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1 High Humidity Shaker Aging to Access Chitin and Cellulose Nanocrystals

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12
13 *KEYWORDS: Chitin, cellulose, biomass, nanocrystal, mechanochemistry, aging, nanomaterial, solid-state*
14

15 **Abstract:** To unlock nature's potential for functional biomaterials, many efforts have been
16 devoted to isolating the nanocrystalline domains within the supramolecular structure of
17 polysaccharides. Yet, low reactivity and yield in aqueous systems along with excessive solvent
18 usage hinders its development. In this report, the first solvent-free pathway to access carboxylated
19 chitin and cellulose nanocrystals with excellent mass balance is described, relying on a new
20 method coined high humidity shaker-aging. The method involves a mild grinding of the
21 polysaccharide with ammonium persulfate followed by an aging phase under high humidity and
22 on a shaker plate. Insights into the mechanism were uncovered, which highlighted the unique role
23 of high humidity to afford a gradual uptake of water by the material up to deliquescence when the
24 reaction is complete. This process was then validated for direct synthesis of nanocrystals from
25 biomass sources including crab and soft wood pulp.

26

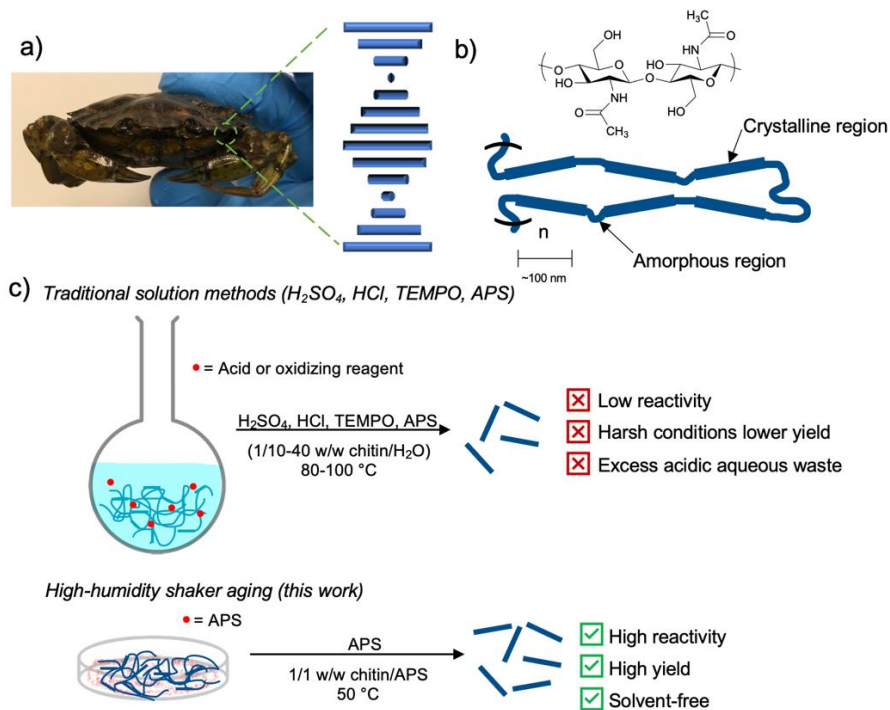
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1 **Introduction:**

