Electronic Supplementary Information

Degradation of Ibuprofen and Acetylsulfamethoxazole by multi-walled Carbon Nanotube Catalytic Ozonation: Surface properties, kinetics and modeling

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Text S1: Method for the determination of rate constants for a macromolecule simultaneously reacting with ozone and serving as the initiator, promoter and inhibitor in the $OH^{\bullet}$ chain reactions in water ozonation

The approach described by Yong and Lin[1, 2] integrated the following three classical models for water ozonation:

1. The transient steady-state concentration of $OH^{\bullet}$[3]:

$$[\cdot OH]=\frac{2k_1[OH^-]+\sum k_{I,i}[M_{I,i}]}{\sum k_{S,i}[M_{S,i}]}[O_3] \qquad (S1)$$

where $[\cdot OH]$ represents the transient steady-state concentration of $OH^{\bullet}$; k_1 represents the 2^{nd}-order rate constant between OH^- and ozone; $[M_{I,i}]$ and $k_{I,i}$ represent the concentration of the initiator and its 2^{nd}-order rate constant with O_3; $[M_{S,i}]$ and $k_{S,i}$ represent the concentration of the inhibitor and its 2^{nd}-order rate constant with $OH^{\bullet}$, respectively.

2. The R_{ct} concept[4]:

$$R_{ct}=\frac{\int[\cdot OH]dt}{\int[O_3]dt}=-\frac{\ln\frac{[pCBA]_t}{[pCBA]_0}}{k_{\cdot OH/pCBA}\int[O_3]dt} \qquad (S2)$$

3. Pseudo-1^{st} order ozone decomposition kinetics [3]:

$$-\frac{d[O_3]}{dt}\frac{1}{[O_3]}=k_{obs}$$
$$=3k_1[OH^-]+k_D[M_{D,i}]+k_I[M_{I,i}]+k_P[M_{P,i}]\left(\frac{2k_1[OH^-]+\sum k_{I,i}[M_{I,i}]}{\sum k_{S,i}[M_{S,i}]}\right) \qquad (S3)$$

Eq (S1) can be substituted to Eq (S2) to yield Eq (S4) assuming that pH value (or $[OH^-]$) and the concentrations of initiator ($[M_{I,i}]$) and inhibitor ($[M_{S,i}]$) do not change during the ozonation.

$$R_{ct}=\frac{\int\left(\frac{2k_1[OH^-]+\sum k_{I,i}[M_{I,i}]}{\sum k_{S,i}[M_{S,i}]}\right)[O_3]dt}{\int[O_3]dt}=\frac{2k_1[OH^-]+\sum k_{I,i}[M_{I,i}]}{\sum k_{S,i}[M_{S,i}]} \qquad (S4)$$

Assuming that MWCNT can simultaneously react with ozone and serve as the initiator, promoter and inhibitor in the $OH^{\bullet}$ chain reactions, Eq (S4) can be rewritten as Eq (S5) with the addition of *tert*-butanol as an external inhibitor (denoted as S with a rate constant of k_{SS} with $OH^{\bullet}$) in the system [1].

$$R_{ct}=\frac{2k_1[OH^-]+k_I[MWCNT]}{k_{SS}[S]+k_S[MWCNT]} \qquad (S5)$$

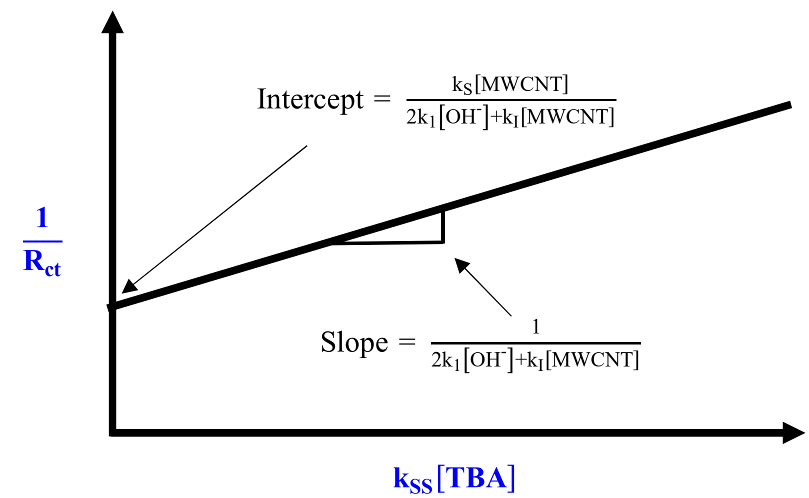
where k_I represents the initiation rate constant of MWCNT (unit: $L(mg\ CNT)^{-1}s^{-1}$), k_S represents the inhibition rate constant of MWCNT (unit: $L(mg\ CNT)^{-1}s^{-1}$), k_{SS} represents the 2^{nd}-order rate constant between *tert*-butanol and $OH^{\bullet}$ (k_{SS}=6.0×10^8

$M^{-1}s^{-1}$).[5]

The reciprocal of Eq (S5) gives Eq (S6).

$$\frac{1}{R_{ct}} = \frac{k_{SS}[S]+k_S[MWCNT]}{2k_1[OH^-]+k_I[MWCNT]} \quad (S6)$$

Ideally, a linear relationship exists between $\frac{1}{R_{ct}}$ and $k_{SS}[S]$ as shown below. k_I and k_S can then be determined from the slope and intercept, respectively.

