Supplementary information for

Employing a novel O_3/H_2O_2+$BiPO_4$/UV synergy technique to deal with thiourea-containing photovoltaic wastewater

Text S1. HPLC Analytical Methods

The separation was performed on a 300Extend-C18 column (3.5μm, 4.6×150mm, Agilent, USA) with a flowrate of 1 mL/min at 30℃. The mobile phase was composed with 60% water (containing 0.1% formic acid) and 40% methyl alcohol. The sample injection volume was 10μL and the detection wavelength was set at 236nm.

Text S2. UPLC-IMS-QToF-MS Analytical Methods.

The mineralization byproducts of thiourea were analyzed via high resolution mass spectrometry analysis, carried on a Water I-Class Acquity UPLC(Waters, UK) coupled with a Vion IMS QToF(Waters, UK) using a SeQuant ZIC-HILIC column(100 mm × 2.1 mm i.d., 3.5 μm) (Merck, Germany). The mobile phase A was 50 mM ammonium formate in water, and mobile phase B was acetonitrile. Metabolites were separated via gradient elution under the following conditions: 0–10 min, 90–50% B; 10–12 min, 50–90% B; 12–15 min, 90% B; and the column was maintained at 45 °C. The flow rate was 0.4 mL/min. The parameters of high-resolution mass spectrometry analysis on full scan mass spectrometry were as follows: MS range, *m/z* 50–1000; scan time, 0.3 s; CE 6 eV; desolvation temperature, 500 °C; source temperature, 120 °C; desolvation gas, 1000 L/h; cone gas, 50 L/h; capillary voltage, 2000 V. The lock correction (lock sprayer reference: mass,556.2766 *m/z*; interval, 0.5 min; sample time, 0.5 min; CE, 6 eV; flow

rate 10 μL/min) enabled isotopic *m/z* screen, with tolerance of 3 mDa mass error, the expected adduct –H. Data were acquired and processed using UNIFI 1.8.1.

Table S1 Analysis of variance (ANOVA) for the prediction of TOC by the quadratic model

Factors	Statistic					
	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remark
Model	1979809	9	219978.8	320.5533	< 0.0001	significant
X_1-H2O2	1842704	1	1842704	2685.19	< 0.0001	significant
X_2-O3	16768.22	1	16768.22	24.43466	0.0017	significant
X_3-pH	19296.7	1	19296.7	28.11917	0.0011	significant
X_1X_2	19299.58	1	19299.58	28.12337	0.0011	significant
X_1X_3	9347.308	1	9347.308	13.6209	0.0077	significant
X_2X_3	292.0168	1	292.0168	0.425527	0.5350	
X_1^2	56907.21	1	56907.21	82.92524	< 0.0001	significant
X_2^2	5064.43	1	5064.43	7.379892	0.0299	significant
X_3^2	13777.19	1	13777.19	20.07613	0.0029	significant
Pure Error	1470.797	4	367.6993			
Cor Total	1984613	16				
R^2	0.99758					
Adj R^2	0.994467					
Adeq Precision	54.68905					

Table S2 Analysis of variance (ANOVA) for the prediction of H_2O_2 residue by the quadratic model

Factors	Statistic					
	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remark
Model	668.5874	9	74.28749	5.404299	0.0184	significant
X_1-H2O2	295.245	1	295.245	21.47861	0.0024	Significant
X_2-O3	26.645	1	26.645	1.938382	0.2065	
X_3-pH	20.48	1	20.48	1.489888	0.2618	
X_1X_2	67.24	1	67.24	4.891605	0.0626	
X_1X_3	75.69	1	75.69	5.506329	0.0513	
X_2X_3	8.41	1	8.41	0.611814	0.4597	
X_1^2	3.260632	1	3.260632	0.237206	0.6411	
X_2^2	11.88379	1	11.88379	0.864527	0.3834	
X_3^2	165.528	1	165.528	12.0419	0.0104	significant
Pure Error	78.512	4	19.628			
Cor Total	764.8094	16				
R^2	0.874188					
Adj R^2	0.71243					
Adeq Precision	8.835728					

