

Simultaneous Generation of Hydroxyl and Hydrogen Radicals from H^+/OH^- Pairs Caused by Water-Solid Contact Electrification

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Experimental Section

Chemicals. SiO₂ microspheres used in this study were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). 5,5-dimethyl-1-pyrroline N-oxide (DMPO), resazurin, and 2',7'-dichlorodihydrofluorescein diacetate (DCFH-DA) were obtained from Sigma-Aldrich company (Shanghai, China). Deuterium oxide (D₂O) was purchased from Meryer Biochemical Technology Co., Ltd. (Shanghai, China) Na¹⁵NO₃ was obtained from Guangzhou test research Technology Co., Ltd. (Guangzhou, China) All other chemical reagents used in this study were purchased from Sinopharm Chemical Reagent Co, Ltd. (Shanghai China).

Construction of Water–solid contact model. The devices consisted of a sealing cylindrical tube with 4 cm (diameter) × 10 cm (length) and two gas bottles. The two gas bottles are connected by Teflon tubes in front and behind the sealing cylindrical tube, respectively. Then, adding 100 mL of water to two gas bottles, and 15g of SiO₂ nanoparticles to the sealing cylindrical tube. Different flow rates (50, 100, 200 mL/min) of argon gas pass through the first gas bottles, the sealing cylindrical tube, and the second gas bottles successively to construct the water–solid contact model for this study.

Fluorescence imaging. DCFH-DA and resazurin were used in the experiments as fluorescent probes for oxidizability and reducibility of SiO₂ during water–solid contact, respectively. Dilute DCFH-DA (v/v = 1/1000) in reconstituted loading buffer solution was prepared as the working solution. The working concentration of resazurin is 100 nM. After a period of contact between water and SiO₂ nanospheres, DCFH-DA and resazurin aqueous solution was added into the SiO₂ nanospheres, and then they were placed under an inverted fluorescence microscope for the observation. 488 and 570 nm laser were applied as an excitation light source, respectively. The exposure time was fixed.

Measurements of radicals. Hydroxyl radicals (•OH) and hydrogen radicals (•H) were trapped by 50 mM DMPO and detected by a Bruker A300-10/12 electron spin resonance (ESR) spectrometer (Germany) at ambient temperature.

Nitrate reduction and nitrite oxidation. 1 M nitrate or nitrite was dissolved in the first gas bottles of the water–solid contact model system. After a period of contact between the nitrate or nitrite solution and SiO₂ nanospheres, the nitrate and nitrite concentration in the second gas bottles was determined via ion chromatography (Dionex ICS-6000, Thermo Fisher Scientific, USA). The mass spectrometry data were collected using a linear ion trap mass spectrometer ((Thermo-Fisher, Waltham, MA). The nano-ESI mode was employed for sample introduction, with samples collected in positive ion mode and an applied voltage controlled at 1.5 kV.

Potential change and current density experiments. O₂ plasma was used to increase the surface hydroxyl groups density and thermal annealing was used to reduce the surface hydroxyl groups density of the glass substrate. The commercial SiO₂ substrate was used as the control. The Boehm titration method was used to determine the hydroxyl density of the material surface. The SiO₂ substrate was cut into a 0.5 × 0.5 cm square and a 2 g sample was dissolved into 25 mL anhydrous ethanol, followed by adding 75 mL of 20 wt% NaCl solution. The solution was stirred slowly and a pH meter (Mettler, SevenExcellence) was used to detect the overall pH change of the solution in real time. The pH of the solution was adjusted to 4 with 0.1 M HCl. After the pH was stabilized, 0.1 M NaOH solution was slowly added dropwise to bring the pH of the solution back to 9 and the amount of NaOH was recorded. The density of hydroxyl groups per square nanometer on the surface of the material was calculated according to the following equation:

$$N = \frac{CVN_A \times 10^{-3}}{S}$$

where C is the concentration of NaOH (mol/L), V (mL) is the volume of NaOH consumed as the pH rises from 4 to 9, N_A is Avogadro's constant, and S is the surface area of the samples.

