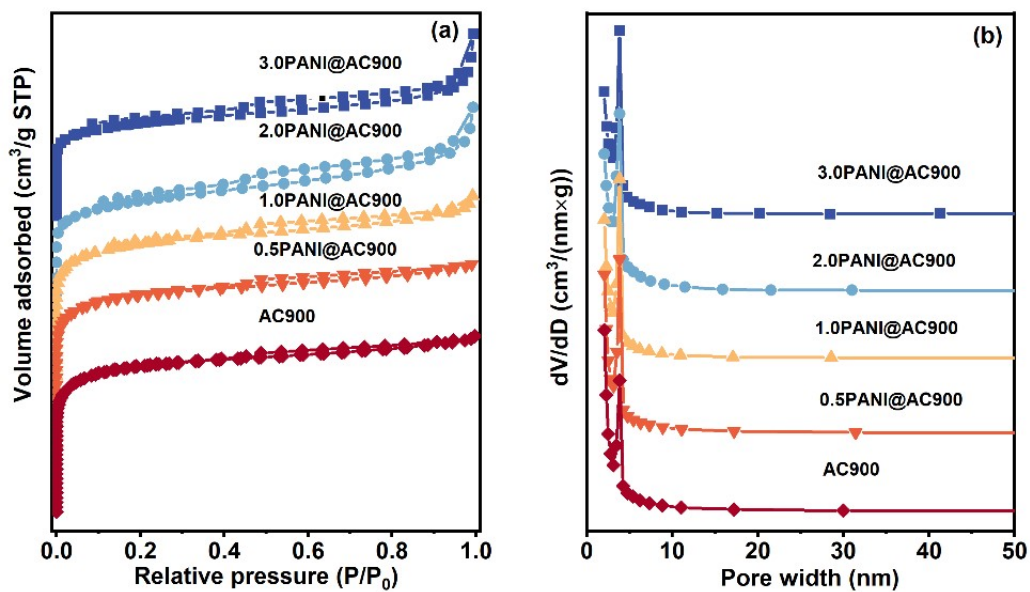


Fig. S2. N₂ adsorption/desorption isotherms of x PANI@AC900 (a) and the corresponding pore size distribution curves calculated from the Barrett-Joyner-Halenda (BJH) method (b).

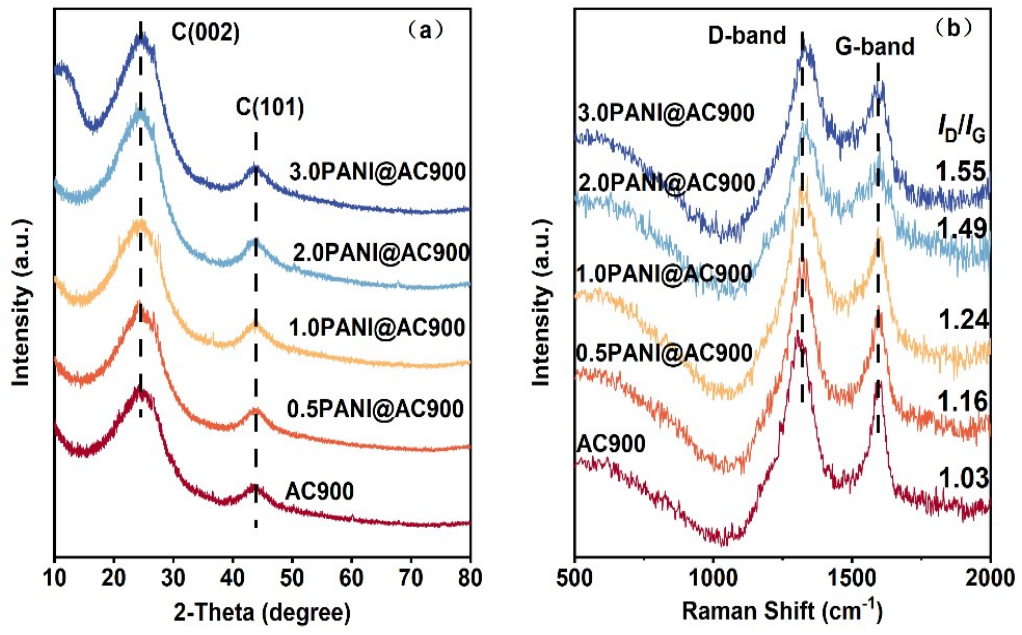


Fig. S3. XRD patterns (a) and Raman spectra (b) of x PANI@AC900.

