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Aqueous Synthesis of Compressible and Thermally Stable Cellulose Nanofibril–Silica Aerogel for CO₂ Adsorption

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Supporting Information

ABSTRACT: Cellulose nanofibrils (CNF)–silica aerogels have been facilely synthesized via a one-step in situ aqueous sol–gel process of polymerizing and aging the silica precursor in the presence of CNFs to encompass the superior dry compressive strength and flexibility of CNF aerogels and the thermal stability of silica aerogels. Sodium silicate (Na₂SiO₃) was hydrolyzed and polymerized in the presence of CNFs at varied ratios to synthesize hydrogels whose storage and loss modulus confirmed CNFs to function as the structural skeleton. At the optimal 8:2 CNFs/Na₂SiO₃ composition, the hydrogels with homogeneously dispersed silica and CNF can be freeze-dried into hierarchically mesoporous aerogels with ultralow density of 7.7 mg/cm³, high specific surface of 342 m²/g, and pore volume of 0.86 cm³/g. This robust sol–gel approach employs naturally abundant silica and cellulose in aqueous system to generate improved CNF–silica aerogels that had much higher compressive strength and modulus of up to 28.5 and 177 kPa and structural flexibility than silica aerogel and enhanced thermal stability and specific surface over CNF aerogel. Further functionalization of CNF–silica aerogels via organosilane reaction introduced primary amine groups capable of capturing CO₂ with an adsorption capacity of 1.49 mmol/g.

KEYWORDS: cellulose nanofibril, silica, aerogel, sol–gel synthesis, CO₂ adsorption

INTRODUCTION

Aerogels are ultralight and highly porous materials that can be made up of varied organic or inorganic materials and are often characterized by low thermal and acoustic conductivity owing to the over 99% trapped air.^{1,2} Silica and cellulose, the most abundant inorganic and polymer on earth respectively, have been extensively investigated for aerogel preparation.^{3–8} Silica and cellulose aerogels, albeit sharing many of the same general aerogel characteristics, differ due to their intrinsic material property discrepancy, most notably different in their thermal and mechanical properties. Silica aerogel is highly thermally stable but extremely brittle to collapse under gentle pressure or even capillary forces.^{9,10} In contrast, cellulose aerogels are ductile and flexible, capable of withstanding compressive deformation of up to 80%¹¹ and even more resilient in wet compressive strength^{12,13} but decomposes at moderately elevated temperatures of 300 °C or less.

To overcome the intrinsic brittleness of silica aerogels, it is most common to incorporate flexible organic skeletons of synthetic polymers, such as poly(hexamethylene diisocyanate),^{9,14} epoxy,¹⁵ polybenzobisthiazole,¹⁶ polystyrene,¹⁷ polyacrylonitrile,¹⁸ and resorcinol-formaldehyde¹⁹ to form organic–inorganic composite aerogels. Cellulose has also been investigated in reinforcing silica aerogel by impregnating preformed cellulose hydrogel/aerogel with silica precursors such as tetraethyl orthosilicate (TEOS)^{20–23} or sodium silicate solution²⁴ in a two-step gelation–impregnation procedure. In these practices, cellulose hydrogel is generally preformed by

dissolving cellulose in *N*-methylmorpholine *N*-oxide,²² LiOH–urea,^{20,24} NaOH–thiourea,²³ NaOH–ZnO,²⁵ or ionic liquid (1-ethyl-3-methylimidazolium acetate)–dimethyl sulfoxide (DMSO),²¹ then regenerating in a nonsolvent. The disadvantages of this gelation–impregnation method include the copious organic solvents needed for both cellulose dissolution and regeneration, and the loss of native cellulose I crystal structure from dissolution.

More recently, the fabrication of cellulose aerogels from aqueous nanocellulose suspension has been shown to be more promising and green.^{12,13,26–31} Similarly, nanocellulose–silica aerogel can also be prepared by immersing nanocellulose aerogels cross-linked by Kymene resin,^{32,33} bacterial cellulose hydrogel 3D network,^{34,35} and silylated nanofibrillated cellulose bioscaffold³⁶ in silica precursor. In contrast to the two-step gelation–impregnation process, a one-step homogeneous dispersion and simultaneous gelation of nanocellulose and silica precursor are more attractive. However, current practice mostly employs organic silica precursors, such as TEOS^{37,38} and methyltrimethoxysilane,³⁹ which requires re-dispersing nanocellulose into a common DMSO³⁹ or alcohol solvent^{37,38} and therefore is more expensive and environmentally unfavorable.⁴⁰