2 Nanomaterials coming from polysaccharides such as cellulose and chitin have received
3 exceptional attention in the past couple of decades owing to their properties such as high aqueous
4 colloidal dispersibility, tensile and mechanical strength, gelling ability, high aspect ratio,
5 biocompatibility, as well as liquid crystalline self-assembly.^[1] They have found a number of
6 applications in the general fields of catalysis, pharmaceuticals, templating, textiles, adhesives, and
7 much more.^[1a, 1b] Cellulose nanocrystals (CNCs) coming from woody cellulosic biomass for
8 example are produced industrially up to the ton scale per day by 10 organization worldwide,^[2]
9 while chitin nanocrystals (ChNCs) from crustacean shells have yet to be developed on the
10 industrial scale, but proven to have great promise in initial applications.^[3] They both exist within
11 biomass as organized domains, with chitin organizing in the so-called “Bouligand structure”
12 surrounded by a matrix of proteins and calcium carbonate (**Figure 1a**).^[4] To liberate the
13 nanocrystals within the biopolymer, the amorphous regions must be selectively cleaved *via* acidic
14 or oxidative pathways (**Figure 1b**). Usually, solutions of mineral acid (HCl, H₂SO₄) or oxidants
15 such as 2,2,6,6-Tetramethylpiperidyl-1-Oxyl (TEMPO) or ammonium persulfate (APS) are used
16 to induce partial depolymerization of the polysaccharide into nanocrystals (**Figure 1c**).^[5] The
17 challenge in these methods relies on the fact dilute concentrations are required to preserve the
18 delicate crystalline structure while the low aqueous solubility of bulk cellulose and chitin
19 drastically reduces reactivity, all resulting in waste generation.



1
 2 **Figure 1:** (a) Natural self-assembly of chitin fibers into the Bouligand structure as existed within
 3 the shells of the pictured green crab. (b) The chitin polysaccharide chemical structure as well as
 4 its macromolecular depiction divided into amorphous and crystalline regions, with a scale-bar to
 5 show the reader the approximate dimensions of the crystalline regions. (c) Schematic comparing
 6 the classic solution-based method using various reagents with the high-humidity shaker aging
 7 method in this work.

8
 9 Mechanochemistry is rapidly establishing itself as an effective tool to cut on
 10 solvent/aqueous waste,^[6] and it has been explored for the valorization of biomass, in the context
 11 of biopolymers deconstruction^[7] and functional materials fabrication.^[8] It is commonly used as
 12 pre-treatment to solution-based chemical methods and thus seen essentially as a physical method
 13 to break bonds. For example, cellulose nanocrystals (CNCs) were made from bamboo pulp by
 14 Huang and coworkers, in a sequence where ball-milling was used as a minor pre-treatment,

1 followed by the solution-based synthesis with phosphotungstic acid.^[9] More recently,
2 mechanochemistry has been used as a reactive medium, such as in the work of van de Ven and
3 coworkers who produced CNCs via cryogrinding cellulose with alkaline chloroacetate.^[10] Yet such
4 mechanochemical methods cause a loss of crystallinity in polysaccharides, which limits the ability
5 to form high quality nanocrystals with high yield.^[11] Herein we report the exploration of a spectrum
6 of mechanochemistry and aging-based techniques to achieve high yield/low impact synthesis of
7 excellent quality chitin and cellulose nanocrystals and the discovery a novel way to perform
8 mechanochemistry via high humidity shaker-aging.

9 **Results and discussion:**

10 Initially, we ball milled dry powders of chitin and APS for 30 min at 29.5 Hz and attempted
11 to suspend the resulting product in water. APS was selected as a mild, cheap and environmentally
12 benign oxidant, able to afford carboxylated nanocrystals, which are more colloiddally stable as
13 compared to mineral acid-based nanocrystals.^[12] Large sediments were observed at the bottom of
14 the vial, indicative of untransformed bulk chitin even after ultrasonication and vigorous stirring
15 (**Figure S1**). Analysis *via* dynamic light scattering (DLS) of the same suspension after brief
16 ultrasonication confirmed particles were too large to be ChNC. An increase in reaction time to 90
17 min milling did not afford any significant ChNC liberation. XRD patterns of the resulting powders
18 revealed the crystallinity remained high after 30 min of milling with APS (crystallinity index
19 (CrI)=66%) but dropped rapidly after 90 min (CrI=49%, reference 66% for bulk chitin), (see
20 supplementary info and **Figure S2**), ruling out increased milling time as a viable path.

