Supporting Information

N-Nitrosamines Formation from Secondary Amines by Nitrogen Fixation on the Surface of Activated Carbon

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Text (2)

TABLES (2)

FIGURES (2)

Text S1. Chemicals

Standard-grade NDMA, *N*-nitrosodibutyl amine (NDBA), dibutyl amine (DBA), sodium nitrite, hydrochloric acid, sulfuric acid, nitric acid, 30% hydrogen peroxide, 50% hydroxylamine solution (in water), 4-methoxybenzenesulfonyl chloride, acetone, dichloromethane, sodium phosphate monobasic and dibasic, sodium borate, sodium bicarbonate, sodium carbonate, sodium hydroxide, and *tert*-butanol (TBA) were obtained at >98% purity from Sigma-Aldrich (St. Louis, MO) or Fisher Scientific (Pittsburgh, PA). DMA was obtained in the form of DMA hydrochloride from both Sigma-Aldrich and Fisher Scientific, and in the form of 40% solution (in water) from Sigma-Aldrich. All reagents were used without further purification. High purity deionized (DI) nanopure water (18.2 MΩ-cm at 25 °C) was generated from a Millipore (Billerica, MA) Milli-Q® water purification system and used to prepare reaction solutions. The isotopes NDMA-d_6, DMA-d_6 hydrochloride, ^{15}N-DMA, ^{15}N-nitrite sodium, and ^{15}N-ammonium chloride were obtained from Cambridge Isotope Laboratories (Andover, MA).

Text S2. Carbon Characterization

*(1) BET Measurements***.** The specific surface area and pore size distribution of the AC particles were determined via the BET and BJH methods, respectively. The isotherms of N_2 gas adsorption used in these methods were collected at 77 K, using relative pressures of 0.05-1 P/P_0. A TriStar II 3020 surface area and porosity measurement system (Micromeritics Inc., GA) was used for these measurements. Both the BET and BJH analyses were performed using Micromeritics software. The relative pressure range of P/P_0 from 0.05 to 0.2 was used for multipoint BET calculations. Ultra high purity gases (99.99%, Airgas) were used for all experiments. The samples were prepared by drying under a vacuum at 80°C for at least 12 h,

followed by degassing under a N_2 gas flow at 300°C for at least 2 h prior to weighting and gas sorption measurements.

*(2) SEM and EDS Measurements***.** Scanning electron microscopic (SEM) studies of the AC particles were carried out using a LEO 1530 SEM microscope (LEO, Japan, now Nano Technology Systems Division of Carl Zeiss SMT, USA). The in-lens secondary electron detector was used for the studies, most of which were performed using an accelerating voltage of 10 kV and a working distance of 8-9 mm. Energy dispersive spectroscopy (EDS) was performed by EDS systems attached to the SEM.

*(3) XPS Measurements***.** X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo K-Alpha XPS system (Thermo Scientific, USA) equipped with an Al K-α radiation as a source, with an energy resolution of 1 eV for the survey scans and 0.1 eV for high-resolution scans of individual characteristic peaks. The X-ray gun produced a 400 μm spot size, and an electron flood gun was used to minimize charging. The system vacuum level was below 10^{-8} torr during the data collection. An emission angle of 90^{o} was used.

Table S1. Potential Enhanced *N*-Nitrosation by AC Particles: Dependence on Nitrite Concentration

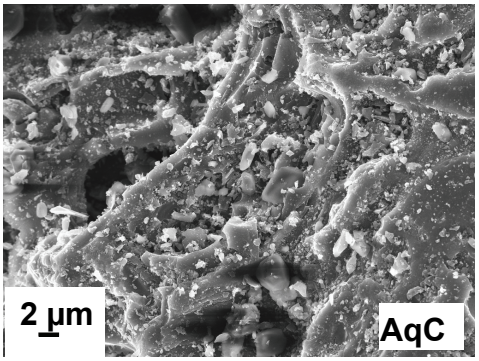
Samples	**NDMA (nano moles)**	**^{15}N-NDMA (nano moles)**
DMA (no nitrite)	0.53 ± 0.01	0.00 ± 0.00
DMA+ 50 nM ^{15}N-Nitrite	0.58 ± 0.01	0.00 ± 0.00
DMA + 100 nM ^{15}N-Nitrite	0.57 ± 0.00	0.00 ± 0.00
DMA+ 500 nM ^{15}N-Nitrite	0.55 ± 0.04	0.03 ± 0.00
DMA + 1,000 nM ^{15}N-Nitrite	0.43 ± 0.03	0.09 ± 0.00
DMA+ 100,000 nM ^{15}N-Nitrite	0.45 ± 0.00	9.78 ± 0.14

