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Wafer-Scale Vertically Aligned Carbon Nanotubes Locked by *in Situ* Hydrogelation Towards Strengthening Static and Dynamic Compressive Responses

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Abstract

Wafer-scale vertically aligned carbon nanotube/poly (vinyl alcohol) (VACNT/PVA) hydrogels were fabricated by infiltration of PVA among VACNTs and subsequent *in situ* hydrogelation. Owing to the homogeneous PVA infiltration, uniform distribution and orientation of the CNTs are well retained, which in turn provide large CNT-PVA interfaces throughout the resulting hydrogels. Compared to bare PVA hydrogels, such composite hydrogels perform significantly enhanced longitudinal compressive responses upon both static and dynamic loadings, achieving improvements of up to 25.2– and 9.0–fold in strength and loss modulus, respectively. The novel scalable fabrication of VACNT/PVA hydrogels and their attractive performances hold great potential for a wide range of applications.

Keywords: vertically aligned carbon nanotubes, poly (vinyl alcohol), composite hydrogels, compressive mechanical properties, dynamic mechanical analysis

1. Introduction

Hydrogels, three-dimensional polymer networks with high water contents, flexibility and lubricity have been considered as good candidates for various applications such as strain/stress sensors for motion detection,^[1] cushion materials for sports shoes^[2] and artificial muscles in soft robotics.^[3] However, bare hydrogels usually suffer from limited mechanical strength and damping due to lack of an efficient energy dissipation mechanism,^[4] which severely hinder their further practical applications. As such, many efforts have been devoted to strengthening the hydrogels by incorporating nanomaterials such as metal oxides^[5]/carbon nanoparticles,^[6] carbon nanotubes (CNTs)^[7] and graphene oxide (GO) nanosheets.^[2] Among them, CNTs with superior mechanical strength and modulus are particularly promising nanofillers because of their exceptionally high aspect ratio. Nevertheless, the resulting reinforcements are still unsatisfactory attributing to the limited CNT-matrix interfacial area, resulting from agglomeration of random CNTs within matrix due to substantial inter-tube van der Waals attractions.^[8]

To date, many strategies have been developed to address the abovementioned problems, including improving the dispersion of CNTs by either significant mechanical energy input with the aid of ultrasound and ball milling, or chemical modification involving the usage of strong acids/oxidants and reactive plasma.^[9] However, the CNTs treated by such harsh processes normally suffer from shortened tube length and impaired intrinsic structures, which are detrimental to their resulting reinforcements. On the other hand, instead of random CNTs, utilizing vertically aligned CNTs (VACNTs) as continuous reinforcements could be a feasible approach to achieve uniform distribution and alignment of CNTs across the dimensions of composite structures, without sacrificing their structural integrity or intrinsic characteristics.^[10] The resulting aligned CNTs reinforced composites such as

CNT/epoxy,^[10h-j] CNT/polyimide^[10k] and CNT/polydimethylsiloxane^[10a] have also been reported with improved thermal, electrical and mechanical properties. Despite these advantages, composite hydrogel infiltrated by macroscale VACNTs, which is expected to exhibit large CNT-matrix interfacial area and thus perform reinforced mechanical response, has not been investigated due to collapse-prone structure of hydrophobic VACNTs when treated with aqueous solutions.^[8a]

Herein, wafer-scale continuous VACNTs (5 mm in length) reinforced poly (vinyl alcohol) (VACNT/PVA) composite hydrogels have been fabricated by infiltration of PVA among hydrophilized VACNTs and subsequent *in situ* hydrogelation. The as-prepared composite hydrogels perform significantly enhanced longitudinal compressive responses upon both static and dynamic loadings. In addition, such hydrogels can be easily dehydrated to obtain corresponding composites with excellent electrical and thermal transports. This work not only provides a novel scalable fabrication approach for various VACNT/polymer hydrogels, but also highlights the great potential of the resulting composites with multifunctional applications.

