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Finely Dispersed Single-Walled Carbon Nanotubes for Polysaccharide Hydrogels

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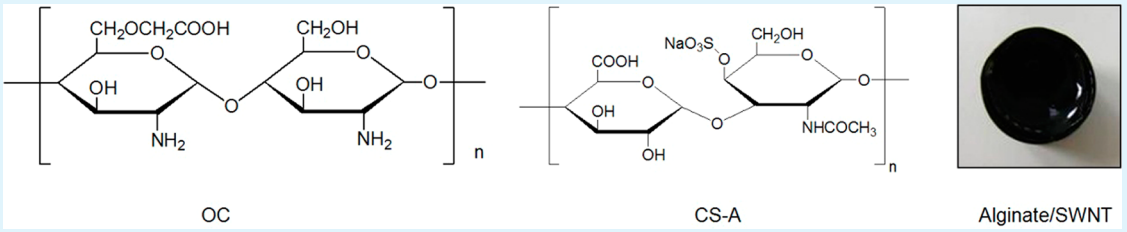
Supporting Information



ABSTRACT: Here we demonstrate a polysaccharide hydrogel reinforced with finely dispersed single-walled carbon nanotubes (SWNTs) using biocompatible dispersants O-carboxymethylchitosan (OC) and chondroitin sulfate A (CS-A) as a structural support. Both of the dispersants can disperse SWNTs in aqueous solutions and hydrogel matrix as individual tubes or small bundles. Additionally, we have found that compressive modulus and strain of the hydrogels reinforced with SWNTs were enhanced as much as two times by the addition of a few weight percent of SWNTs. Moreover, the SWNT-incorporated hydrogels exhibited lower impedance and higher charge capacity than the alginate/dispersant hydrogel without SWNTs. The OC and the CS-A demonstrated much higher reinforcing enhancement than a commercially available dispersant, sodium dodecyl sulfate. Combined with the experimental data on the mechanical and electrical properties, the biocompatibility of OC and CS-A can provide the possibility of biomedical application of the SWNT-reinforced hydrogels.

KEYWORDS: *O-carboxymethylchitosan, chondroitin sulfate A, reinforced hydrogel, SWNT, biocompatibility, alginate*

1. INTRODUCTION

Although hydrogels are widely used in diverse biomedical applications because of their soft nature, biocompatibility, the ability to incorporate large amounts of water, and resemblance to native extracellular matrix,[1−8] poor mechanical and electrical properties of the hydrogels often limit their practical applications.[9−13] To improve the mechanical and electrical properties of hydrogels, there have been several attempts to incorporate carbon nanotubes (CNT) into a hydrogel matrix, including hyaluronic acid, alginate, chitosan, and polyvinyl alcohol.[11−17] Studies to improve biocompatibility of CNT incorporated hydrogels have also been reported.[11] To fully exploit high strength and stiffness of nanotubes in composites, the nanotubes should be debundled and well-dispersed in the matrix. Single-walled carbon nanotubes (SWNTs) typically tend to aggregate into bundles through intertube van der Waals forces; the resulting bundles have lower surface area to volume ratio, which reduces their reinforcement value.[18,19] Two approaches are often adopted to disperse CNTs: surface functionalization and surfactant stabilization.[20−27] It has been reported that the surface functionalization compromises structural and electrical properties of CNT due to defects formed on their sidewalls,[28] whereas the surfactant stabilization maintain original states of CNT. Despite the improved structural property, there have been only few reports on biomedical applications of the CNT/hydrogel composites because nonbiocompatible dispersants, such as poly(methacrylic acid) and cetyltrimethylammonium bromid, have been used to disperse CNTs in hydrogels. Undoubtedly, biocompatibility of surfactants is of great importance, but only few surfactants are known to be biocompatible.[29]