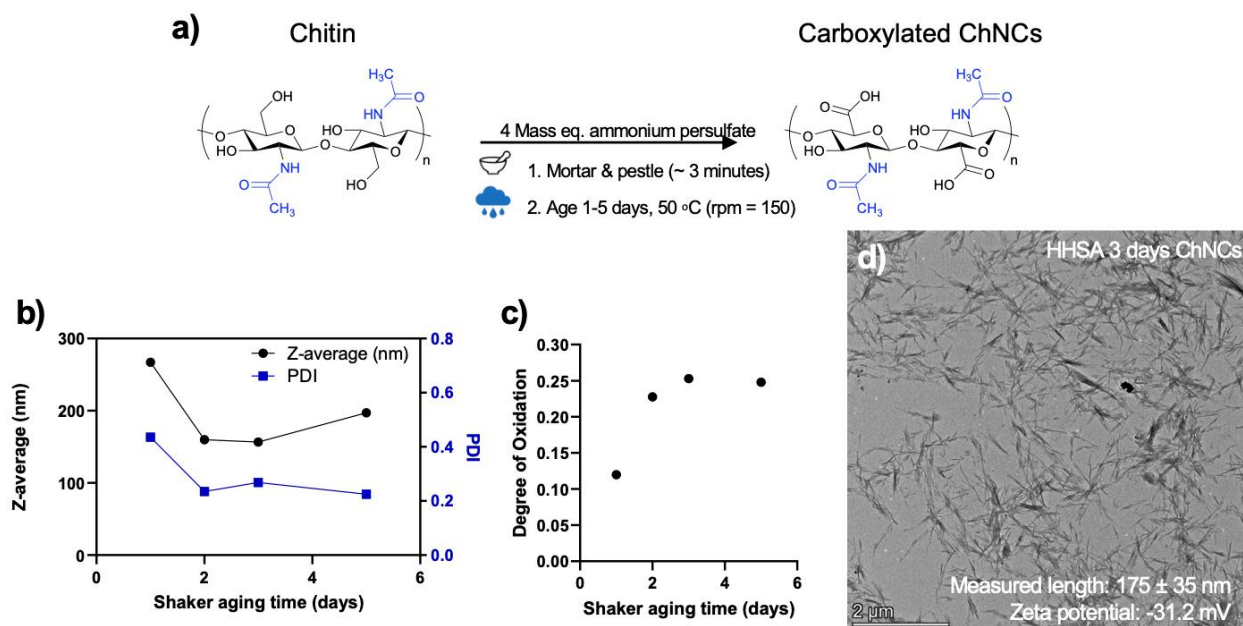
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22 Aside from mechanochemistry, which focuses on shearing and grinding to induce
23 mechanical force needed to break bonds, accelerated aging has emerged as another powerful and

1 low-energy technique to produce high quality materials in the solid phase, as exemplified by
2 Frišćić and coworkers who produced zeolitic imidazolate frameworks in this fashion.^[13] We
3 recently used this technique to deacetylate chitin and ChNCs into chitosan and chitosan
4 nanocrystals (ChsNCs) respectively, in settings where pure mechanochemistry was too harsh on
5 the materials.^[14] This idea has also been explored for the production of CNCs by Konturri and
6 coworkers who used HCl vapor to induce hydrolysis at the surface of cellulose-based cotton fibers,
7 ^[15] although in this case vigorous sonochemical treatments were still necessary to liberate the
8 CNCs, and the demonstration was only done qualitatively on a small scale. Spurred by this, we
9 investigated whether accelerated aging could be the solid-state method to achieve high reactivity
10 for the liberation of ChNCs. After initial APS and chitin grinding for 30 minutes, the mixed solid
11 samples were placed into a controlled relative humidity chamber at slightly elevated temperature
12 of 50 °C for 3 days (**Figure S3, Supplemental Information**). While the resulting product yielded
13 an opaque suspension indicative of ChNC formation, both DLS (**Table S1, Entry 1**) and
14 transmission electron microscopy (TEM) confirmed that the reaction was still largely incomplete
15 with aggregates still present within the sample (see supplementary information - **Figure S3**). A
16 control experiment was also done where we substituted the 30 min ball milling pre-treatment with
17 just mortar and pestle mixing for 3 minutes before 3 days aging, which also incurred similar
18 aggregation in the product (**Table S1, Entry 2**). The XRD of the mortar and pestle sample also
19 indicated that this mixing technique did not affect the crystallinity value, displayed by the CrI of
20 the sample having no change from the initial chitin CrI (**Figure S2**). Importantly, we noticed that
21 water adsorbed on the material from the humidity chamber was essential for oxidation to take
22 place. This was reminiscent of the conditions of Konturri who used HCl vapours to trigger
23 hydrolysis in a filter paper,^[15] in which is it critical the vapour reaches all the sample for the