The potential changes of the SiO₂ substrate with different surface hydroxyl groups density were obtained by (KPFM) experiments. Experiments were performed on a atomic force microscope (AFM) instrument (Multimode 8 Bruker, USA). AFM probe (NSC18, Mikro-Mash, USA; Au coated; tip radius: 25 nm; spring constant: 2.8 N m⁻¹) was used as the conductive tip. At the same time, we also used conductive glass as the substrate and cooperated with the Keithley 6514 electrometer to detect the drop of DI water on the conductive glass with different surface hydroxyl groups to record the change of the current.

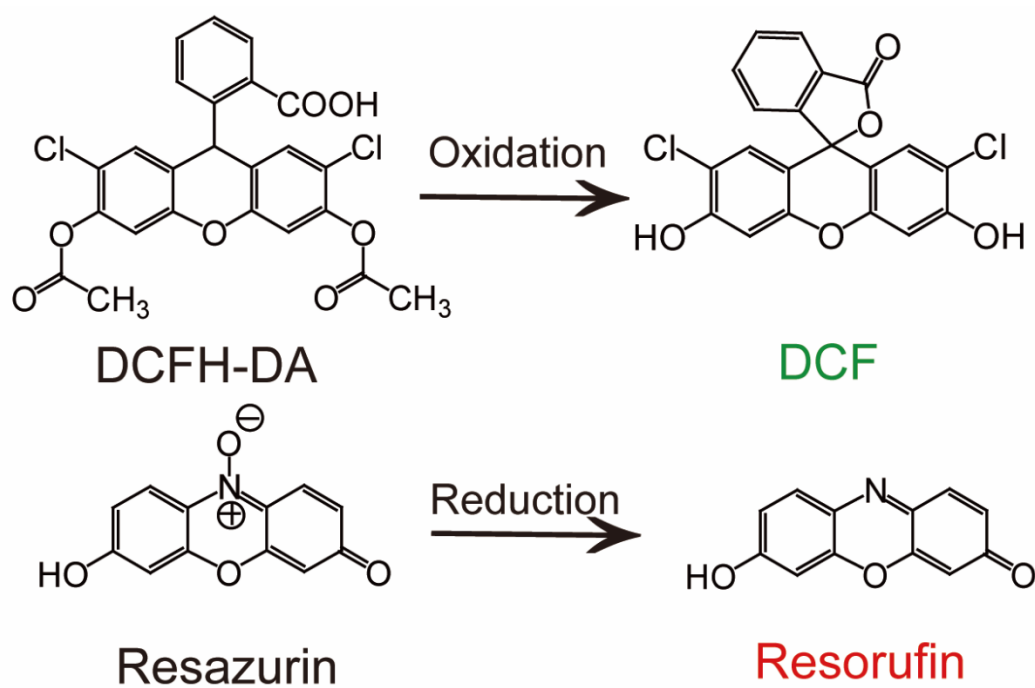


Figure S1. (A) Reaction scheme between DCFH-DA and ROS; (B) Reaction scheme between Resazurin and reductive species.