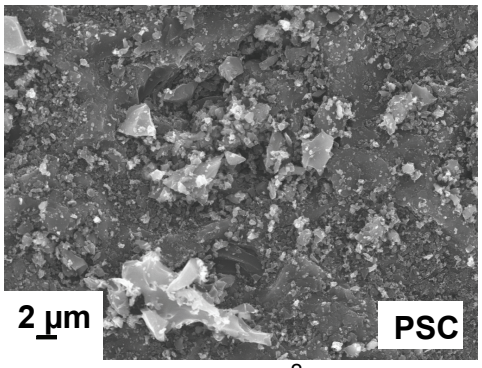
Experiments were conducted at pH 7.5, using 222 µM DMA, 200 mg PSC carbon, 3 h particle drying time; Instrument detection limit for NDMA = 2 pico moles; Mean ± standard deviation (n = 3)

Table S2. Trace Metal Analysis of AC Particles

Element	**AqC** (mg/g of AC)	**PSC** (mg/g of AC)	**F400** (mg/g of AC)
Iron	7.900	0.052	**8.480**
Aluminium	**3.403**	1.907	0.301
Copper	0.015	0.003	**0.018**
Nickel	0.004	0.001	**0.009**
Sodium	**0.487**	0.349	0.277
Potassium	**5.393**	4.536	0.027
Manganese	0.004	0.004	0.004
Phosphorus	0.150	0.114	**0.759**
Sulfur	0.055	0.019	**0.648**
NDMA Yield [7]	*0.29%*	*0.10%*	*0.05%*

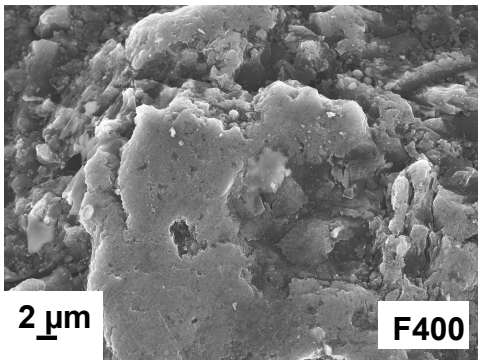
Note: Bold values represent the highest concentration for respective metals among AC particles