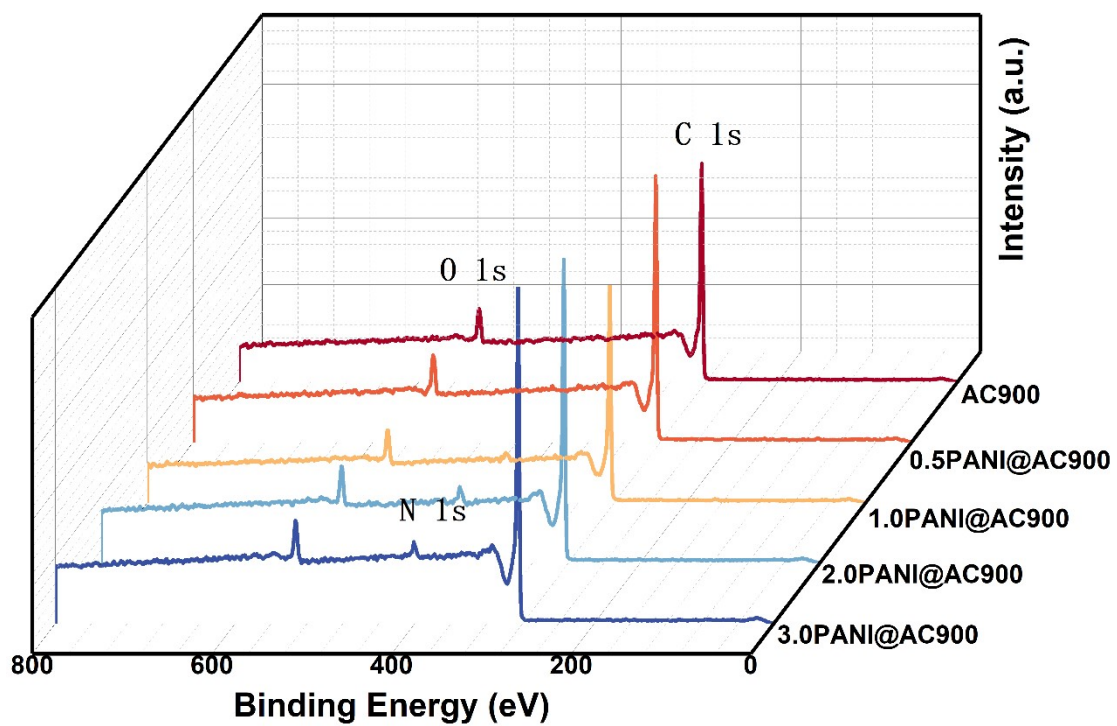


Fig. S4. XPS survey spectra (a) and O1s spectra (b) of x PANI@AC900.

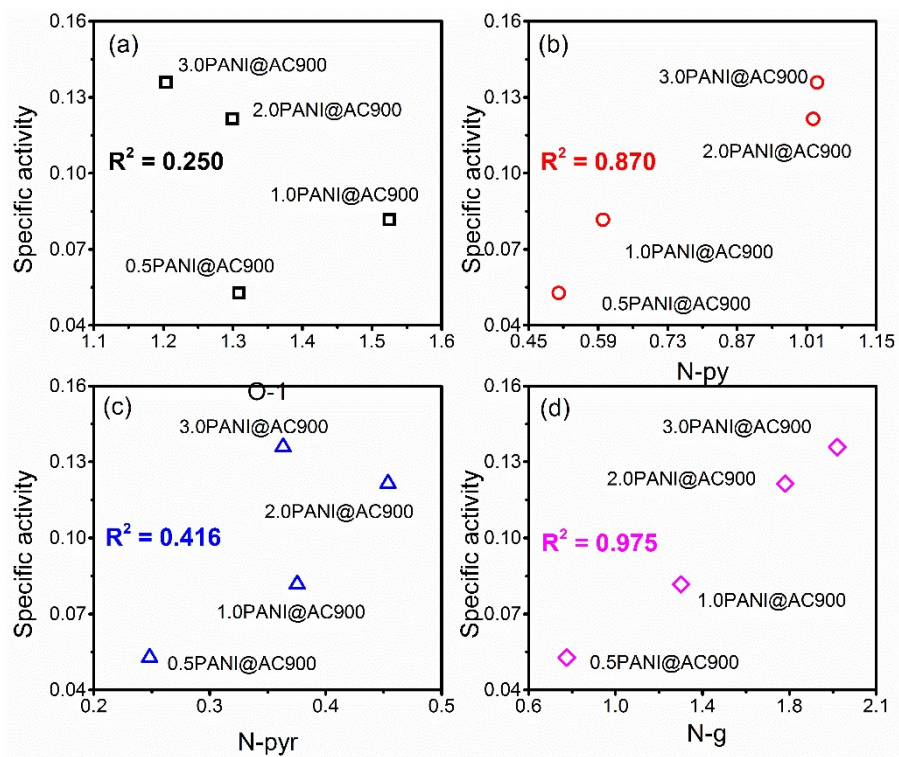


Fig. S5. The *specific activity* as functions of O-1 **(a)**, N-py **(b)**, N-pyr **(c)** and N-g **(d)**.

