Support information

Acid Hydrolysis of Chitin in Calcium Chloride Solutions

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Table of Contents

Number of pages in the supporting information: 24

Number of figures in the supporting information: 18

Number of tables in the supporting information: 11

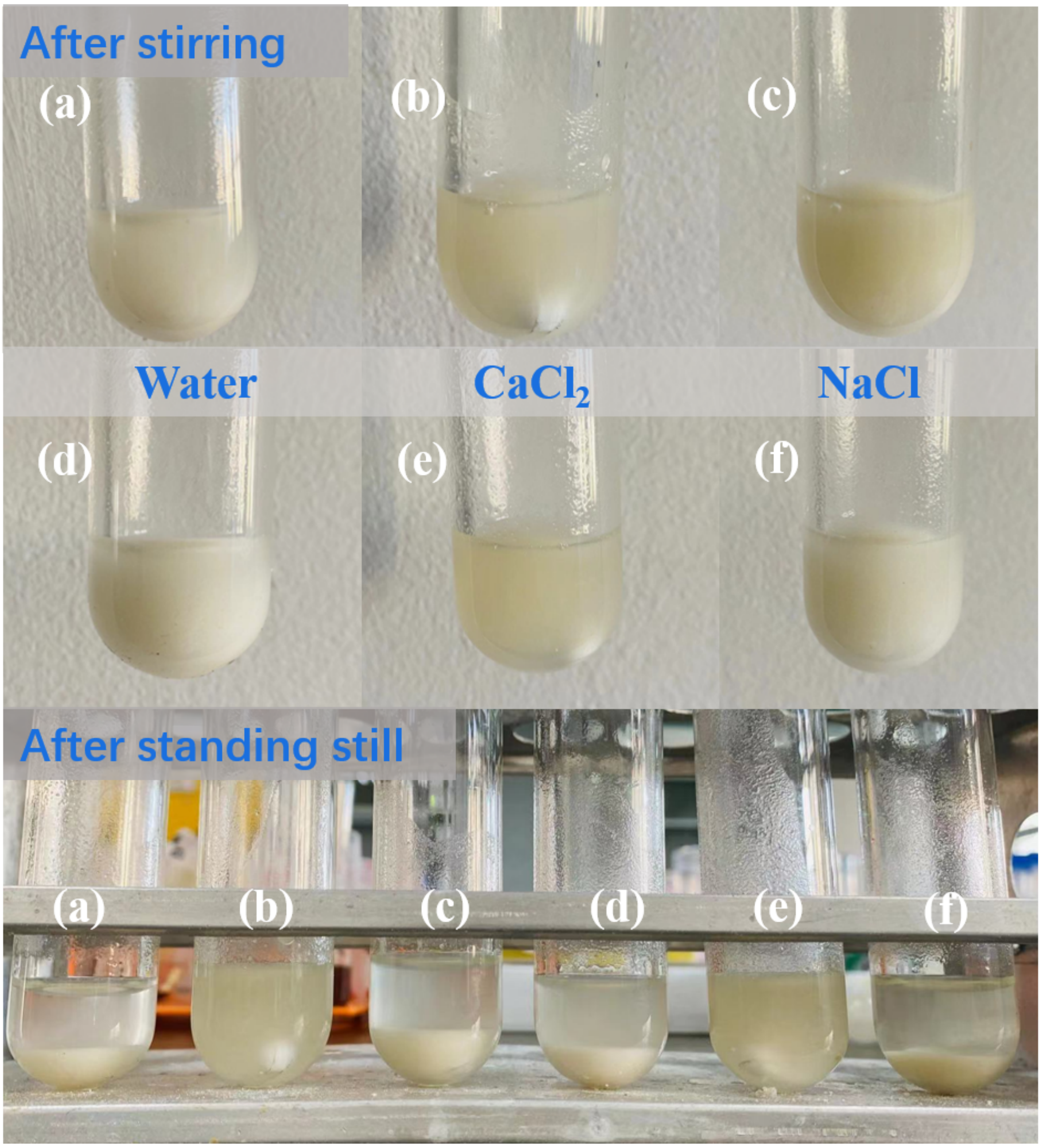

Fig. S1 Chitin samples in different solvent systems after stirring and after standing still: chitin with aging in (a) water (b) $CaCl_2$ (c) NaCl; chitin without aging in (d) water (e) $CaCl_2$ (f) NaCl. (The concentrations of $CaCl_2$ solution and NaCl solution are 50 wt% and 30 wt%, respectively.)

Table S1 Yields of by-products from NAG or chitin under different aging and hydrolysis conditions