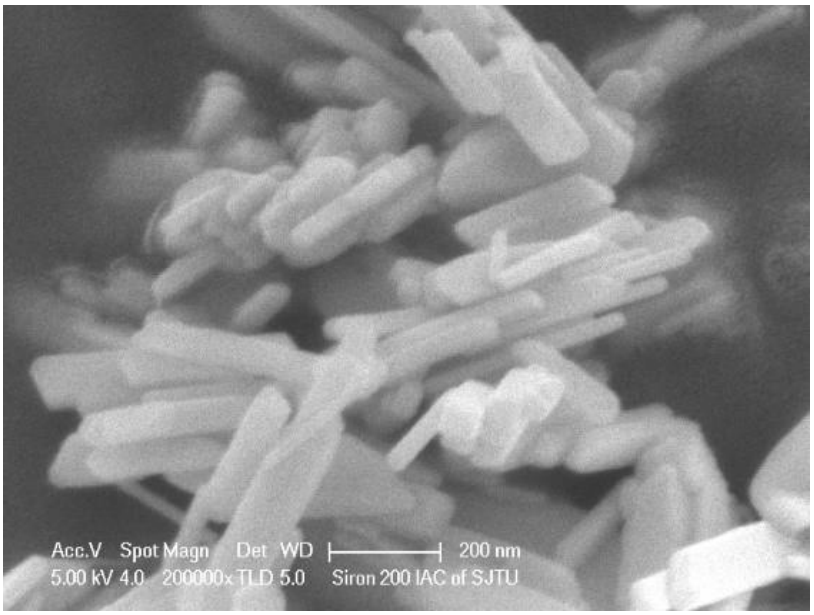


Figure S1 SEM images of $BiPO_4$

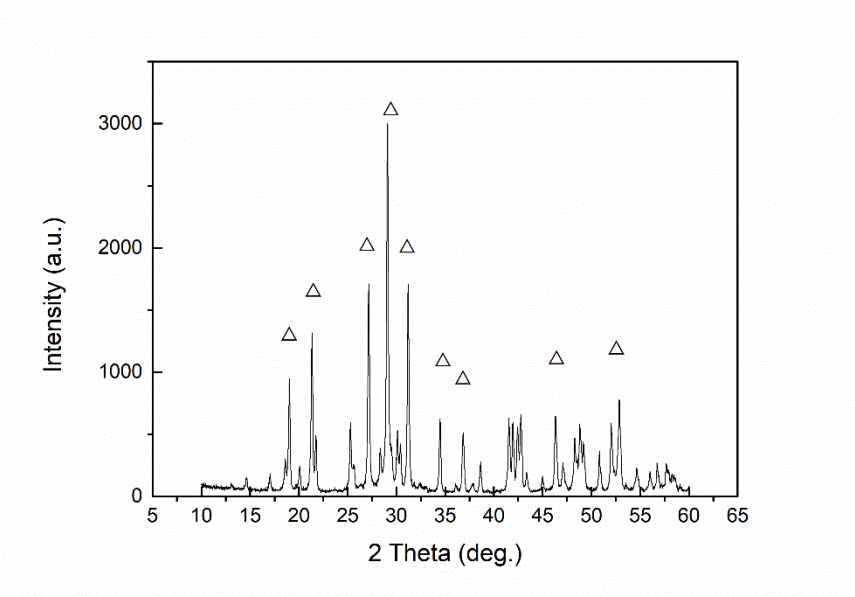


Figure S2 XRD pattern of $BiPO_4$

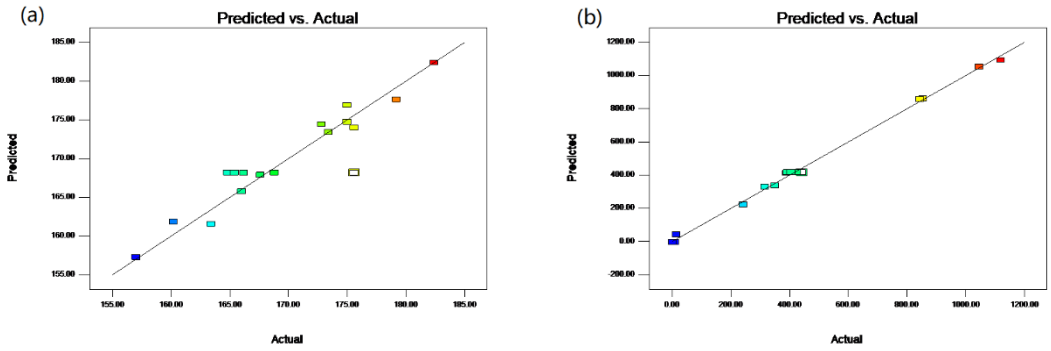