We have reported O-carboxymethylchitosan (OC)[30] and chondroitin sulfate A (CS-A)[31] (Figure 1a and 1b) to disperse SWNTs in aqueous solutions. We found that these dispersants noncovalently wrap around SWNTs without damaging their structures, thus preserving the mechanical and electrical properties of SWNTs. Additionally, it has been reported that alginate is able to form hydrogen bonds with polysaccharides, such as chitosan,[32] cellulose,[33] pullulan,[33] and glucomannan,[34] as well as other materials, such as peptide,[35] gelatin,[36] poly(ethylene oxide),[37] etc. This hydrogen bond plays an important role in the stability of alginate hydrogels.[35] Specifically, the intermolecular hydrogen bonds between O-carboxymethylchitosan (OC) and alginate has been experimentally shown in the previous study by Fan L. et al.[38] Hydrogen bonding also occurs in CS-A-based materials.[39,40]

On the basis of our previous study, we postulated that alginate (Figure 1c) is compatible with OC and CS-A, because they are all polysaccharides. The SWNT-reinforced hydrogel using OC and CS-A as a dispersant can not only, because of

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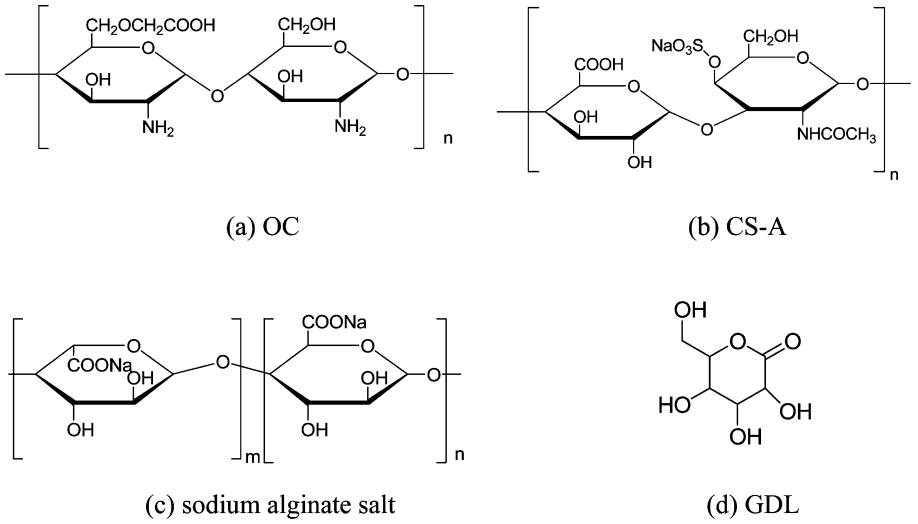

Figure 1. Chemical structures of (a) OC, (b) CS-A, (c) sodium alginate salt, (d) GDL.

their biocompatibility, improve its mechanical and electrical properties but also could be a good candidate for biomedical applications, such as implantable electrodes and biofuel cells, where biocompatibility plays a major role in the device performance.[41,42]

In this article we report alginate/SWNT composite hydrogels, in which SWNTs are dispersed by polymer-wrapping. Sodium alginate was gelled by divalent calcium ions supplied by calcium carbonate in the presence of D-glucono-δ-lactone (GDL) (Figure 1d). Compressive properties, water swelling, electrical impedance, and charge capacity of the composite hydrogels were measured and analyzed.

2. EXPERIMENTAL DETAILS

2.1. Materials. All chemicals were purchased form Sigma-Aldrich (Singapore) and theyr are in research grade and used as received. The synthesis procedure of OC has been reported previously.[30] SWNTs were bought from Chengdu Organic Chemicals Co. Ltd. (China). The received SWNTs were heated in air at 350 °C for 1 h and refluxed in 3 M HCl for 10 h to remove the impurities. The purified SWNTs were then collected onto a filter paper via vacuum filtration and thoroughly washed with deionized (DI) water until the washing water dripping from the filter paper was neutral in pH. The solid on the filter paper was lyophilized (Christ Alpha 1−2 plus model) to a loose powder which was utilized for all subsequent purposes.