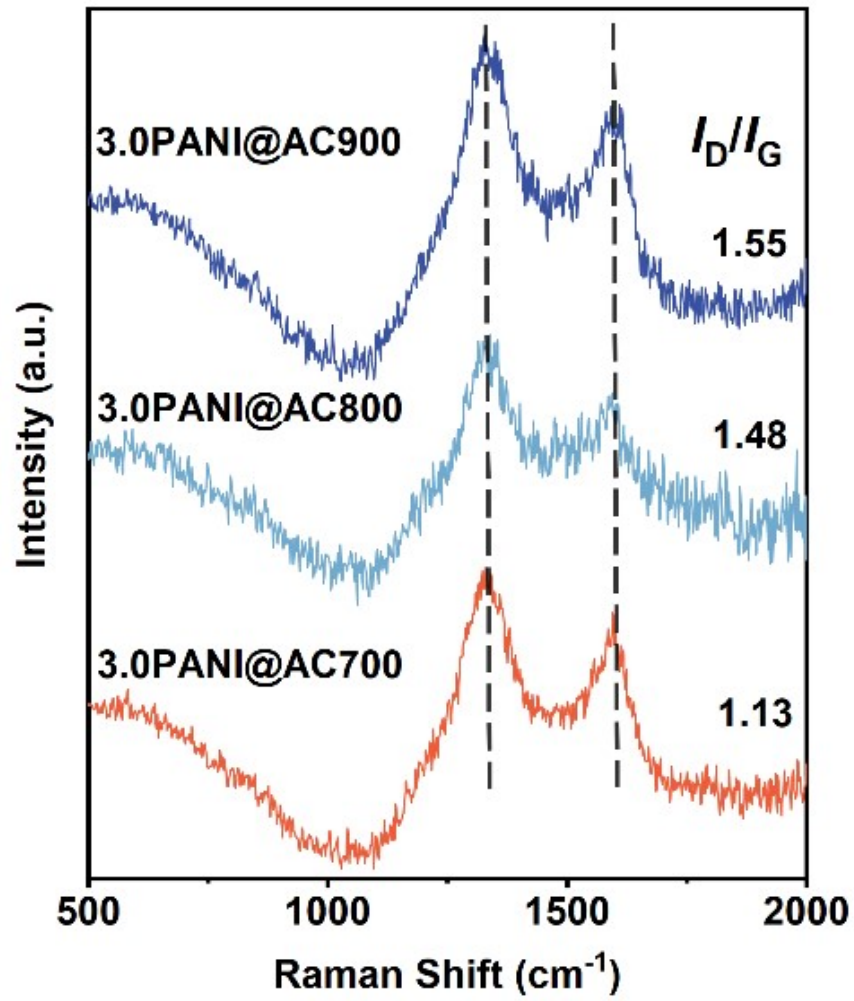


Fig. S6. Raman spectra of 3.0PANI@AC-T (T=700, 800, 900°C)

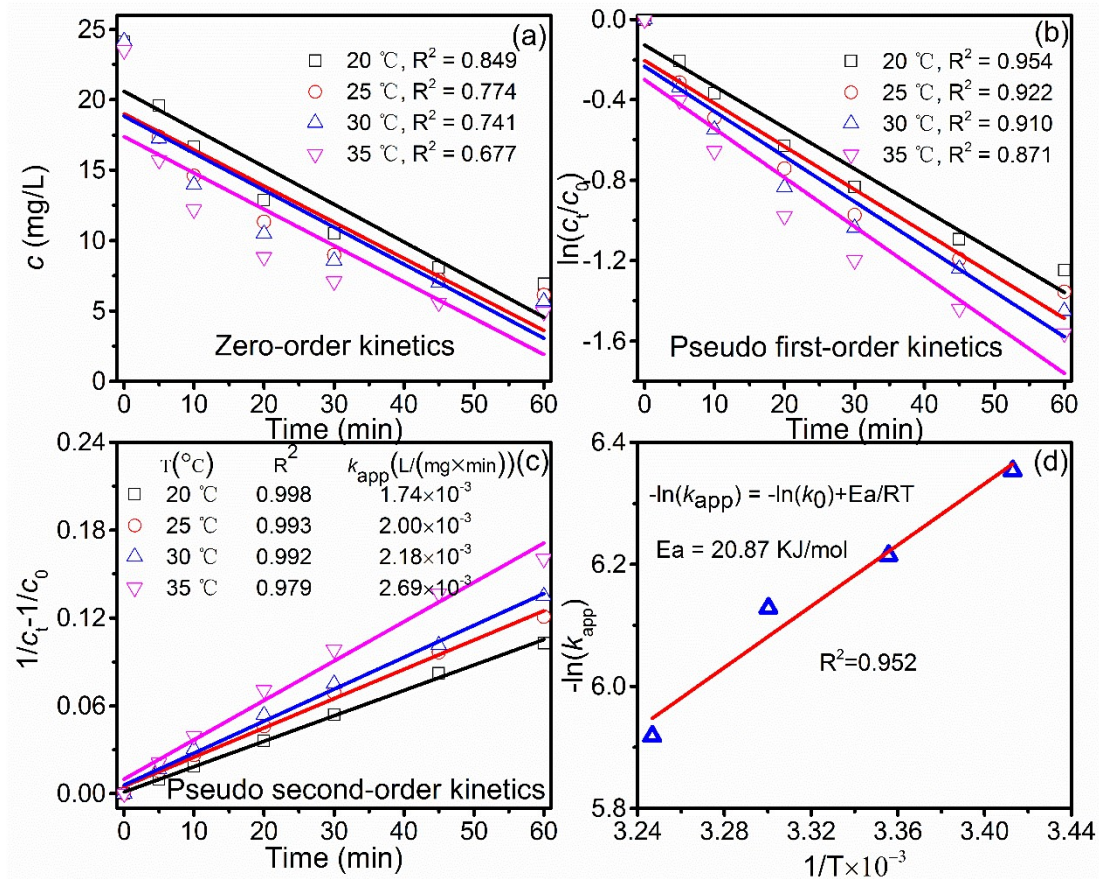


Fig. S7. Kinetics study of TC degradation using 3.0PANI@AC900: (a) the zero-order kinetics, (b) the pseudo first-order kinetics, (c) the pseudo second-order kinetics and (d) the calculation of activation energy based on Arrhenius equation.

