Electronic Supplementary Material (ESI) for Nanoscale Advances.

SUPPORTING INFORMATION

Synthesis of Microporous Silica Nanoparticles to Study Water Phase Transitions by Vibrational Spectroscopy

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List of Methods and Figures:

Materials

Materials: Polyoxyethylene (5) nonylphenylether (IGEPAL CO-520), cyclohexane (HPLC, >99.7%), anhydrous ethanol (>99.5%), methanol (HPLC, >99.9%), 1-hexanol (98%), Zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$, >99.9%), Copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, >99.9%), tetraethylorthosilane (TEOS, >99.9%), Ammonia Hydroxide (NH_4OH, 5M), Hydrochloric Acid (37%) were purchased from Sigma-Aldrich, hydroxyl-terminated polyamidoamine dendrimer G_x-OH PAMAM (x=4-7) in water were purchased from Dendritech. Ultrapure deionized (D.I.) water was generated using a Millipore Milli-Q plus system. All reagents were used as received without further purification.

Sample ID	Overall Diameter (OD) (nm)	Mesopore Diameter (MD) (nm)	Ratio (OD/MD)	Dendrimer Generation	Dendrimer Molarity (mM)	Metal Molarity (mM)	TEOS Amount (mL)
Zn@G_4-OH@SiO_2 (ethanol/water)	47.9 ± 3.5	15.0 ± 2.2	3.1	4	1.342	21.5	248
Zn@G_4-OH@SiO_2 (methanol/water)	44.6 ± 4.5	14.2 ± 3.6	3.2	4	1.342	21.5	248
Zn@G_4-OH@SiO_2 (hexanol/water)	22.0 ± 2.5	4.0 ± 0.9	5.6	4	1.342	21.5	248
Zn@G_4-OH@SiO_2 (water)	30.9 ± 2.4	4.7 ± 1.2	6.6	4	1.342	21.5	248
Zn@G_5-OH@SiO_2	30.2 ± 2.4	2.7 ± 0.6	11.2	5	1.342	43.0	248
Zn@G_6-OH@SiO_2	29.5 ± 2.3	2.3 ± 0.5	13	6	0.776	49.7	319
Zn@G_7-OH@SiO_2	28.2 ± 2.0	<1.5	>20	7	0.557	71.3	237

All Solutions Contain:	
IGEPAL CO-520	10mL
Cyclohexane	170mL
NH_3OH	0.8mL
Total Volume	~185mL

Figure S1: Synthetic overview to produce individually silica nanoparticle species.