2. Results and Discussion

Figure 1. Fabrication of freestanding and flexible wafer-scale VACNT/PVA composite hydrogels. Step

I : VACNT a

was gradually exchanged by homogenous infiltration of aqueous PVA solution among the VACNTs. Step III: By cyclic freezing/thawing was applied to PVA, by which the oriented morphology and uniform distribution of the VACNTs were well preserved.

Figure 1 illustrates the fabrication process of VACNT/PVA composite hydrogels. The 5-mm long VACNTs grown on a 4-inch Si wafer were firstly treated with sodium dodecyl benzene sulfonate (SDBS, see the Experimental Section for more details) to improve their hydrophilicity. Then the SDBS was gradually exchanged with aqueous PVA solution until a homogeneous infiltration of PVA among the VACNTs was obtained. Next, cyclic freezing/thawing was applied to enable *in situ* hydrogelation of PVA, by which freestanding and flexible wafer-scale VACNT/PVA composite hydrogels were successfully fabricated. The morphology and structure changes of the VACNTs before (**Figure 2a–c**) and after PVA infiltration (Figure 2d–f) were further studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) characterizations. It is observed that the highly oriented structure of VACNTs within the VACNT/PVA composites was not affected by PVA infiltration. Meanwhile, the CNT-PVA interfaces display intimate contact without physical gaps, indicating strong adhesion between CNTs and PVA polymer chains.^[11]

Figure 2. Morphology and structure characterizations of VACNTs before a–c) and after PVA infiltration d–f). SEM a,d) and TEM b,c,e,f) images of VACNTs and VACNT/PVA composites, respectively. The aligned morphology and uniform distribution of VACNTs are well retained within the VACNT/PVA composites.

Figure 3. a) Raman spectra, b) XRD patterns and c) TGA profiles of CNT, PVA and composite VACNT/PVA. Crystalline structures of the CNT and PVA hydrogels are well preserved for the VACNT/PVA composite hydrogels with 2.23 wt% (CNT:PVA) CNT filling.

Next, Raman, X-ray diffraction (XRD) and thermogravimetric analysis (TGA) were further employed to verify crystalline structure and thermal behavior of the VACNTs before and after PVA infiltration. As shown in the Raman spectra (**Figure 3a**), characteristic D (1334.3 cm⁻¹) and G (1571.8 cm⁻¹) peaks with high G/D intensity ratio (I_G/I_D)^[12] of initial CNTs could be clearly identified with no noticeable changes for the VACNT/PVA composites, indicating that the good crystalline structure of CNTs is not altered by PVA infiltration. It is noted that the XRD pattern (Figure 3b) of VACNT/PVA hydrogels exhibits similar diffraction peaks with that of bare PVA hydrogels,^[13] suggesting that the crystalline structure of composite hydrogels is not affected by CNTs. As shown in Figure 3c, the VACNT/PVA hydrogels exhibit dramatic 86.27% weight loss before 160 °C attributing to the water evaporation, showing similar water content with bare PVA hydrogels (86.60%).^[13] Upon continuous heating, further weight losses of 13.43% at 650 °C and 0.30% at 800 °C can be observed due to the decompositions of PVA and CNT, respectively. The weight fraction of CNT (CNT:PVA) was then calculated to be 2.23 wt% (corresponding to volume fraction of 1.28%). In addition, the VACNT/PVA hydrogels possess improved swelling capability than

the bare PVA hydrogels (with equilibrium swelling ratios of 338.43% and 287.28%, respectively), which is beneficial for their practical applications.

Figure 4. a) VACNT/PVA hydrogels are able to fully recover after longitudinal compression at a strain of as high as 75%. b) Compressive stress-strain curves of the viscoelastic composite hydrogels at various applied strains demonstrate their c) significantly enhanced compressive strengths (C. S.) and energy dissipation ratios (E. D. R.) reinforced by VACNTs.

