Supporting Information

Amino-modified zirconia aerogels for the efficient filtration of NO_2: Effects of water on the removal mechanisms

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Number of Tables: 6; Number of Figures: 7.

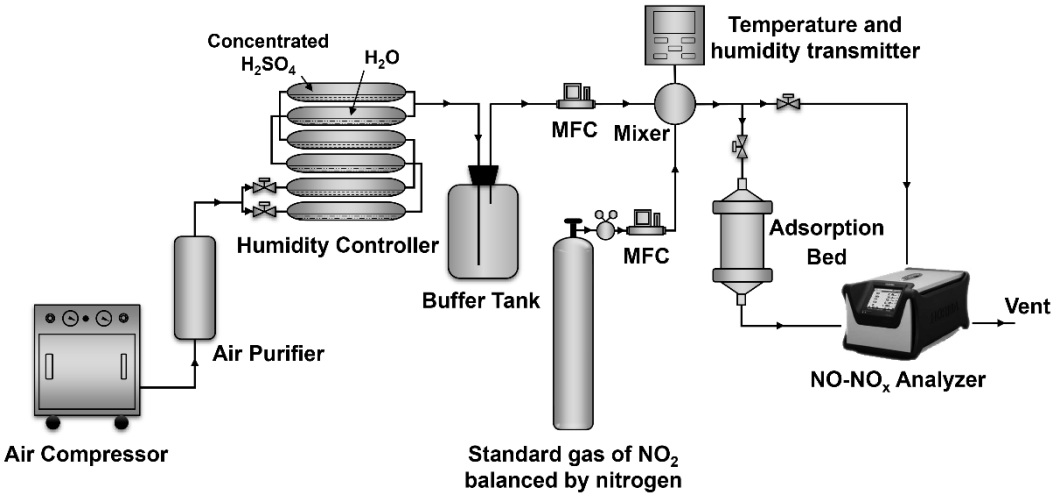

Figure S1. Tube breakthrough system for granule samples.

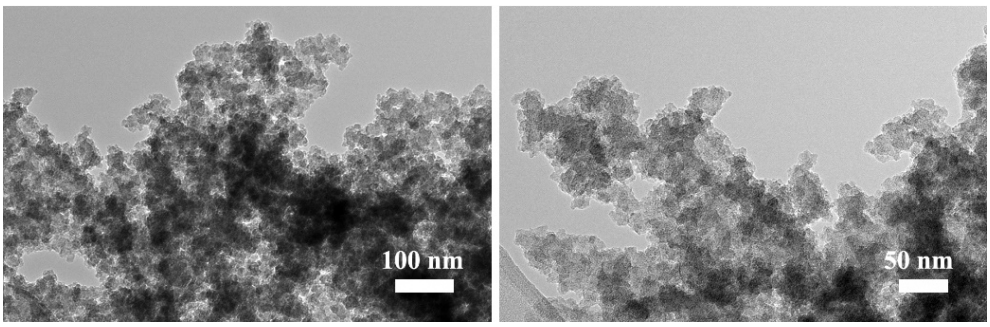

Figure S2. TEM images for AMZA-4.

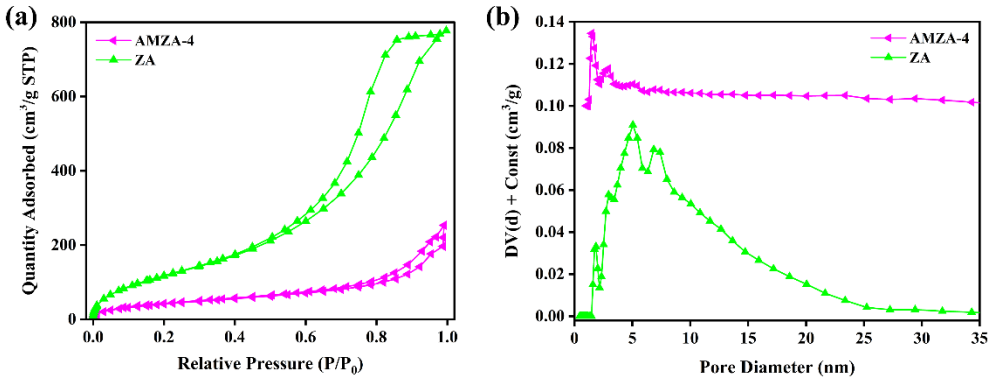

Figure S3. (a) Ar adsorption-desorption isotherms at 87 K and (b) NLDFT pore size distribution of the ZA and AMZA-4 aerogel samples.