2.2. Preparation of Alginate Solution. To make 2 wt % alginate solutions, we added 0.9 g of sodium alginate to 45 mL of deionized water and stirred it at room temperature for 1 day to ensure that the alginate was completely dissolved. One-hundred ninety-eight grams of calcium carbonate was added into 45 mL of alginate solution. The mixture was sonicated (SONICS, VCX-750, 150 W) for 30 min (10 s on/10 s off cycle in ice) in order to break the calcium carbonate into small particles.

2.3. Preparation of Dispersed SWNT Solutions. Two weight percent polymer (OC or CS-A) solution was used to disperse SWNTs. Using a 1 wt % SWNT (the concentration of SWNTs was based on the weight of alginate) in hydrogel as an example, 3 mg of SWNTs were added into a 5 mL polymer solution. The mixture of SWNTs and polymer solution was sonicated at 100 W with tip sonication in water-ice bath continuously for 1 h.

2.4. Preparation of Alginate Hydrogels. A 24-well polystyrene cell culture dish was used as the gel formation mold. 1.5 mL alginate solution and 6.6 mg calcium carbonate was used for one gel sample. To make hydrogels without SWNTs, we added a mixture of 6.6 mg of calcium carbonate in 1.5 mL of alginate solution into each well, followed by 0.5 mL of pure polymer (OC or CS-A) solution. This mixture was stirred until it was homogeneous. Then, 23.5 mg of D-glucono-δ-lactone (GDL)[43] (a divalent calcium ions supplier) (Figure 1d) was added into each well and the mixture was stirred another 20 min. The final mixture was left standing for 2 days at room temperature to harden. To prepare SWNT-reinforced hydrogels, we added 0.5 mL polymer-SWNTs solution of 0.5 mL pure polymer solution instead. The SWNT content varied from 0.5 wt % to 5.0 wt %. Another set of alginate gels using a commercial surfactant, SDS, was also prepared for comparison.

2.5. Mechanical Measurement. Hydrogel compression stress−strain tests were performed at 25 °C with an Instron 5543 mechanical tester with a 10 N load cell. Compression tests were done with the surface of the hydrogels flat and parallel. The hydrogels were cut to small pieces with a thickness and diameter of 0.5 and 1.5 cm, respectively, to obtain flat and parallel surfaces for mechanical testing. At least 5 samples were tested for each type of alginate hydrogel.

A typical stress−strain graph determined from these tests (see Figure S1 in the Supporting Information), the definition of the primary modulus (E_1), the secondary modulus (E_2), and the ultimate compressive stress are presented in the Supporting Information.

2.6. Swelling Measurement. Hydrogels were lyophilized for 24 h and then immersed in water for saturation. Then the hydrogels were removed from the water and quickly dried on filter paper to eliminate residual surface water. The percentage of swelling (S%) was calculated as eq 1

$$S\% = 100\frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \quad (1)$$

2.7. Electrical Properties Measurement. Electrical properties of SWNT-reinforced hydrogels were analyzed by cyclic voltammetry (CV) and electrical impedance spectroscopy (EIS) using a CHI 660 electrochemical workstation in the standard three cell configuration. An Au disk electrode with a diameter of 2 mm was used as the working electrode. A platinum wire and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Before modification of the working electrode with hydrogel, all electrodes were cleaned by polishing with 1, 0.3, and 0.05 μm aluminum powder, followed by sonication in DI water for 5 min. After the mechanical cleaning, the electrodes were immersed into 0.5 M H_2SO_4 and swept between −0.4 and 1.4 V until the CV curve of the unmodified electrodes became stable. Ten μL of the prepared hydrogel precursor solution containing Ca^{2+} ions was dropped on top of the Au electrode using a micropipet and then kept for two days in a humid environment before the electrical properties measurement.