1 reaction to proceed. In our system, we reasoned diffusion to layers deeper than the surface could
2 be a limiting factor. To aid in this, we sought a gentle agitation method, in the form of a shaker
3 incubator chamber. With this modification, we used mortar and pestle to mix PG chitin and APS
4 together before proceeding to the proposed high humidity shaker aging (HHSA) at 50 °C and 98
5 % relative humidity (**Figure 2a**). This strategy was very successful, as after 1 day, both the Z-
6 average value from DLS data as well as the polydispersity index (PDI) had dropped to 267.2 nm
7 and 0.436, respectively (**Figure 2b, Table S1 Entry 3**). After 3 days of aging, DLS analysis
8 displays the lowest Z-average value of 156.7 nm, with a PDI of 0.268, which is similar to the
9 ChNCs produced in solution (**Table S1, Entry 5**).^[16] In parallel, conductometric titration
10 experiments were used to deduce the amount of carboxylate functionalities found on the ChNCs
11 after HHSA (**Figure 2c**). The sample with 3 days of aging showed a peak of a degree of oxidation
12 (DO) of 0.25, which is higher than the solution based method.^[16] This high DO leads to high
13 dispersity and colloidal stability as demonstrated by a representative TEM image of the 3 day-aged
14 sample, which has a measured length of 173 ± 35 nm (**Figure 2d**), as well as a ζ -potential value
15 of -31.2 mV. By ¹³C cross polarization (CP) magic-angle spinning (MAS) nuclear magnetic
16 resonance (NMR) and Attenuated total reflectance (ATR) Fourier transform infrared (FTIR)
17 spectroscopy, we observed minimal to no change to the polysaccharide backbone structure
18 throughout the HHSA process (**Figure S4, S5**). Quantitative NMR also confirmed no deacetylation
19 took place in this process. The FTIR carboxyl C=O stretch peak usually at around 1720 cm⁻¹ is
20 very low in signal, which is a common feature for carboxylated ChNCs.^[12, 17] Overall, these
21 experiments show that ChNCs are effectively produced from chitin by HHSA, as a critical method,
22 with ball milling being merely a mixing component.