Table S1. Texture properties of the ZA and AMZA-4 aerogel samples derived from Ar porosimetry at 87 K

Sample	$V_{micro}/(cm^3 \cdot g^{-1})$	$V_{total}/(cm^3 \cdot g^{-1})$	$\frac{V_{micro}}{V_{total}}/\%$
ZA	0.02	0.97	2
AMZA-4	0.02	0.58	3

Table S2. Comparison of the bulk density for ZA and AZMA-4 aerogels

Sample	Density ($cm^3 \cdot g^{-1}$)
ZA	0.39
AMZA-4	0.45

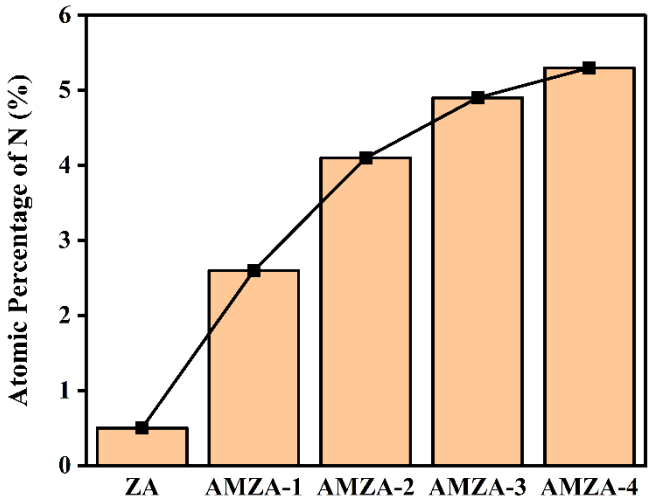

Figure S4. Atomic percentage of the surface N element derived from XPS survey scans for samples obtained with different APTES amount.

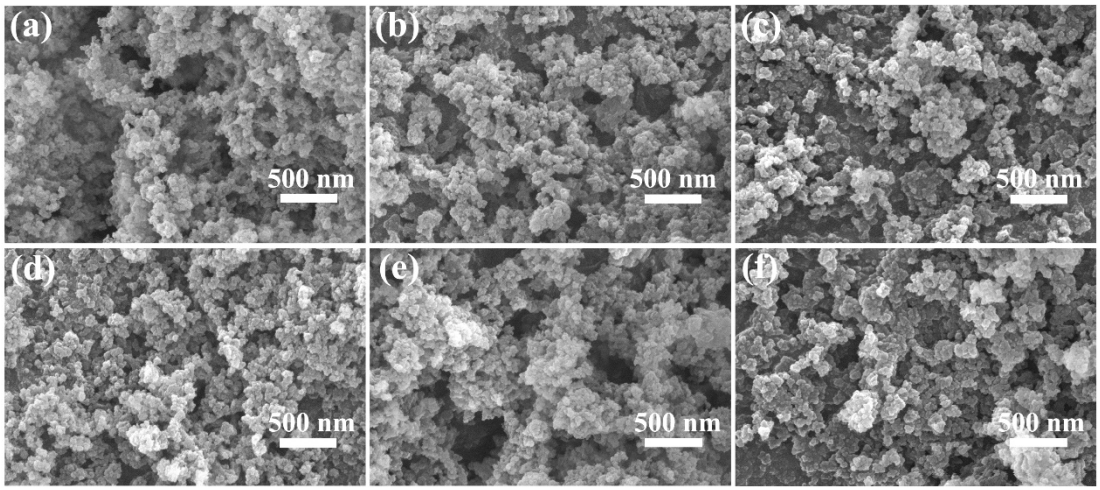

Figure S5. SEM images of (a) fresh AMZA-4 sample and those exposed to NO_2 under different humidity conditions: (b) RH 0-15%, (c) RH 0-50%, (d) RH 50-50%, (e) RH 80-80%, and (f) RH 0-80%.

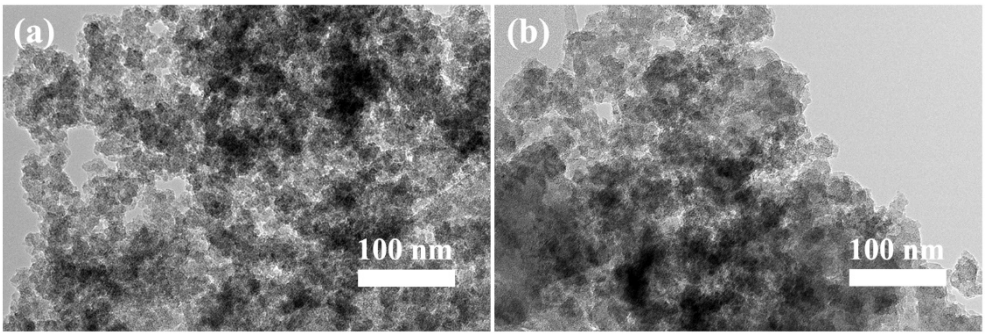

Figure S6. TEM images of the AMZA-4 sample (a) prior to and (b) following NO_2 adsorption at RH 0-80%.