During measurement, CV was performed between −0.6 and 0.8 V with a scan rate of 0.1 V/s and alternating current (AC) impedance was measured between 1 HZ to 100 KHZ with an AC amplitude of ±5

mV. The charge capacitance of the hydrogel modified electrode was calculated by eq 2:

$$\text{charge storage capacitance} = CV \text{ area}$$

$$\text{charge storage capacity} = \frac{CV \text{ area}}{2 \cdot \text{scan rate}} \quad (2)$$

3. RESULTS AND DISCUSSION

3.1. Morphology Observation. To make the SWNT-reinforced hydrogels, we finely dispersed SWNT in the OC and CS-A solutions with an assistance of sonication. After gelation with GDL for 2 days at room temperature, the mixture with/without SWNT turned into relative rigid gels. Figure 2 shows

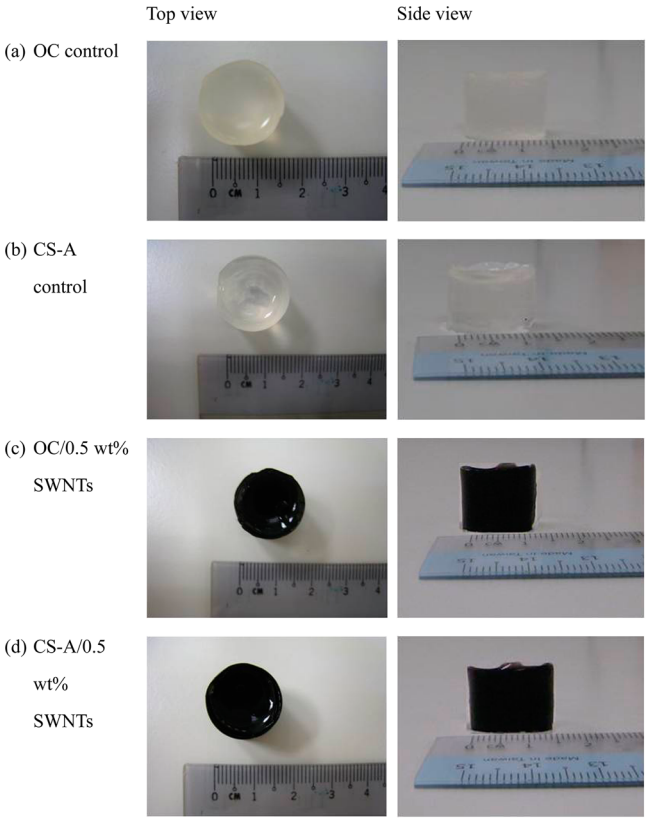

Figure 2. Photographs of representative hydrogels: (a) control with OC dispersant, (b) control with CS-A dispersant, (c) with 0.5 wt % SWNTs using OC, (d) with 0.5 wt % SWNTs using CS-A.

the gross visual appearance of alginate hydrogels made with and without SWNTs. Both OC and CS-A controls without SWNTs are translucent, whereas those containing SWNTs are opaque black with no visible color difference between gels containing different amount of SWNT.

3.2. Mechanical Property Analysis. To confirm our hypothesis that alginate may be compatible with OC and CS-A, we investigated the mechanical properties of the SWNT-reinforced hydrogels using OC and CS-A as dispersants by three parameters, i.e., the ultimate compressive stress (σ_u), primary modulus (E_1), and secondary modulus (E_2). Figure 3 shows the obtained σ_u, E_1, and E_2 of hydrogels made with OC and CS-A and various SWNT contents. For the purpose of comparison, SDS, a commercial surfactant, was used as a control. The numerical data are presented in Tables S1−S3 in the Supporting Information.