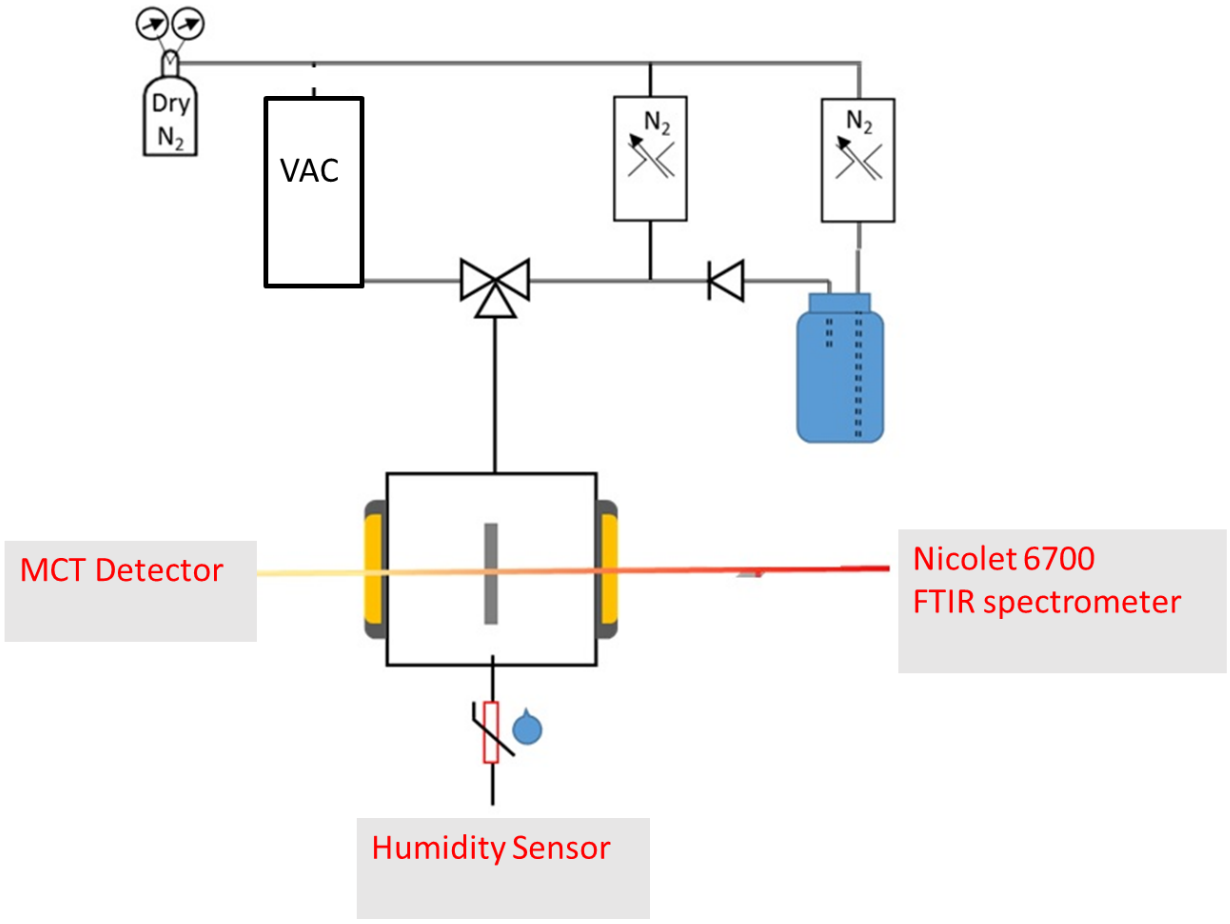

Figure S2: Diagram of transmission FTIR vapor cell setup used to analyze synthesized silica nanoparticles.