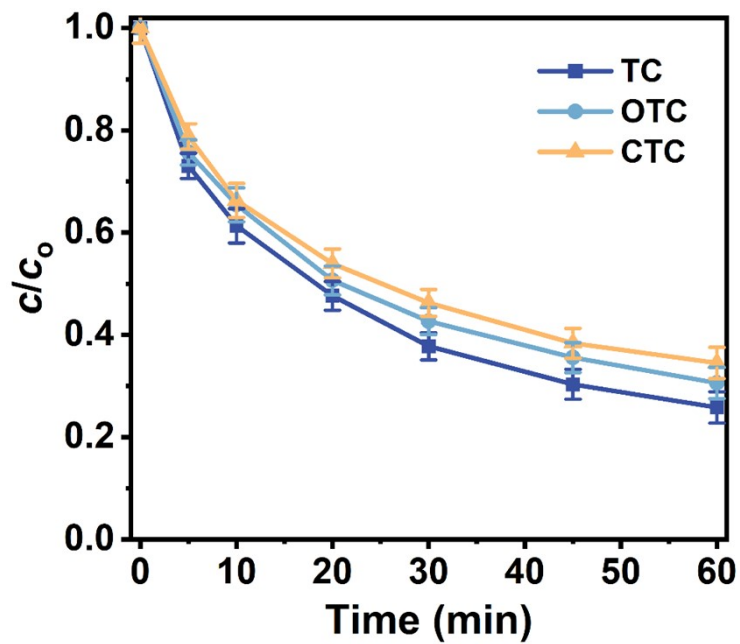


Fig. S8. Catalytic degradation of different TCs using 3.0PANI@AC900 (Experiment conditions: 25 °C, $c_0 = 25$ mg/L, $c_{PS} = 1.68$ mM, $c_{cat.} = 0.4$ g/L).