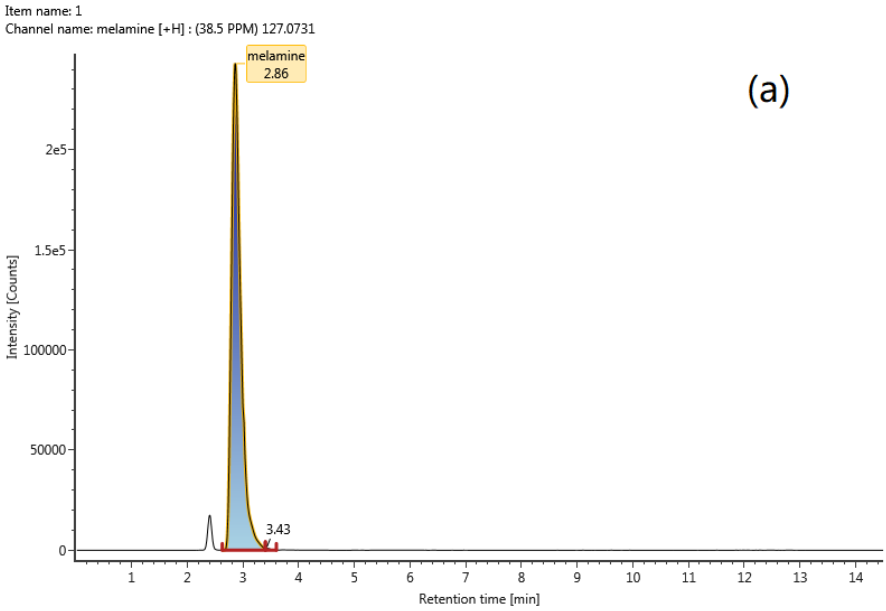
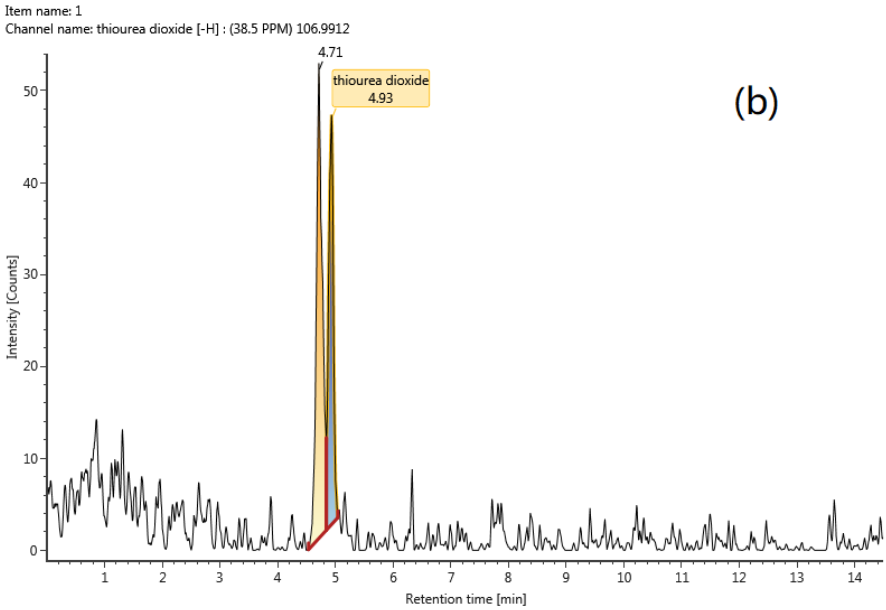


Figure S3 Validation of TOC and H_2O_2 residue model using the plot of predicted values versus observed experimental data.





