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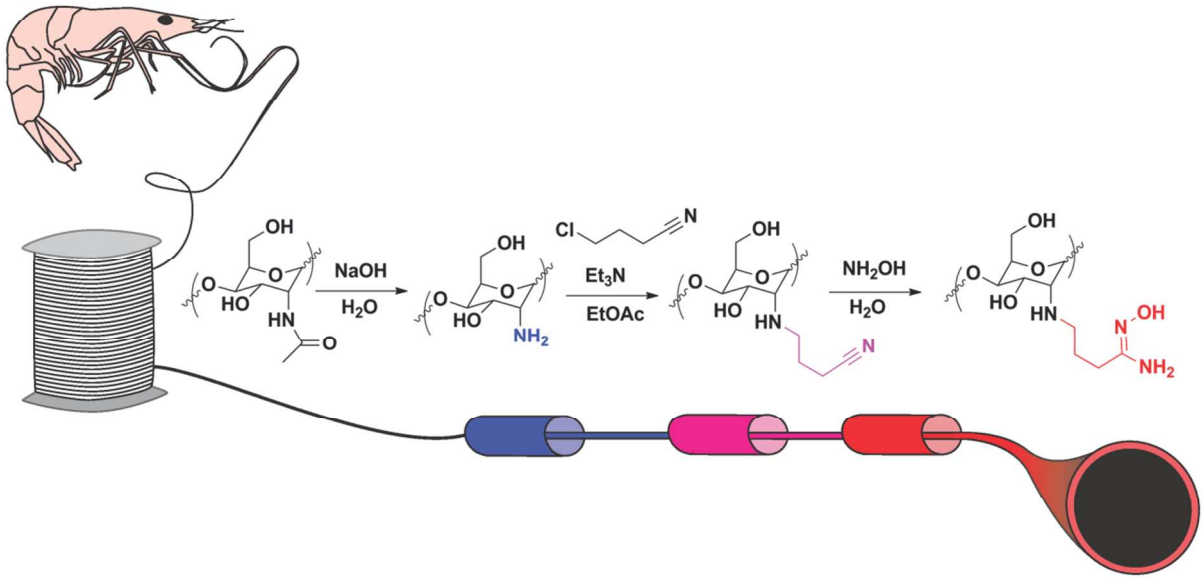

A platform was developed for the surface modification of ionic liquid-spun chitin fibers, that provides the physical properties of chitin with chitosan's functional properties on the surface.

Surface Modification of Ionic Liquid-Spun Chitin Fibers for the Extraction of Uranium from Seawater: Seeking the Strength of Chitin and the Chemical Functionality of Chitosan

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Abstract

Chitin fibers, prepared by extracting chitin directly from shrimp shell waste and dry-jet wet spinning from the resulting ionic liquid (1-ethyl-3-methylimidazolium acetate) solution in a one-pot process, were surface modified by taking advantage of the insolubility of chitin in common solvents (e.g., water, organics). In this proof of concept example, the chitin fiber surfaces were first deacetylated using aqueous NaOH to make available the primary amine (the functional group of chitosan) on the surface. Further treatment of the fibers allowed for the task-specific tailoring of the functionality (here we appended amidoxime for the extraction of aqueous uranyl ions from seawater). Compositional analysis and physical property measurements (e.g., tensile strength and thermal decomposition) of the fibers before and after surface modification indicated minimal change to the bulk material; however, spectroscopy and sorption studies of uranyl ions from aqueous solution demonstrated surface modification. The lower cost, one-pot process used in this study resulted in weak and brittle fibers, suggesting that additional purification of the chitin before pulling fibers will greatly improve the strength and utility of the resulting material. Overall, a platform has been developed for the surface modification of chitin fibers that provides both the physical properties of chitin and the functional properties of chitosan, resulting in an advanced material from a biorenewable resource with reduced chemical input.

Introduction

Chitin and its deacetylated derivative chitosan (Fig. 1) are renewable biopolymers that have numerous applications in today's society.[1-5] Yet, chitin generated from the seafood industry is routinely disposed of as solid waste at great cost and land use.[6-8] Increasing beneficial reuse of this material is an economic and environmentally sound goal.

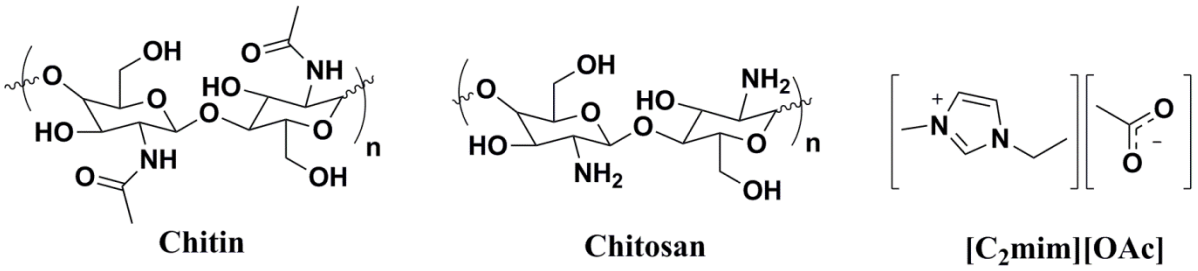


Fig. 1. Chemical structures of chitin, chitosan, and 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]).

Currently, the industrial method for the isolation of chitin utilizes strong acids and bases which can compromise the integrity of the biopolymer by decreasing the naturally high molecular weight.[9,10] In addition, this process also partially converts chitin into chitosan, which has a different set of properties. Chitosan is normally prepared by the treatment of chitin with strong base to convert the N-acetyl groups to primary amines. This process also typically decreases the molecular weight of the material, and there are many studies which have attempted to reduce this loss in molecular weight.[11,12]

The properties of chitin and chitosan are quite different and depend significantly on two main structural features, degree of deacetylation (%DDA) and molecular weight.[11,13] With increased %DDA, the polymer becomes more soluble in acidic solutions, as well as becoming more easily modified chemically due to the amine functional groups. While this processing provides routes to new materials, the decreased molecular weight affects properties such as strength, solubility, and biodegradability which can change significantly.[11] For applications using chitosan, the modification of the entire polymer before making the final material degrades strength and includes unnecessary or wasted chemicals from unnecessary derivatization. The harsh initial processing conditions to obtain chitin combined with the degradation of desired properties upon deacetylation of the entire polymer, severely limits the resulting material properties and potential applications.[14]