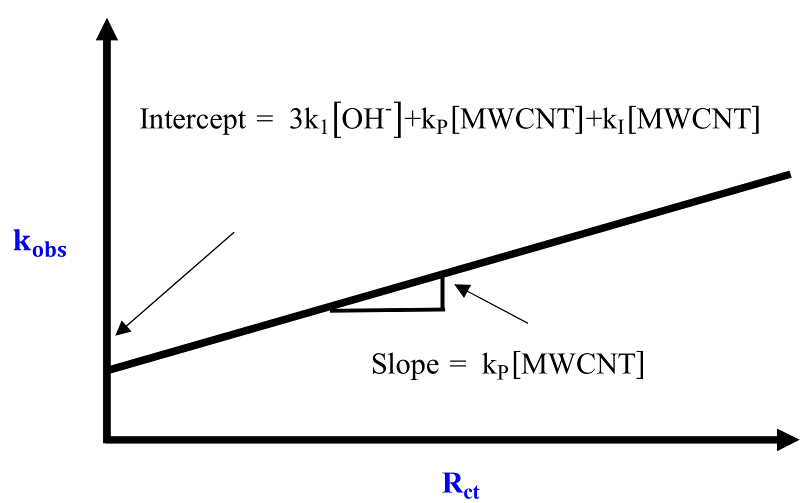


In the same system, substituting Eq (S3) to Eq (S1) gives Eq (S7):

$$-\frac{d[O_3]}{dt}\frac{1}{[O_3]} = k_{obs}= 3k_1[OH^-]+k_D[MWCNT]+k_I[MWCNT]+k_P[MWCNT]R_{ct} \quad (S7)$$

where k_D represented the direct reaction rate constant of MWCNT, k_P represented the promotion rate constants of MWCNT (unit: $L(mg\ CNT)^{-1}s^{-1}$).

A linear relationship should exist between k_{obs} and R_{ct} as shown below. k_p and k_D can then be determined from the slope and intercept, respectively.