To investigate reinforcing effects of VACNTs on mechanical responses of composite hydrogels, systematic longitudinal compressions were carried out. Similar with bare PVA hydrogels (Figure S1a), VACNT/PVA hydrogels are able to fully recover after compression up to a 75% strain (**Figure 4a**), showing their excellent shape-recovery characteristics resulting from highly cross-linked polymer chains formed after cyclic freezing/thawing (Figure S1b and Figure 2d). Meanwhile, corresponding stress-strain curves at strains of 25, 50 and 75% (Figure 4b) exhibit a nonlinear stress-strain relationship (strain stiffening^[14]) of the hydrogels, indicating their natural viscoelastic characteristic.^[13] Upon continuous compression, PVA chains within hydrogels tend to become uniformly oriented, while the interactions between PVA chains and H₂O molecules lead to a hardening effect. In the meantime, VACNT/PVA hydrogels perform significantly higher compressive stresses and

larger hysteresis loops than bare PVA hydrogels at respective strains, suggesting their better performances in mechanical strength and energy dissipation.

As summarized in Figure 4c, compressive strengths (C. S.) of 0.081, 0.16 and 0.47 MPa can be achieved when strains of 25, 50 and 75% are applied for composite hydrogels, which are respectively 25.2–, 7.8– and 2.4–fold higher than those of the bare PVA hydrogels. These impressive reinforcements contributed by 2.23 wt% VACNTs are obviously better than those of randomly dispersed CNTs or GO within hydrogels (3.5 wt% and 0.8 wt% additions lead to 113% and 36% increases in C. S.,^[15] respectively). As reported, the crystallinity and water content have significant impacts on mechanical properties of hydrogels.^[13] Considering that the crystalline structure (Figure 3b) and water content (from 86.60% to 86.27%) of the composite hydrogels are not affected by CNTs, the enhanced mechanical performances of VACNT/PVA hydrogels can be attributed to the reinforcing effects of VACNTs. As identified by the abovementioned SEM and TEM analysis (Figure 2), the VACNT/PVA composites exhibit well-bonded interfaces between CNT and PVA. Therefore, a commonly used theoretical model $Y_c = (\eta_o \eta_l Y_f - Y_m)V_f + Y_m$ ^[16] could be applied for the as-prepared VACNT/PVA hydrogel, where Y is modulus, V is volume fraction, c, f and m stand for composite, filler and matrix, respectively. η_o is the orientation efficiency factor, which has values of 0.2, 0.375 and 1 for random distributed, in plane aligned and aligned fibers, respectively. The uniform distribution and continuous alignment of VACNTs enable the composite hydrogels take full advantages of their superior axial mechanical strength and modulus.^[10a,16] Meanwhile, the VACNTs with ultra-high aspect ratio of $\sim 3 \times 10^5$ maximize the length efficiency factor η_l (approaches 1 when fiber aspect ratio is larger than 10),^[16] which facilitate the homogeneous stress distribution and minimize the presence of stress concentration centers, leading to the efficient load transfer upon loading. In addition, the VACNT/PVA hydrogels perform excellent energy dissipation ratios (E. D. R.) of 39.76,

51.46 and 61.15% at 25, 50 and 75% strains, respectively, which are 5.7–, 4.3– and 1.5–fold higher than the counterparts of bare PVA hydrogels. This is attributed to the large interfacial areas resulting from nanoscale dimension and high aspect ratio of CNTs,^[17] which contribute to significant frictional energy loss caused by additional CNT-PVA and CNT-CNT interactions upon compression.^[10a,18] Moreover, the nanotube structure and excellent thermal conductivity of VACNTs enable immediate dissipation of strain energy through on-tube oscillations and in form of heat, respectively.^[19]

Figure 5. VACNT/PVA and bare PVA hydrogels show a) frequency and b) strain dependent storage (E'), loss (E'') modulus and damping ratio ($\tan \delta$) upon dynamic longitudinal compressions. Moreover, the composite hydrogels perform effective improvements in E' and E'' over entire ranges of applied frequency and strain, which are particularly significant at larger strains.