23



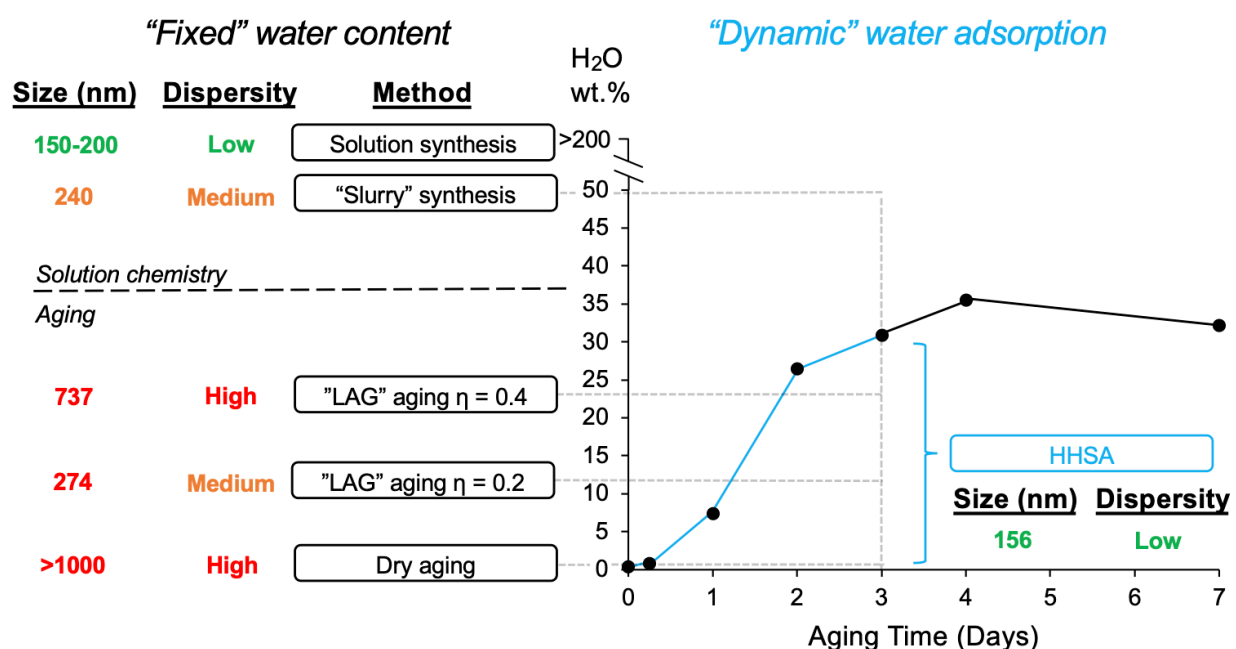
1
 2 **Figure 2:** (a) Scheme for shaker aging under humidity to make ChNCs. (b) Results from dynamic
 3 light scattering showing the Z-average value (black dots and lines) and polydispersity index (blue
 4 dots and lines) of the resulting ChNC suspension in relation to the aging time. (d) Representative
 5 TEM micrograph of carboxylated ChNCs with 3 days of HNSA.

6
 7 We then explored the mechanism of APS oxidation within our solid-state system, which
 8 has been little studied.^[18] From negative control experiments, it is determined that both the
 9 formation of radicals as well as the need for water is essential in this reaction to afford the oxidation
 10 of chitin (See **Supplemental Information** for more details). An important observation that is seen
 11 within all HNSA reactions is the uptake of water within the solid mixture of APS and chitin. To
 12 better understand the role of water adsorption in this reaction, we experimentally determined the
 13 kinetics of water adsorption within our solid mixture by following its content within the solid
 14 sample over the course of 7 days under HNSA (**Figure 3**) using thermogravimetric analysis
 15 (TGA). Almost no water sorption happened up to 6 hr of HNSA until a “threshold” was reached,

1 and rapid, autocatalytic adsorption of water into the solid mixture took place between 1 day and 2
2 days (up to 60% of all water adsorption happened between days 1 and 2). After 2 days, the rate of
3 water adsorption decreased, deliquescence was achieved at 3 days and a plateau was reached
4 between the timepoints at days 4 and 7. Upon analyzing this curve, we wondered if keeping the
5 water constant within the reaction vessel could favor the reaction. This is in tune with efforts in
6 the area of mechanochemistry to provide catalytic amounts of liquid which in some cases can
7 drastically catalyze or even chemically alter the reaction, dubbed the term liquid-assisted grinding
8 (LAG).^[19] We investigated two different values of LAG: $\eta = 0.2$ and $\eta = 0.4$, in order to simulate
9 the initial and final stages of the rapid water sorption progress in the water content experiment
10 (**Figure 3**). Resulting material morphology was analyzed by DLS (**Table S1**) and TEM
11 micrographs (**Figure S7**), and revealed aggregates of ChNCs for $\eta = 0.4$, with a high Z-average
12 value of 736.7 nm with PDI = 0.285 (**Table S1, Entry 7**), while the $\eta = 0.2$ sample shows smaller
13 sizes of 274.2 nm with PDI 0.268 (**Table S1, Entry 8**), although still higher than HHSA samples.
14 This comparison reveals that LAG was not successful in offering the high quality ChNCs seen
15 with HHSA. Specifically, $\eta = 0.2$ LAG aging, with water content equivalent to 1-day HHSA,
16 seems to provide good initial results, but the particle size and dispersity remained high, as if the
17 reaction was not completed. On the other hand, $\eta = 0.4$ LAG aging, with water content equivalent
18 to 2-day HHSA, the Z-average value was more than 3 times higher than the 2-day HHSA sample
19 they both have relatively similar water contents of 21 % and 26 %, respectively, hinting that
20 starting off at high water content is not efficient, possibly because APS radical formation is too
21 fast at high water content. A further control experiment was done to mimic the slurry condition
22 found after day 3 aging, in which deliquescence is reached (“slurry” synthesis). While the reaction
23 proceeded under these conditions, both the DLS Z-average (240.0 nm) and PDI values (0.313)