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Scheme 1. Synthesis of Aminated CNF/Silica Aerogel via Sodium Silicate Hydrolysis and Condensation in the Presence of CNF To Form Hydrogel and Amination of Aerogel

Toward a more streamlined integration and green process, a facile one-step sol–gel process involving all aqueous dispersible precursors was developed to fabricate cellulose nanofibrils (CNFs)–silica aerogel. The synergistic gelation of CNF and sodium silicate in aqueous suspension is conceptually different from prior works that involved multiple steps or organic silica precursors as discussed in previous sections. Silica aerogels have been produced from sodium silicate, an inexpensive and water-soluble silicon source⁴¹ alone or in mixture with cellulose dissolved in NaOH.²⁵ The fact that aqueous sodium silicate readily gels makes it ideal for hybridizing with cellulose nanofibrils in aqueous suspension. The gelation of CNFs with sodium silicate was probed by their viscoelastic behaviors over time to elucidate the interaction between CNF and silica as well as the hydrogel formation. The gradual growth of silica nanoparticles on CNFs is observed under atomic force microscope (AFM), and the derived aerogel was systematically characterized for the morphologies, chemical structure and composition, specific surface area and pore size, mechanical properties, and thermal stability. In addition, the silica in the aerogel introduces silanol groups to facilitate reaction with organic silane to add novel functionalities to the aerogels, which has been demonstrated to react with (3-aminopropyl)triethoxysilane (APTES) to introduce amine groups for CO₂ adsorption. While CO₂ adsorption by APTES is a typical method, the preparation of dry resilient CNF/silica aerogel using this new and sustainable method is novel, and the CNF scaffold could offer the typically brittle pure silica gel dry strength and yet very low density from sodium silicate precursor.

EXPERIMENTAL SECTION

Materials. Cellulose nanofibrils (CNFs) were derived from cellulose isolated from rice straw by 2,2,6,6-tetramethylpyperidine-1-oxyl (TEMPO) mediated oxidation employing 5 mmol/g NaClO/cellulose at pH 10 by adding 0.5 M NaOH, followed by mechanical blending (Vitamix 5200) at 37 000 rpm for 30 min.⁴² Sodium metasilicate nonahydrate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, crystalline, certified, Fisher Scientific), hydrochloric acid (1 N, certified, Fisher Scientific), anhydrous ethanol (histological, Fisher Scientific), *tert*-butanol (certified, Fisher Scientific), and 3-aminopropyltriethoxysilane (APTES, 99%, Sigma-Aldrich) were used as received without further

purification. All water used was purified using a Milli-Q plus water purification system (Millipore Corporate, Billerica, MA).

Fabrication of CNF–Silica Aerogel. CNF–silica aerogel was synthesized via a sol–gel process using TEMPO oxidized cellulose nanofibrils and aqueous sodium silicate as precursors (Scheme 1). Aqueous sodium silicate was hydrolyzed into silicic acid, which polymerizes into polysilicic acid and then condenses to silica (Scheme 1).⁴³ Aqueous sodium silicate (0.6 wt %) with pH adjusted to 5 by adding 1 mol/L HCl was freshly prepared and mixed with 0.6 wt % CNFs at 9:1, 8:2, 6:4, and 4:6 (by volume) CNF/sodium silicate ratios. CNF–silica hydrogel was formed by aging each mixture (10 mL) for 48 h at ambient condition, then washing with 0.2 mol/L HCl. These CNF–silica hydrogels were solvent exchanged to *tert*-butanol, frozen (−20 °C), and then freeze-dried (−50 °C, 0.05 mbar) in a freeze-drier (FreeZone 1.0 L benchtop freeze-dry system, Labconco, Kansas City, MO). For surface amination, the 4:6 CNF–silica hydrogel (10 mL) was solvent exchanged with anhydrous ethanol into alcogel, saturated with APTES in 10–30 wt % APTES/ethanol (10 mL) for 24 h, and then reacted with water in freshly prepared ethanol (10 mL) containing 0.6–1.8 mL of water (with respect to 10–30 wt % APTES) for 24 h. The amine-functionalized alcogel was then solvent exchanged to *tert*-butanol and freeze-dried as previously described.