Recently our group has shown that high purity, high molecular weight chitin can be extracted directly from shrimp shell waste in a one-pot process using ionic liquids[15,16] (ILs, defined as salts that melt below 100 °C[17]). Chitin fibers, films, and beads can be prepared directly from these IL solutions by coagulating them with an antisolvent such as water.[15] Indeed, in one application we have found that the chitin we extracted directly from shrimp shells could be easily electrospun into chitin nanofibers as a direct result of its much higher MW compared to commercially available chitin sources.[18,19] The preparation of fibers, films, beads, and other materials with chitin, rather than with chitosan, results in materials which have the strength of chitin, but lack the chemical functionality of chitosan.[20]

We have sought ways to combine the favorable properties of both materials, such as the reactivity of chitosan with the toughness and insolubility of chitin, while preserving their biodegradability. Because chitin is insoluble in virtually every solvent, it is especially suited to surface-selective functionalization. Surface functionalization has the potential to preserve many of the good properties that are lost by completely converting chitin to chitosan. Because only a small fraction of the chitin would need to be converted, the physical properties should correspond to those of bulk chitin. However, for applications such as metal adsorption where the reactivity occurs at the surface, both the capacity and reactivity of surface-functionalized chitin should be indistinguishable from those where the entire material has been converted. Further, by controlling the surface area (e.g., by electrospinning nanofibers of chitin[18,19]), one has control over the capacity of each fiber for chemical modification.

The solubility of high MW chitin in ILs provides a ready route to these materials. The chitin can be extracted directly from crustacean shells in a single step and directly spun into fibers, cast as films, or coagulated as beads. (If high purity chitin is required, the extracted chitin can first be coagulated as a floc and redissolved prior to preparing the final material, but at added cost.[15,16,18,19]) The insolubility of these chitin materials in aqueous media allows direct surface functionalization *via* deacetylation with base followed by reaction at the exposed amine. Such a strategy should greatly reduce the amount of time, energy, and chemicals needed to prepare functionalized chitin materials. The combination of IL-based forming of chitin followed by surface functionalization leads to a platform for making a plethora of new functional materials[14] which overcome the disadvantages of both chitin (lack of solubility and lack of reactive amines) and chitosan (lack of strength and lack of durability).

In this paper, we have selected one possible application for these fibers from a U.S. Department of Energy project aimed at developing high capacity adsorbents for the extraction of uranium from seawater[21] as a proof-of-concept demonstration. Successful implementation would require a fiber strong enough to withstand deployment in the sea, with the chemical functionality required to append the uranium selective extractant to the fiber surface. The current benchmark process is to use a sorbent made by grafting uranyl-selective amidoxime functional groups[22,23] onto synthetic polyethylene polymers using high energy irradiation techniques.[24] A recent cost analysis indicated that the adsorbent comprises 43% of the total cost for extracting uranium from seawater,[25] and research has focused on lowering the cost through increasing adsorbent capacity and recycling by increasing the surface area[26-28] or developing alternative functional groups to amidoxime.[29,30] Even though polyethylene polymers are a major source of anthropogenic marine pollution[31,32,33] and are made from nonrenewable petroleum, there has been little emphasis on lowering the cost or environmental impact of the process by changing the sorbent backbone to a more suitable material.

The strength, durability, and water resistance of polyethylene materials are sufficient for long term marine deployment,[34] however, in our opinion, the main reason for the use of polyethylene is simply that it was the first polymer backbone used and it worked. We believe that the material which will ultimately be used in this application must address the environmental concerns about polyethylene while meeting or exceeding its performance. We have thus proposed an alternative strategy to use a naturally available waste material, shrimp shells, to obtain a high molecular weight chitin which could be used to prepare strong, high surface area, biodegradable sorbents. Here, we demonstrate the preparation, characterization, and utilization of chitin fibers *via* dry-jet wet spinning of a solution of chitin extracted from shrimp shells in 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]), and the surface functionalization of the fibers with the uranyl-selective amidoxime functional group.

Experimental

Chemicals

Reagents were used as obtained from Sigma-Aldrich, Milwaukee, WI, unless otherwise noted. All solvents were 'solvent grade' and used as received without additional purification. 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]) was purchased from Iolitec (Ionic Liquids

Technologies, Inc., Tuscaloosa, AL). Deionized (DI) water was acquired from an in-house system (Culligan Water Systems, Chattanooga, TN) with a measured resistivity of 17.4 MΩ. Dried shrimp shells were received from the Gulf Coast Agricultural and Seafood Cooperative in Bayou La Batre, AL where the shrimp shells were dried at a specialized facility by pressing with a screw press to eliminate the majority of the water, followed by heating at up to 160 °C in a fluidized bed dryer until the material had a final moisture content of less than 5 wt%. The material received from the drying facility was ground using an IKA Works Universal Grinding Mill (Wilmington, NC) and sieved to give a powder with a particle size of <250 μm. Ground shrimp shells were further dried in a Precision Scientific Econotherm Laboratory Oven, Model 1025 (Winchester, VA) at 80 ºC for 24 h. 'Regenerated and purified chitin' refers to chitin that has been extracted from shrimp shells using [C_2mim][OAc], coagulated, washed, sonicated in water, and then dried in the oven at 80 ºC for 24 h.[15]

Preparation of Chitin Fibers from Shrimp Shells (SS Fibers)

Extraction of chitin from dried shrimp shell was performed using a domestic microwave oven (SHARP Carousel R-209KK, Mahwah, NJ) using a previously reported procedure.[15,16] *CAUTION!* Care must be taken when using microwave heating because [C_2mim][OAc] is an efficient microwave absorber and heating occurs rapidly, which can easily lead to degradation of the ILs, and/or chitin, or even explosions of sealed systems.