Entry	Substrate	Aging temperature (K)	C/A ratio	Hydrolysis temperature (K)	NAG yield/conversion [a] (%)	By-products yield (%)					
						5-HMF	Formic acid	Levulinic acid	Acetic acid	Lactic acid	3A5AF
1	chitin	313	8:1	393	51.0	0.6	0.1	1.1	0.4	2.8	0.3
2	chitin	-	8:1	393	5.91	0.8	0	0	0.3	1.3	0.2
3	chitin	-	4:1	393	6.33	0.8	0.0	0.6	0.5	1.8	0.2
4	chitin	318	8:1	393	37.2	0.5	0	-	0.2	0	0.3
5	chitin	328	8:1	393	32.3	0.8	0.1	-	0.5	3.0	0.3
6	chitin	313	8:1	403	28.1	1.1	0.1	3.7	0.6	3.5	0.3
7	NAG	313	8:1	403	51.6	0.8	0	1.8	0.2	1.8	0.2
8	NAG	313	8:1	393	55.7	0.9	0	2.0	0.2	1.8	0.2

[a] Entry 7 and Entry 8 show NAG conversion instead of yield.

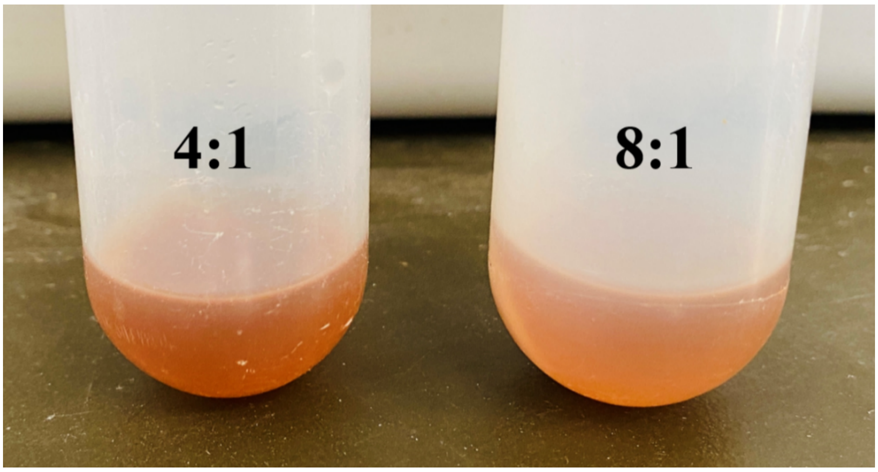

Fig. S2 Colour of hydrolysis products at acid concentrations of 4:1 and 8:1. (Samples were aged for 48 h at 313 K and hydrolysed at 393 K for 60 min.)