Characterization. The dynamic rheological properties of CNF–silica hydrogels were measured at 25 °C using a AR1000-N rheometer (TA Instruments) equipped with two parallel acrylic plates (20 mm diameter) separated by 2 mm. The oscillatory time sweep of each fresh CNF and sodium silicate mixture was carried out under a constant 2 Pa oscillation stress and 1 Hz frequency. The oscillatory frequency sweep of cured CNF–silica hydrogel was conducted under a constant oscillation stress of 1 Pa.

The progressive growth of silica nanoparticles onto CNFs during static aging was observed by atomic force microscopy (AFM, Asylum-Research MFP-3D) at 5, 24, and 48 h. Each respective gel (10 μL) was diluted in 10 mL of water and sonicated for 5 min (Branson 2510, Branson Ultrasonics Corp.), and then 10 μL of the dispersed hydrogel was deposited onto a freshly cleaved mica surface and air-dried. AFM was scanned using tapping mode with OMCL-AC160TS standard silicon probe in air under ambient condition at 1 Hz and imaged at 512×512 pixel resolution.

The cross-sectional morphology of CNF–silica aerogel was visualized using field emission scanning electron microscope (FE-SEM) (XL 30-SFEG, FEI/Philips, USA) at a 5 mm working distance and 5 kV accelerating voltage. The elemental compositions were measured using energy-dispersive spectroscopy (EDS, EDAX,

Figure 1. (a) Photograph of 0.6 wt % of CNF, silica, and 8:2 CNF–silica aged for 48 h. Viscoelastic properties of CNF–silica hydrogels: (b) storage modulus G' and (c) loss modulus G'' during time sweep; (d) G' and G'' of hydrogels aged (48 h) and protonated (0.2 N HCl) during frequency sweep.

AMETEK, Inc.) of the FE-SEM at a magnification of 500 $\times$ with a 10 kV accelerating voltage and a 5 mm working distance.

Fourier transform infrared (FTIR) spectra of CNF–silica aerogels as transparent KBr pellets (1:100, w/w) were obtained from a Thermo Nicolet 6700 spectrometer. The spectra were collected at ambient condition in the transmittance mode from an accumulation of 128 scans at a 4 cm^{-1} resolution over the regions of 4000–400 cm^{-1} . Thermal gravimetric analyses (TGA) were performed under purging N_2 (50 mL/min) at 10 $^{\circ}\text{C}/\text{min}$ from 25 to 500 $^{\circ}\text{C}$ using a TGA-50 analyzer (Shimadzu, Japan). The specific surface area and pore characteristics of CNF–silica aerogels were determined by N_2 adsorption at 77 K using a surface area and porosity analyzer (ASAP 2000, Micromeritics, USA). Approximately 0.1 g of each sample was degassed at 35 $^{\circ}\text{C}$ for 24 h prior to measurement. The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method from the linear region of the isotherms in the 0.06–0.20 relative P/P_0 pressure range. Pore size distributions were derived from desorption branch of the isotherms by the Barrett–Joyner–Halenda (BJH) method. The total pore volumes were estimated from the amount adsorbed at a relative pressure of P/P_0 of 0.98.

The compressive behaviors were performed on 20 mm diameter and 10 mm thick aerogels at a constant 1 mm/min rate on Instron 5566 equipped with a 5 kN load cell. Young's modulus was determined from the initial slope of σ – ϵ curve. The yield stress (σ_y) was determined at the end of elastic region, and the ultimate stress (σ_u) was determined at strain $\epsilon = 0.8$.

CO_2 Adsorption. The CO_2 adsorption by the amination functionalized CNF–silica aerogel was carried out using TGA following a previously reported procedure.^{44,45} The CO_2 adsorbed in the aerogel (approximately 5 mg) was driven off by heating under N_2 to 105 $^{\circ}\text{C}$ for 1 h, then cooled to room temperature under flowing N_2 . The CO_2 adsorption was initiated by switching from N_2 to CO_2 and monitored by the weight gain for 3.5 h.