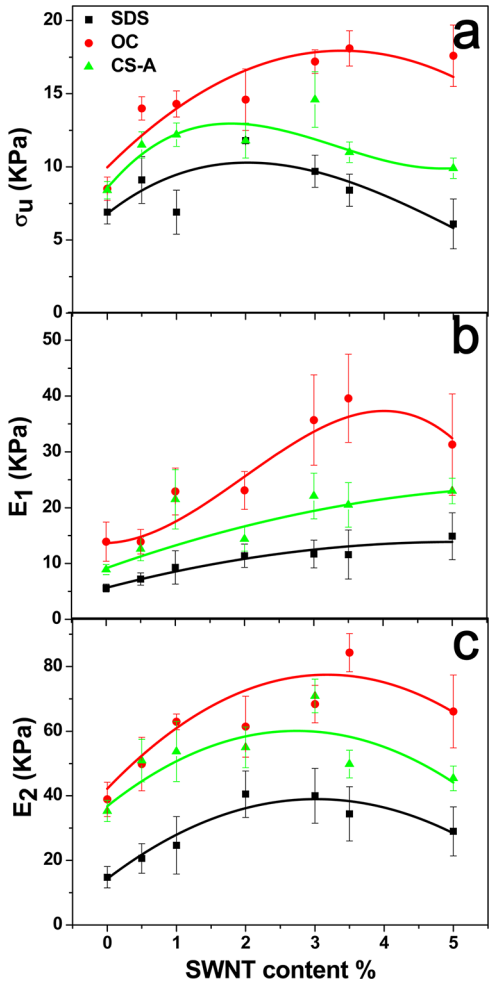

Figure 3. Effect of SWCNTs content on the (a) ultimate compressive stress (σ_u), (b) primary modulus (E_1) and (c) secondary modulus (E_2) of alginate hydrogels using SDS, OC, and CS-A as dispersants.

The compressive strength and moduli of all the hydrogels made with OC or CS-A are higher than those with SDS. Among those two biocompatible dispersants, OC exhibits better compressive properties than CS-A. For all samples, the measured mechanical properties improve with increasing SWNT content at low contents, followed by plateau or decline at the higher range of tested SWNT contents.

Specifically, using OC as a dispersant, σ_u, E_1, and E_2 of the hydrogels increase with SWNT contents and reached a maximum at around 3.5 wt %. With 3.5 wt % SWNT, the ultimate compressive stress (18.1 ± 1.2 kPa) and secondary modulus (84.3 ± 5.9 kPa) are more than two times those of pure alginate gel (σ_u = 8.5 ± 0.8 kPa, E_2 = 38.9 ± 5.5 kPa), whereas E_1 (39.6 ± 7.9 kPa) increases to almost 3 times that of pure alginate gel (13.9 ± 3.5 kPa). Beyond 3.5 wt % SWNTs, the E_1 and E_2 moduli decrease and σ_u does not increase. We postulate that at SWNT loading higher than the observed optimal loading, there is significant SWNT reaggregation during the prolonged gelation period.

Using CS-A dispersant, σ_u and E_2 of the hydrogels increase with SWNTs content and reached a maximum at around 3 wt %. σ_u and E_2 of hydrogel dispersed with CS-A (14.6 ± 1.9 kPa and 70.9 ± 5.2 kPa) are around two times higher than those of the CS-A control (8.4 ± 0.6 kPa and 35.3 ± 3.3 kPa). E_1 plateaued at 3 wt % SWNT.

With SDS surfactant, at the optimum SWNT content of about 2 wt %, the σ_u (11.8 ± 1.2 kPa) and E_2 (40.5 ± 7.2 kPa) are nearly two times those of pure alginate gel (σ_u = 6.9 ± 0.8 kPa, E_2 = 14.8 ± 3.3 kPa); E_1 plateaued at 2 wt % SWNT (up to 14.9 ± 4.2 kPa) to 3 times of pure alginate (5.6 ± 0.7 kPa).