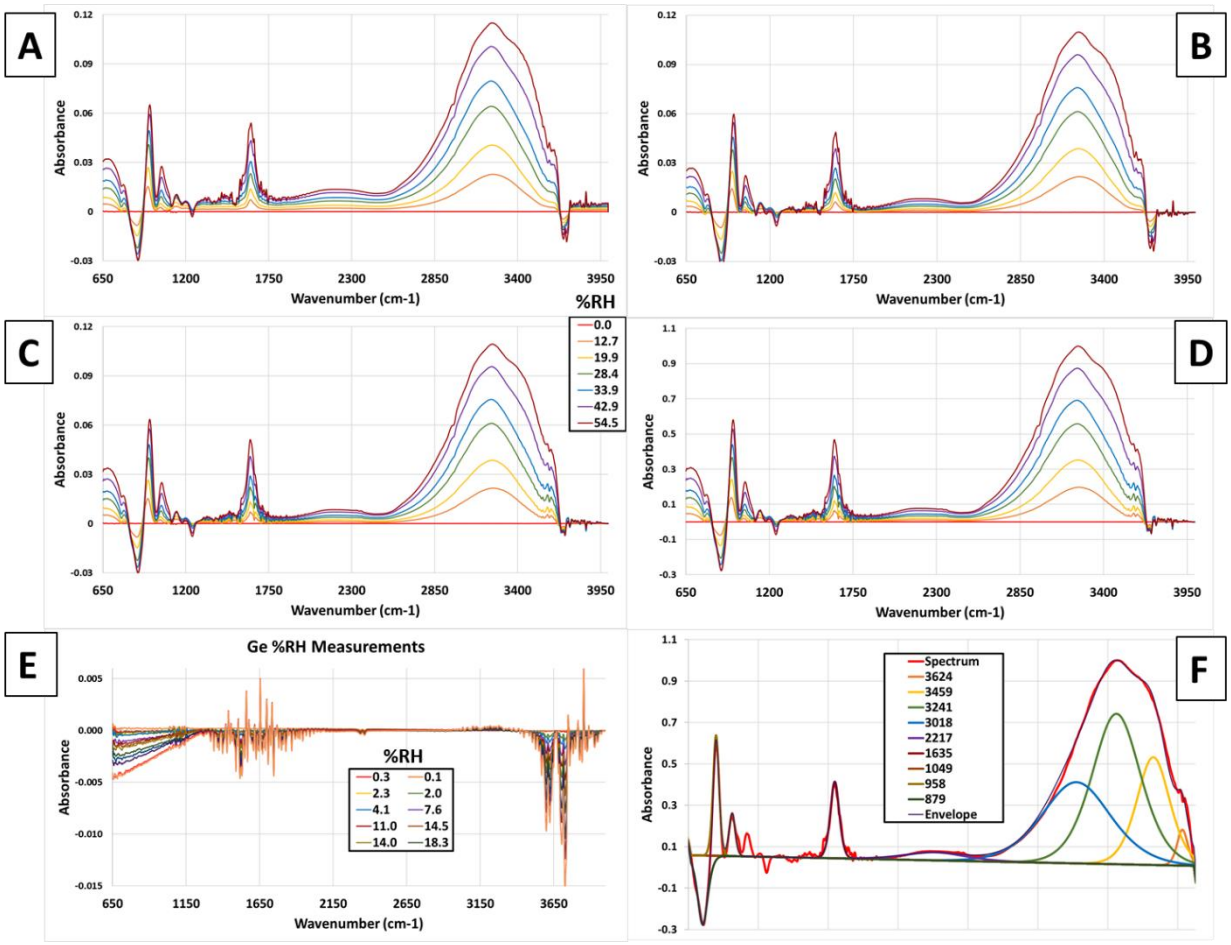

Figure S3: Spectral series for Zn@G4-OH@SiO2 show data processing steps with (A) raw spectra, (B) baseline normalized, (C) atmospheric water vapor subtracted, (D) normalized to the 3250cm^{-1} peak, (E) hydration series of blank Ge under the same vapor conditions, and (F) final fitted spectra of Zn@G4-OH@SiO2 at maximum hydration at 309K.