RESULTS AND DISCUSSION

In synthesizing CNF–silica aerogels via a sol–gel process of aqueous CNF and sodium silicate as precursors, the viscoelastic behaviors of aqueous CNF and aged aqueous sodium silicate, both at 0.6% as well as their mixtures, were monitored. The aqueous CNF alone appeared viscous and flowed freely as shown to drop to the bottom of the inverted glass vial (Figure 1a), exhibiting a higher loss modulus (G'') than the storage modulus (G') over time (Figure S1, Supporting Information) to indicate well dispersed CNFs due to the electrostatic repulsion of their ionized surface carboxylates. The aged sodium silicate solution was also viscous and flew freely to the bottom of the inverted glass vial, indicating weak silica networks, especially at such low silica content. The gelation of CNF and silica network upon aging was far more obvious in the case of 8:2 CNF–silica hydrogel that remains at the top of the inverted glass vial. Considering the lack of gelation for each individual component, the clear gelation of CNF–silica hydrogel was hypothesized as a result of synergistic complexation between CNF and silica network upon aging, possibly through the hydrogen bonding between the CNF surface hydroxyls and free hydroxyls on the colloidal silica (Figure S2, Supporting Information). It should be noted that acid induced CNF gelation only occurs under extremely acidic conditions upon addition of strong acid at pH 2.⁴⁶ The sodium silicate solution cannot induce gelation by protonation of the acid groups as its pH is close to the pK_a of CNF carboxylic acid.

At all CNF–sodium silicate compositions studied, gelation of CNF and silica network upon aging appeared spontaneous as indicated by the higher G' than G'' upon mixing (Figure S3,

Figure 2. Morphological evolution of 8:2 CNF–silica hydrogels. The elongated white fibril-like structures represent CNF, and the white particles represent silica. AFM height images of dispersed hydrogel after (a, d) 5 h, (b, e) 24 h, and (c, f) 48 h aging.

Supporting Information). In fact, the sol–gel transition point occurred prior to the measurement. At 9:1 and 8:2 CNF–silica ratios, the G' increased rapidly first and then gradually over time (Figure 1b), whereas the G'' leveled off (Figure 1c), indicating continuing gelation during the aging process. However, as CNF contents lowered, G' of 6:4 and 4:6 CNF–silica hydrogels peaked in shorter time and then gradually decreased over time with the G'' surpassing G' at 2164 and 334 s, respectively (Figure S3, Supporting Information), indicative of gel to solution transition induced by the plate oscillation. That hydrogels weakened with higher silica contents suggests that CNFs provide the primary skeletal gel network while the condensed colloidal silica serves to bridge and interconnect CNFs within the gel networks. The 8:2 CNF–silica hydrogel had the highest G' value, indicative of the strongest network and the most synergistic bridging between CNF and silica at this composition.

To further improve the mechanical properties of the aged hydrogels, CNF surface carboxylates were protonated by immersion in 0.2 N HCl to enhance inter-CNF hydrogen bonding. Such effect was clearly shown by the more than 2 orders of magnitude higher G' as compared to those without acid protonation treatment (Figure 1b and Figure 1d). Under all compositions, the G' is also more than 1 order of magnitude higher than the G'' , indicating that the weak gel structure of 6:4 and 4:6 CNF–silica hydrogel was also strengthened by acid treatment. The G' values of 9:1, 8:2, 6:4, and 4:6 CNF–silica hydrogels at 1 Hz oscillation were 3898, 2924, 1666, and 613 Pa, respectively, following the same decreasing trend with decreasing CNF composition, as the acid primarily protonates CNF surface carboxylate groups to induce more gelation. In addition, by acid protonation and washing, Na^+ has been removed from CNF and therefore could not affect the mechanical properties.

The hydrolysis of sodium silicate to silicic acid that polymerizes via condensation reaction to form colloidal silica was monitored over time with AFM imaging (Figure 2). After 5 h of aging, silica nanoparticles in ~ 5 nm diameters were observed among less than 2 nm thick CNFs in the hydrogel (Figure 2a and Figure 2d). Further aging to 24 h led to more numerous silica nanoparticles of similar sizes on the surfaces of CNFs (Figure 2b and Figure 2e), indicating CNF surfaces as nucleation sites for silica nanoparticles as well as the possible role of CNFs in regulating the size of silica nanoparticles during aging at up to 24 h. Aging for 48 h produced more numerous and larger silica nanoparticles of around 10–15 nm thick among CNFs (Figure 2c and Figure 2f). These large nanoparticles are thought to be grown from the small nucleus as shown in Figure 2b rather than aggregating from many individual silica nanoparticles as they are stable even after 5 min sonication. While hydrolysis of sodium silicate is expected to be relatively swift, the condensation, polymerization, and nucleation of colloidal silica take hours and its further growth into large silica nanoparticles requires even longer time.

