

Electronic Supporting Information

Silicon Carbon Nanoparticles-based Chemiluminescence Probe for Hydroxyl Radical in PM_{2.5}

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Materials and methods

Chemicals.

3-aminopropyltrimethoxysilane (APTMS, 97%) and potassium superoxide were purchased from Aladdin (Milwaukee, WI, USA). Titanium trichloride solution (TiCl₃) was obtained from Kelong Chemical Reagent Company (Chengdu, China). Other reagents were bought from Chengdu United Institute of Chemical & Reagent. The pH 4 phosphate buffer solution (PBS) of 0.1 M was prepared with H₃PO₄–NaH₂PO₄. Ultrapure water (18.2 MΩ/cm) was obtained from a Mili-Q ultrapure system. All chemicals were at least of analytical grade.

Synthesis of SiC nanoparticles (SiC NPs).

The APTMS as precursor was mixed with 15 mL water to a final concentration of 1.0 M, which was heated hydrothermally in a stainless-PTFE reactor at 220 °C for 6 hrs. After centrifugation (8000 rpm, 10 min) to remove large particles, the SiC NPs were dialysed against water with a dialysis membrane (MW: 300) for 12 hrs to separate from the residual unreacted species. Finally, a transparent and little brown aqueous solution containing SiC NPs was obtained. The

concentration of SiC NPs was calculated based on the APTMS precursor concentration.

Characterization.

Transmission electron microscopy (TEM) and high-resolution TEM images were recorded using a Quanta 200 FEG (FEI company). X-ray diffraction (XRD) measurements were carried out via a BRUKER D8 diffractometer (40 mA/40 kV), using Cu $K\alpha_1$ radiation ($\lambda = 1.54 \text{ \AA}$) over the 2θ range of 5° to 70° . X-ray photoelectron spectroscopy (XPS) (Model PHI 5000) was used to characterize the as-prepared SiC NPs. Binding energies were corrected by using the $4f_{7/2}$ peak at 84.0 eV as a standard. And the SiC NPs was investigated with a Varian 640 Fourier transform infrared (FTIR) spectrophotometer (Varian, USA). The PL spectrum was recorded using the F-7000 spectrometer operated with instrument settings: 700 V of high voltage, 5 nm excitation slit and 5 nm emission slit. The UV-Vis spectrometer (U-2910) was used to analyze the UV-Vis absorbance of SiC NPs solution. The CL detection were operated on the Ultra Weak Luminescence Analyzer (BPCL-2-TGC) with the flow pump (BT100-02) using a speed-controller. The HPLC equipment used was an Agilent 1100 LC including a BinPump and a VWD detector. The electron spin resonance (EPR) spectra were recorded with Bruker E-500 and the following instrument settings: microwave power 2.0 mW, modulation frequency 100 kHz, and modulation amplitude 0.1 mT to analyze the CL mechanism.

1. Chemiluminescence Spectra.

The flow injection analysis system for determination of hydroxyl radical concentration consisted of three lines. Typically, the SiC NPs (35.9 mg/mL) solution of pH 2.0 was injected through a six-valve injector with water as carrier and mixed with Ti(III) solution at near neutral before entering the detector, which finally reacted with H_2O_2 within the mixing coil in front of the PMT.

The flow rates were 20 rpm/min for all solutions. The CL signals were detected and recorded with the BPCL luminescence analyzer. The peak height of the signal recorded was measured relative to CL intensity.

2. XRD spectrums of SiC NPs

The X-ray diffraction (XRD) pattern of the prepared SiC NPs, shown in Figure S1, appeared a relatively broad peak at a value of 2θ of 23 °C, indicating the amorphous nature of the carbon structure.¹