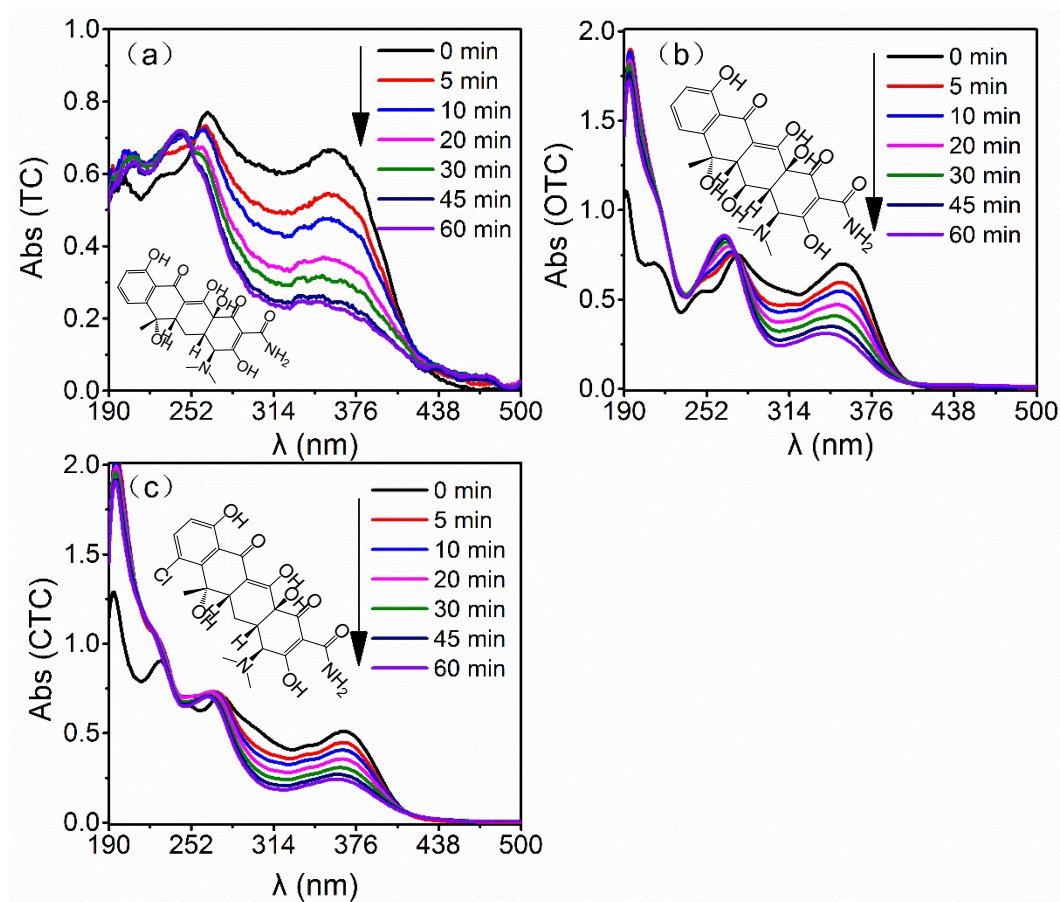


Fig. S9. UV-vis spectra of TCs at different reaction time using 3.0PANI@AC900

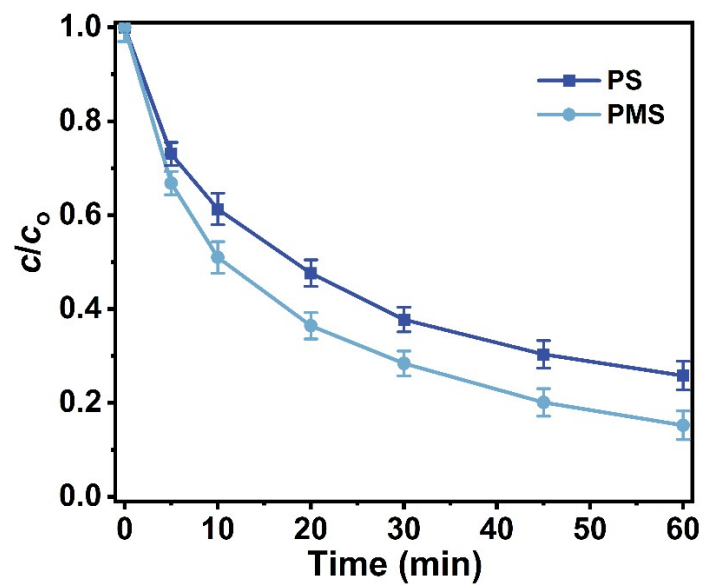


Fig. S10. Catalytic degradation of TCs using 3.0PANI@AC900 (Experiment conditions: 25 °C, $c_0 = 25$ mg/L, $c_{\text{PS/PMS}} = 1.68$ mM, $c_{\text{cat.}} = 0.4$ g/L).