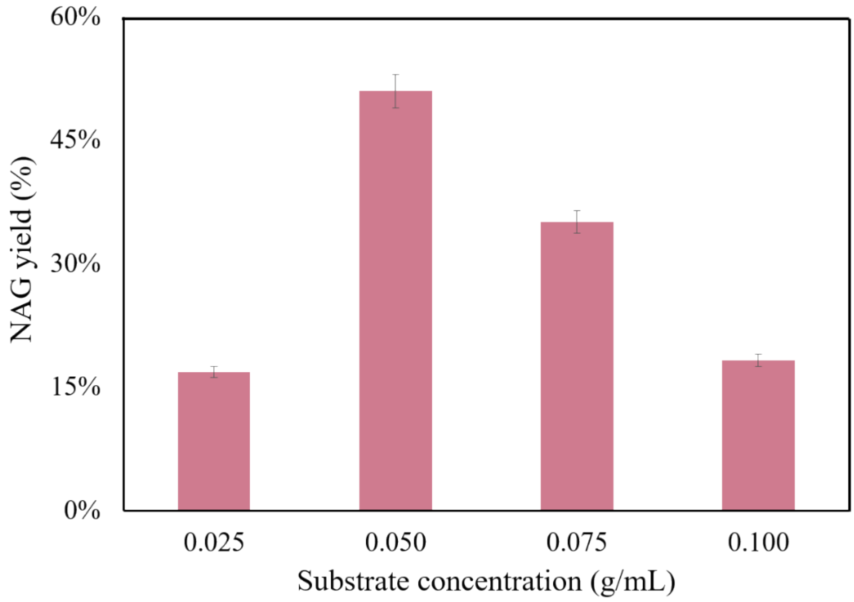

Fig. S3 NAG yield under different substrate concentration. Reaction conditions: chitin was aged at 313 K for 48 h (C/A ratio as 8:1) and hydrolyzed in 50 wt% $CaCl_2$ at 393 K for 1 h.

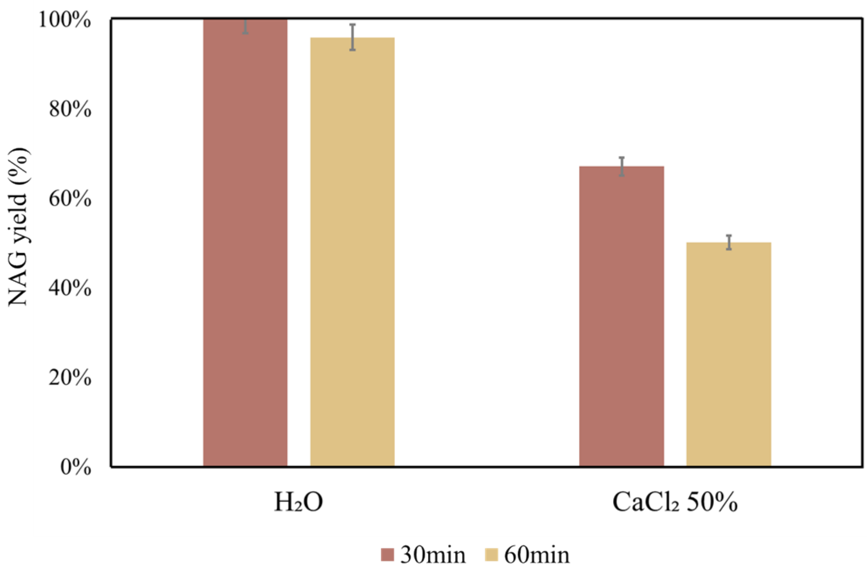

Fig. S4 NAG decomposition tests in water and 50 wt% $CaCl_2$ solution. Reaction conditions: 0.2 g NAG in 4 mL solvent, heated at 393 K for 1 h.

