Synergistic Interface Engineering in ZnO@CNT Catalysts: Electronic Modulation for Switching Peroxydisulfate Activation toward a $^1O_2$-Dominated Non-Radical Pathway

S1. Experimental materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$；AR,99%), multi-walled carbon nanotubes (CNTs), 2-methylimidazole (2-MI; AR,99%), 2,2,6,6-tetramethylpiperidine (TEMP; AR,99%), methanol (MA; AR,99%), potassium persulfate (PDS; $K_2S_2O_8$), sulfamethoxazole (SMX；AR,99%) ,p-Benzoquinone (p-BQ; AR,99%), L-histidine(L-His; 99%), tert-butanol (TBA; AR,99%), sodium bicarbonate ($NaHCO_3$; AR,99%), sodium perchlorate, sodium nitrate ($NaNO_3$; AR,99%), humic acid (HA; AR,99%), and sodium hydroxide (NaOH; AR,96%). Methanol (chromatographically pure), ciprofloxacin (CIP; AR, 99%), diclofenac (DF; AR, 99%), bisphenol A (BPA; AR, 99%). All chemicals were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. All reagents were of analytical grade and used without further purification.

S2. Characterizations

Scanning electron microscopy (SEM) and energy spectrum analysis (EDX) systems were used to characterize the surface morphology and elemental distribution of the ZnO@CNT composites, and X-ray diffractometry (XRD,

Cu Kα radiation source, λ = 1.5406 Å) was used for physical structure analysis. Electrochemical impedance spectroscopy (EIS, CHI1650E) was used to electrochemically analyze the samples. The degradation of various contaminants was tested by HPLC (Agilent Technologies 1260 Infinity II). Condition: column: Hypersil ODS C18 150*4.6mm; T=35 ℃; u = 1.0 ml/min. We used spin trapping (DMPO, TEMP) techniques to detect $SO_4^{-}\cdot$, ·OH, $O_2^{-}\cdot$, and $^1O_2$ radicals, and electron paramagnetic resonance (EPR) was used to detect DMPO-$SO_4^{-}\cdot$, DMPO-·OH, DMPO-$O_2^{-}\cdot$, and TEMP-$^1O_2$ signals. Different samples were prepared in order to capture $SO_4^{-}\cdot$, ·OH, $O_2^{-}\cdot$, and $^1O_2$ radicals. For example, the ·OH and $SO_4^{-}\cdot$ samples were prepared from 50 μL of DMPO, 0.5 mL of deionized water and 0.5 mL of reaction solution, while the $^1O_2$ sample was prepared from 50 μL of TEMP and 0.5 mL of reaction solution. The samples were then sent to a BRUKER A300 spectrometer for analysis, with the test conditions set to a modulation amplitude of 1.0 G, a time constant of 10.24 ms, a transition time of 81.92 ms, and a scan time of 83.89 s. We used Win-EPR and SimFonia version.

S3. Software for data processing and analysis

The degradation kinetics were fit by the pseudo first-order model and the apparent rate constant (k) was calculated according to Eq. (B1):

$$\ln (C_t / C_0) = -k\, t \qquad \text{(B1)}$$

where Ct is the target pollutant concentration at a certain reaction time (t), and C0 is the initial concentration of target pollutant.

S4. Theoretical calculations

The DFT calculations were conducted by employing the universal generalized gradient correlation function and Vienna ab initio simulation package (VASP5.4). A plane-wave basis set with cutoff energy at 400 eV within the framework of the projector augmented wave method was adopted. The Gaussian smearing width was set to 0.2 eV. The Brillouin zone was sampled with 3 × 3 × 1 K points. All atoms were allowed to converge to 0.01 eV Å-1. The condensed Fukui function could be calculated as:

Nucleophilic attack: $f_k^+ = q_N^k - q_{N+1}^k$ (B2)

Electrophilic attack: $f_k^- = q_{N-1}^k - q_N^k$ (B3)

Radical attack: $f_k^0 = (q_{N-1}^k - q_{N+1}^k)/2$ (B4)

Where qk was the atom charge of atom K at corresponding state, and the values of Fukui Index of the reactive sites were usually larger than other regions.