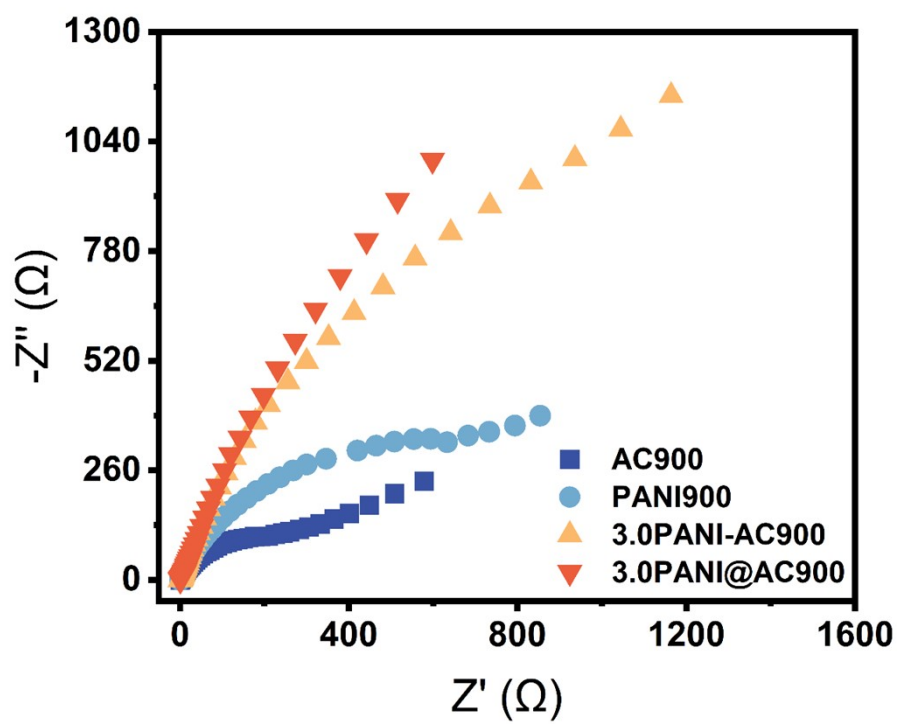


Fig. S11. Electrochemical impedance spectroscopic analysis of x PANI@AC900

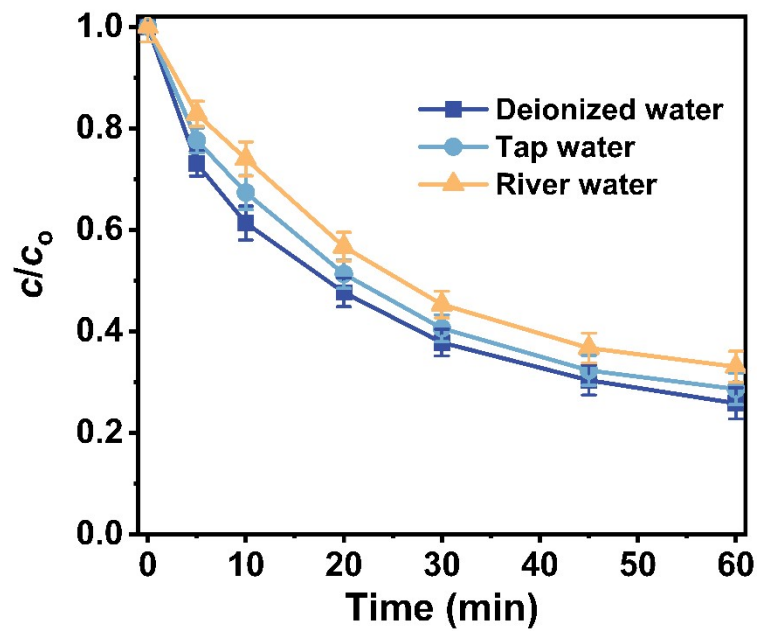
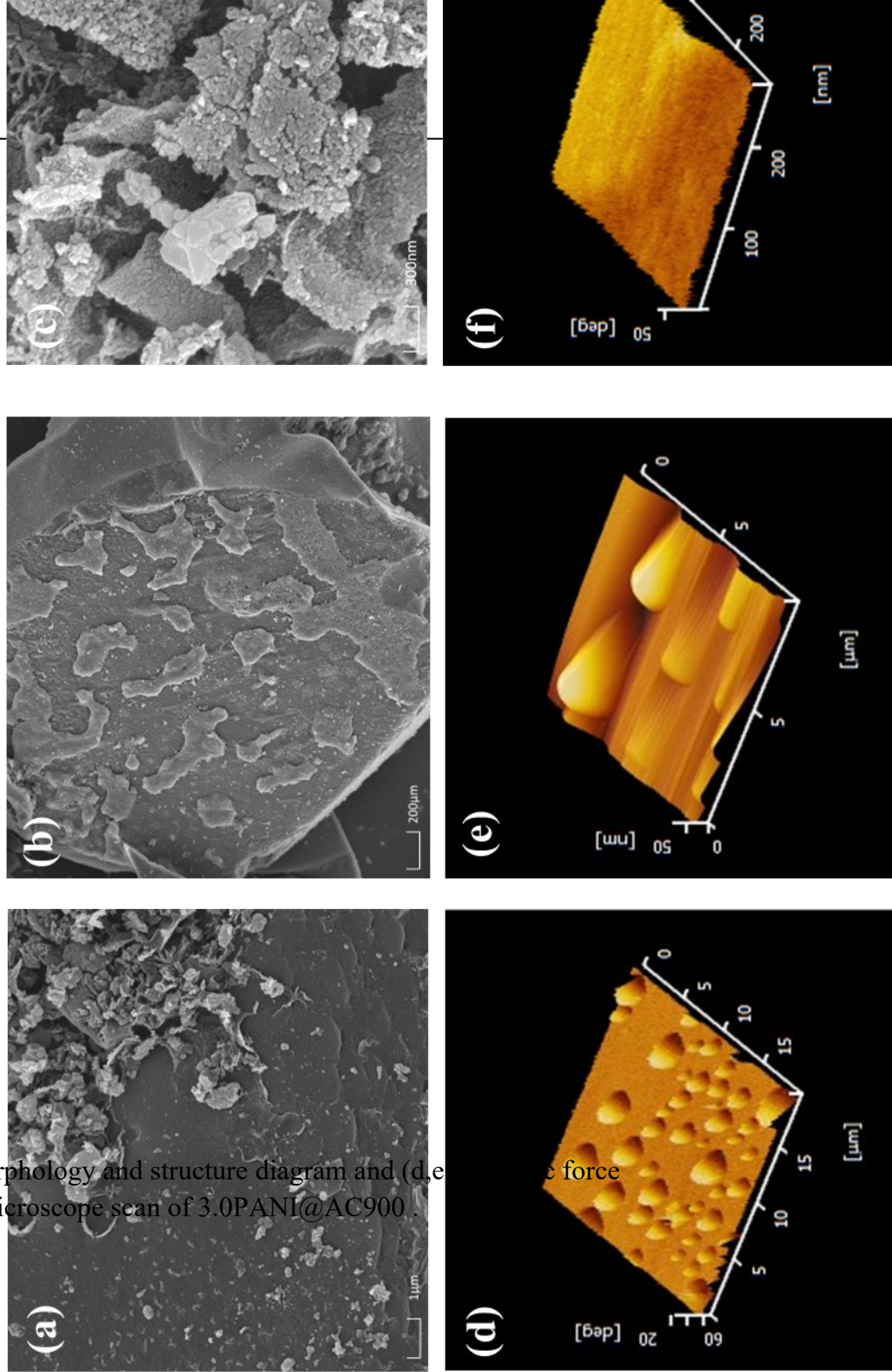


Fig. S12. TC degradation in 3.0PANI@AC900/PS system with real water samples.