All solutions were made in a similar fashion with an appropriate mass of shrimp shell being added to a mass of IL corresponding to a final weight percent (wt%). For example, a 6 wt% solution was prepared by mixing 19.290 g ground shrimp shell in 301.044 g [C_2mim][OAc] to give a total mass of 320.330 g. The mixture was heated at full power for six 10 s long pulses, followed by 48 5 s long pulses for a total heating time of 5 min. The solution was stirred by hand with a glass stirring rod between pulses and was observed to darken slightly with time during the heating. After dissolution, the solution was centrifuged to remove insoluble materials, loaded into four 60 mL syringe tubes, and degassed in an oven at 80 °C overnight resulting in approximately 60 mL of solution per syringe.

The four syringes filled with chitin-IL solution were used to prepare chitin fibers following a dry-jet wet spinning method as described previously for producing cellulose and chitin fibers from IL solution.[35,15] The spinning setup consisted of a syringe pump (for controlled rate of

extrusion), a water bath (for coagulation of chitin and dissolution of IL), godets within the water bath (for fiber stretching), and a spool (for collection of spun fibers). After degassing, each syringe was attached to the syringe pump (Model No. NE-1010, New Era Pump Systems, Inc., Farmingdale, NY) with a temperature jacket and controller set to 80 °C. Each solution was extruded into a 0.6 m long water bath after a small air gap (~1.5 cm). The regenerated chitin filament was led through the pair of godets twice, to provide adequate fiber stretching and elongation, and then collected onto a spool. The syringe pump was set at an extrusion rate of 1.5 mL/min. The voltage setting for the motor spinning the godets was 4.2 V. DI water was used as the coagulant. Each spool of fibers was then placed in a 600 mL beaker and soaked in 500 mL DI water for 2 days, exchanging the water several times to remove the residual IL. Four spools containing approximately 1 g (dried weight) of fibers each were obtained. One set of fibers (SS fibers) was air dried for analysis, while the remaining three spools of fibers were stored in water until the desired surface modification was complete.

Deacetylation of Chitin Fibers (DA Fibers)

Three of the four spools of chitin fibers were treated in the standard method for preparing chitosan. The amounts of reagents were chosen to ensure an excess. About 1 g SS of fibers was removed from each of three spools and placed in separate 400 mL beakers. To each beaker was added 200 mL of 1.25 M NaOH and a magnetic stir bar. The beakers were covered with watch glasses and the mixtures were heated at 80 °C for 8 h with stirring. After 8 h, the fibers appeared to lighten in color, and the liquids were decanted. Each set of DA fibers was washed with DI water a total of three times (3 x 100 mL) with swirling. One set of DA fibers was air dried for analysis while the remaining two sets of fibers were carried through immediately to the next modification without drying. No visible changes were observed during this process.

Nitrile Functionalization of Deacetylated Fibers (CN Fibers)

Two of the three sets of DA fibers were treated to append a nitrile to the primary amine. The amounts of reagents were chosen to ensure an excess. 200 mL of ethyl acetate was added to each portion of ~1.00 g DA fibers. 293 µL (0.321 g, 3.10 mmol, 0.5 eq.) 4-chlorobutyronitrile and 441 µL (0.320 g, 3.20 mmol, 0.51 eq.) triethylamine were then added and the mixtures were covered with a watch glass and heated at 50 °C overnight. After completion, the liquids were

decanted and 50 mL ethyl acetate was added to the fibers and swirled to wash the fibers of residual reagents. The CN fibers were washed a total of three times with 50 mL ethyl acetate each. One set of CN fibers was carried through to the final step, while one set was dried in air for analysis. No visible changes were observed.

Amidoxime Functionalization of Nitrile Fibers (AO Fibers)

In the final step, CN fibers were treated with hydroxylamine to convert the nitrile group to an amidoxime group. Here, 200 mL of DI water was added to a 400 mL beaker containing ~1.00 g CN fibers and a magnetic stir bar. 0.570 µL (0.614 g, 9.30 mmol) 50% hydroxylamine in water was then added to ensure an excess and the reaction mixture was covered with a watch glass and stirred at 80 °C overnight. The liquid was decanted and the AO fibers washed with 3 x 50 mL water using a swirling action. No visible changes were observed. These fibers (AO fibers) were dried in air for analysis.

Fiber Characterization

The chitin content of the dried shrimp shell and fibers were measured by the Black and Schwartz method.[36] Infrared (IR) spectra were obtained in the range ν_{max} = 400–4000 cm^{-1} on a Bruker Alpha FT-IR instrument, Bruker Optics Inc. (Billerica, MA) with an attenuated total reflection (ATR) sampler by pressing solid samples directly against the ATR diamond. IR spectra were recorded on whole fibers, as well as fibers ground by hand into a powder.

X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS 165 Multitechnique Electron Spectrometer (Kratos Analytical Ltd, Manchester, U.K.). Samples were loaded on copper tape. Monochromated Al-Kα radiation was used as the excitation source. Peaks were plotted in binding energy space and assigned based on reference data from the PHI *Handbook of X-Ray Photoelectron Spectroscopy*.[37]

Thermogravimetric analyses (TGA) were conducted with a Mettler-Toledo (Columbus, OH) DSC/TGA 1. The instrument's internal temperature was calibrated by observing the melting points of Au, Zn, and In. Samples of 5–10 mg were analyzed in 70 µL alumina pans under an air atmosphere. All samples were heated from room temperature to 75 ºC with a 30 min isotherm at 75 °C in order to ensure excess volatiles or residual solvents were removed. Following the

isotherm, samples were heated to 1000 ºC at 5 ºC/min, then held at 1000 ºC for 30 min. Decompositions temperatures were recorded as the onset to 5% weight mass loss ($T_{5\%dec}$).

The tensile properties of the fibers were determined using a MTS Q-Test 25 machine (Eden Prairie, MN) equipped with a specially designed pneumatic grip suitable for thin and flexible fiber testing. A load cell of 22.4 N capacity was used for load measurement. The cross head speed was maintained at 1.27 mm min^{-1} from an initial cross head distance of 15.24 cm. For this measurement, additional fibers of each type were prepared following the exact protocol from above. Before drying, the fibers were cut into approximately 38 cm pieces, laid on the bench top, and then air dried. Fibers were inspected and those with no visible defects were chosen for testing. Cross-sectional areas were measured using digital calipers with 0.0254 cm precision at seven points along the fiber spaced approximately 2.5-5 cm apart and averaged. The tensile strength of the fibers was measured using single fibers and at least seven fibers of uniform cross-section from each type were tested.