1 were higher than that of the sample after 3 days HHSA (Z-average = 156 nm, PDI = 0.268). This
 2 outlines that it is not simply the amount of water that is present within the sample that matters, but
 3 the gradual increase in water content while the reaction is proceeding that is the catalyzing factor
 4 deciding the controlled depolymerization of chitin into ChNCs. This is the first time this
 5 observation has been reported for aging as a solid-state reaction pathway depending on gradual
 6 water adsorption.

7



8

9 **Figure 3** Varying methods with a "fixed" water content value throughout the time of reaction,
 10 with comparison between solution chemistry and aging with general figure of merits in size and
 11 yield. All reactions were conducted under 50 °C and 3 days, while "solution synthesis" represents
 12 general solution-based hydrolysis methods using APS as an oxidant. "Dynamic" water adsorption
 13 over time monitored by TGA for the HHSA reaction found in the solid mixture of chitin (300 mg)
 14 and APS (1.2 g) under 98 % relative humidity and 50 °C.

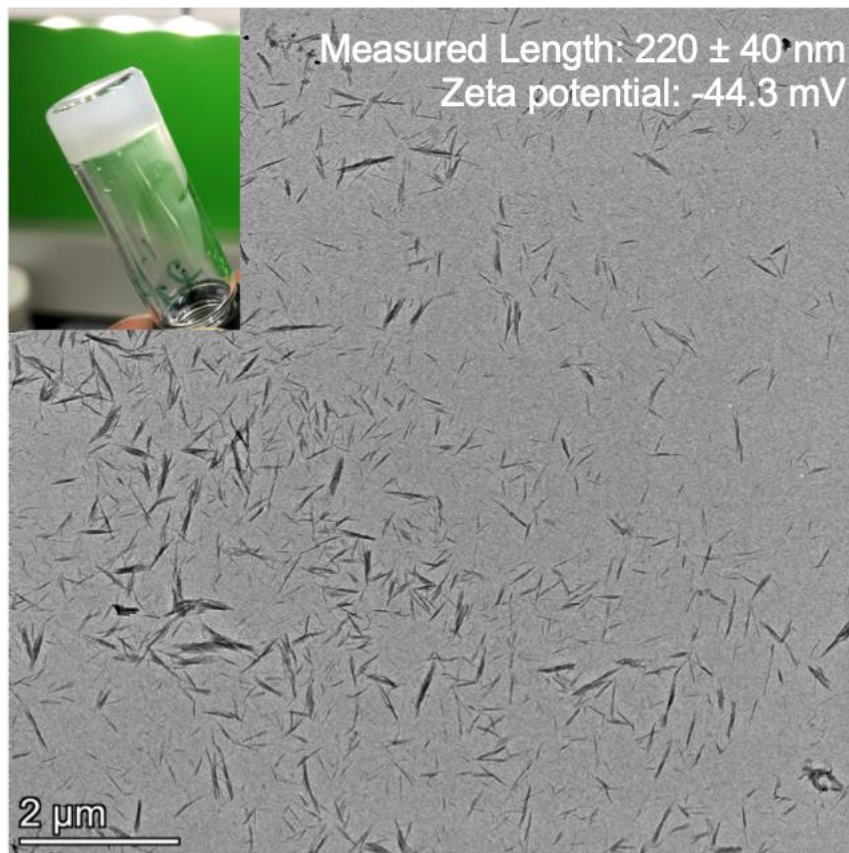
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1 In HHSA, it can be envisioned that slow water adsorption is occurring from the APS and chitin
2 solid mixture within a high humidity environment that is allowing for ultra-high aqueous
3 concentrations of persulfate radical and hydrogen peroxide to be generated in *situ* within the solid
4 mixture (**Figure S8**). In this case, as water slowly starts to penetrate the solid mixture, ultra-high
5 concentrations of sulfate radicals and peroxides may form which can effectively cleave the
6 amorphous regions of chitin and liberating space for more water to permeate through and react
7 with local APS. The timing here seems crucial so that radical formation, gradual hydrolysis, and
8 water permeation take place at similar pace to afford a homogeneous material in the end. This is
9 the first time that ChNCs can be made from chitin starting from the solid-state, which is as
10 comparable to traditional solution-based synthesis techniques in terms of making highly disperse
11 nanocrystals with no aggregation.