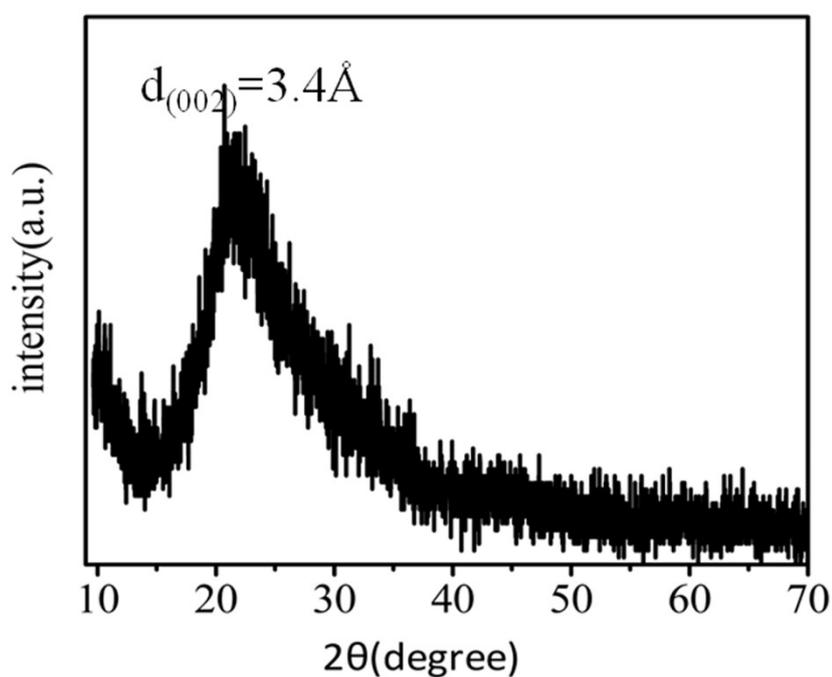


Figure S1. (a) XRD pattern of SiC NPs.

3. XPS spectrums of SiC NPs

The C 1s spectra of the as-prepared SiC NPs in Figure S2 b revealed four peaks centering at 284.3, 284.8, 285.5 and 287.7 eV, while the binding energy at 284.3 eV was ascribed to sp^2 C-C bonds and at 284.8 eV was assigned to C-H bonds. The binding energies at 285.5 and 287.7 eV were identified as C-N and C=O bonds, respectively. The existence of 287.7 eV implied that

the APTMS units were partially oxidized in the process of synthesis. This result was consistent with the FTIR spectrum (Fig. 1c). In the Si 2p spectrums of the SiC NPs and SiC NPs /·OH, the binding energies at 102 and 102.7 eV were identified as Si-O-C and Si-O-Si bonds, respectively.