The CNF–silica hydrogels were further solvent-exchanged to *tert*-butanol and then frozen and freeze-dried into aerogels. The stronger 9:1, 8:2, and 6:4 CNF–silica hydrogels showed no observable dimensional change after solvent exchange and freeze-drying, producing white aerogels with similar densities of 7.9, 7.9, and 7.7 mg/cm^3 , respectively. Slight shrinkage observed for the 4:6 CNF–silica aerogel led to a higher density of 10.5 mg/cm^3 . To retain aerogel dimensions, the dominant presence of CNFs is clearly necessary to maintain the skeletal structural integrity. In all cases, the ultralow densities of 7.7–10.5 mg/cm^3 indicate that porosities are above 99% (see Supporting Information), although the exact porosity is impossible to be determined without the actual composition of the aerogel.

Figure 3. Cross-sectional SEM images of aerogels: (a–c) 9:1, (d–f) 8:2, (g–i) 6:4, and (j,l) 4:6 CNF–silica compositions.

Figure 4. (a) FTIR and (b) EDS spectra of CNF–silica aerogels.

The SEM images of the CNF–silica aerogel cross sections show hierarchically porous structures (Figure 3). The 9:1 (Figure 3a and Figure 3b), 8:2 (Figure 3d and Figure 3e), and 6:4 (Figure 3g and Figure 3h) CNF–silica aerogels showed similar tens to hundreds micrometer sized cellular porous network structures, whereas the 4:6 (Figure 3j and Figure 3k) CNF–silica aerogel had more irregular and plate-like

structures with the disappearance of large macropores, possibly from silica aggregates as observed under AFM image. Closer inspection of the pore cellular walls/films at higher magnification showed 30–40 nm wide elongated fiber-like morphologies in 9:1 (Figure 3c) and 8:2 (Figure 3f) CNF–silica aerogels and disappearance of large macropores and presence of more large film pieces in both 6:4 (Figure 3i) and

Figure 5. N_2 adsorption–desorption of CNF–silica aerogels: (a) isotherm; (b) pore size distribution.

Figure 6. Mechanical and thermal properties of the CNF–silica aerogels: (a) compressive stress–strain curves, with inset showing curves at strain below 0.12; (b) Young's modulus and ultimate stress; (c) TGA; (d) DTGA.

4:6 (Figure 3l) CNF–silica aerogel. For all CNF–silica aerogels, mesopores ranging from a few nanometers to several tens of nanometers could be observed at high magnification images, along with the macropores observed at low magnification, indicating the hierarchical porous structure. The main morphological changes with increasing silica content include the less regular cellular aerogel morphology from self-assembled CNF and more clearly aggregated morphologies assembled from silica.

The FTIR of CNF–silica aerogel were clearly evident of CNF peaks at 3400, 2900, 1060, and 897 cm^{-1} , corresponding to the O–H, C–H, C–O stretching vibrations, $\text{C}_1\text{--O--C}_4$ deformation of the β -glycosidic linkage, and the prominent peak at 1728 cm^{-1} from the carbonyl stretching of carboxylic acid groups in CNFs (Figure 4a). With decreasing CNF/silica ratio, the peak intensity at 897 cm^{-1} decreased and the

intensities for the two peaks at 798 and 467 cm^{-1} assigned to Si–O–Si stretching in silica increased. This increased silica content was corroborated by the EDS spectra (Figure 4b), showing that the silicon peak significantly increased with increasing silica content or decreasing CNF/silica ratios. Atomic silicon content determined from EDS was 0.5, 3.9, 9.5, and 19.3 wt % for 9:1, 8:2, 6:4, and 4:6 CNF–silica aerogels, respectively (Table S1, Supporting Information), all lower than the original compositions likely due to the loss of some silica during washing and solvent exchange. EDS mapping of the 4:6 CNF–silica aerogel showed homogeneous distribution of C, O, and Si (Figure S4, Supporting Information), confirming uniformly mixed CNF and silica within CNF–silica aerogels and consistent with AFM and SEM imaging.

Figure 7. Surface silanization of 4:6 CNF–silica aerogel with 3-aminopropyltriethoxysilane (APTES): (a) N_2 adsorption–desorption isotherm; (b) pore size distribution; (c) FTIR spectra; (d) CO_2 adsorption curves.