Among the three dispersants, OC appears to be most effective in improving the compressive properties, while SDS is the least. This is probably because, in OC and CS-A dispersants, particularly the former, the presence of O and N atoms promotes hydrogen bonding with the alginate matrix (Figure 1). Because of abundant amine groups present in OC, which likely facilitate the formation of more hydrogen bonds with alginate matrix than CS-A,[32] the OC hydrogel exhibits better mechanical properties than CS-A hydrogel. The less ionizable hydroxyl, carboxyl, and amine groups on OC would afford more sites for hydrogen bonding than CS-A, which contains highly ionizable sulfate group. The multiple sites of interaction on a single macromolecule of OC and CS-A may promote stress transfer between alginate matrix and SWNT to account for their higher increase in compressive properties compared to the small molecule SDS. Both OC and CS-A have hydroxyl and carboxyl groups, which are able to form hydrogen bonds with alginate matrix.

To understand the influence of SWNT incorporation on the swelling behavior of the hydrogels, we investigated the swelling ratios of the specimens with OC, CS-A, and SDS dispersants and tabulated the results in Table 1. Most of the specimens

Table 1. Swelling Ratios for Hydrogels Using OC, CS-A, and SDS as Dispersants

	swelling ratio		
SWNT content %	OC	CS-A	SDS
control	19.83 ± 0.10	19.41 ± 0.06	20.27 ± 0.04
0.5	16.86 ± 0.09	17.87 ± 0.04	19.41 ± 0.06
1	17.18 ± 0.16	17.18 ± 0.09	18.23 ± 0.17
2	20.28 ± 0.11	18.61 ± 0.04	19.41 ± 0.10
3	16.86 ± 0.04	17.18 ± 0.02	20.74 ± 0.17
3.5	15.95 ± 0.07	16.24 ± 0.12	19.41 ± 0.04
5	16.24 ± 0.03	17.52 ± 0.09	16.54 ± 0.07

exhibited high swelling ratios compared to previous reports, for example, swelling ratio of less than 10 for MWCNT-modified gelatin gel,[44] CNT/PVA hybrid hydrogels,[16] and the CNT-incorporated alginate microsphere.[13] A slight decrease in the swelling ratio upon SWNT incorporation was observed, indicating that SWNT inhibited the swelling of the gel matrix.[44] There was no significant difference in the water uptake capacity when the SWNT content was lower than 3.5 and 2% for SDS and OC samples, respectively, whereas the swelling ratio for CS-A samples was not changed regardless of the SWNT content.

3.3. Electrical Property Analysis. The electrical properties of SWNT-reinforced hydrogels were characterized with charge capacitance and electrochemical impedance spectroscopy, which are important properties for implantable recording/stimulating electrodes.[45] Alginate hydrogel precursor solution containing finely mixed SWNTs were dropped on gold electrodes (2 mm in diameter) and gelled for electrochemical measurements (gel thickness of ~3 mm). Figure 4 shows the electrodes covered with hydrogels without or with SWNT using OC as a dispersant.

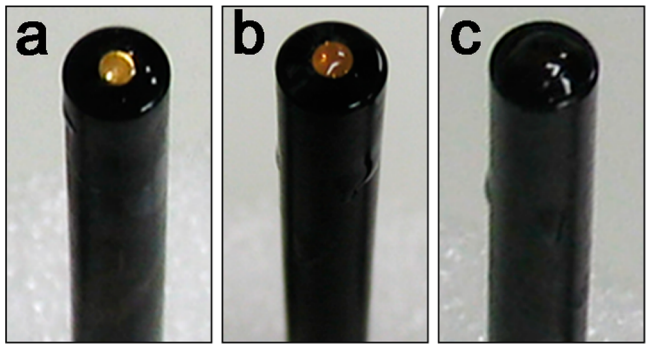

Figure 4. Electrodes modified with hydrogels containing a dispersant, (a) OC (control), (b) 0.5% and (c) 2% SWNT using OC as dispersants.

