

## **Supporting Information**

### **Undiscovered multiple roles of multivalent cations in the pollutant removal from actual water by persulfate activated by carbon materials**

Han-Chao Zhang, Jiang-Jin Han, Xin Zhang, Pu-Can Guo, Dong-Hua Xie, Guo-Ping  
Sheng\*

CAS Key Laboratory of Urban Pollutant Conversion, Department of Environmental  
Science and Engineering, University of Science and Technology of China, Hefei,  
230026, China

#### **\*Corresponding author:**

Prof. Guo-Ping Sheng

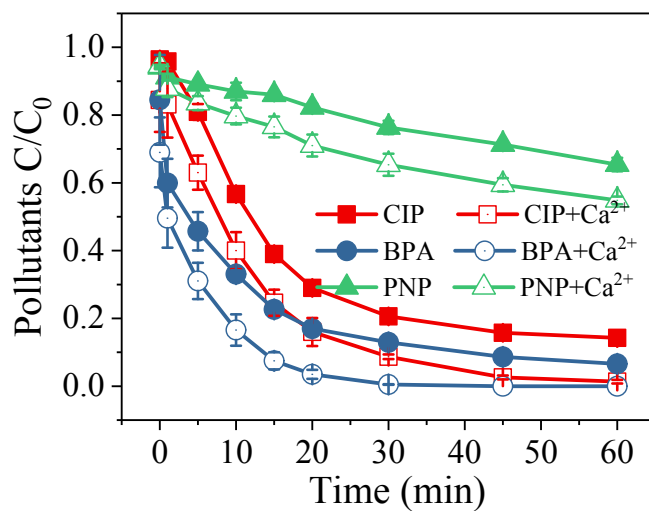
Fax: +86-551-63601592

E-mail: [gpscheng@ustc.edu.cn](mailto:gpscheng@ustc.edu.cn)

This supporting information contains 11-page document, including 4 figures and 5  
tables as well as this cover page.

## **Text S1**

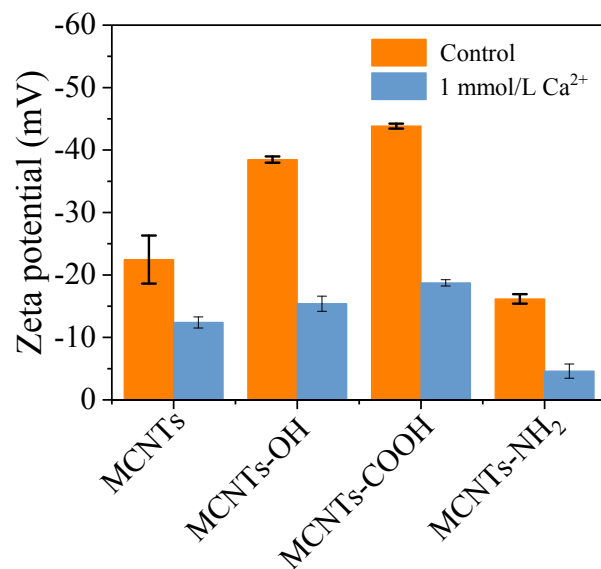
**Linear sweep voltammetry measurement.** The Linear sweep voltammetry (LSV) measurement was conducted at room temperature in a three-electrode configuration with an electrochemical workstation (CHI 760E, Chenhua Instrument Co., China). The MCNTs was coated on the fluorinated tin oxide glass as the working electrode, and the Pt was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. A 20 mmol/L boric acid buffer was used as the electrolyte. The current at a working electrode was measured with increasing the potential from 0.2 to 1.4 V with a scan rate of 20 mV/s.