In addition to static loading, complex dynamic compressions with various frequencies or strains are also anticipated for structural hydrogels.^[20] Therefore, the viscoelastic responses (longitudinal) of the VACNT/PVA hydrogels were further characterized. **Figure 5a** shows storage (E'), loss modulus (E'') and damping ratio ($\tan \delta$) of the VACNT/PVA and bare PVA hydrogels as functions of frequency at a 0.5% strain. Besides the positive frequency dependence of E' and E'' ,^[21] both hydrogels show the E' that is more than 1 order of magnitude higher than respective E'' over entire applied frequency range (0.1–100 Hz), suggesting their elasticity and rigidity.^[22] Meanwhile, the VACNT/PVA hydrogels exhibit

stably higher E' and E'' (1.9– and 1.4–fold, respectively) than bare PVA hydrogels at respective frequencies, which agrees well with what observed during static compressions. To study the effect of strain on E' and E'' of hydrogels, dynamic compressions at strains varying from 0.3 to 10% were further carried out (Figure 5b). Upon loading frequency of 1 Hz, both PVA and VACNT/PVA hydrogels show strain-dependent E' and E'' , which are generally stable at strains less than 1% and increase when strain is larger. Particularly, the reinforcements in E' and E'' (especially for E'') of VACNT/PVA hydrogels become more obvious at higher strains. When applied strain reaches 10%, significant enhancements of 4.5–fold in E' (from 0.08 to 0.36 MPa) and 9.0–fold in E'' (from 0.008 to 0.072 MPa) can be achieved for the composite hydrogels as compared to bare PVA hydrogels, respectively. The strengthened van der Waals interactions and mechanical interlocking at strong CNT-PVA interfaces under larger strains contribute to better load transfer and thus higher E' .^[23] On the other hand, more interaction sites are activated at CNT-PVA and CNT-CNT interfaces upon larger applied strains, which greatly facilitate stick-slip frictional energy dissipation^[18b,18c,23,24] of the VACNT/PVA hydrogels and lead to comparable damping (E'' and $\tan \delta$) improvements with those of the aligned CNT/polymer composites.^[18b,25]

Figure 6. Mechanical-resistance responses of the VACNT/PVA hydrogels. Relative change in resistance as functions of a) compressive strain and b) cycles (at a 50% strain).

Moreover, considering the excellent compressibility of the hydrogels and outstanding electrical conductivity of the CNTs, the VACNT/PVA composite hydrogels are expected to perform good mechanical-resistance responses.^[26] As shown in **Figure 6a**, the relative change in resistance ($\Delta R / R_0 = (R_0 - R) / R_0$, where R_0 and R are the longitudinal resistances of the composite hydrogel without and with applied compressive strain, respectively) of the VACNT/PVA hydrogels increases almost linearly with the applied strain, and is reversible over the loading-unloading cycle. The slope reflects their gauge factor (the sensitivity to strain, defined as $(\Delta R / R_0) / \text{strain}$) of 0.80 that is comparable with those of the CNT/polymer and CNT/elastin cryogel strain sensors.^[26,27] This strain sensitivity can be attributed to the increased inter-tube contacts upon compression loading, which contribute to more conducting paths and thus smaller resistances.^[27] In addition, no obvious change can be found in the real-time resistance variation profile of the VACNT/PVA hydrogels upon cyclic compression at a 50% strain (Figure 6b), indicating their excellent cyclic mechanical resistance responses. These outstanding elasticity and strain/stress dependent resistance enable the VACNT/PVA hydrogels with promising strain/pressure sensor applications.

Figure 7. Comparison of longitudinal electrical and thermal conductivities of dehydrated VACNT/PVA composites with those of previously reported aligned CNT (ACNT) and randomly dispersed CNT (RCNT) based polymer composites.