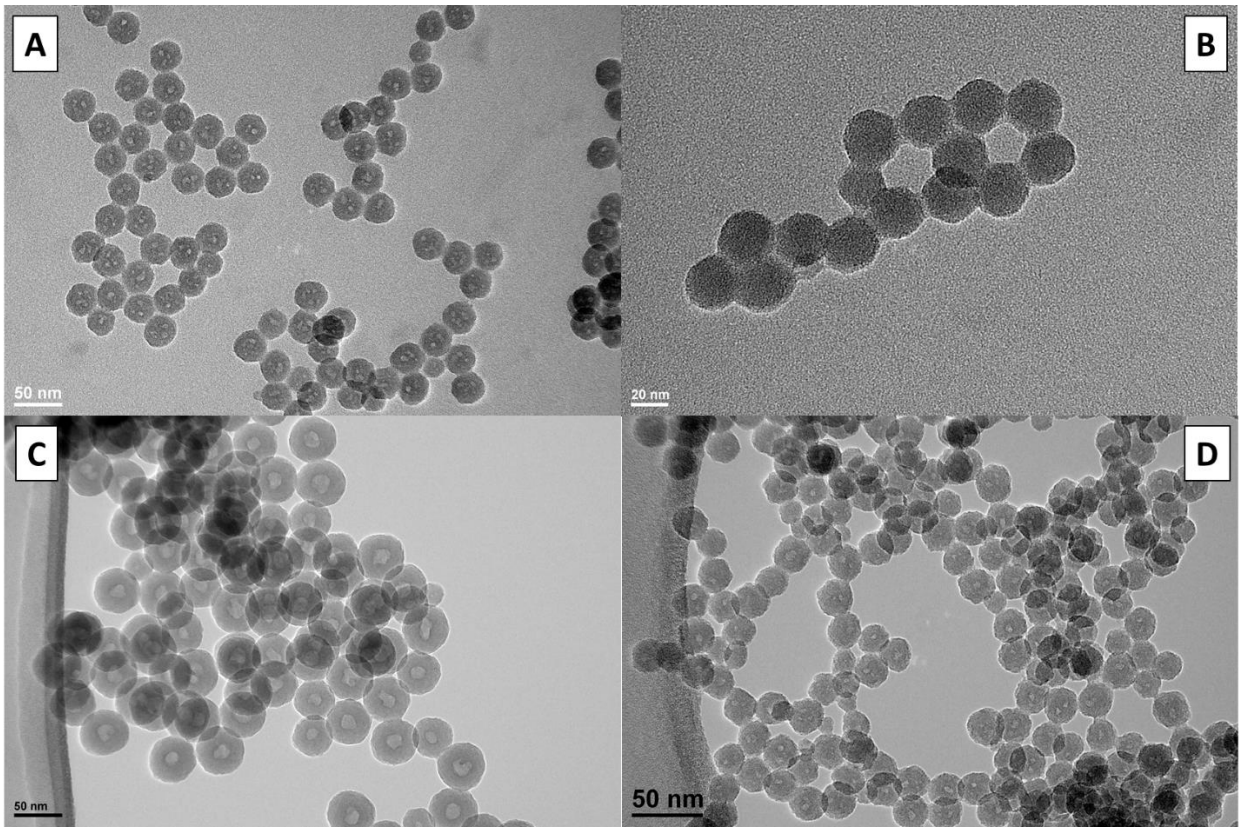

Figure S4: TEM images used for statistical analysis of overall particle and internal mesopore sizes for (A) Zn@G_4-OH@SiO_2 (water), (B) Zn@G_7-OH@SiO_2, (C) Zn@G_4-OH@SiO_2 (ethanol/water), and (D) Zn@G_4-OH@SiO_2 (hexanol/water).