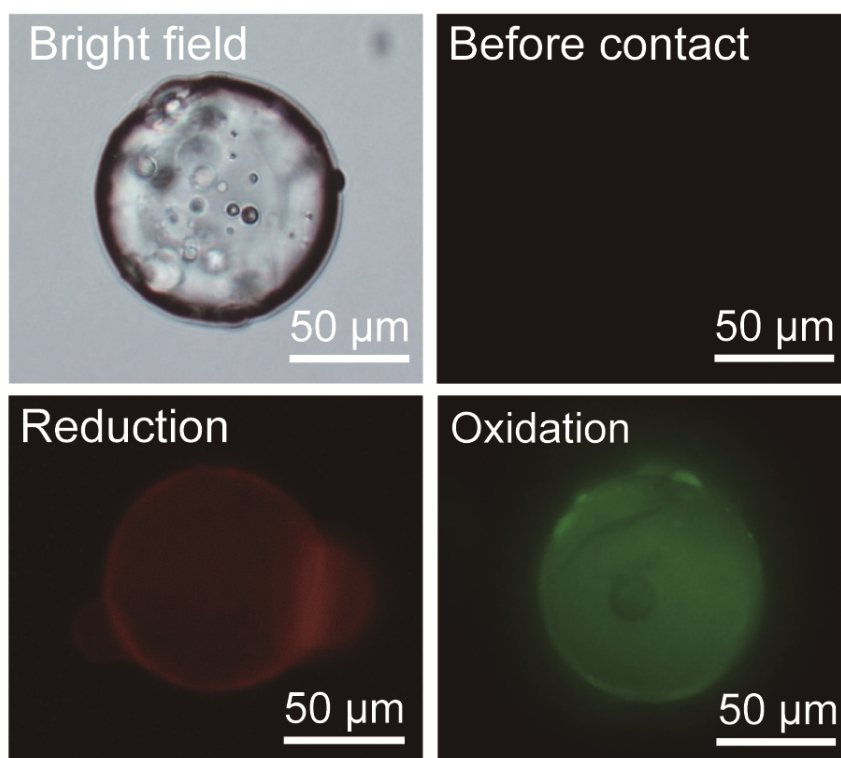


Figure S2. (A) Typical brightfield microscopy image of a SiO₂ microsphere; (B) The fluorescence image of a SiO₂ microsphere after contact with water-carrying argon gas (obtained by bubbling the gas into Resazurin aqueous solution with concentration of 100 nM) under 570 nm laser excitation; (C) The corresponding fluorescence image of the SiO₂ microsphere before the contact in B. (D) The fluorescence image of a SiO₂ microsphere after contact with water-carrying argon gas (obtained by bubbling the gas into diluted DCFH-DA solution ($v/v = 1/10000$)) under 488 nm laser excitation; (E) The corresponding fluorescence image of the SiO₂ microsphere before the contact in D.

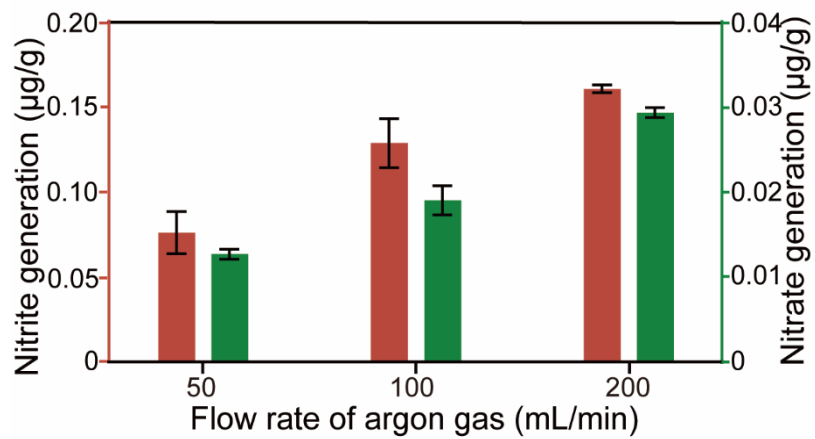


Figure S3. Nitrite and nitrate generation during water-solid contact depended on Flow rate of argon gas.