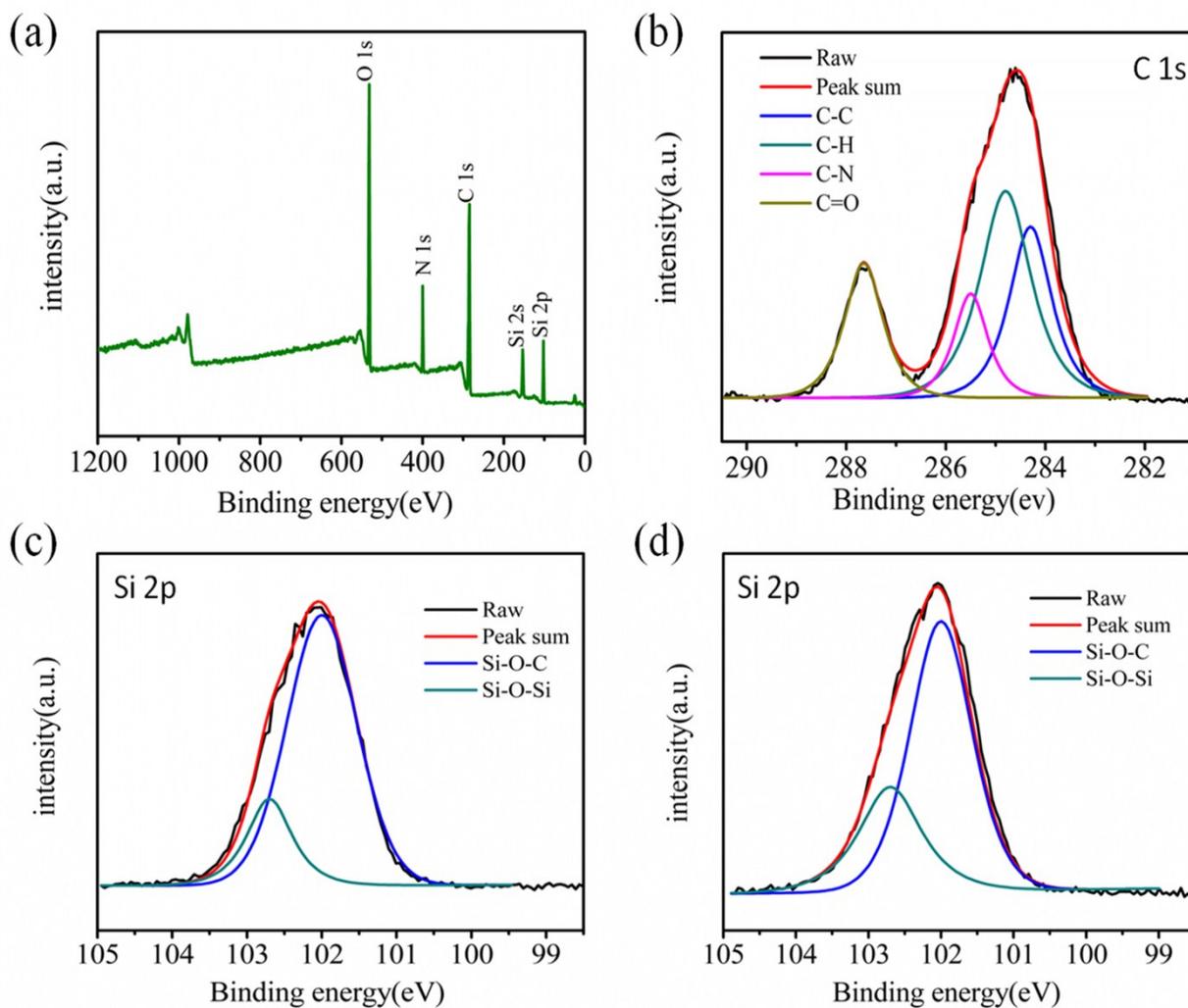


Figure S2. (a) XPS survey spectra of the SiC NPs. (b)The XPS spectra of C 1s and (c) Si 2p of the SiC NPs.

(d)Si 2p XPS spectrum of SiC NPs-·OH.

4. CL kinetic profile of Fenton reaction and reaction mechanisms

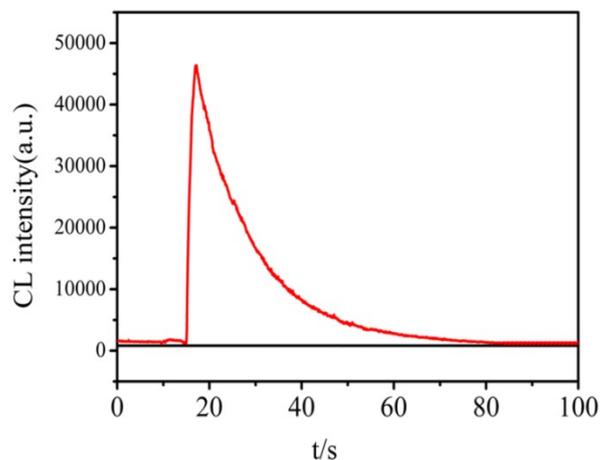


Figure S3. CL kinetic profile obtained when H_2O_2 was added into SiC NPs- Fe^{2+} solution. Conditions: H_2O_2 50 mM, SiC NPs 35.9 mg/mL, Fe^{2+} 5.0×10^{-3} M.

Table S1. Significant Additional Kinetic Model Reactions

reaction	Rate constant	ref
$\text{Ti}^{3+} + \text{H}_2\text{O}_2 \longrightarrow \cdot\text{OH} + \text{Ti}^{4+} + \text{HO}\cdot$	$\square 200 \text{ M}^{-1}\cdot\text{S}^{-1}$	2
$\cdot\text{OH} + \text{Ti}^{3+} \longrightarrow \text{Ti}^{4+} + \text{HO}\cdot$	$3 \times 10^8 \text{ M}^{-1}\cdot\text{S}^{-1}$	2
$\cdot\text{OH} + \text{H}_2\text{O}_2 \longrightarrow \text{HO}_2\cdot + \text{H}_2\text{O}$	$2.7 \times 10^7 \text{ M}^{-1}\cdot\text{S}^{-1}$	3
$\cdot\text{OH} + \cdot\text{OH} \longrightarrow \text{H}_2\text{O}_2$	$5.5 \times 10^9 \text{ M}^{-1}\cdot\text{S}^{-1}$	3
$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \longrightarrow \cdot\text{OH} + \text{Fe}^{3+} + \text{HO}\cdot$	$55 \text{ M}^{-1}\cdot\text{S}^{-1}$	4
$\text{Fe}^{3+} + \text{HO}_2\cdot \longrightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+$	$1.3 \times 10^6 \text{ M}^{-1}\cdot\text{S}^{-1}$	4