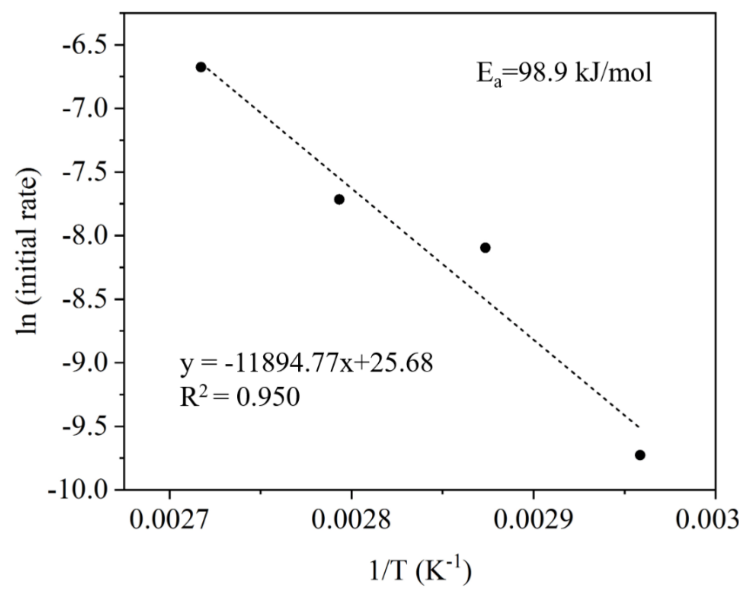

Fig. S5 Arrhenius plot of initial rates based on NAG concentration at 338 K-368 K for 20-70 min.

Table S2 The detailed results of NAG concentration with respect to time at various temperatures for the Arrhenius plot (chitin conversion is lower than 30 wt%).

Temperature (K)	Time (min)	NAG concentration (mol/L)	slope	ln (slope)
338	35	4.46E-03	2.96E-03	-9.726
	50	4.73E-03		
	65	5.83E-03		
	70	6.14E-03		
348	40	7.05E-03	2.87E-03	-8.097
	50	1.10E-02		
	60	1.24E-02		
	70	1.68E-02		
358	30	8.13E-03	2.79E-03	-7.716
	40	2.69E-02		
	50	3.85E-02		
	70	5.69E-02		
368	20	8.13E-03	2.72E-03	-6.676
	30	2.69E-02		
	50	3.85E-02		
	60	5.69E-02		