12
13 We validated the versatility of this new method by producing high quality carboxylated
14 CNCs from microcrystalline cellulose, in 3 days, with a ζ -potential = -44.3 mV, Z-average = 202.1
15 nm and PDI = 0.192 determined by DLS. Fully dispersity of CNCs was achieved, while TEM
16 confirmed the length of the crystallites at 220 ± 40 nm (**Figure 4**). CNC produced by this novel
17 method have the same properties as the ones made through other methods in terms of size and
18 polydispersity.^[20] Importantly, we obtained CNC in high yield of 61 % up to 1 g reaction scale,
19 better than the solution based method . Furthermore, a process mass intensity (PMI) calculation
20 was done comparing the HHSA method to a standard solution-based method with APS as the
21 oxidizing agent, which verifies that the amount of water and reagent needed to make CNCs using
22 HHSA is an order of magnitude below that of the solution-based method, with PMI values of 12.5
23 compared to 203 for the traditional method (**Supporting Information**). Finally, the resulting CNC

1 are also superior in that they are easily suspendable, with suspensions stable over the course of 3
2 months, with similar ζ -potential values before and after. At a concentration range of 5 wt. %, the
3 carboxylated CNC suspension depict gel-like behavior, as shown in the inset of **Figure 4**.
4 Interestingly, their ζ -potential -44.3 mV are at least 10 mV more negative than CNCs from
5 industrial sources.^[20]

6



7

8 **Figure 4:** Unstained TEM image of carboxylated CNCs made from microcrystalline cellulose
9 using HHSA method. Inset shows of a 5.75 wt. % suspension of carboxylated CNCs.

10

11 To further streamline polysaccharide nanocrystals fabrication, we used raw chitinous
12 biomass - powdered green crab shell- and soft wood pulp, to directly access ChNCs and CNC

1 respectively. Soft wood pulp CNCs afforded excellent dispersions and whiskers similar to the one
2 made from cellulose (**Figure S9**). With green crab shells, TEM revealed that ChNCs are isolated
3 as into individual whiskers (**Figure S10**), while minerals from the shell were also present in the
4 form of small black dots, identified to be calcium-rich by energy dispersive X-ray spectroscopy
5 (EDX) (**Figure S11**). Interestingly, this provides context that the APS oxidation of green crab
6 shells does not get rid of the calcium carbonate present within it, but still selectively
7 depolymerizing chitin. This work has the potential to afford a new valorisation route for crustacean
8 shell, as an important biowaste stream.

9 **Conclusion**

10 In conclusion, HNSA is a new method to achieve solid-state reactivity for the formation of
11 ChNCs and CNCs. In contrast to mechanochemistry, which focuses on shearing and grinding to
12 induce mobility, HNSA is a “softer” form of mechanochemistry focusing on the progression
13 between pure solid mixtures and slurries, in which control of relative humidity is the key in
14 promoting gradual water adsorption and thereby radical-based oxidation reactivity. The as-made
15 ChNCs and CNCs have comparable properties to traditional solution-made ones, while their
16 synthesis has a higher yield and a much improved PMI to the solution based methods.

17

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4

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