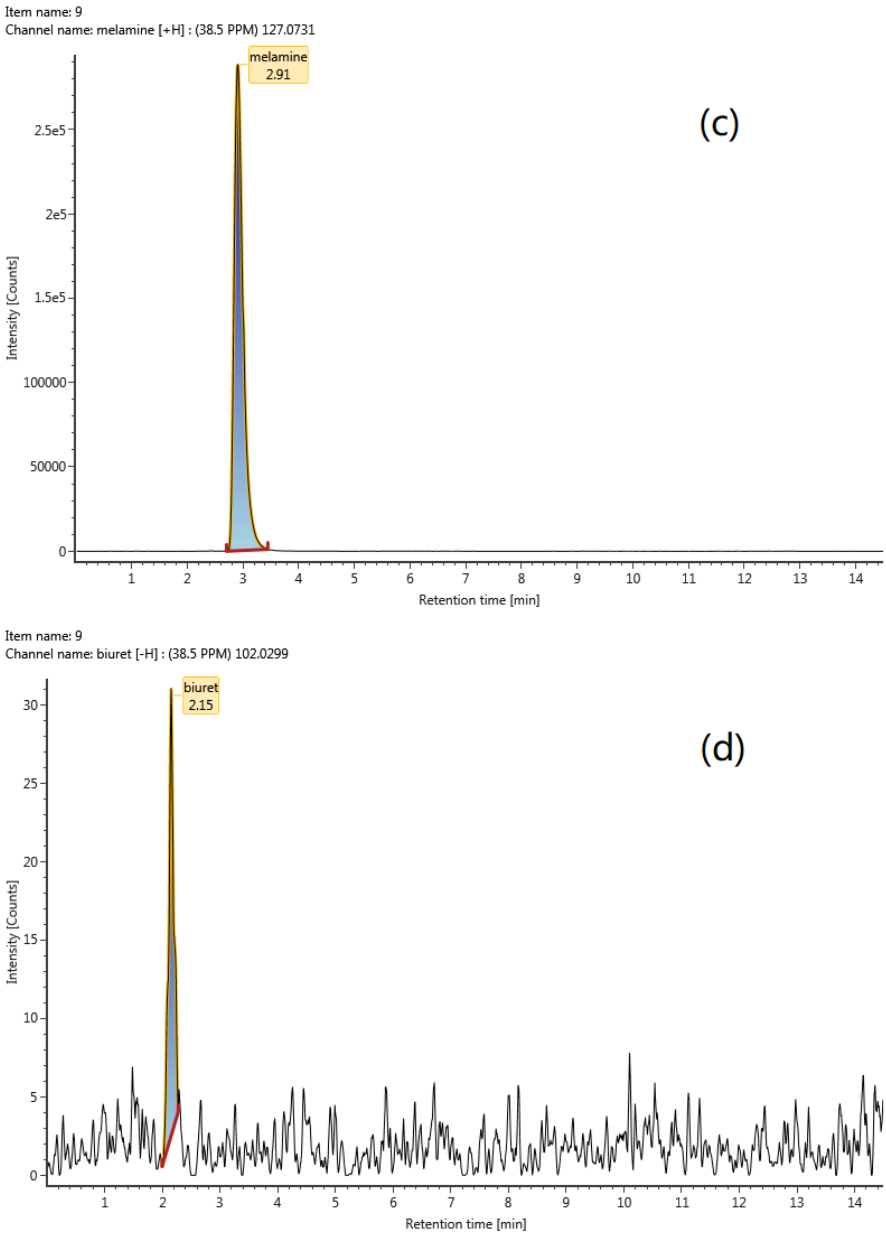


Figure S4 UPLC-IMS-QToF-MS Analysis data. (a)&(b): Intermediates after O_3/H_2O_2, (c)&(d): Intermediates after $BiPO_4$