All CNF–silica aerogels showed a combination of type II and type IV BET nitrogen adsorption–desorption isotherms with hysteresis loops at relative pressure above 0.6 without a saturation limit at higher relative pressure (Figure 5a) and type H3 hysteresis loop typical of mesopores (2–50 nm) as well as aggregated structure of plate-like particles and slit-shaped pore structures,⁴⁷ consistent with the presence of silica nanoparticles. While the total pore volumes of all aerogels are in close range from 0.7 to 0.86 cm^3/g , their pore size distribution exhibited two peaks centered at 7 and 60 nm with the larger pores dominating in those with CNFs as majority, then gradually shifted to smaller pores as silica contents increase (Figure 5b). The specific surface also increases from 152 to 342 m^2/g with increasing silica ratio, indicating silica and interspacings between silica and CNF contributing more specific surface in the aerogels containing more silica (Table S2, Supporting Information).

To further probe the mesoporous structure of the individual component within aerogel, the 4:6 CNF–silica aerogel was calcined in air to burn off CNFs. The calcinated aerogel retained the shape but shrank in diameter and was all white in color, indicating absence of carbon residues from cellulose (Figure S5a,b, Supporting Information). The mesoporous structures are lost after calcination, as indicated by the lack of hysteresis loop in the BET adsorption–desorption isotherm as well as the disappearance of the 6 nm peak (Figure S5c,d, Supporting Information). Consequently, the BET specific surface areas decreased significantly from 342 to 87 m^2/g , and the pore volume also decreased from 0.70 to 0.22 cm^3/g (Table S3, Supporting Information). These observations are consistent with the notion that the mesopores are primarily located at the interspacings between cellulose nanofibrils and

silica and that CNFs and silica nanoparticles are homogeneously mixed at the nanoscale.

The compressive stress–strain curves of all CNF–silica aerogels exhibited three compression stages (Figure 6a) that are similar to those for pure CNF aerogel,²⁶ including the initial elastic regions showing an abrupt increase of the stress with increased strain at up to 0.04, a plastic deformation region from 0.04 to 0.6 strain where the stress increases slowly with increasing strain once passing the yield point, and the last densification stage where the stress increases abruptly with increasing strain from 0.6 to 0.8 strain, indicating all to be flexible and deformable under stress. This is in shear contrast to typical silica aerogels that shatter under even very low stress. The slope for the initial stress–strain curve is obviously steeper for the aerogel with higher CNF content, corresponding to higher Young's modulus. Both the Young's modulus and ultimate stress increased with increasing CNF contents, with respective 43, 75, 164, and 177 kPa and 17.5, 17.8, 20.3, and 28.5 kPa for 4:6, 6:4, 8:2, and 9:1 CNF–silica aerogels (Figure 6b). The increasing mechanical properties of CNF–silica aerogels follow the same trend as their respective hydrogels, again supporting that CNFs function as the structural skeleton to be responsible for the mechanical properties of aerogels.

The thermal stability of the CNF–silica aerogels was investigated using TGA, showing the degradation temperatures at the maximum weight loss rate in the similar range from 289 to 313 $^{\circ}C$, higher than 269 $^{\circ}C$ for CNF,⁴² decreasing weight loss rate of 0.68, 0.64, 0.48, and 0.35% $^{\circ}C^{-1}$, and higher char residues at 500 $^{\circ}C$, i.e., 7.3, 11.5, 21.8, and 39.2% for 9:1, 8:2, 6:4, and 4:6 CNF–silica aerogels, respectively (Figure 6c and Figure 6d), all affirming improved thermal stability with increasing silica content. As expected, the initial weight loss at

below 150 °C due to evaporation of absorbed moisture was 7.9, 7.9, 8.6, and 10.7% and increased with higher silica content.

Considering its highest specific surface and thermal stability, as well as relative good compressive properties and flexibility, the 4:6 CNF–silica aerogel was further reacted with (3-aminopropyl)triethoxysilane to introduce surface amine groups for CO₂ adsorption. Following amination with 30% APTES, both specific surface and total pore volume of the CNF–silica aerogel significantly reduced from 342 to 11 m²/g and from 0.73 to 0.05 cm³/g, respectively (Table S4, Supporting Information). With increasing APTES amination, the type IV hysteresis gradually disappeared and the adsorbed quantity significantly reduced, turning into a typical type II adsorption–desorption isotherm (Figure 7a and Figure 7b), typical for macroporous or nonporous materials. The significantly reduced surface area and pore volume as well as the change into macroporous or nonporous structure indicate that the mesopores in CNF–silica aerogel were filled by APTES after amination. This reduced surface area and pore volume have been observed previously,⁴⁸ and maintaining high specific surface area and large pore volume after amination should be of great interest to maximize the following CO₂ adsorption capacity.