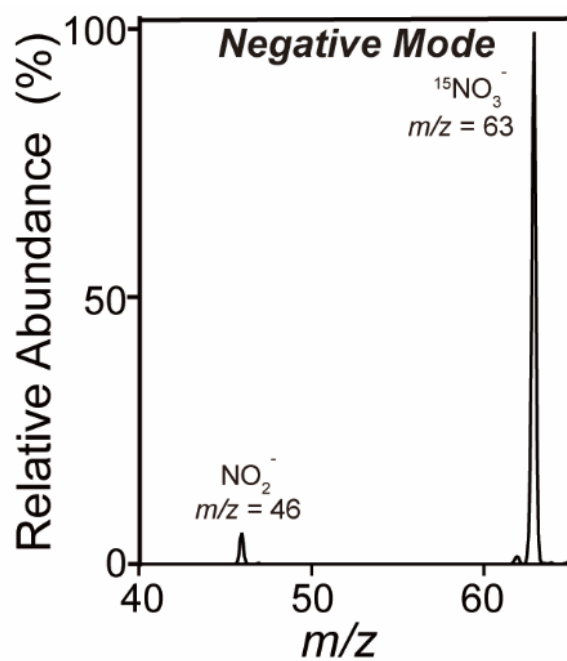


Figure S4. MS spectrum in the negative mode of NO₂⁻ and ¹⁵NO₃⁻ before the contact between SiO₂ and moist argon gas containing both nitrate and nitrite anions.

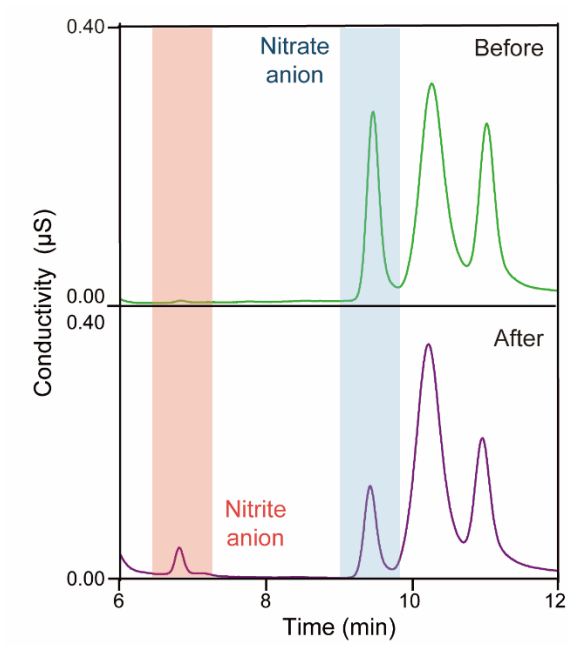


Figure S5. Ion chromatography spectra reveal the reduction of NaNO_3 before and after the contact.