To further broaden the application scope, VACNT/PVA composites were fabricated by dehydrating the composite hydrogels and their electrical and thermal transports were systematically investigated (**Figure 7**).^[10j,28] Excitingly, a dramatic 8 orders of magnitude increase in longitudinal electrical conductivity (from 1.97×10^{-10} to 2.13×10^{-2} S cm⁻¹, Figure S2) can be achieved for the VACNT/PVA composites with only 2.23 wt% of VACNT filling, attributing to the efficient electron conduction along continuous VACNTs which is free of resistive barriers.^[10f,10g,12,29] This excellent conductivity of VACNT/PVA composites is several (~2–4) orders of magnitude higher than those of randomly dispersed CNT (RCNT)/PVA composites,^[29a,30] and is comparable with or better than those of other aligned CNT (ACNT)/polymer composites with similar level of CNT loading.^[31] In addition, the VACNT/PVA composites exhibit an improved longitudinal thermal conductivity of 1.83 W m⁻¹ K⁻¹, which is 3.9-fold higher than that of bare PVA (0.47 W m⁻¹ K⁻¹) and is competitively better than most CNT/polymer composites with similar CNT fraction.^[10c,21,32] This impressive enhancement is due to that the continuously aligned CNTs within VACNT/PVA can serve as efficient heat-conducting paths without being influenced by thermal interfacial resistance.^[19b] Meanwhile, the 5-mm length of the CNTs is much longer than mean free paths of phonons, enabling stable transport of phonons with various wavelengths.^[12] These electrically and thermally conductive VACNT/PVA composites show promising flexible electronic and thermal management applications.

3. Conclusions

Wafer-scale VACNT/PVA composite hydrogels have been successfully fabricated by infiltration of PVA among VACNTs and subsequent *in situ* hydrogelation. By using this

method, the uniform distribution, aligned morphology and crystallinity of CNTs are well preserved within the composite structure. As a result, the as-prepared composite hydrogels perform outstanding longitudinal compressive responses upon both static and dynamic loadings, attributing to continuous reinforcements of uniformly distributed VACNTs and the resulting large CNT-PVA interfaces. Particularly, impressive enhancements of up to 25.2-, 5.7-, 4.5- and 9.0-fold in strength, energy dissipation ratio, storage and loss moduli, respectively, can be achieved for the VACNT/PVA hydrogels. In addition, such hydrogels can be easily dehydrated to obtain corresponding composites with significant 8 orders of magnitude electrical and 3.9-fold thermal conductivity improvements. This work not only provides a novel scalable fabrication approach for various VACNT/polymer hydrogels, but also highlights the great potential of the resulting composites with multifunctional applications.

4. Experimental Section

Materials: 4-inch wafer-scale VACNT arrays (5-mm tall) were purchased from Aixtron Ltd. Sodium dodecyl benzene sulfonate (SDBS, technical grade) and PVA (MW = 89 000–98 000, 99%) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification.

Fabrication of VACNT/PVA Hydrogels: Firstly, VACNT arrays were treated with aqueous SDBS solution (10 mg mL⁻¹) overnight to improve their hydrophilicity. Next, the SDBS was gradually exchanged with aqueous PVA solution (13.6 wt%) assisted by mechanical shaking, achieving a homogeneous infiltration of PVA among the VACNTs. Finally, the VACNT/PVA composite hydrogels were achieved by *in situ* hydrogelation of PVA after 5 cycles of freeze/thaw process, which is composed of a freezing step (21 h at -20 °C) and a

subsequent thawing step (3 h at 25 °C). For comparison, bare PVA hydrogels were also prepared with similar process.

Measurements of Water Content and Swelling Ratio: First, the hydrogel samples ($15 \times 15 \times 5 \text{ mm}^3$) were dried at 40 °C in vacuum for 10 h to ensure that all the water component have been removed. Then, the dried samples were immersed in DI water to swell until their masses became unchanged. Next, the samples were taken out from the water and blotted with filter paper before weighing. The water content and the equilibrium swelling ratio (ESR) of the hydrogel sample were respectively calculated according to water content = $(m_0 - m_1) / m_0 \times 100\%$ and ESR = $(m_2 - m_1) / m_1 \times 100\%$, where m_0 , m_1 and m_2 are the masses of the hydrogel sample, dried sample and swollen sample, respectively.