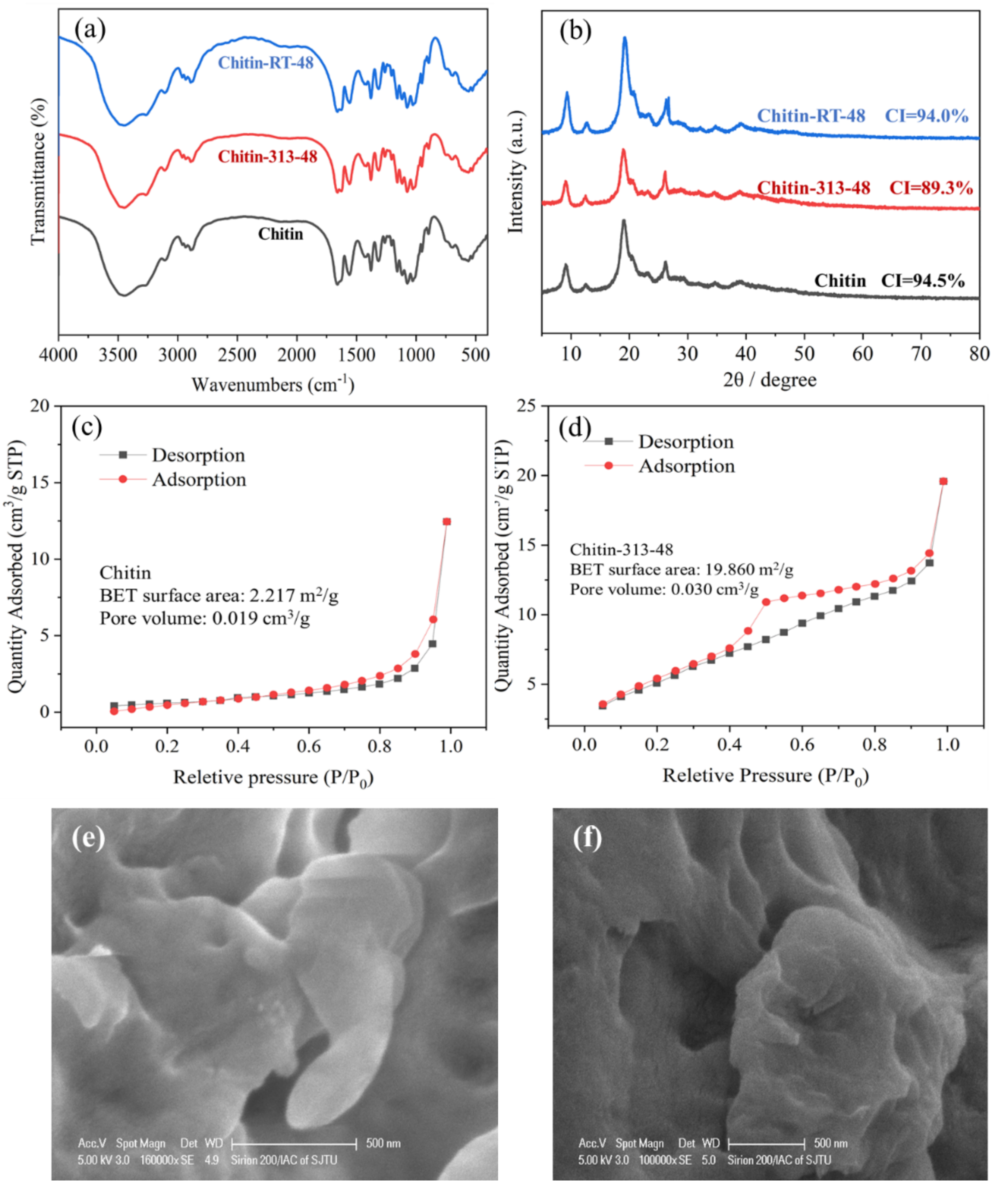

Fig. S6 (a) FTIR of chitin, chitin-313-48, chitin-RT-48; (b) XRD of chitin, chitin-313-48, chitin-RT-48; BET of (c) chitin; (d) chitin-313-48; SEM of (e) chitin; (f) chitin-313-48.