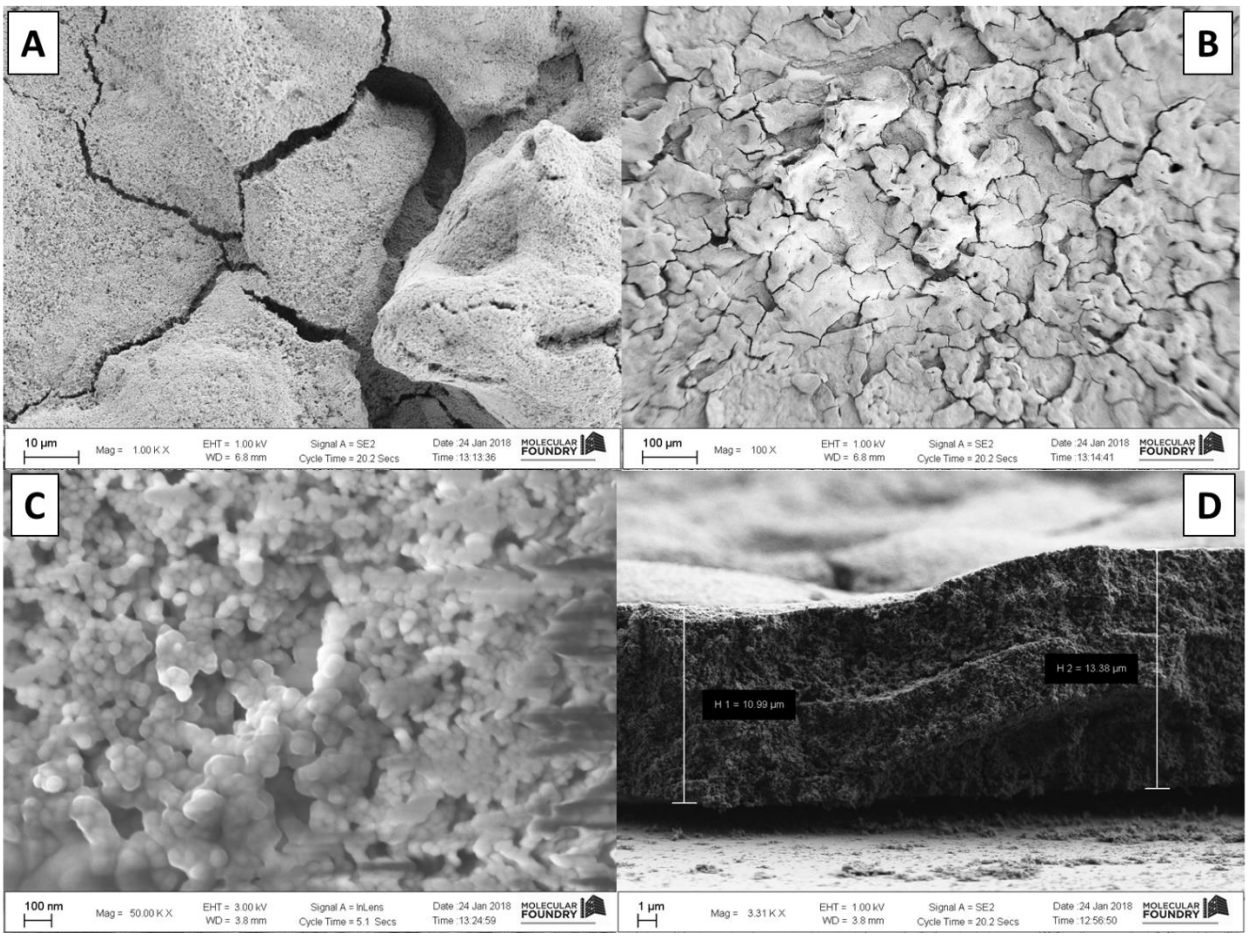

Figure S5: SEM images showing typical packing and film thickness using the example of Zn@G_4-OH@SiO_2.

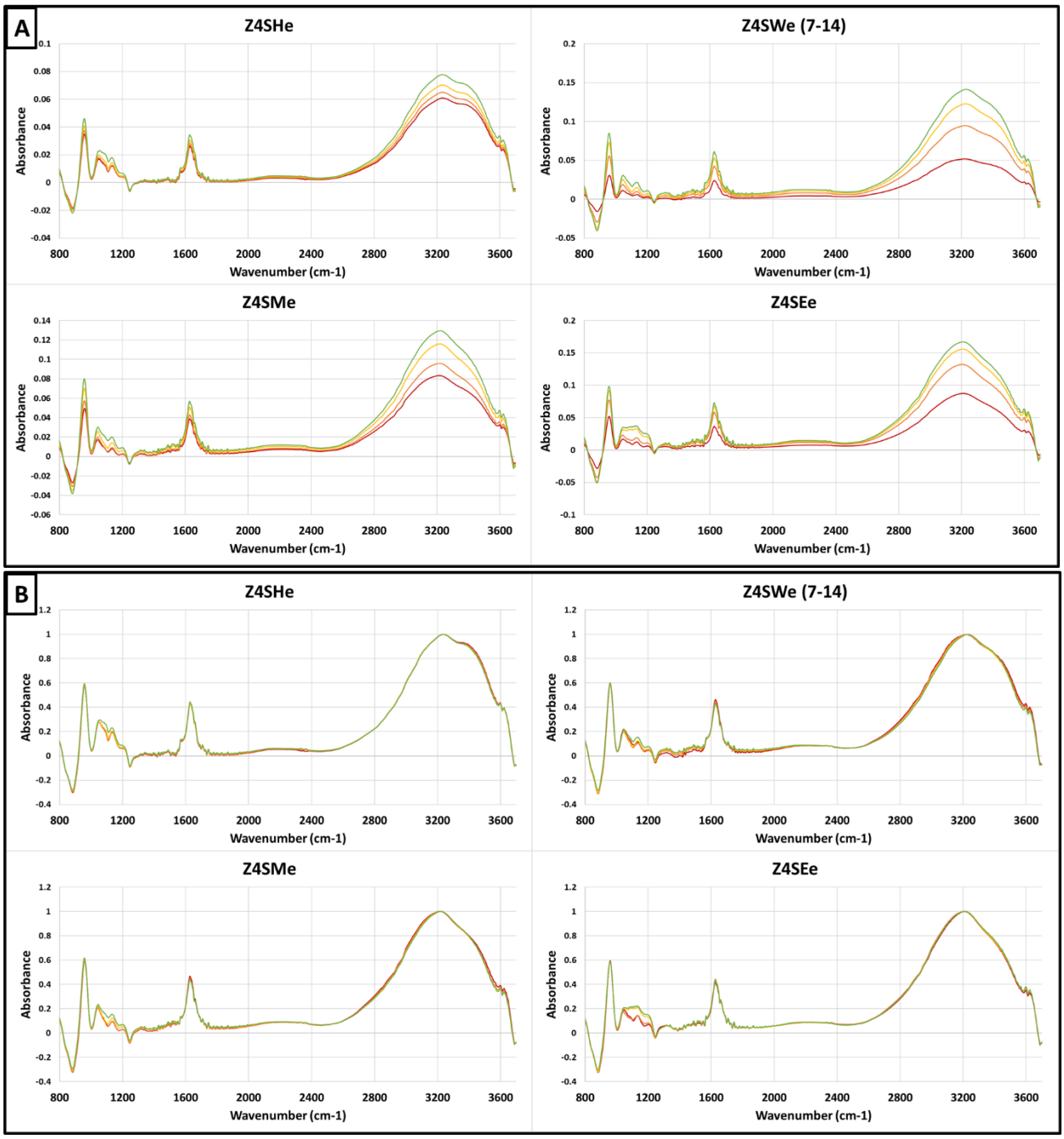

Figure S6: Figure shows the lack of variation in FTIR spectrum due to changes in film thickness (red thinnest ~10 µm to green thickest ~30 µm). Top four spectrum are raw and bottom four normalized to 3250 cm^{-1} peak.