Static Compression Tests: Static compressive properties (longitudinal, along CNT alignment direction) of VACNT/PVA hydrogels were determined using a Universal Testing System (Instron 5567, Instron, USA) in a quasi-static fashion at room temperature. Square-shaped VACNT/PVA hydrogel sample ($15 \times 15 \times 5 \text{ mm}^3$) was firstly loaded on center of lower platen, a compression rod with 50 mm diameter was then applied onto the sample with a controlled speed. The compressions were all conducted within confinement of the smaller upper platen. To comprehensively investigate compressive behaviors of the VACNT/PVA hydrogels, strains of 25, 50 and 75% were applied at a strain rate of $100\% \text{ min}^{-1}$. Corresponding tests were also done for bare PVA hydrogels as comparison. Strain and stress were calculated using displacement of the compression rod divided by original height of the sample and compressive loading force over cross-sectional area of the sample, respectively. All the measurements were repeated at least three times to extract average values.

Dynamic Mechanical Analysis: Dynamic compressive viscoelastic properties (longitudinal, along CNT alignment direction) of VACNT/PVA hydrogels were characterized with a

dynamic mechanical analyzer (DMA Q800, TA Instruments, USA) at room temperature. Square-shaped VACNT/PVA hydrogel samples with dimensions of $10 \times 10 \times 5 \text{ mm}^3$ were tested using a parallel-plate compression clamp. Storage and loss modulus as functions of applied strain and frequency were respectively collected under multi-strain (0.3–10%, at 1 Hz) and multi-frequency (0.1–100 Hz, at 0.5% strain) modes with a preload force of 0.01 N. Corresponding tests were also carried out for bare PVA hydrogels as comparison. All the measurements were repeated at least three times to obtain average values.

Measurement of Mechanical-Resistance Response: The longitudinal resistance of the VACNT/PVA hydrogel ($20 \times 10 \times 5 \text{ mm}^3$) was measured with the sourcemeter (Keithley 2400, USA) by putting two probes onto its top and bottom surfaces, which were further fixed by two paralleled plastic platens with the help of screw and bolt to ensure good contacts (as shown in Figure S3). The mechanical-resistance response was then measured by monitoring the resistance in real-time when the compressive strain was applied to the composite hydrogel by tightening/loosening the screw.

Thermal Conductivity Measurements: Composite VACNT/PVA hydrogels were freeze dried to obtain corresponding VACNT/PVA composites, which were then cut into disks with diameter of 12.7 mm and thickness of 5 mm and measured using Laser Flash technique (DLF 1200, TA Instruments, USA). Prior to measurement under Ar atmosphere at room temperature, spray coating of a thin graphite layer was applied on two sides of the samples to maximize absorption and emissivity. The data was fitted using Cowan model with pulse correction to extract thermal diffusivity. Thermal conductivity was finally obtained according to $\lambda = \alpha \cdot \rho \cdot C_p$, where λ is thermal conductivity, α is thermal diffusivity (as extracted), ρ is density (as measured) and C_p is heat capacity (measured by Modulated Differential Scanning Calorimeter, MDSC, TA 2920, TA Instruments, USA). Bare PVA was measured as well for

comparison. The measurements were repeated three times for each sample to confirm the reproducibility.

Characterization: Morphologies of VACNT arrays, PVA and VACNT/PVA composites were characterized by scanning electron microscopy (SEM, LEO 1550). Nanostructures of CNTs and VACNT/PVA composites were investigated by transmission electron microscopy (TEM, Tecnai G2 F20 X-Twin). Raman spectroscopy (WITEC CRM200 Raman system) with a 532 nm laser was used to study crystalline structures of the CNTs before and after PVA infiltration. X-ray diffraction (XRD, Shimadzu XRD-6000) was adopted to investigate crystallinities of PVA hydrogels with and without VACNT filling. Thermogravimetric analysis (TGA, Shimadzu DTG-600H thermal analyzer) under constant air flow of 50 mL min⁻¹ were applied to study thermal behaviors of the CNT, PVA and VACNT/PVA hydrogels. Electrical conductivities of the PVA and VACNT/PVA composites were analyzed with a precision semiconductor parameter analyzer (Keithley 4200) using a probe station (Karl Suss PA200) by a two-probe configuration measurement method at room temperature.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no competing financial interest.

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