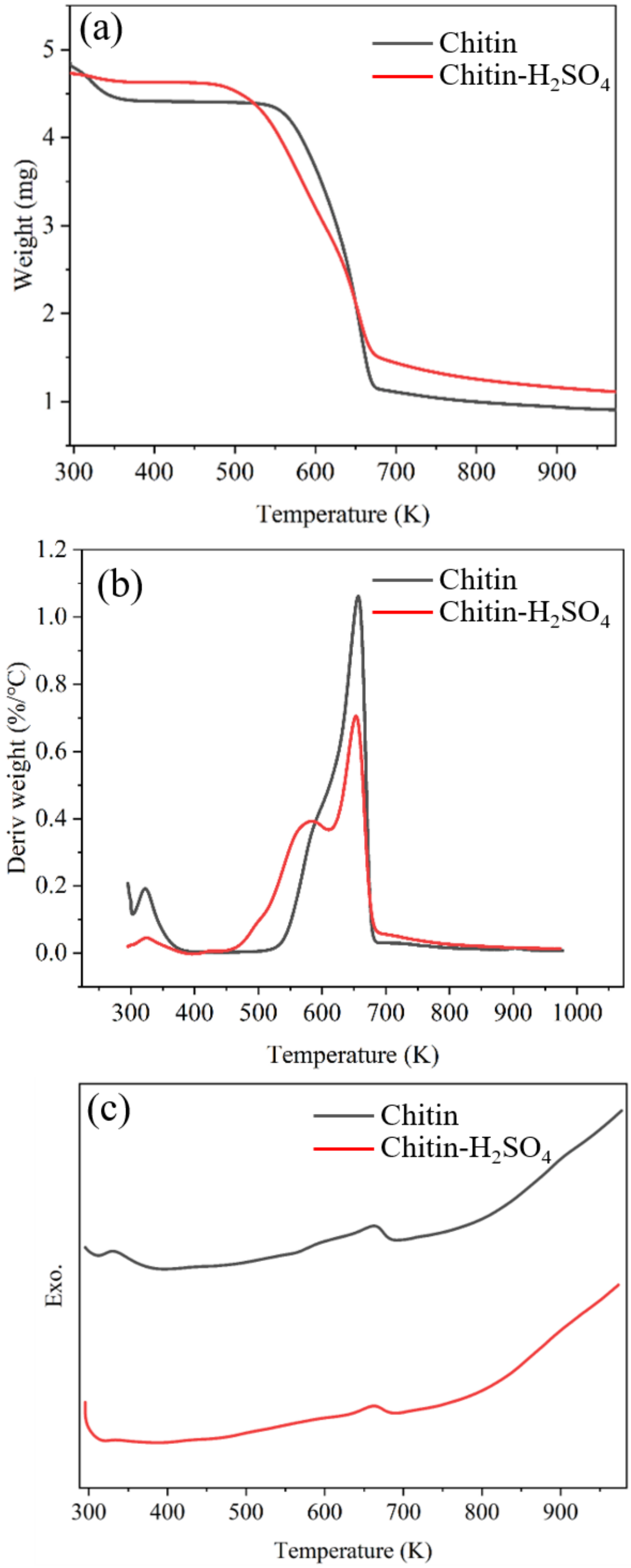

Fig. S7 (a) TGA, (b) DTG and (c) DSC of chitin and Chitin-H_2SO_4.

Table S3 Solubility of chitin under different aging conditions.

Samples	Aging temperature (K)	Aging time (h)	Chitin to acid molar ratio	Additive	Solubility (%)
Chitin	-	-	-	-	0
Chitin-RT-24	RT	24	10:1	-	14.9
Chitin-RT-24	RT	24	8:1	-	19.2
Chitin-RT-24	RT	24	6:1	-	21.5
Chitin-RT-24	RT	24	4:1	-	22.8
Chitin-313-48	313	48	8:1	-	20.8
Chitin-313-48	313	48	8:1	10 μL H_2O	19.4
Chitin-313-48	313	48	8:1	20 μL H_2O	21.9
Chitin-313-48	313	48	8:1	60 μL H_2O	23.1
Chitin-313-48	313	48	8:1	80 μL H_2O	26.3