Radiotracer Distribution Experiments

CAUTION! ^{233}U is a radioactive alpha and gamma emitter and appropriate training and laboratory safety methods should be observed. Minimize handling time and activity used to reduce exposure. Consult and comply with all local regulations regarding storage and disposal of radioactive materials.

Distribution ratios were determined by measuring activities in counts per minute (cpm) using a Packard Cobra-II gamma counter (Meriden, CT). All dry weight distribution ratios were determined radiometrically by batch contacts of the fibers with the desired solutions at 25(1) °C. The dry weight distribution ratios were calculated as in eq. 1:

$$\mathbf{D_w} = \left(\frac{A_o - A_f}{A_f}\right)\left(\frac{V_{(aq)}}{m_R(dwcf)}\right) \quad \textbf{(1)}$$

where A_o is the count rate in solution prior to contact with the fiber, A_f is the count rate in solution after contact with the fiber, V is the volume (mL) of solution in contact with the fiber, m_R is the mass (g) of wet fiber, and the dry weight conversion factor (dwcf) allows conversion to the dry mass of fiber.

To determine the dry weight conversion factor for each type of fiber, clean one dram (3.70 mL) borosilicate glass shell vials were dried to constant weight in the oven at 110 °C and their

tare weights were recorded. Approximately 4-5 mg of each of the four fibers were placed in the tared vials and the fibers were then dried to constant weight in the oven at 110 °C. The mass of the dried fibers was divided by the mass of the wet fibers to determine the dry weight conversion factor (dwcf). The dwcfs were measured in triplicate for each fiber and were determined to be: 0.93(1), 0.964(3), 0.96(1), and 0.963(7) for SS, DA, CN, and AO fibers, respectively. The averaged values were used for all calculations using eq. 1.

Each batch uptake experiment was performed by adding 5 μL of 1 μCi/1 μL aqueous $^{233}UO_2Cl_2$ to 1.3 mL of DI water, gently mixing, and removing a 150 μL aliquot for gamma counting (A_o). A total of 1 mL of the remaining solution (V) was added to a known mass (~2.5 mg) of wet fibers (m_R). The mixture was then shaken at 75 rpm on a New Brunswick Scientific C25 Incubator shaker table (Edison, NJ) at 25 °C. Aliquots of each solution were taken for counting at 1.5, 4, 22, 44, and 144 h. To remove aliquots, the solutions were centrifuged for 2 min at 2000x*g* (3800 rpm) to separate the phases and a 150 μL aliquot (A_f) of the supernatant was taken for gamma counting. Dry weight distribution ratios (D_w) for each fiber were calculated from the change in activity at 144 h using eq. 1.

Results and Discussion

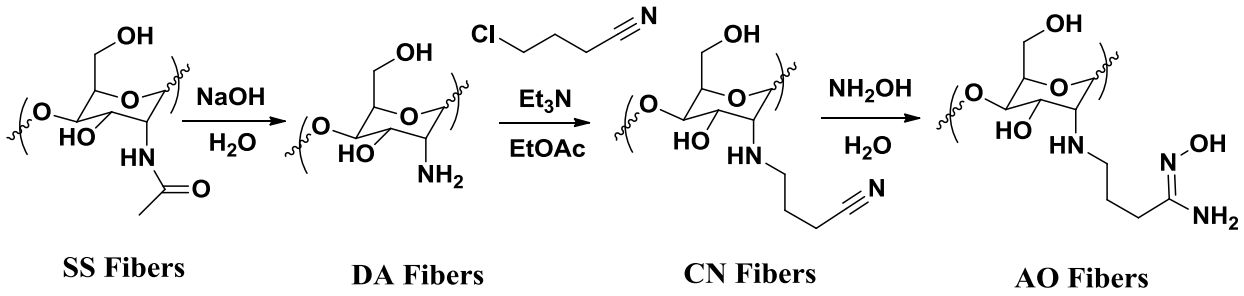
Preparation and Surface Modification of Chitin Fibers

Since both cost and biodegradability were motivating factors[25] for using chitin, a decision was made to use the raw extracted chitin in a one-pot process, rather than extracting the chitin, purifying it *via* coagulation in water, and then redissolving the chitin prior to use. From prior work, we anticipated that this could lead to higher amounts of impurities in the fibers (see below) and some sacrifice in overall strength.[15] Nonetheless, the simplicity of this process or some small variation of it would keep chemical and energy usage to a minimum.

While the four types of chitin fibers were prepared several times to conduct all experiments, when comparing the four types within this study and for each type of experiment, all fibers were prepared from the same batch of shrimp shell extract spinning solution. The spinning solution was prepared by extraction of ca. 19 g dried shrimp shell (6 wt%) in $[C_2mim][OAc]$ followed by centrifugation to remove any insoluble residue. The extract solution was then loaded into four 60 mL syringes which were degassed in an oven at 80 °C overnight. Each syringe was used to

dry-jet wet spin a spool of about 1 g of chitin fibers using techniques and equipment we have previously reported for chitin and cellulose.[15,35] Each spool of chitin fibers was washed with DI water and further soaked for 1-2 days to remove residual IL. One spool of the chitin fibers (designated SS fibers) was removed and dried in air, while the remaining spools were kept in water until used in the next step.

Surface modification of the chitin fibers followed the reaction pathways noted in Scheme 1 taking advantage of the insoluble nature of chitin. First, SS fibers were taken off the three spools, placed in separate beakers, and each stirred in 400 mL of 1.25 M aqueous NaOH at 80 °C for 8 h to deacetylate the surface. The solutions were decanted from the fibers which were then washed three times with 100 mL DI water. Approximately 1 g of the fibers (designated as DA fibers) were set aside for analysis and the remaining fibers were carried on to the next step.