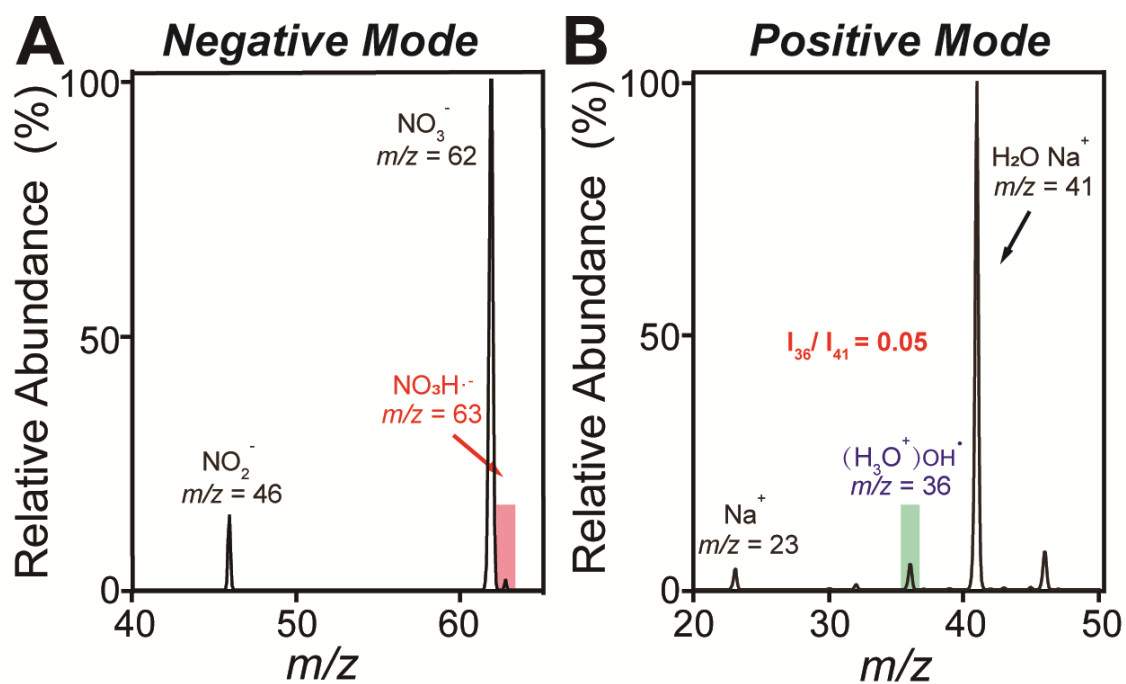


Figure S6. MS spectra reveal the reduction of NaNO_3 after the contact (A) Negative mode and (B) Positive mode.

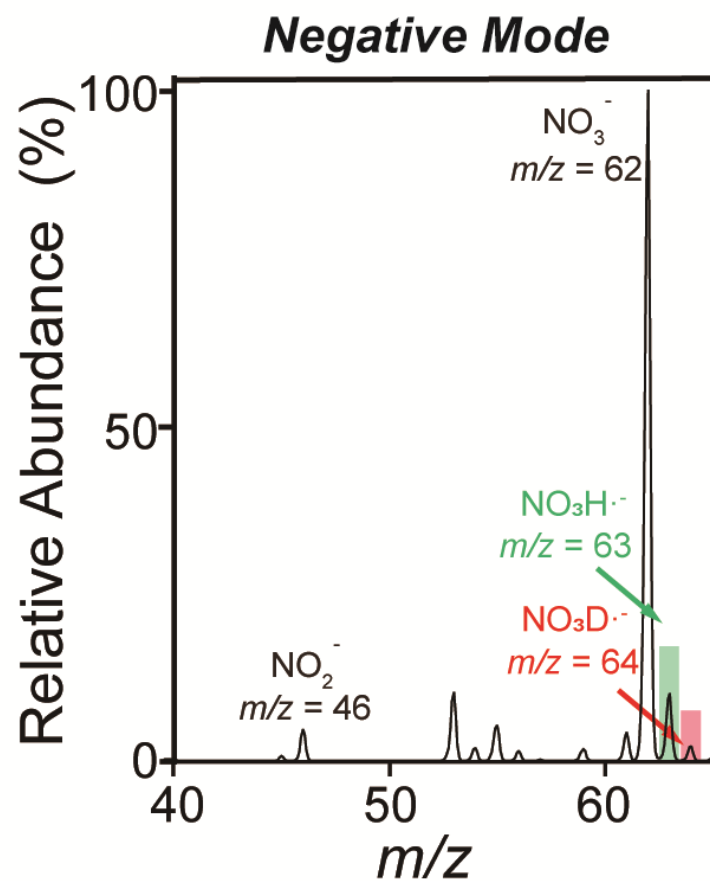


Figure S7. The MS spectrum reveals the reduction of NaNO_3 after the contact between D_2O -carrying argon gas and SiO_2 .