Table S3. Comparison of texture properties of the AMZA-4 samples derived from N_2 porosimetry at 77 K before and after NO_2 adsorption

Sample/ RH	Breakthrough time/min	S_{BET}/($m^2 \cdot g^{-1}$)	V_{meso}/($cm^3 \cdot g^{-1}$)	V_{total}/($cm^3 \cdot g^{-1}$)	$\frac{V_{meso}}{V_{total}}$/%	D_{avg}/nm
AMZA-4	–	197.0	0.65	0.67	97	27.8
0-15%	130	175.8	0.60	0.62	97	31.3

0-50%	197	151.3	0.54	0.56	96	30.9
50-50%	205	156.5	0.50	0.51	98	32.5
80-80%	220	127.4	0.45	0.46	98	34.3
0-80%	362	103.8	0.39	0.40	98	39.2

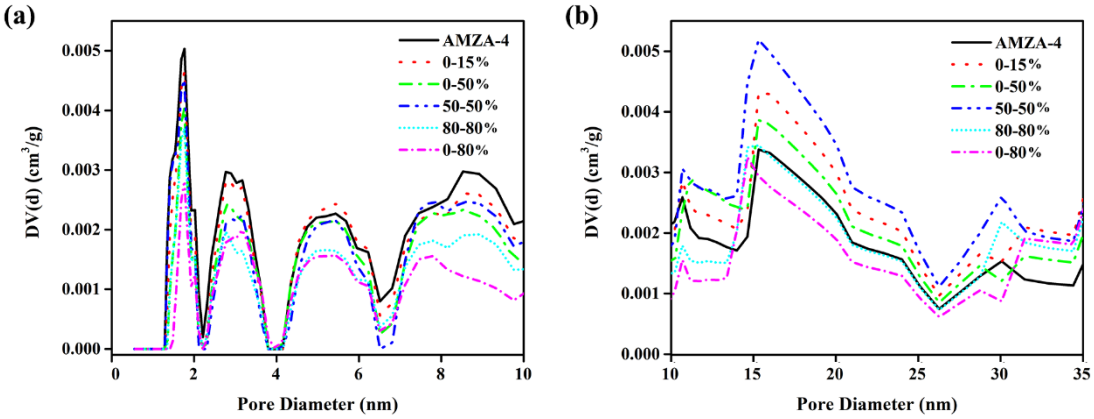

Figure S7. Alterations in the DFT pore size distributions of AMZA-4 samples after NO_2 adsorption under different humidity conditions: (a) the pore < 10 nm, (b) the pore in the range of 10~35 nm. Data were derived from N_2 porosimetry at 77 K.

Table S4. The surface elemental composition and atomic percentage of AMZA-4 before and after NO_2 adsorption

Sample/RH	Atomic percentage/%					ΔO/ΔN
	C	N	O	Zr	Si	
AMZA-4	29.7	5.3	44.5	1.3	19.2	–
0-15%	29.2	5.8	45.1	1.2	18.7	1.2
0-80%	27.0	6.7	46.4	1.3	18.6	1.4
80-80%	27.1	6.2	46.9	1.4	18.4	2.7

Table S5. Ratios of different NO_2 adsorption products and percentages of protonated amino groups under different humidity conditions

Sample/RH	Nitrates/ (nitroamines + nitrosamines)	Percentages of protonated amino groups $-NH_3^+/(-NH_3^+ + -NH_2)$
AMZA-4	–	0.26

0-15%	0.40	0.31
0-80%	1.97	0.36
80-80%	1.07	0.43

Table S6. Existing patterns and relative atomic percentage of the N element on the AMZA-4 surface before and after NO_2 exposure

Sample/RH	Species	FWHM/eV	Peak position/eV	Peak area	Fraction/%
AMZA-4	$-NH_2$	2.0	399.4	21696.6	73.7
	$-NH_3^+$	2.0	401.2	7738.9	26.3
0-15%	$-NH_2$	1.9	399.6	19472.1	52.9
	$-NH_3^+$	1.8	401.1	8817.4	23.9
	Nitrosamine	1.4	402.2	3238.4	8.8
	Nitramine	1.3	406.5	2884.6	7.8
	Nitrate	1.6	407.0	2422.5	6.6
0-80%	$-NH_2$	2.0	399.8	14092.5	45.2
	$-NH_3^+$	1.8	401.6	8017.9	25.7
	Nitrosamine	1.3	402.5	1551.1	4.97
	Nitramine	1.1	406.3	1506.9	4.83
	Nitrate	1.4	407.0	6033.9	19.3
80-80%	$-NH_2$	1.9	399.7	11733.0	40.6
	$-NH_3^+$	1.9	401.4	8599.2	29.7
	Nitrosamine	1.4	402.3	2355.6	8.2
	Nitramine	1.1	406.4	1769.4	6.1
	Nitrate	1.4	407.0	4453.5	15.4