5. Optimizing conditions.

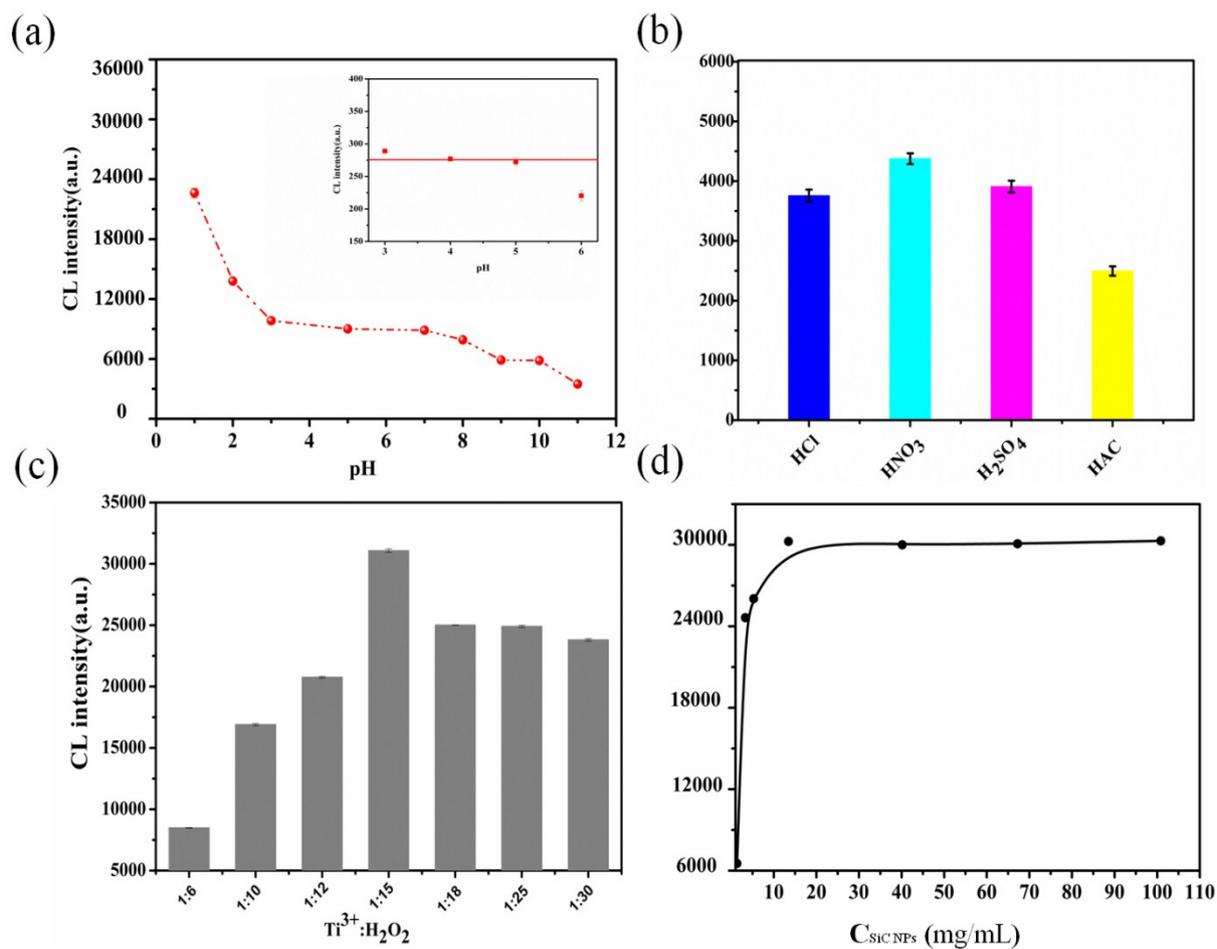


Figure S4. (a) Effect of pH on the CL intensity of SiC NPs. The inset showed effect of titanium solution with different pH on the CL intensity. Conditions: Ti(III) solution, 3.7×10^{-4} M. (b) Effect of different acids media on the CL intensity of SiC NPs- \cdot OH system under the same pH. (c) Effect of concentration ratio of titanium ion to hydrogen peroxide on CL intensity of SiC NPs- \cdot OH system. (d) Influence of concentrations of SiC NPs on the CL intensity.