(Experiment conditions: 25 °C, $c_0 = 25$ mg/L, $c_{PS} = 1.68$ mM, $c_{cat.} = 0.4$ g/L).

Fig. S13. (a,b,c)Morphology and structure diagram and (d,e) Atomic force microscope scan of 3.0PANI@AC900 .



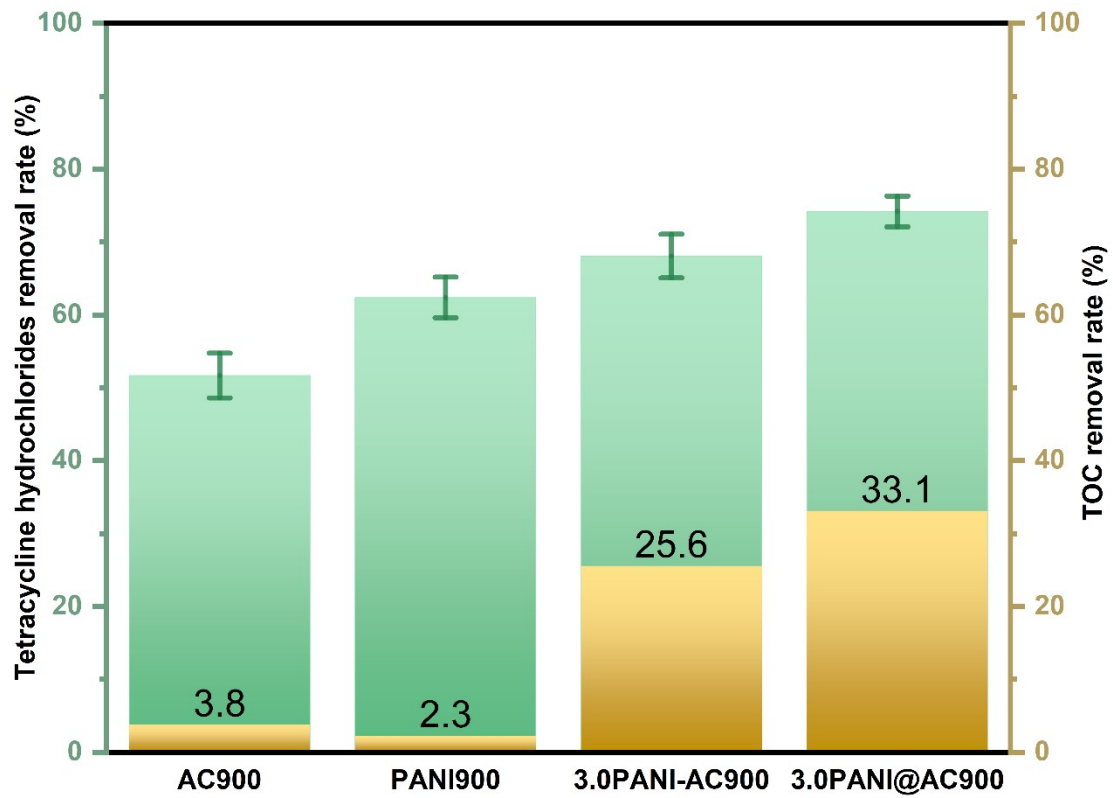


Fig. S14. The TOC removal efficiencies of different samples.