S5. Degradation efficiency of SMX by ZnO@CNT with different loadings

As shown in the degradation trends, SMX removal efficiency increased with ZnO loading from 5% to 20%, but a decline was observed at 25%

loading. Specifically, at 30 minutes of reaction time, the degradation efficiencies of ZnO@CNT-5, 10, 15, 20, and 25 were 72.3%, 84.6%, 90.3%, 91.2%, and 88.2%, respectively. This trend indicates that 15-20% loading represents the optimal range, with 15% loading showing near-peak performance. More importantly, when evaluating ZnO utilization efficiency, the incremental improvement from 15% to 20% loading was minimal (only 0.9% increase in efficiency), while the 25% loading showed decreased performance due to particle aggregation and reduced active site accessibility, as confirmed by our characterization studies. From an economic perspective, ZnO@CNT-15 achieves comparable performance to ZnO@CNT-20 while using 25% less ZnO precursor, representing a more cost-effective formulation. Additionally, moderate loading of 15% provides better long-term stability prospects, as excessive metal oxide loading can accelerate catalyst deactivation due to particle aggregation and potential mass transfer limitations. Therefore, considering the balance between catalytic performance, material utilization efficiency, and practical applicability, ZnO@CNT-15 was selected as the optimal catalyst for detailed mechanistic studies in this work.