6. Cyclic voltammograms

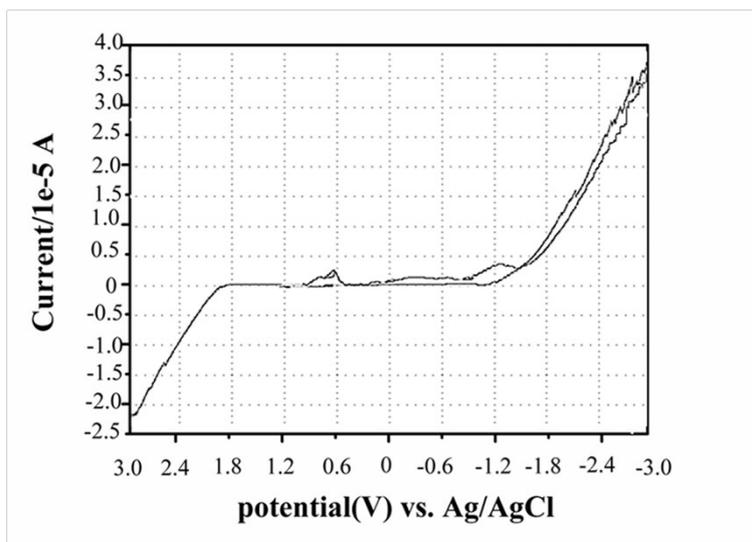


Figure S5. Cyclic voltammograms recorded for the control solution without SiC NPs at pH 2.0.

7. General selectivity study.

In the flow injection analysis (FIA) system for selectivity study, the SiC NPs solution was injected through a six-valve injector and mixed with different ROS within the mixing coil. And the respective ROS were generated as follows: superoxide solution ($O_2^{\cdot-}$) was prepared by adding KO_2 (10 mg) to dry dimethyl sulfoxide (10 mL) and stirred vigorously for 10 min;⁵ singlet oxygen (1O_2) was chemically generated by the reaction between H_2O_2 (100 mM) and $NaClO$ (100 mM);⁵ alkoxy radical ($RO\cdot$) was generated as a product of $t\text{-BuOOH}$ (100 mM) in the presence of $Fe(II)$ (100 mM);⁶ and hydroxyl radical ($\cdot OH$) was generated from the reaction of $Ti(III)$ (6.3×10^{-3} M) with H_2O_2 (50 mM).

8. Quantifying $\cdot OH$ in HPLC.

As described above, $\cdot OH$ was generated from the reaction of $Ti(III)$ with H_2O_2 . The determination of $\cdot OH$ relied on the concentrations of corresponding adduct formaldehyde-2,4-dinitrophenylhydrazine (HCHO-DNPH) produced from the reaction of 2,4-dinitrophenylhydrazine (DNPH) with formaldehyde. It should be noted that a standard addition

method was applied here, owing to the low sensitivity of HPLC and high deviation of the HPLC peak area resulting from the low amount of formaldehyde generated. The standard curve of HCHO-DNPH concentration vs relative HPLC peak area was shown in Figure S 3b. For the determination of $\cdot\text{OH}$ generated from Ti(III) and H_2O_2 , 250 mM of DMSO was firstly mixed with different concentrations of Ti(III) and H_2O_2 to produce formaldehyde quantitatively: Ti(III) which was diluted half with deionized water ($3.15 \times 10^{-3}\text{M}$) and H_2O_2 solution (50 mM) were both diluted by taking 0.3, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0, and 6.0 mL into 100 mL flask, respectively. And then $3 \times 10^{-7}\text{M}$ formaldehyde was spiked and continually reacted at $25\text{ }^\circ\text{C}$ for 10 min. Consequently, 5 mL of $\text{H}_3\text{PO}_4\text{-NaH}_2\text{PO}_4$ at pH 4.0 and 0.2 mL of DNPH of 6 mmol L^{-1} were added into the solution and diluted to 10 mL with deionized water. Finally, the mixture was maintained for 30 min and analyzed by HPLC-UV.