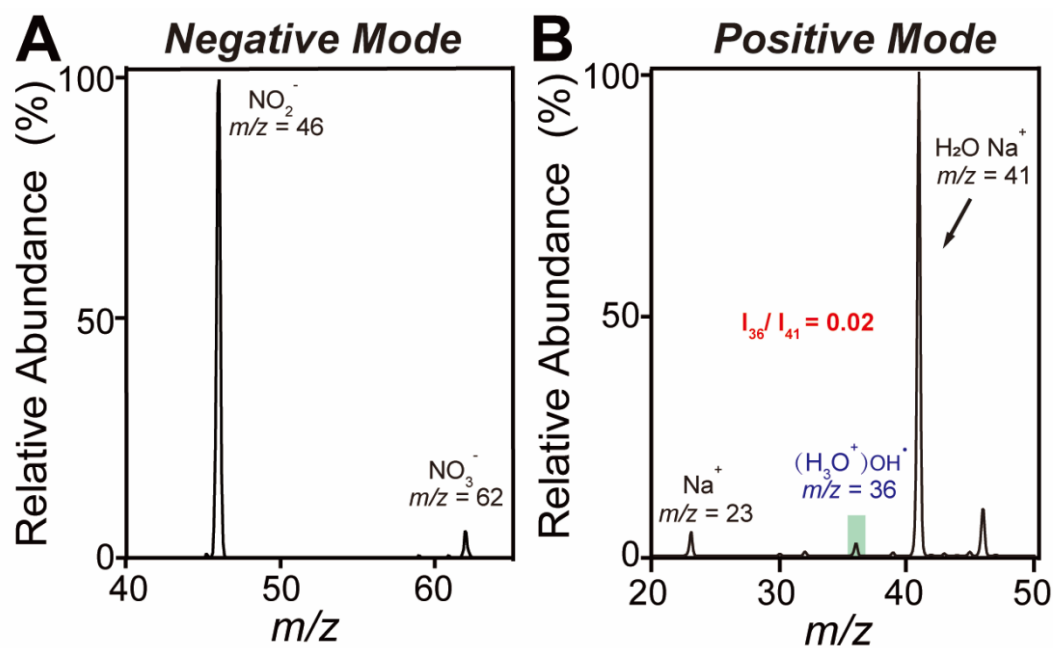


Figure S8. MS spectra reveal the oxidation of NaNO_2 after the contact (A) Negative mode and (B) Positive mode.

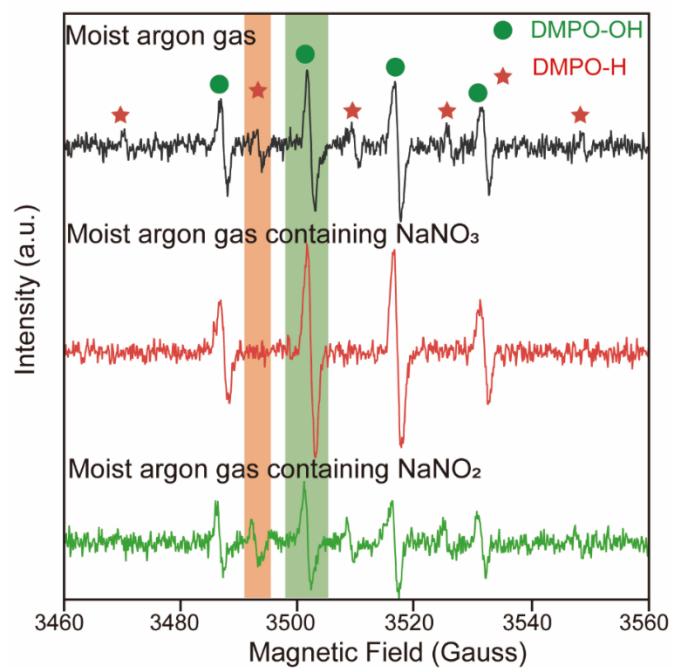


Figure S9. ESR spectra of hydroxyl and hydrogen radicals are generated when SiO₂ contacts with moist argon gas, moist argon gas containing NaNO₃, and moist argon gas containing NaNO₂, respectively.

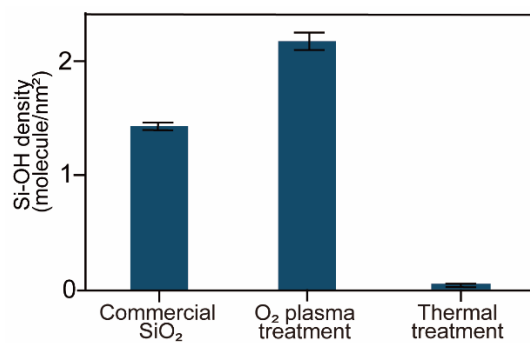


Figure S10. The Si-OH density of the commercial SiO₂ sample, and SiO₂ samples treated by O₂ plasma and annealing at 500 °C, respectively.