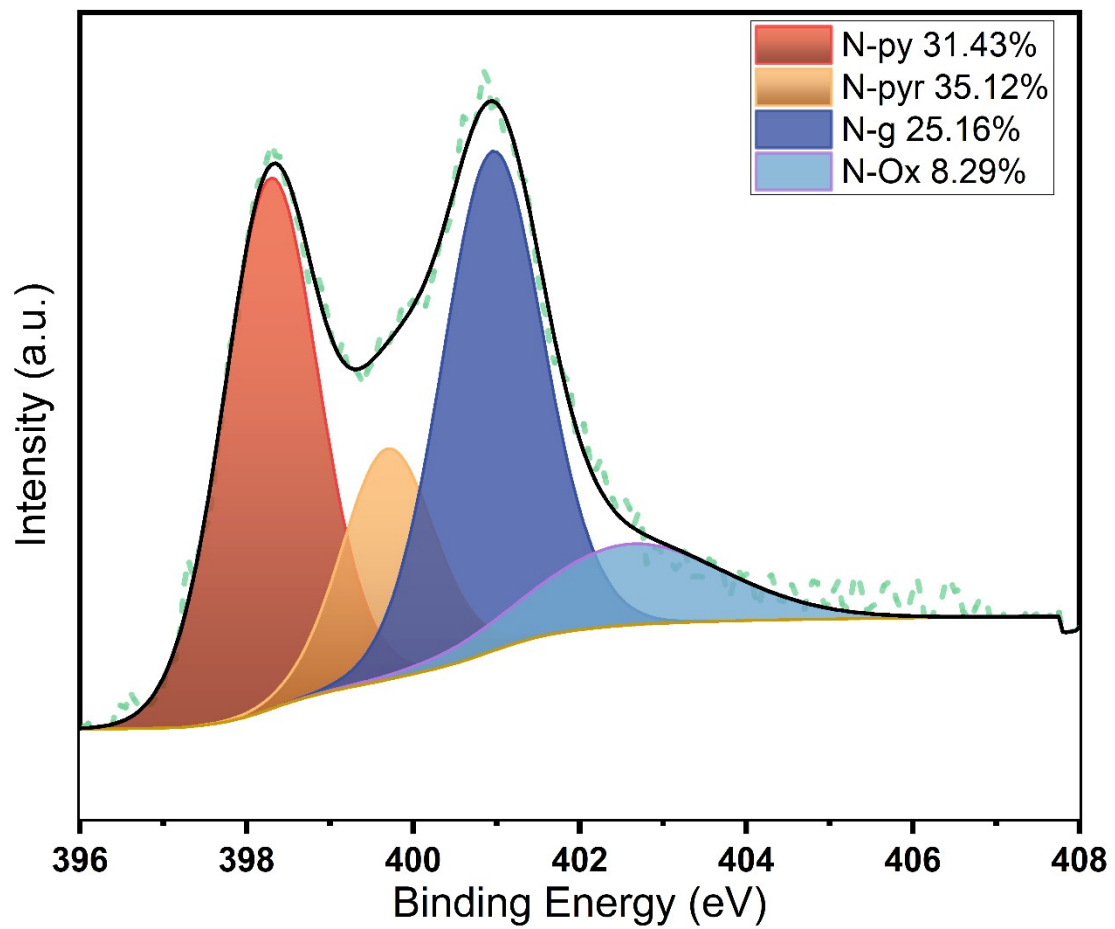


Fig. S15. XPS spectra of 3.0PANI@AC900 after use

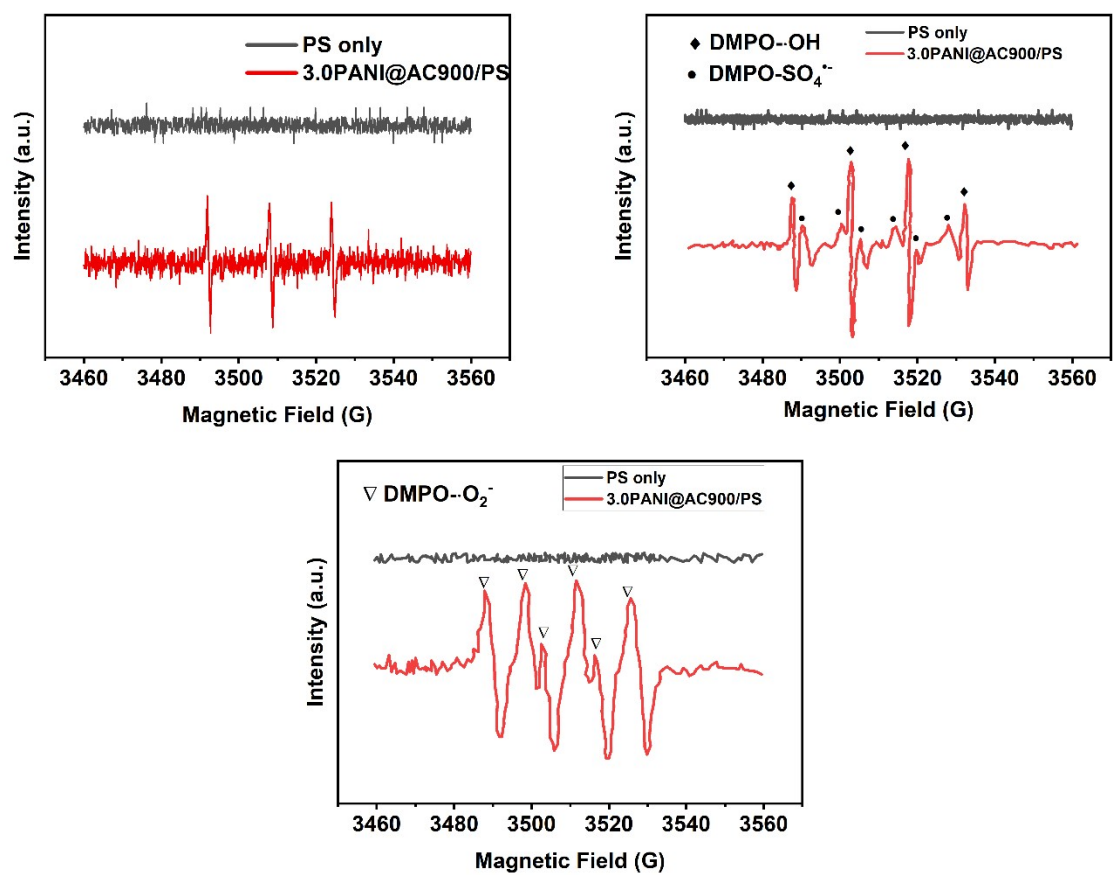


Fig. S16. EPR spectra of 3.0PANI@AC900/PS system at 5 min with the existence of (a) TEMP-¹O₂, (b)DMPO-SO₄•⁻, DMPO-HO• and (c)TEMP-O₂•⁻.