Scheme 1. Synthetic scheme for the surface modification of chitin fibers using a typical method for deacetylation of chitin1 and a chemical route previously used by our group to append amidoxime groups onto imidazolium cations.[38]

To attach the uranyl-selective amidoxime ligand to the now free amine groups on the chitin fiber surface, a two-step reaction was conducted. Two ~1 g portions of the DA fibers in separate beakers were stirred in an ethyl acetate solution containing 0.0155 M 4-chlorobutyronitrile and 0.0160 M triethylamine at 50 °C overnight. The reaction solutions were then decanted and each set of fibers was washed three times with 50 mL ethyl acetate resulting in the nitrile-functionalized fibers (designated CN fibers). An approximately 1 g portion of the CN fibers were air dried and kept for analysis. The other ~1 g portion of CN fibers was then stirred in 0.047 M aqueous hydroxylamine at 80 °C overnight. The solution was decanted and the fibers were washed three times with DI water to provide the amidoxime-functionalized (AO) fibers.

In total ~1 g each of SS, DA, CN, and AO fibers were prepared and air dried before characterization and analysis. The fibers were flexible but brittle, with no visible degradation as a result of any of the surface treatments. Optical microscopy images (ESI Figs. S1-S4) show fibers that are very rough on the surface and non-uniform with a large number of visual, crystalline impurities, particularly when compared to previously prepared fibers using chitin first coagulated and then redissolved in IL prior to spinning.[15] The DA, CN, and AO fibers appear slightly rougher on the surface than the SS fibers suggesting that treatment to the fibers does remove portions of or change the surface of fibers.

Fiber Characterization

The chitin content of the dried shrimp shell starting material and each type of fiber were measured by the Black and Schwartz method[36] revealing chitin contents of 22(1), 58.3(5), 64(3), 61.8(2), and 63.2(8)% for shrimp shell and SS, DA, CN, and AO fibers, respectively (Table 1). The large increase in chitin content for the fibers when compared to the initial chitin content of the dried shrimp shells was expected since the IL extracts chitin while leaving most of the shell matrix behind as previously reported.[15] The apparent increase of chitin content from the SS fibers to DA fibers suggests that the caustic treatment removes additional non-chitin material from the fibers, whereas further treatment to append the ligand does not. The highly basic conditions of the deacetylation treatment could remove residual proteins in a manner similar to the caustic wash used to purify chitin in the industrial process.[9,10,11]

Table 1. Composition and physical properties of shrimp shells and modified fibers.

	Shrimp Shells	SS Fibers	DA Fibers	CN Fibers	AO Fibers
Chitin Content[a] (%)	22(1)	58.3(5)	64(3)	61.8(2)	63.2(8)
Moisture Content[b] (%)	4.0	7(2)	4(1)	4(2)	4(1)
$CaCO_3$ Content[b] (%)	26	16.9(2)	23.6(1)	29(1)	26(2)
Residual[c] (%)	47	17(1)	9(1)	3(3)	5(1)
Decomposition ($T_{5\%onset}$, °C)	-	274(4)	226(2)	229(8)	265(1)
Fiber Diameter (mm)	-	0.20(5)	0.20(3)	0.25(3)	0.24(2)
Break Stress (MPa)	-	9(2)	9(3)	9(3)	7(1)
Break Elongation (%)	-	6(3)	6(2)	7(2)	5(2)
Yield Stress (MPa)	-	7(2)	5(2)	4(3)	4(1)
Yield Elongation (%)	-	2(1)	2(1)	2(1)	2(1)
Young's modulus (MPa)	-	3(1)	2(1)	2(1)	2(1)

[a]Chitin content determined by the Back and Schwartz method. [b]Determined gravimetrically. [c]Determined by mass balance.

Further analyses were conducted using thermogravimetric analyses (TGA, Fig. 2) on two independent samples of each material. The results for all four fibers are relatively similar with three major mass losses; the initial loss of water during the isotherm at 75 °C, a large mass loss at ~275 °C, attributed to the decomposition of the chitin material,[39] and a third mass loss at 700 °C, characteristic of $CaCO_3$ decomposition to CaO and CO_2. Moisture content appears to decrease slightly upon treatment from 7% in SS fibers to 4% in DA, CN, and AO fibers.

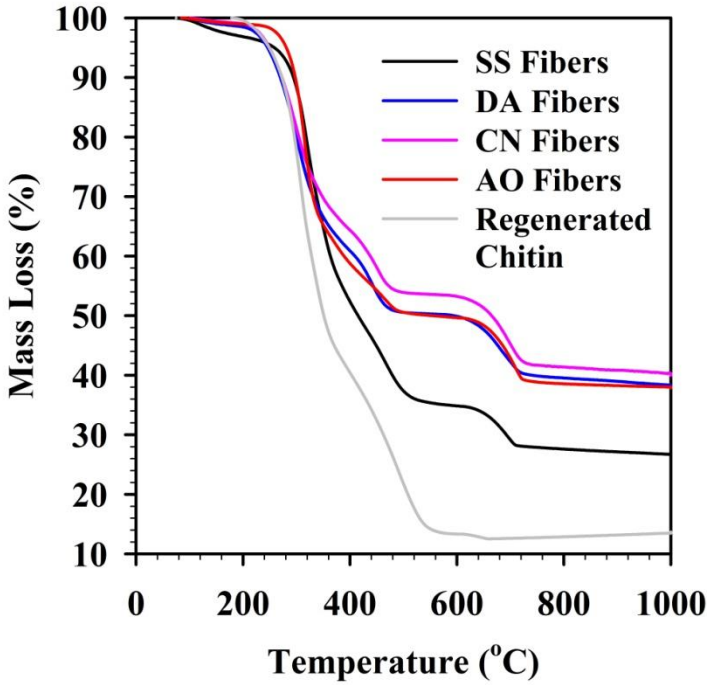


Fig. 2. Thermogravimetric analysis of SS (black), DA (blue), CN (pink), and AO (red) fibers, as well as regenerated and purified chitin (grey).

All of the fibers have relatively similar thermal decomposition temperatures ($T_{5\%onset}$) with values of 274(4), 226(3), 229(8), and 265(1) ^{o}C for SS, DA, CN, and AO fibers, respectively. SS fibers show the most deviation between the other fibers, showing a much smaller residual ash content (25% compared to ~40% for the other fibers). We believe this is due to a higher protein content in the SS fibers. Treatment with NaOH is the common method for removal of proteins when extracting chitin from shrimp shells.[9,11] A decrease in thermal decomposition temperature between chitin (SS fibers) and chitosan (DA fibers) as seen here has been reported before for chitosan and chitin.[39]

The $CaCO_3$ content of each fiber was determined using the decomposition of $CaCO_3$ at 700 °C by calculating mass loss as CO_2. Values of 16.9(2), 23.6(1), 29(1), and 26(2)% $CaCO_3$ were determined for SS, DA, CN, and AO fibers, respectively (Table 1). The relative increase in $CaCO_3$ content for the surface treated fibers is most likely due to the removal of proteins by the NaOH treatment as discussed above. The fiber residuals were calculated through mass balance and the trend follows a general decrease in residual with increasing treatment to the fibers.