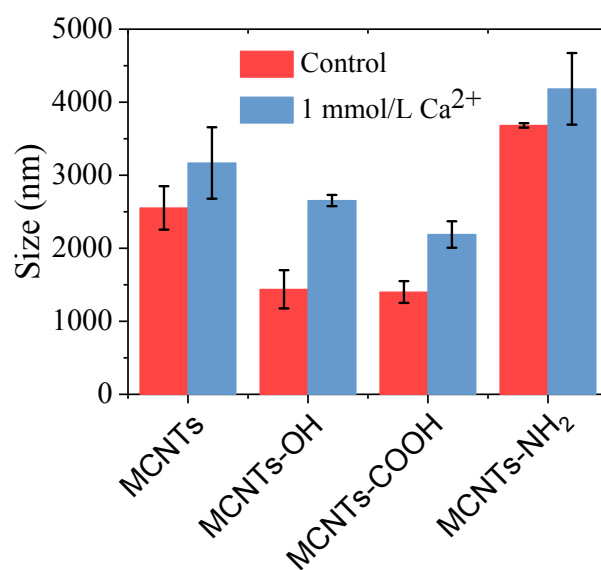
**Figure S1.** Effect of  $\text{Ca}^{2+}$  on the CIP, BPA, and PNP degradation kinetics in the PDS

activation by the MCNTs. Reaction conditions:  $[\text{CIP}] = [\text{BPA}] = [\text{PNP}] = 2 \text{ mg/L}$ ,

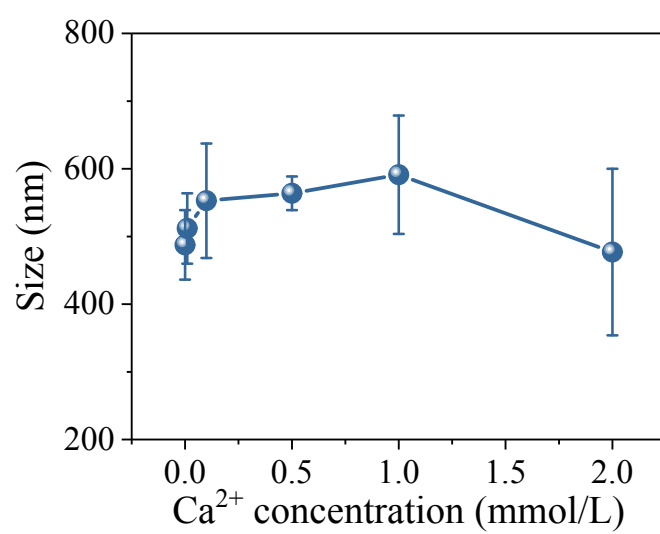
$[\text{MCNT}] = 100 \text{ mg/L}$ ,  $[\text{PDS}] = 1 \text{ mmol/L}$   $[\text{Ca}^{2+}] = 1 \text{ mmol/L}$ , pH 7.0.



**Figure S2.** Effect of  $\text{Ca}^{2+}$  on the zeta potential of various MCNTs with various functional groups. Reaction conditions: [MCNT], [MCNT-OH], [MCNT-COOH], [MCNT-NH<sub>2</sub>] = 100 mg/L, [ $\text{Ca}^{2+}$ ] = 1 mmol/L, pH 7.0.



**Figure S3.** Effect of  $\text{Ca}^{2+}$  on the hydrodynamic size of various MCNTs with various functional groups. Reaction conditions: [MCNT], [MCNT-OH], [MCNT-COOH], [MCNT-NH<sub>2</sub>] = 100 mg/L, [ $\text{Ca}^{2+}$ ] = 1 mmol/L, pH 7.0.



**Figure S4.** Effect of  $\text{Ca}^{2+}$  on the hydrodynamic size of SRNOM in the solution.

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**Table S1. characteristics of four actual waters**

|                     | DOC<br>(mg-C/L) | TN<br>(mg/L) | NH <sub>4</sub> <sup>+</sup> -N<br>(mg/L) | NO <sub>3</sub> <sup>-</sup> -N<br>(mg/L) | TP<br>(mg/L) | UV <sub>254</sub> |
|---------------------|-----------------|--------------|---|---|--------------|-------------------|
| <b>SC Effluent</b>  | 6.8±0.9         | 17.5±0.1     | 0.974±0.115                               | 4.27 ± 0.12                               | 0.112±0.006  | 0.089±0.007       |
| <b>river water</b>  | 8.4±1.2         | 14.9±2.0     | 0.460±0.019                               | 4.10 ± 0.01                               | 0.064±0.001  | 0.134±0.009       |
| <b>lake water</b>   | 9.6±1.8         | 12.1±0.8     | 0.270±0.012                               | 3.27 ± 0.17                               | 0.125±0.006  | 0.120±0.012       |
| <b>ground water</b> | 2.6±0.8         | 7.6±0.8      | 0.022±0.005                               | 1.15± 0.35                                | 0.040±0.003  | 0.02±0.001        |