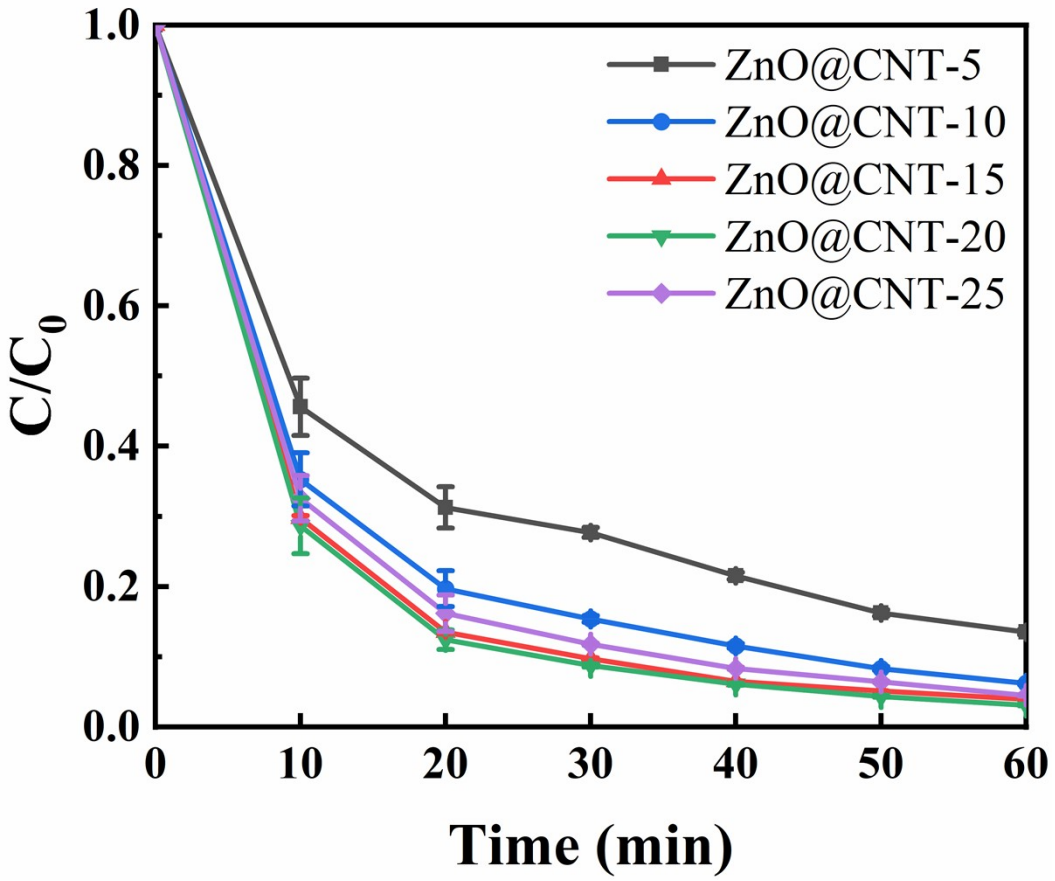


Fig. S5. Degradation efficiency of SMX by ZnO@CNT with different loadings

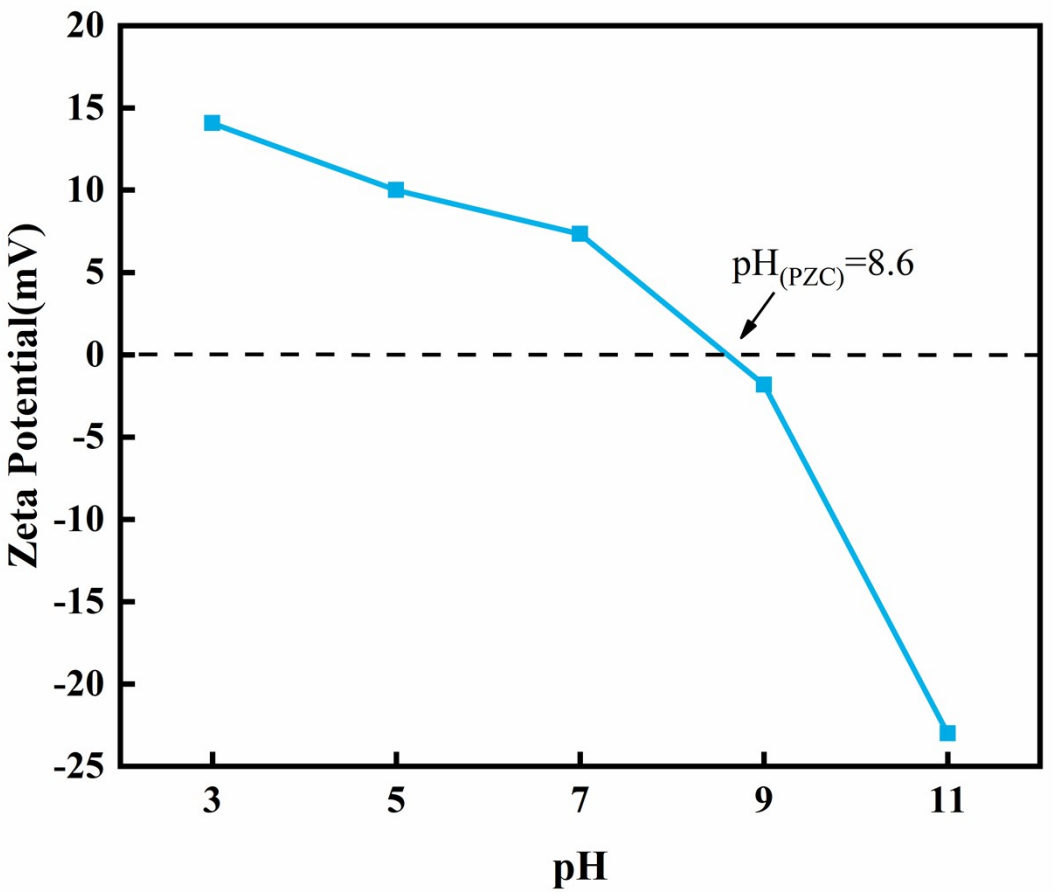


Fig. S6. Zeta potential of ZnO@CNT at different pH conditions.