Attenuated total reflectance infrared (ATR-IR) spectroscopy was used to study the surface of the fibers by placing them directly on the surface of the ATR sample window, as well as to study the bulk material by grinding the fibers prior to measurement. A portion of the normalized spectra of the unground fibers are presented in Fig. 3 (full spectra are in ESI, Fig. S5). All unground fibers show similar spectra characteristic of chitin with subtle, yet significant, differences. The spectra contain bands common with chitin including ν_{OH} = 3443 cm^{-1}, ν_{NH} = 3275 cm^{-1}, ν_{CH} = 2930 cm^{-1}, and characteristic amide bands at ν_{CO} =1650 cm^{-1}, ν_{CN} = 1631 cm^{-1}, ν_{NH} = 1561 cm^{-1}, and $\nu_{(amide\ band\ III)}$ = 1315 cm^{-1}.[40]

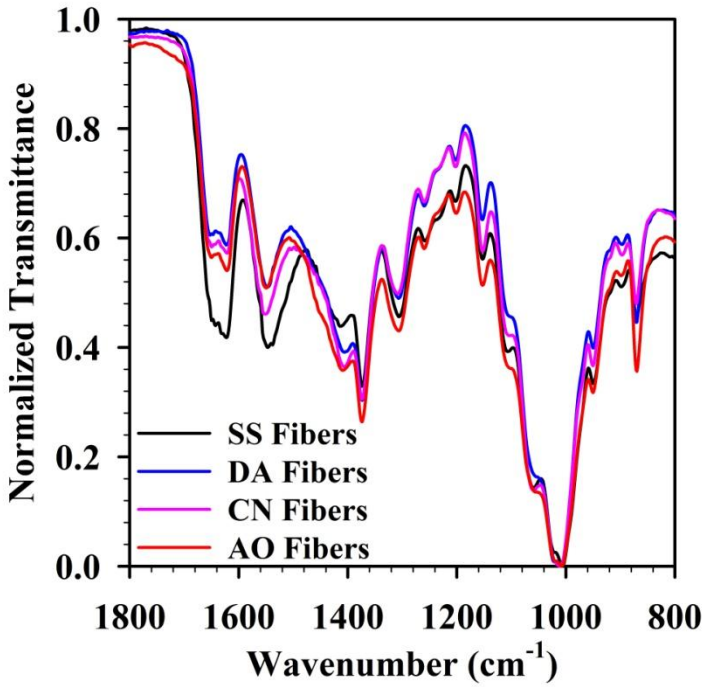


Fig. 3. A portion of the normalized IR spectra for unground SS (black), DA (blue), CN (pink), and AO (red) fibers.

A few changes which occur in the spectra upon treatment of SS fibers are noteworthy. The bands at 3443, 3275, and 2930 cm^{-1} change in intensity. The change in the higher wavenumber bands could be due to increased moisture content and therefore increased hydrogen bonding as has been shown before.[38] The band at 2930 cm^{-1} undergoes a significant change in intensity though we have been unable to identify the cause. Within the lower range of 1200-1800 cm^{-1}, the most significant changes are from the decrease and sharpening of the bands at 1650 and 1631 cm^{-1}, as well as the increase in intensity of the band at 1420 cm^{-1}. Both changes are indicative of

a change in the deacetylation of the material and the most significant changes occur with the treatment to prepare the DA fibers which, as indicated in the chitin content measurement (Table 1), resulted in a relatively significant composition change.

To characterize the interior part of the fiber which was not exposed to the treatment baths, the fibers were dried and ground to a fine particle size and the IR spectra were recorded using the same parameters as the unground fibers. A portion of the spectra of the ground fibers are shown in Fig. 4, along with the spectra of ground shrimp shells and $CaCO_3$ for comparison (full spectra are in ESI, Fig. S6). All ground fibers were compared to their unground fiber individually and comparative spectra are available in the ESI (Figs. S7-S10).

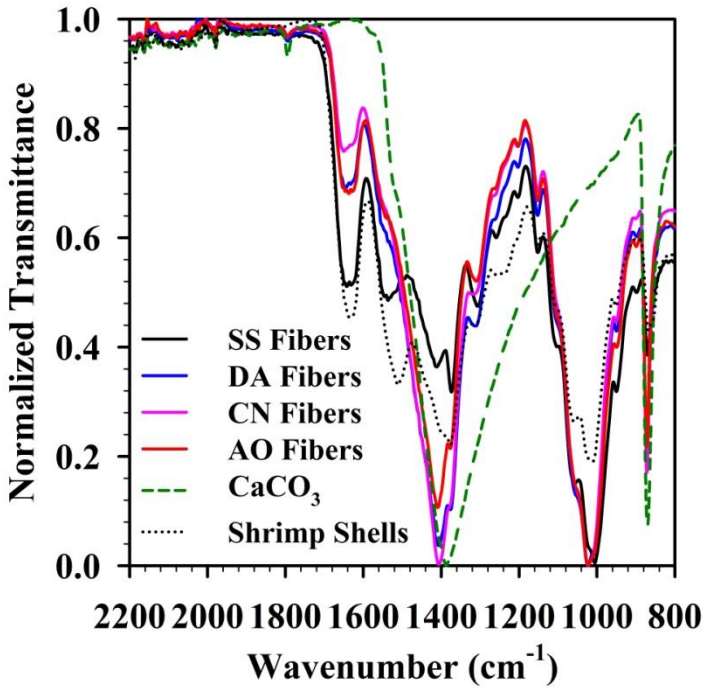


Fig. 4. A portion of the normalized IR spectra for ground SS (black), DA (blue), CN (pink), and AO (red) fibers, $CaCO_3$ (dashed green), and dried shrimp shells (dotted black).