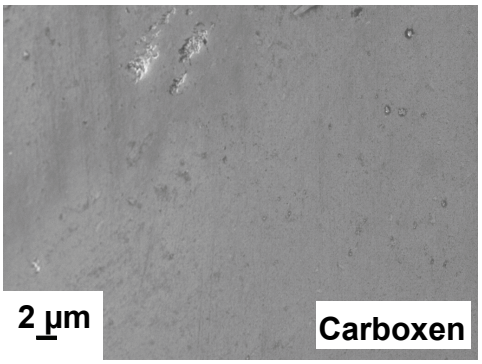




S_{BET} = 1202 m^2 / g 1114 m^2/g

NDMA formed = 1.65 ± 0.10 nmoles 0.56 ± 0.07 nmoles

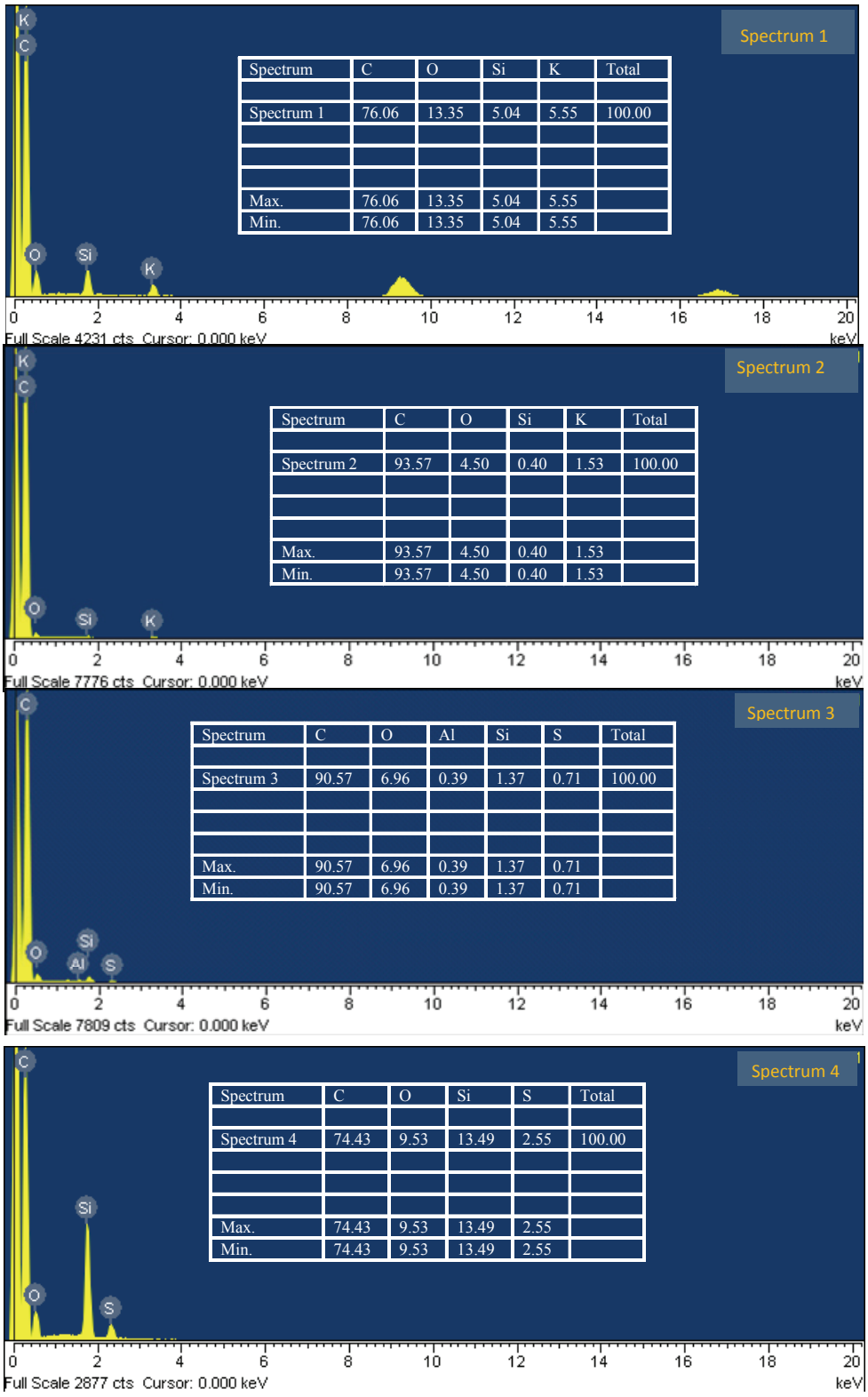




S_{BET} = 1044 m^2/g 858 m^2/g

NDMA formed = 0.54 ± 0.06 nmoles 0.07 ± 0.02 nmoles

Figure S1. SEM images of four carbon surfaces at the same resolution



Spectrum	C	O	Si	K	Total
Spectrum 1	76.06	13.35	5.04	5.55	100.00
Max.	76.06	13.35	5.04	5.55	
Min.	76.06	13.35	5.04	5.55	

Spectrum	C	O	Si	K	Total
Spectrum 2	93.57	4.50	0.40	1.53	100.00
Max.	93.57	4.50	0.40	1.53	
Min.	93.57	4.50	0.40	1.53	

Spectrum	C	O	Al	Si	S	Total
Spectrum 3	90.57	6.96	0.39	1.37	0.71	100.00
Max.	90.57	6.96	0.39	1.37	0.71	
Min.	90.57	6.96	0.39	1.37	0.71	

Spectrum	C	O	Si	S	Total
Spectrum 4	74.43	9.53	13.49	2.55	100.00
Max.	74.43	9.53	13.49	2.55	
Min.	74.43	9.53	13.49	2.55	

Figure S2. Spectrum 1: EDS for AqC, Spectrum 2: EDS for PSC, Spectrum 3: EDS for F400, and Spectrum 4: EDS for Carboxen 572 (All Results in Weight Percent)