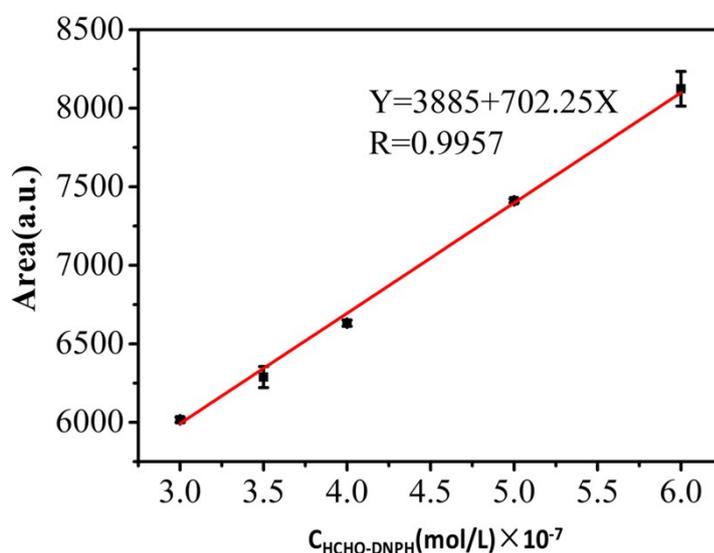


Figure S6. Standard curve for the determination of HCHO-DNPH concentration.

9. CL intensities with different concentrations of $\cdot\text{OH}$

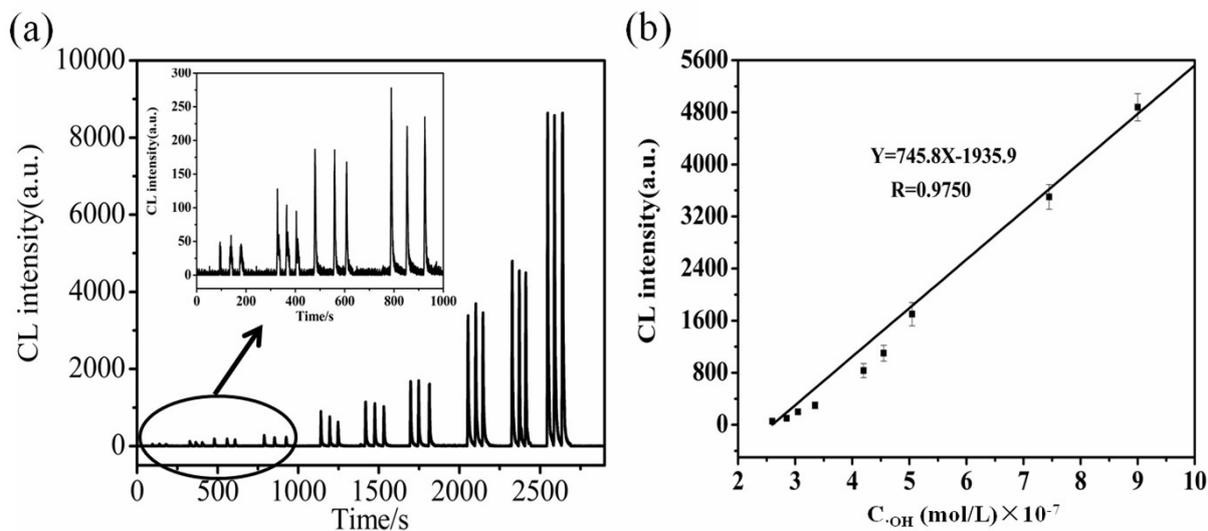


Figure S7. (a) CL signals in flow injection system and (b) The CL intensities as a function of concentration of $\cdot\text{OH}$.

10. Preparation of $\text{PM}_{2.5}$ solution

$\text{PM}_{2.5}$ samples were acquired from the Chengdu department of Environment Monitoring Station by using a Met One Instruments (BAM 1020) equipped with a $\text{PM}_{2.5}$ filter type. After collection, the filter with $\text{PM}_{2.5}$ samples and the blank filter were both transferred into 0.01 M PBS solution with $\text{pH}=7$. Then shaken the solution with filter for 15 min on a Daigger Vortex Genie 2, sonicated for 30 min at 200 W, and then shaken again for 15 min. After that, removed the filter from the suspension and dried. Then $\text{PM}_{2.5}$ suspensions were finally acquired after vacuum distillation at $25\text{ }^\circ\text{C}$. The amount of $\text{PM}_{2.5}$ removed from the filter was calculated by the differences in weight of the filter before and after the above steps. Finally, 2.1 mg/ml of prepared $\text{PM}_{2.5}$ suspension was obtained.