Overall, the spectra of the ground SS fibers are similar to the spectra of the unground fibers indicating the bulk material and surface are similar and characteristic of chitin as expected. However, significant differences between ground and unground DA, CN, and AO fibers were observed with a large increase in the band at ~1400 cm^{-1}. When compared to the overlaid spectrum of $CaCO_3$, the data suggests an increase in the relative $CaCO_3$ concentration with the first treatment of fibers (to make DA fibers), which is also consistent with the removal of some

protein material in the deacetylation step. This correlates well with the TGA and chitin content measurement data presented above, which also indicates that the deacetylation treatment removes protein and perhaps a small amount of chitin. The comparative spectra (ESI Figs. S7-S10) also indicate that the chemical functionality of the surfaces and interiors of the fibers are indeed different.

For additional surface characterization, X-ray photoelectron spectroscopy (XPS) was performed on the unground fibers. All fibers were first analyzed through a survey scan (over a binding energy range of 0 to 1000 eV) to determine the elements present within the top 1-12 nm of the surface of the samples (Fig. S11). Carbon, N, and O were found as expected for chitin, with additional peaks for Ca and Na for certain fibers. Both DA and CN fibers appear to contain Na which would indicate the fibers contain residual NaOH after the deacetylation treatment. The AO fibers do not contain Na, indicating the final treatment within water was significant enough to remove the final traces of Na.

As all steps of the treatment are expected to involve changes to the surface nitrogen atoms, high resolution scans of the N 1*s* region of the spectrum (390-410 eV, shown in Fig. 5) were done to investigate these changes. In contrast to the slight changes observed in the IR data, which indicated the similarities of the bulk composition of the fibers, the major changes in the XPS spectra of different fibers offer unequivocal evidence for surface modification. The differences also correlate with the expected chemical changes. The N 1*s* peak for DA fibers is sharper and at slightly lower binding energy than the N 1*s* peak for DA fibers. As the natural chitin in SS fibers typically contains a certain amount of free amine, the broader N 1*s* peak probably contains contributions from two types of nitrogen atoms, acetylated and deacetylated (or amide and amine nitrogen atoms). Upon deacetylation, the N 1*s* peak sharpened and moved slightly to lower binding energy, indicating that there is now one type of nitrogen atom, and it is more reduced than the nitrogen atoms in natural chitin. Both of these observations are consistent with deacetylation. Further treatment to the CN fiber did not significantly alter the peak present in the DA fibers, though it does appear to broaden slightly which would indicate two nitrogen types are present, a second amine and a nitrile. The AO fibers show a severely broadened N 1*s* peak, which might be expected considering this fiber surface now has three nitrogen atom types; a secondary amine, a primary amine, and oxime. The XPS shifts also correlate with those that have been observed in XPS spectra of amidoxime grafted mesoporous carbon materials.[41]

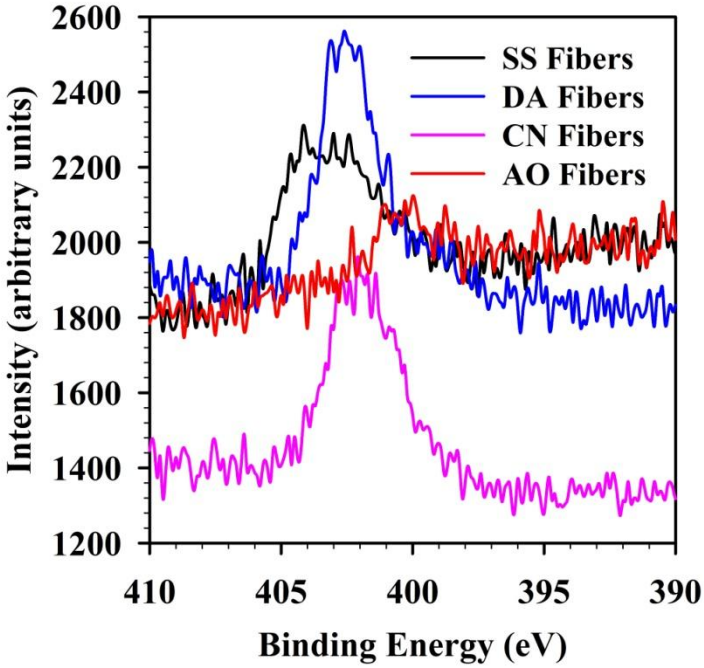


Fig. 5. High resolution XPS scans of the N 1*s* region for SS (black), DA (blue), CN (pink), and AO (red) fibers.

Fiber Physical Properties

The tensile strengths of the fibers were measured using single fibers of ~38 cm length with an initial crosshead distance of 15.24 cm. Seven fibers of each type with uniform cross-sections and no visible flaws were examined for break stress and yield stress (Fig. 6 and Table 1). Fig. 6 shows stress-strain curves for all fibers, each of which display a small linear elastic region with similar slopes, followed by a period of strain hardening that ends in fiber failure. Comparison of the diameter, yield stress, and break stress of the four fiber types revealed that all were similar within measurement error. The tensile strengths are low (9±2 MPa) when compared to the higher tensile strength (237±26 MPa) measured for chitin fibers prepared from IL solutions of chitin which was first extracted, reconstituted and then redissolved before spinning.[15] The brittleness previously observed while drying the fibers was confirmed through the similarities in the values for the break stress and yield stress and is most likely attributed to the significant amount of $CaCO_3$ present within the fibers. This is supported by the low values for the determined Young's modulus (Table 1), which are three orders of magnitude lower than the fibers prepared from the redissolution of regenerated chitin.[15]