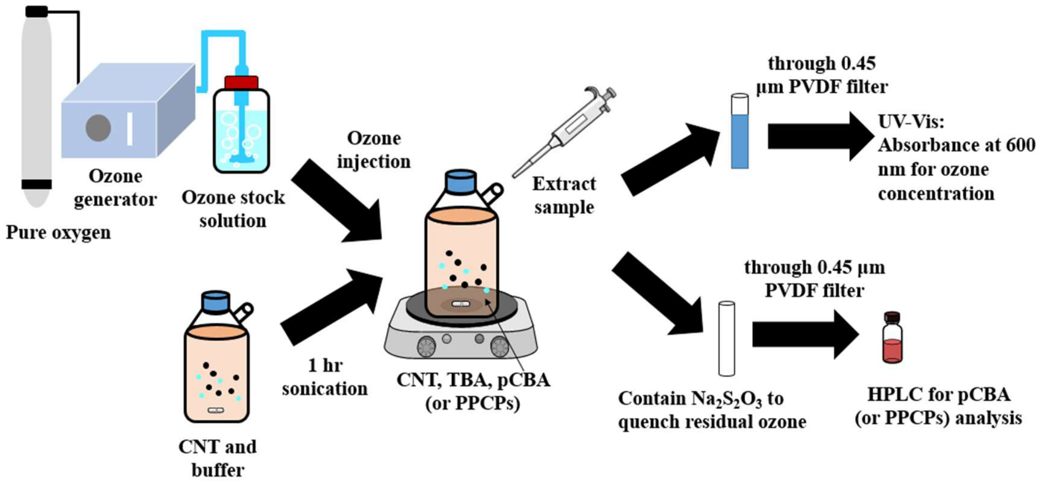


Figure S1. Schematic diagram of ozone experiments

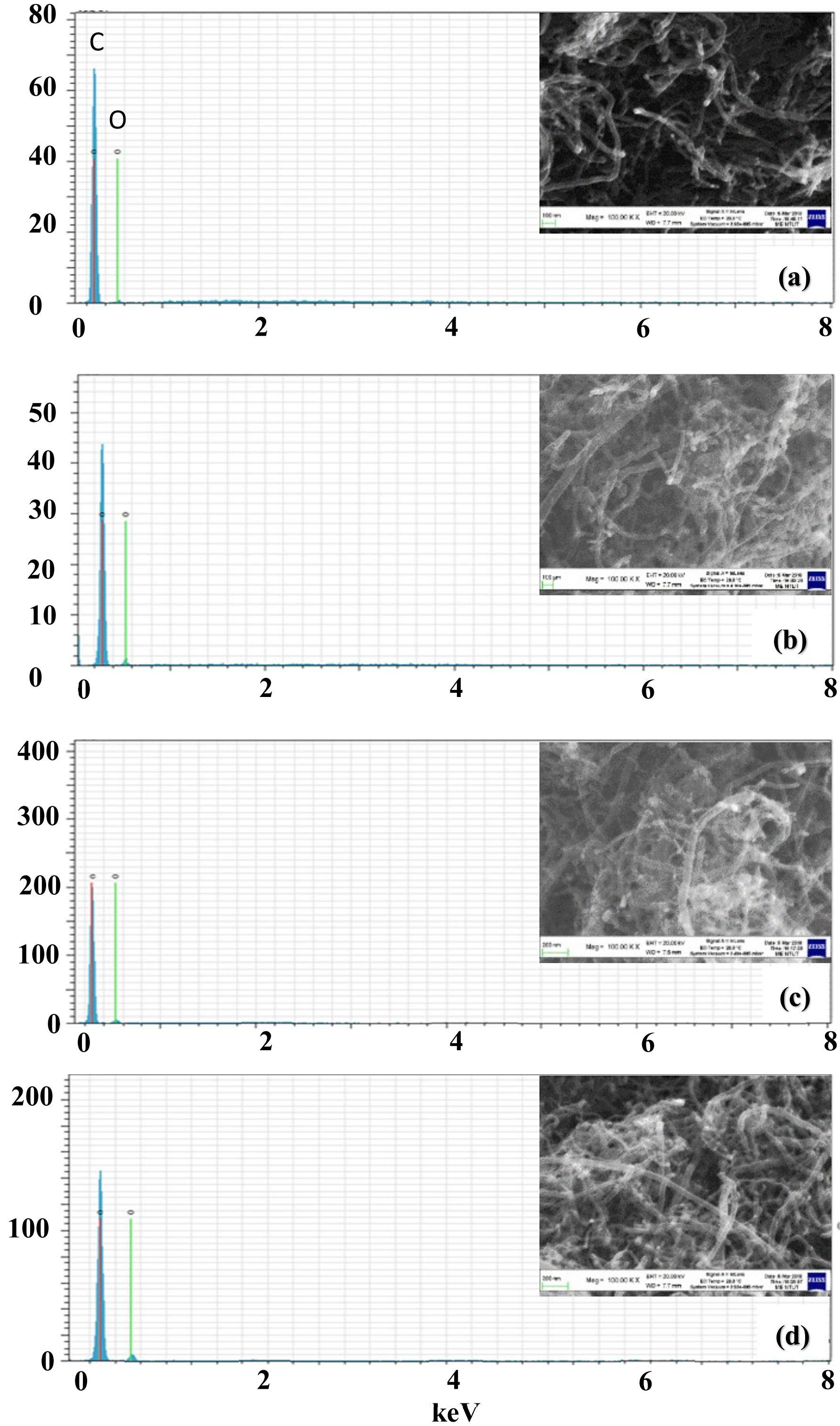


Figure S2. EDS spectra of (a) p-MWCNT, (b) 20-MWCNT, (c) 40-MWCNT and (d) 70-MWCNT.

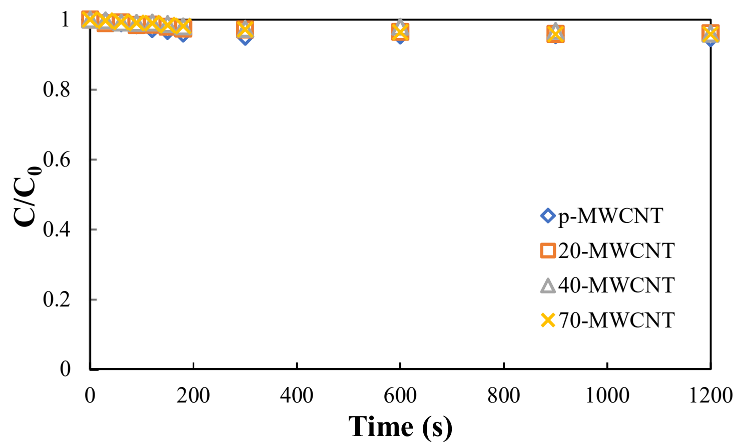


Figure S3. Adsorption of pCBA onto the 4 MWCNTs. Experimental condition: $[pCBA]_0$ = 0.5 μM, $[B_4O_7^{2-}]$ = 5 mM, MWCNT dosage = 20 mg/L, pH = 7.

References

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