FTIR spectra of aminated CNF–silica aerogel showed the disappearance of the CNF carboxyl carbonyl-stretching peak at 1726 cm^{−1} (Figure 7c), possibly due to the APTES amine effect on dissociation of carboxyls into carboxylate ions, lowering the carbonyl stretching to 1600–1650 cm^{−1} or a broad peak at 1627 cm^{−1}. In addition, several new peaks appeared after amination, including the 1109 cm^{−1} from Si–O–C asymmetric stretching, 1305 cm^{−1} from methylene wagging, 1484 cm^{−1} from bicarbonate salts, 1627 cm^{−1} from NH₂ bending, and 3300 cm^{−1} from NH₂ stretching, successfully confirming amination of CNF–silica aerogel by APTES to present the primary amine groups for CO₂ adsorption. The 1109 cm^{−1} peak intensified with the increasing of APTES concentrations, indicating more Si–O–C bonds formed with increasing APTES.

CO₂ adsorption of the aminated CNF–silica aerogels increased with increasing APTES (Figure 7d), showing adsorption capacity of 1.11, 1.25, and 1.49 mmol/g of CNF–silica aerogels aminated at 10, 20, and 30% of APTES, respectively. The 1.49 mmol/g of CO₂ adsorption is higher than some of other amine grafted polymer networks (1.04 mmol/g)⁴⁹ and amine-based nanofibrillated cellulose (1.39 mmol/g).⁵⁰ As the current value was measured using dried CO₂, CO₂ adsorption is expected to be even higher in the presence of moisture at higher relative humidity. As demonstrated by nanofibrillated cellulose–polyethylimine foam containing 44% polyethylimine, its CO₂ adsorption capacity increased from 1.5 to 2.2 mmol/g at relative humidity raised from 40% to 80%.⁵¹ While two amino groups react with one CO₂ to form carbamate in theory, only one amine reacts with one CO₂ in the presence of water, releasing one amino group for further reaction.

CONCLUSIONS

Ultralight, ultraporous, flexible, and thermally stable CNF–silica aerogels have been facilely in situ synthesized by polymerizing and aging silica precursor in the presence of TEMPO oxidized CNFs in an aqueous sol–gel process. The synergistic protonation of CNF surface carboxylate groups

under the acidic condition and hydrogen bonding between CNFs and prehydrolyzed silica precursor facilitated gelation of the aqueous mixtures at concentration as low as 0.6 wt %, which cannot be achieved with either individual component. These low concentrations produced aerogels in hierarchical porous structure with ultralow density of 7.7 mg/cm³, high specific surface of 342 m²/g, and pore volume of 0.86 cm³/g. Both the storage (*G'*) and loss (*G''*) modulus of the CNF–silica hydrogels and the compressive modulus and stress of the CNF–silica aerogels showed CNFs to function as the structural skeleton to achieve optimal mechanical strength for 8:2 CNF–silica hydrogel and aerogels. On the other hand, increasing silica content enhanced the thermal stability as well as enable silane reaction, i.e., APTES amination, of CNF–silica aerogel. The APTES aminated 6:4 CNF–silica aerogel showed CO₂ adsorption capacity as high as 1.49 mmol/g. In essence, the sol–gel process produced robust CNF–silica aerogels whose improved mechanical properties and structural flexibility over silica aerogel and enhanced thermal stability and specific surface area over CNF aerogel may be easily tuned by compositions. These CNF–silica aerogels have the potential for versatile applications as resilient thermal insulating materials, CO₂ adsorbents, and mesoporous scaffolding.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsanm.8b01515.

Storage and loss modulus of CNF suspension; schematics of hydrogen bonding between polysilicic acid and cellulose nanofibrils; viscoelastic properties of CNF–silica hydrogel; EDX mapping for the aerogel; specific surface and pore volume of the aerogels (PDF)

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Notes

The authors declare no competing financial interest.

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