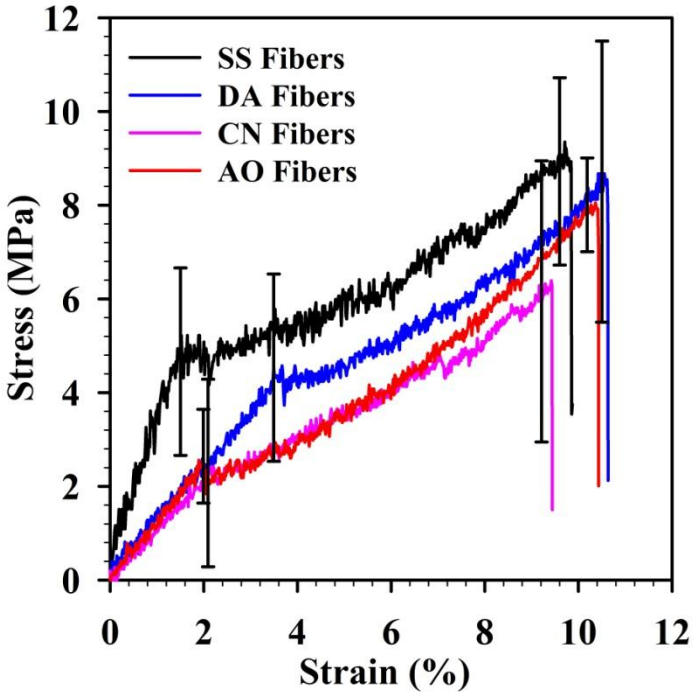


Fig. 6. Stress–strain curves for SS (black), DA (blue), CN (pink), and AO (red) fibers.

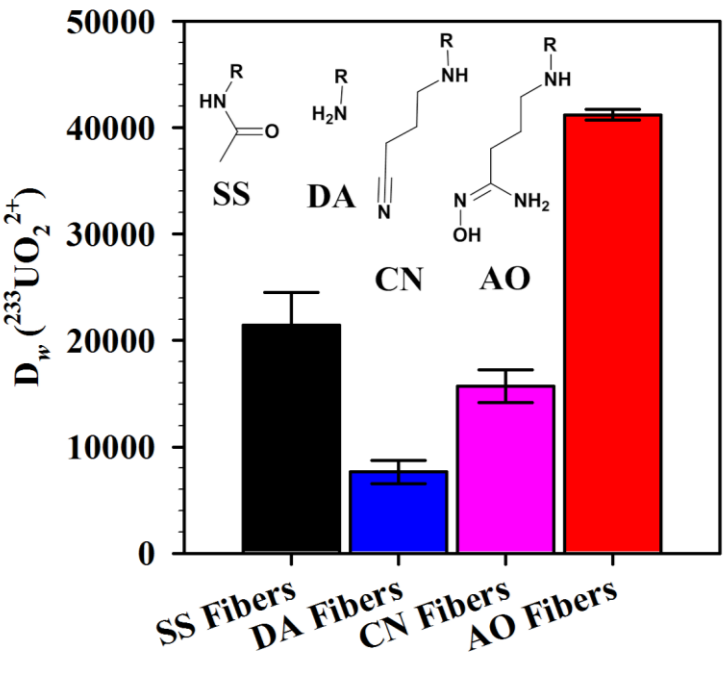
Though the fibers prepared here display significantly weaker tensile strengths, the values suggest that surface modification does not seem to significantly alter the strength and integrity of the bulk chitin fiber. The data suggest that even though the method used here might produce the most cost effective fibers for bulk use, it is likely that the intended application involving deployment in the sea would require much stronger fibers. If this indeed is the case, the extracted chitin could be easily purified by first reconstituting it after extraction followed by redissolution of the now purified chitin material prior to spinning.

Extraction of Uranium

Each of the four types of fibers was tested for their ability to remove UO_2Cl_2 from very dilute aqueous solution. Dry weight distribution ratios were determined radiometrically at 25(1) °C by batch contacts of ca. 2.5 mg of each fiber with 1 mL of DI water spiked with ca. 0.007 µCi of $^{233}UO_2Cl_2$ and shaken for 144 h. Aliquots of the solution were taken for counting at certain intervals to compare uptake kinetics, and dry weight distribution ratios (D_w) for each fiber were calculated from the change in activity at 144 h using eq. 1 (see Experimental). The plot of activity as a function of time is shown in the ESI (Fig. S12) and indicates an exponential

decrease in the activities of all of the samples. AO fibers show the fastest uptake when compared to the other fibers.

The differences in the D_w values (Fig. 7) at 144 h support surface functionalization by showing that each treatment affected uranium uptake. The AO fibers show the highest affinity for UO_2^{2+}, commensurate with the known affinity of the amidoxime functional group for aqueous uranyl ions. The distribution ratios for the other fibers correlate with the hardness of the coordinating/functional group as a Lewis base: SS (amide) > CN (nitrile) > DA (amine). A search of the Cambridge Structural Database shows that uranyl complexes with amides are far more common than complexes with nitrile or primary amine functional groups, with 143, 6, and 1 entries, respectively.[42]



3.

Fig. 7. D_w values for extraction of $^{233}UO_2Cl_2$ from water by SS (black), DA (blue), CN (pink), and AO (red) fibers.

Conclusions

We have prepared chitin fibers in a one pot process using dry-jet wet spinning from the direct extraction of chitin from shrimp shells using $[C_2mim][OAc]$. By exploiting the insolubility of natural chitin, we have developed a platform for surface modification of chitin materials. Building upon traditional methods for deacetylation, which provides access to the primary

amine, we have modified the surface of chitin fibers with a functional extractant (here, amidoxime for the extraction of uranium from seawater), leaving an inner core of chitin that represents the bulk material. The complete compositional analysis and physical properties suggest that surface modification was successful in imparting chemical functionality without significantly altering the bulk properties of the material.

We consider this a platform for functional biorenewable materials which, through the use of surface-appended selective extractants, provide both the physical properties of natural chitin along with the functional properties of synthetically tailored materials. Extraction results support the discussed example as a model for the extraction of uranium from seawater, however, the brittleness of the fibers even before surface modification suggests that the chitin will have to be reconstituted and purified prior to use for increased strength and durability.

Current efforts are focused on increasing the strength of the fibers either by using higher purity chitin or by homogenous blending of other biopolymers prior to spinning. We are also working to increase the capacity of these fibers by increasing the available surface area of these fibers *via* electrospinning. We believe the overall platform demonstrated here (i.e., materials with the internal properties of chitin, but the surface functionality of chitosan) has broad application in separations and environmental remediation, plastics, drug delivery, medical devices, and beyond.[14] This strategy not only reduces the chemical input necessary for providing function, but also provides advanced materials from biorenewable resources and agricultural waste.

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