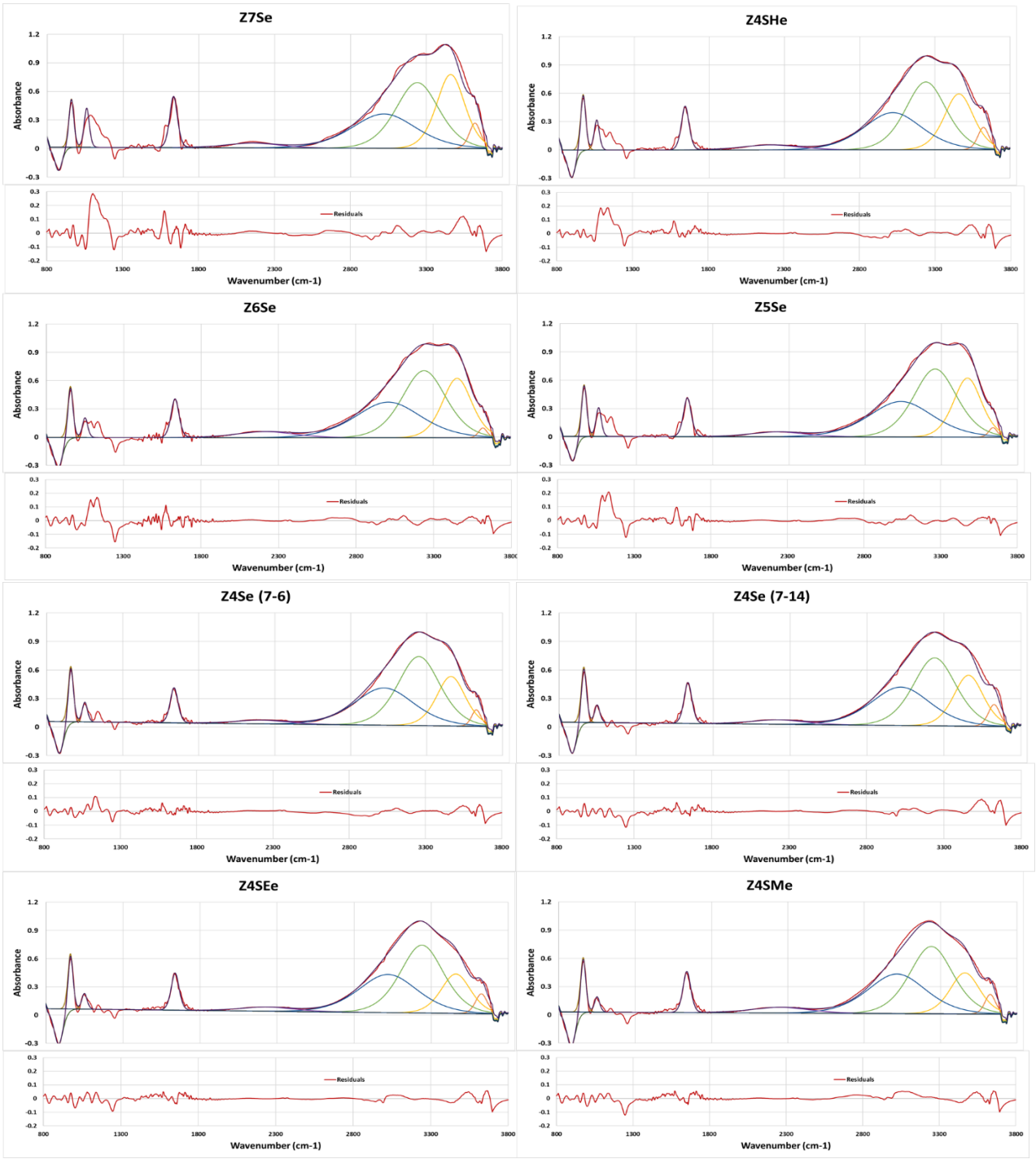

Figure S7: Representative FTIR spectral series and peak fittings with residuals showing variation between measured spectrum and their fits for all individual silica nanoparticle species.