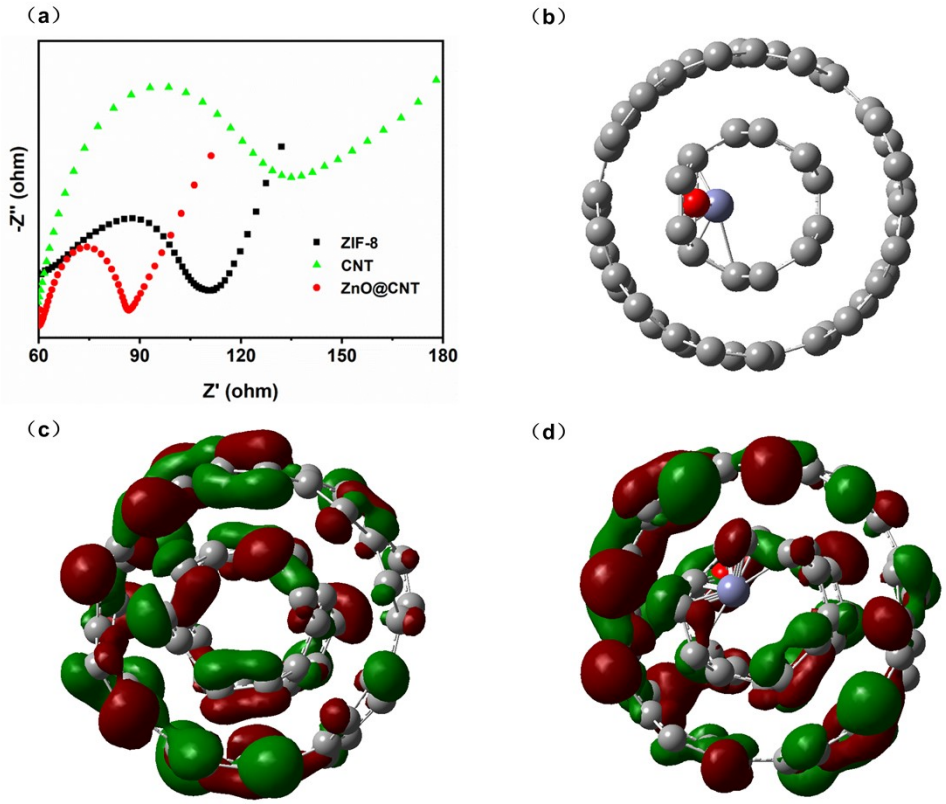


Fig. S7. EIS of ZIF-8, CNT and ZnO@CNT (a); ZnO@CNT Load model (b); Carbon nanotube HOMO diagram (c); ZnO@CNT HOMO diagram (d).

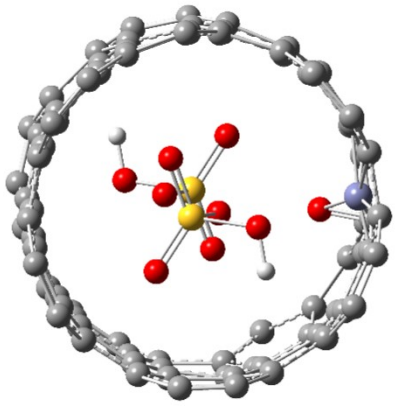


Fig. S8. Potential adsorption models of PDS molecules on ZnO@CNT.

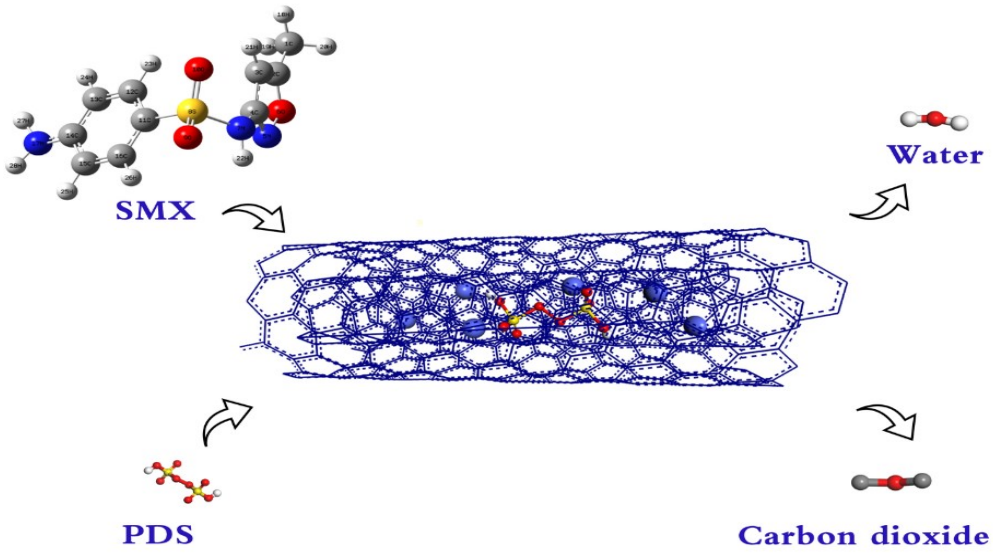


Fig. S9. Degradation mechanism of SMX in ZnO@CNT/PDS system.