11. Metals detection of $\text{PM}_{2.5}$ suspension

Metal concentrations in $\text{PM}_{2.5}$ samples were detected by the ICP-OES on SPECTRO ARCOS. The 0.5 mL of $\text{PM}_{2.5}$ suspension was digested into 25 mL of clarified solution. Three sample

blanks were processed with samples. And the results of metal concentrations detected in PM_{2.5} samples were shown in Table S2.

Table S2. Transition Metals Found in Representative PM_{2.5} Samples (ppm)

Al	As	Ba	Ca	Cd	Co	Cr
486.7±0.1	ND	189.76±0.03	947.5±0.1	ND	ND	ND
Cu	Fe	Mn	Ni	Pb	Si	Zn
0.23±0.02	153.64±0.02	ND	ND	ND	2846.3±0.5	183.23±0.02

12. Effects of some coexistent substances on the detection of ·OH from the PM_{2.5} suspension.

The flow injection analysis system for determination of effects of some substance (e.g., some ions and organic compounds) in the detection of hydroxyl radical concentration from the PM_{2.5} suspension was consisted of two lines. Typically, the SiC NPs (35.9 mg/mL) solution of pH 2.0 was injected through a six-valve injector with water as carrier and reacted with PM_{2.5} solutions which had been mixed with different substances in the mixing coil in front of the PMT. The flow rates were 20 rpm/min for all solutions. The CL signals were detected and recorded with the BPCL luminescence analyzer.

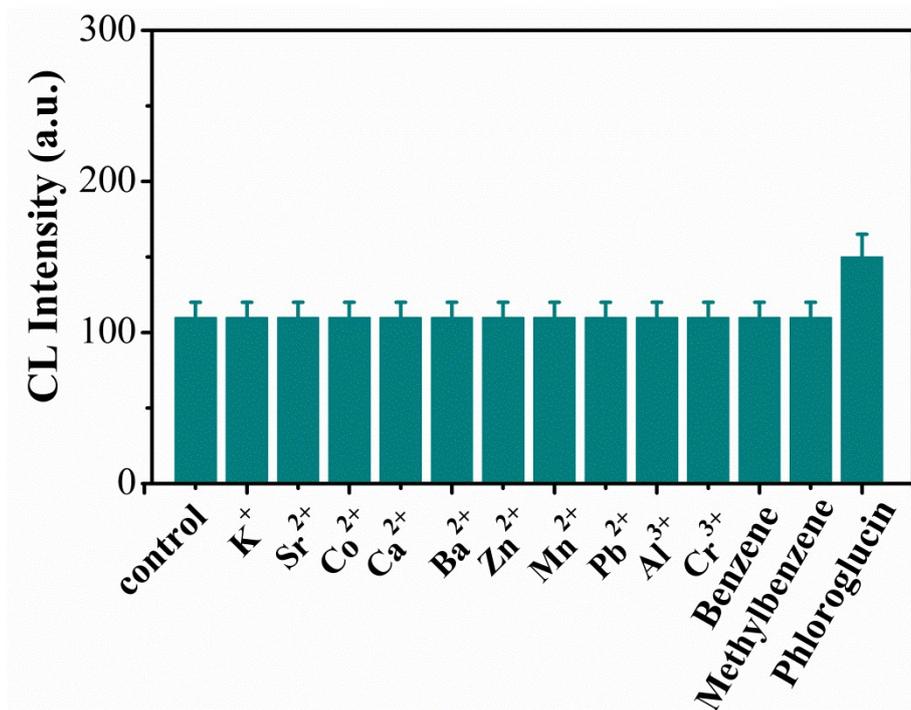


Figure S8. Effects of coexistence substances . Condition: SiC NPs, 35.9 mg/mL; PM_{2.5} suspension, 2.1 mg/mL. The concentrations of other ions were all 1mM; concentrations of some organic compounds were 100μM.

References

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