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DOC: Dissolved organic carbon

TN: Total Nitrogen

TP: Total Phosphorus

**Table S2. HPLC test conditions for various micropollutants.**

|     | mobile phase |              |                         | Flow rate<br>(mL/min) | UV<br>detector<br>(nm) |
|-----|--------------|--------------|-------------------------|-----------------------|------------------------|
|     | methanol     | acetonitrile | 0.1% formic acid        |                       |                        |
| BPA | -            | 40%          | 60%                     | 0.8                   | 273                    |
| CIP | -            | 20%          | 80%                     | 0.5                   | 277                    |
| SMX | 40%          | -            | 60%                     | 0.8                   | 263                    |
| PNP | -            | 80%          | 20% (H <sub>2</sub> O)* | 0.5                   | 318                    |

\*: The mobile phase of PNP was acetonitrile and H<sub>2</sub>O, not 0.1% formic acid.



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**Table S3. element content of different carbon nanomaterials**

|         | MCNTs | MCNTs-<br>OH | MCNTs-COOH | MCNTs-NH <sub>2</sub> | g-MCNTs |
|---------|-------|--------------|------------|-----------------------|---------|
| C at. % | 97.27 | 93.51        | 95.54      | 97.35                 | 99.11   |
| N at. % | 0.21  | 0.23         | 0.18       | 1.12                  | -       |
| O at. % | 2.52  | 6.26         | 4.28       | 1.53                  | 0.89    |

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**Table S4. multivalent cations concentration of actual water before and after CER treated**

|              | Ca <sup>2+</sup> (mg/L) |             | Mg <sup>2+</sup> (mg/L) |       | Fe <sup>2+</sup> (mg/L) |             | Al <sup>3+</sup> (mg/L) |             |
|--------------|-------------------------|-------------|-------------------------|-------|-------------------------|-------------|-------------------------|-------------|
|              | Before                  | After       | Before                  | After | Before                  | After       | Before                  | After       |
| SC Effluent  | 37.47±1.32              | 0.019±0.002 | 6.85±0.83               | n.d.  | 0.028±0.04              | 0.010±0.002 | 0.044±0.008             | 0.005±0.001 |
| River water  | 38.11±2.57              | 0.298±0.125 | 7.12±0.92               | n.d.  | 0.009±0.001             | 0.005±0.001 | 0.039±0.004             | 0.018±0.005 |
| Lake water   | 15.15±0.81              | 0.023±0.010 | 5.45±0.24               | n.d.  | 0.166±0.017             | 0.107±0.011 | 0.18±0.001              | 0.128±0.017 |
| Ground water | 93.70±3.49              | 0.024±0.004 | 22.12±1.27              | n.d.  | n.d.                    | n.d.        | 0.029±0.002             | 0.017±0.003 |

n.d.: not detected

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**Table S5. The pH in the four actual water before and after CER treatment**

|                    | pH     |       | Total organic carbon (mg/L) |            |
|--------------------|--------|-------|-----------------------------|------------|
|                    | Before | After | Before                      | After      |
| Secondary effluent | 7.68   | 8.01  | 6.88±0.44                   | 7.00±0.53  |
| River water        | 8.01   | 7.92  | 9.02±0.72                   | 8.82±0.59  |
| Lake water         | 8.02   | 8.31  | 10.77±0.43                  | 10.90±1.50 |
| Ground water       | 7.73   | 8.05  | 2.78±0.33                   | 3.08±0.75  |

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