Wavenumber (cm^{-1})	Peak Assignment
3735	ν(SiO-H) Isolated Silanol
3624	H-bonded ν(SiO-H) Vicinal Silanol
3459	$\nu_{as}(H_2O)$ Asymmetric Stretch (Bulk Confined Water)
3241	$\nu_{s}(H_2O)$ Symmetric Stretch (Ice-like Surface Water)
3018	Bulk Interfacial/Interparticle water
2127	$\delta(H_2O)$ Bend + Libration
1643	C=O stretch (amide I)
1635	$\delta(H_2O)$ Bend
1543	C-N stretching/C-N-H bending (amide II)
1294, 1065	C-N stretch (tert-amine)
1214	$\nu_{as}(Si\text{-}O)_{LO}$ Surficial Siloxane
1096	$\nu_{as}(Si\text{-}O\text{-}Si)_{TO}$ Surficial Siloxane
1049	$\nu_{as}(Si\text{-}O)$
958	$\nu_{s}(Si\text{-}OH)$ Vicinal Silanol
879, 798	$\nu_{s}(Si\text{-}O\text{-}Si)$ Surficial Siloxane

Figure S8: Wavenumber assignments for dry silica nanoparticles and silica hydration.

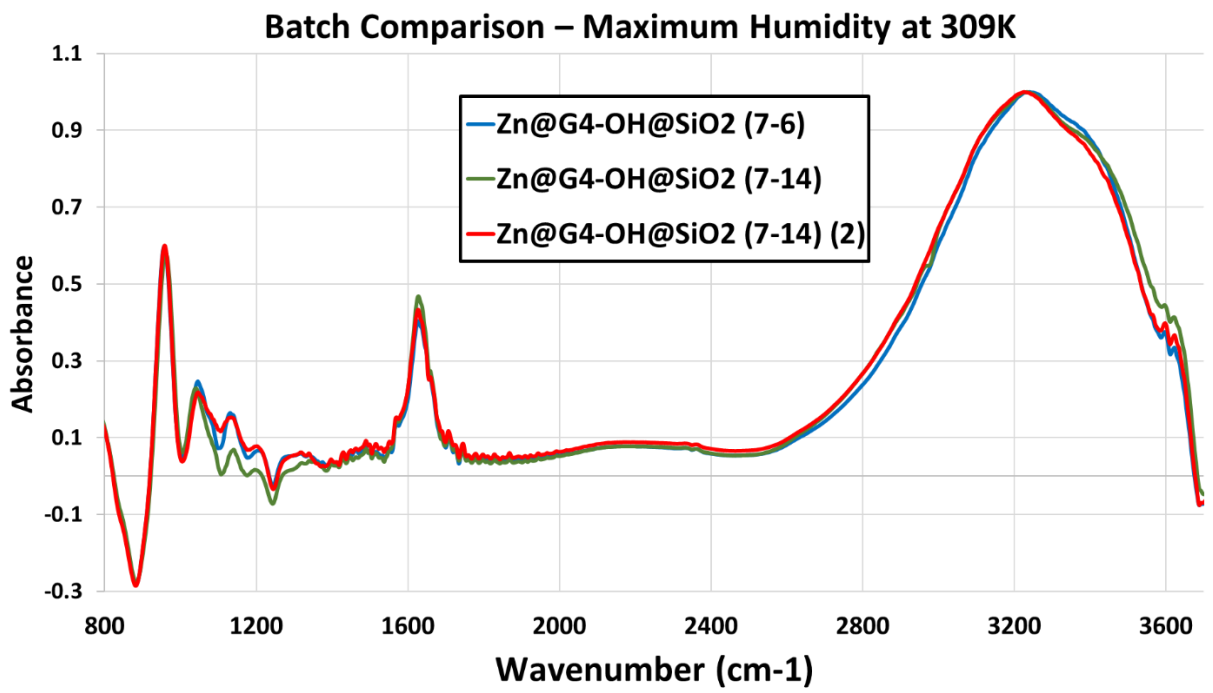

Figure S9: Batch comparison of Zn@G_4-OH@SiO_2 at maximum hydration of ~50% relative humidity and at 309K, showing consistency in measurements between batches.