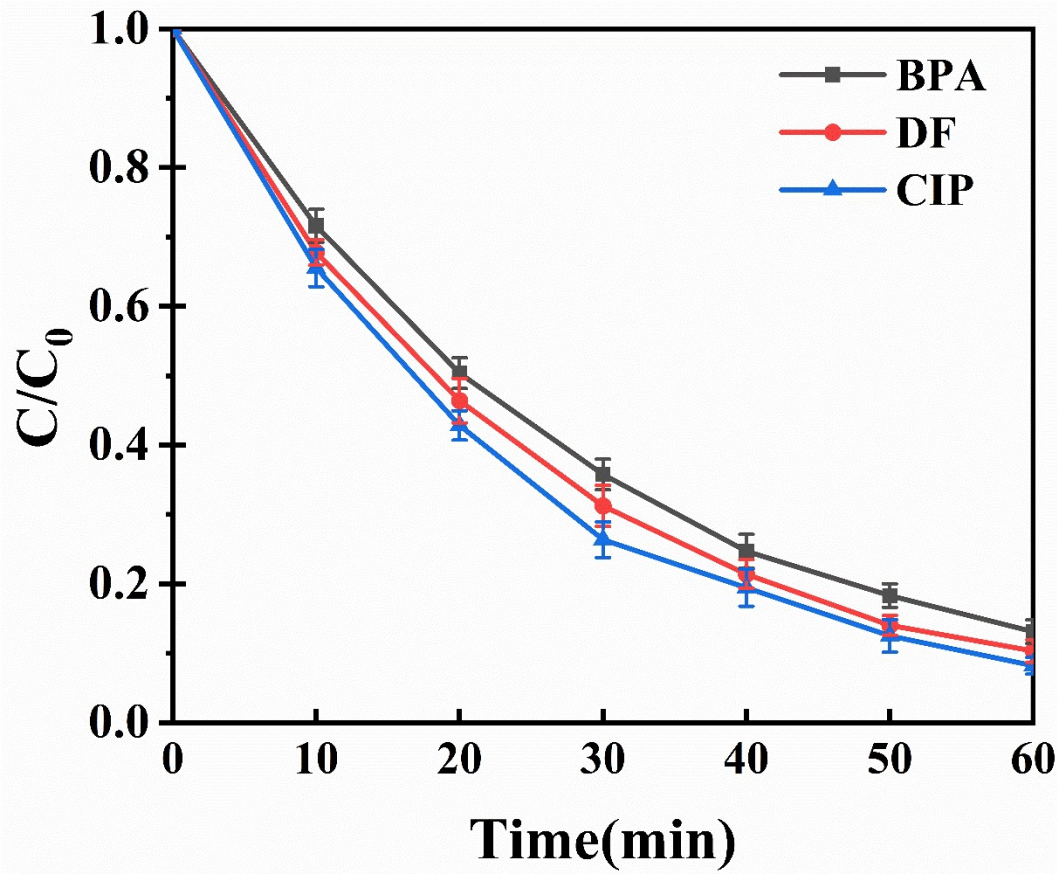


Fig. S10. Degradation performance of ZnO@CNT for CIP, DF and BPA