Figure 5 shows the CSC and the impedance of electrodes modified with hydrogel at various SWNT contents. Hydrogel

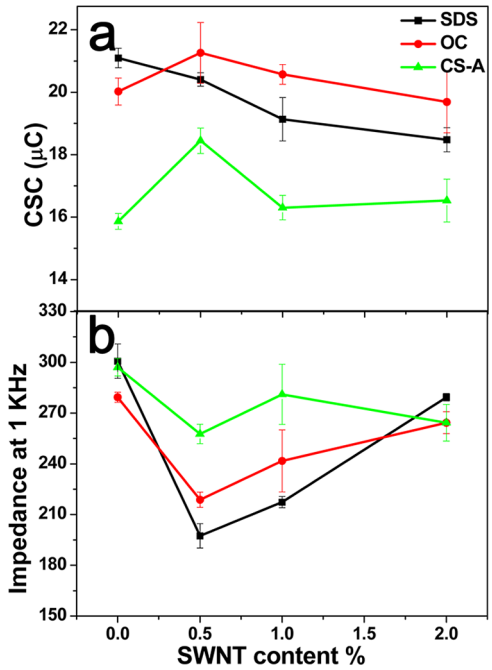

Figure 5. (a) Charge storage capacitance (CSC) and (b) impedance at 1 kHz of hydrogel-modified electrodes as a function of SWNT contents (n = 5).

coatings on electrode generally show a small drop in CSC,[46] which was also observed in our study; the CSC of bare electrode is 25 μC. However, the incorporation of SWNTs dispersed with OC or CS-A into the hydrogel results in an increase of the CSC of modified electrodes. This effect is not linear with SWNT content; the maximum enhancement was at SWNT content of 0.5 wt %. Charge transfer in hydrogels are mainly via the movements of charged ions.,[46] We therefore speculate that, as SWNT content increases, ionic movement in the hydrogel could be significantly hindered by SWNT, resulting in decrease in CSC, whereas such interruption is minimal with low SWNT content in hydrogel. Based on the charge storage capacity, the hydrogel-modified electrode using OC as SWNT dispersant shown an optimal performance, followed by SDS, and then CS-A.

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The impedance of the modified electrodes at biologically important frequency, 1 kHz, was lower than a control (180 Ω) for all dispersants, indicating that the electrical properties of the modified hydrogel were not hindered by the SWNT incorporation. The lowest impedance was achieved when 0.5 wt % SWNT was used regardless of the type of dispersants.

Because of their high ion permeability and biocompatibility, hydrogels have been used for implantable electrodes to mediate foreign body response.[11,47−49] However, relatively poor signal-to-noise ratio was reported for the hydrogel-modified electrode possibly because of an increase of distance between neurons and electrodes.[50] In addition, poor mechanical properties of hydrogels have significantly limited their widespread use, particularly in the place where the hydrogels need to provide structural support, such as bone- and tissue regeneration. We foresee the SWNT-modified electrode favors the electrical signal transduction, thus leading to improved signal recording performance of neural electrodes. Combining the enhanced mechanical strength from incorporated SWNT and the improved biocompatibility by OC and CS-A dispersants, our modified hydrogels have great potential for the tissue-electrode interface, where significant electric transportation is required.

4. CONCLUSION

In this study, SWNTs were used to reinforce alginate hydrogels using biocompatible dispersants, OC and CS-A. SWNT-reinforced hydrogels showed increased compressive properties as large as two times that of unreinforced controls. OC and CS-A, particularly the former, demonstrate much higher reinforcing enhancement than commercial dispersant, SDS. Hydrogels reinforced with 0.5 wt % SWNTs dispersed by OC have lower impedance and higher charge capacity than unreinforced alginate/OC hydrogel. The results show that OC and CS-A could successfully incorporate SWNTs into alginate hydrogel, improving its mechanical and electrical properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table summarizing the mechanical and electrical properties of the hydrogels. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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