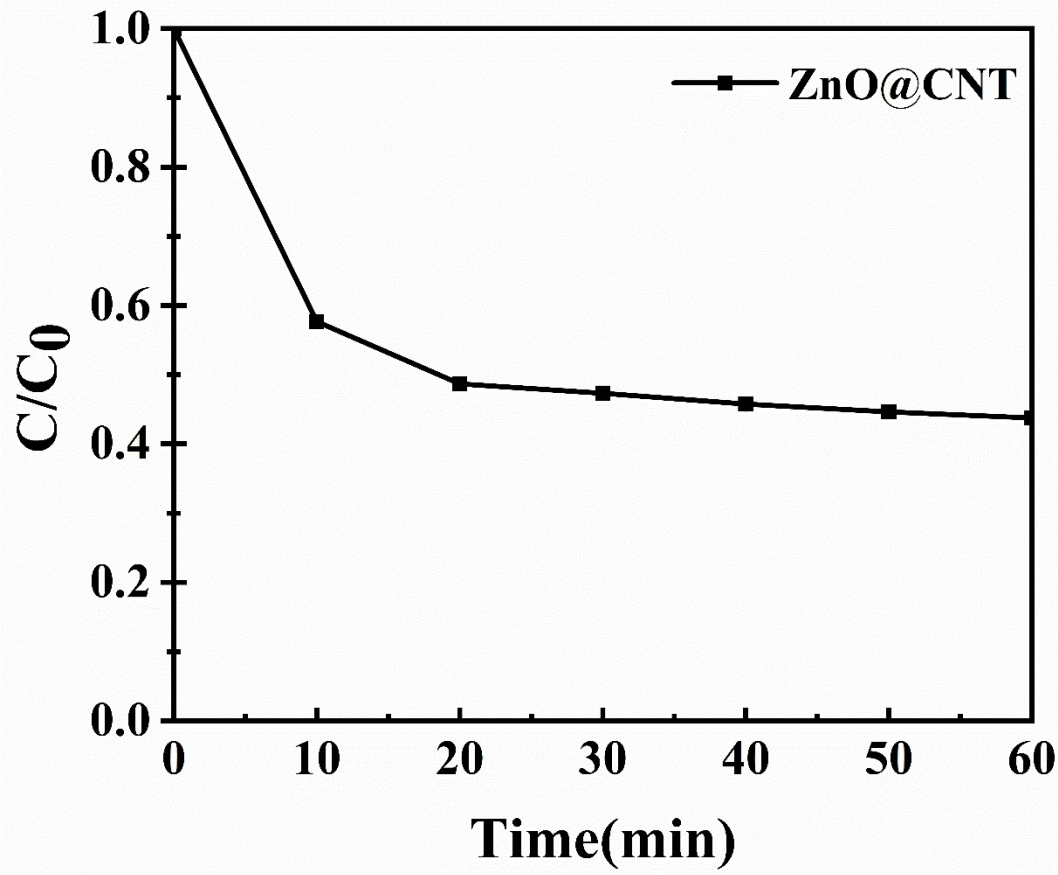
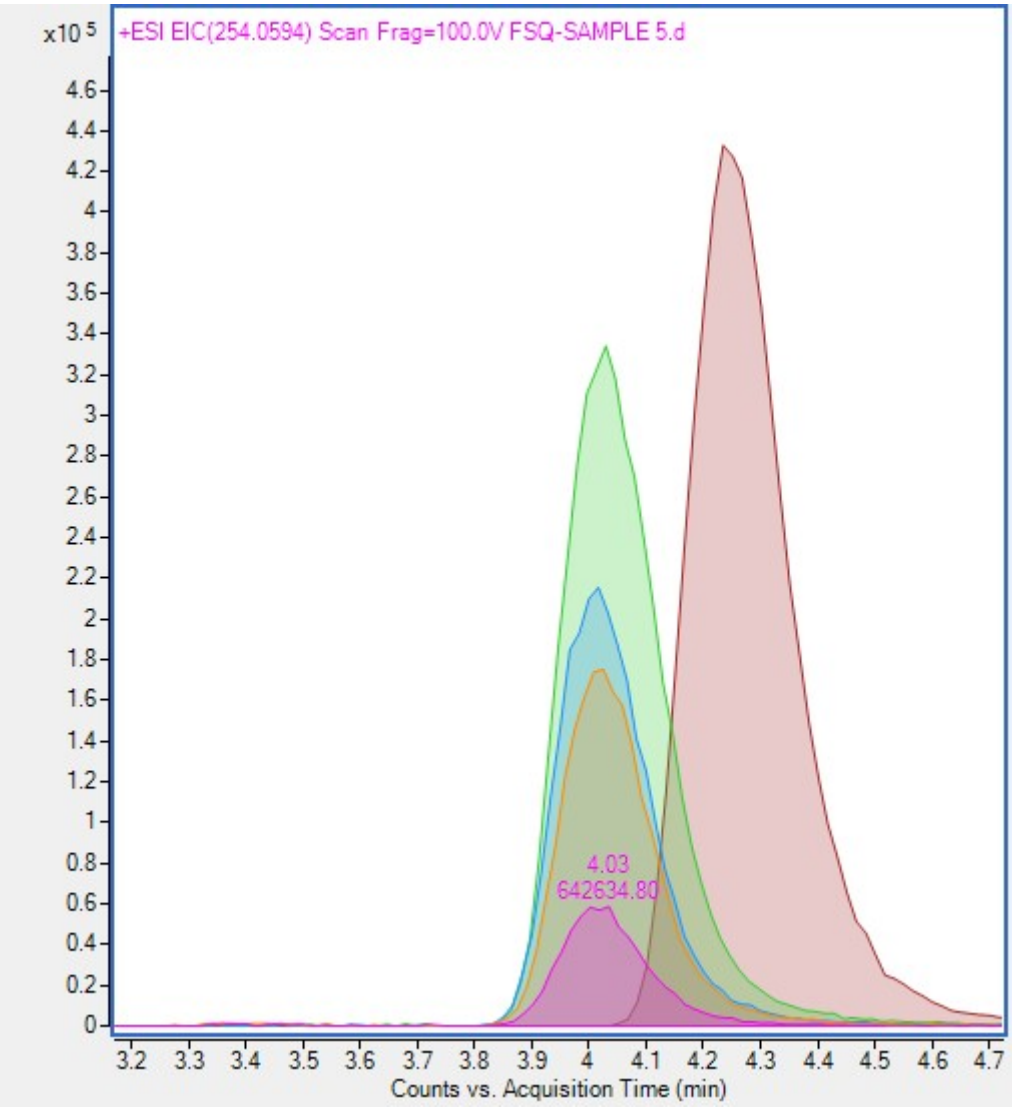


Fig. S11. The TOC of ZnO@CNT/PDS [PDS] = 0.8 g/L, SMX = 20 mg/L, [ZnO@CNT] = 0.2 g/L, [pH] = 9, Temperature = 25 ℃.

97


x10 5
+ESI EIC(254.0594) Scan Frag=100.0V FSQ-SAMPLE 5.d
4.03
642634.80
Counts vs. Acquisition Time (min)

98

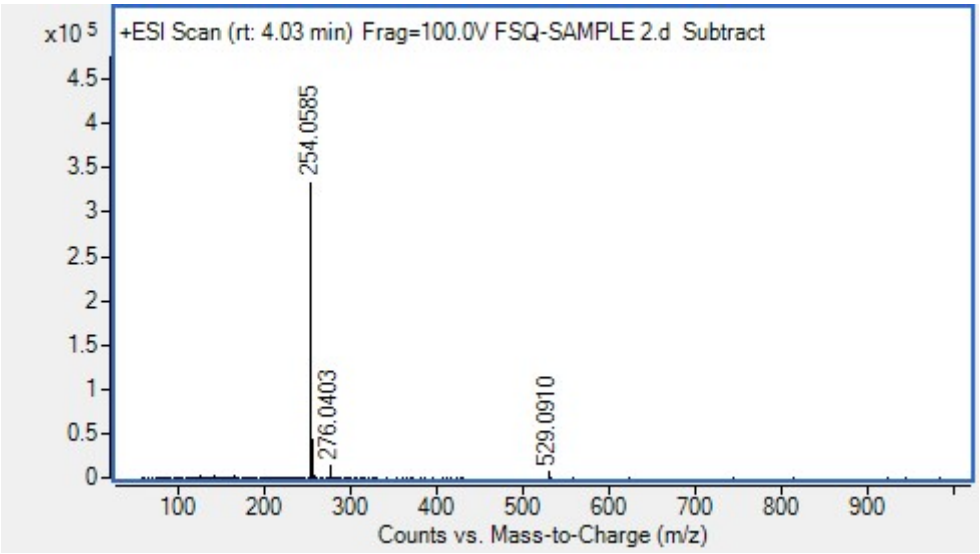

x10 5
+ESI Scan (rt: 4.03 min) Frag=100.0V FSQ-SAMPLE 2.d Subtract
254.0585
276.0403
529.0910
Counts vs. Mass-to-Charge (m/z)

Fig. S12. LC-MS chromatograms of SMX and the transition products