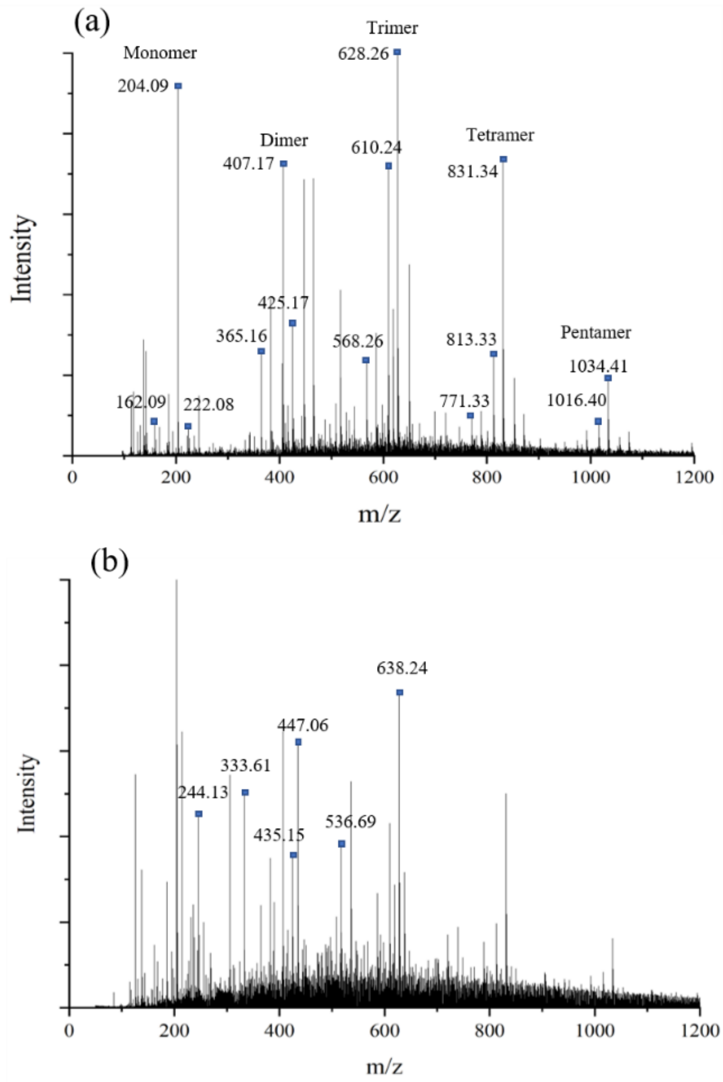

Fig. S8 TOF-MS of (a) chitin-313-48 (b) chitin-313-48 with 30% $CaCl_2$ MSHs.

Table S4 The detailed peak locations of chitin-313-48 and chitin-313-48-$CaCl_2$ dissolved portion in TOF-MS.

Sample	Location (m/z)	Formula	Comment
Chitin-313-48	204.09	$C_8H_{13}NO_5H$	Monomer
	222.08	$C_8H_{14}NO_5 \cdot H_2O$	
	407.17	$(C_8H_{13}NO_5)_2H$	Dimer
	425.17	$(C_8H_{13}NO_5)_2H \cdot H_2O$	
	610.24	$(C_8H_{13}NO_5)_3H$	Trimer
	628.26	$(C_8H_{13}NO_5)_3H \cdot H_2O$	
	813.33	$(C_8H_{13}NO_5)_4H$	Tetramer
	831.34	$(C_8H_{13}NO_5)_4H \cdot H_2O$	
	1016.40	$(C_8H_3NO_5)_5H$	Pentamer
	1034.41	$(C_8H_{13}NO_5)_5H \cdot H_2O$	
	162.09	$C_6H_{11}NO_4$	Glucosamine
	365.16	$C_6H_{11}NO_4 \cdot C_8H_{13}NO_5H$	Glucosamine +Monomer
	568.26	$C_6H_{11}NO_4 \cdot (C_8H_{13}NO_5)_2H$	Glucosamine + Dimer
	771.33	$C_6H_{11}NO_4 \cdot (C_8H_{13}NO_5)_3H$	Glucosamine + Trimer
Chitin-313-48-Ca	244.13	$C_8H_{13}NO_5HCa$	Monomer +Ca^{2+}
	333.61	$(C_8H_{13}NO_5)_3H \cdot H_2OCa$	Trimer +Ca^{2+}
	435.15	$(C_8H_{13}NO_5)_4H \cdot H_2OCa$	Tetramer +Ca^{2+}
	447.06	$(C_8H_{13}NO_5)_2HCa$	Dimer +Ca^{2+}
	536.69	$(C_8H_{13}NO_5)_5H \cdot H_2OCa$	Pentamer +Ca^{2+}
	638.24	$(C_8H_{13}NO_5)_6H \cdot H_2OCa$	Hexamer +Ca^{2+}

Table S5 Elemental analysis of different chitin samples

Samples	C (%)	N (%)	H (%)	S (%)*
chitin	6.53	45.49	7.45	<0.10
chitin-313-48	6.45	44.72	7.46	0.41

* In elemental analysis, content of less than 0.1% means that the element is undetectable.

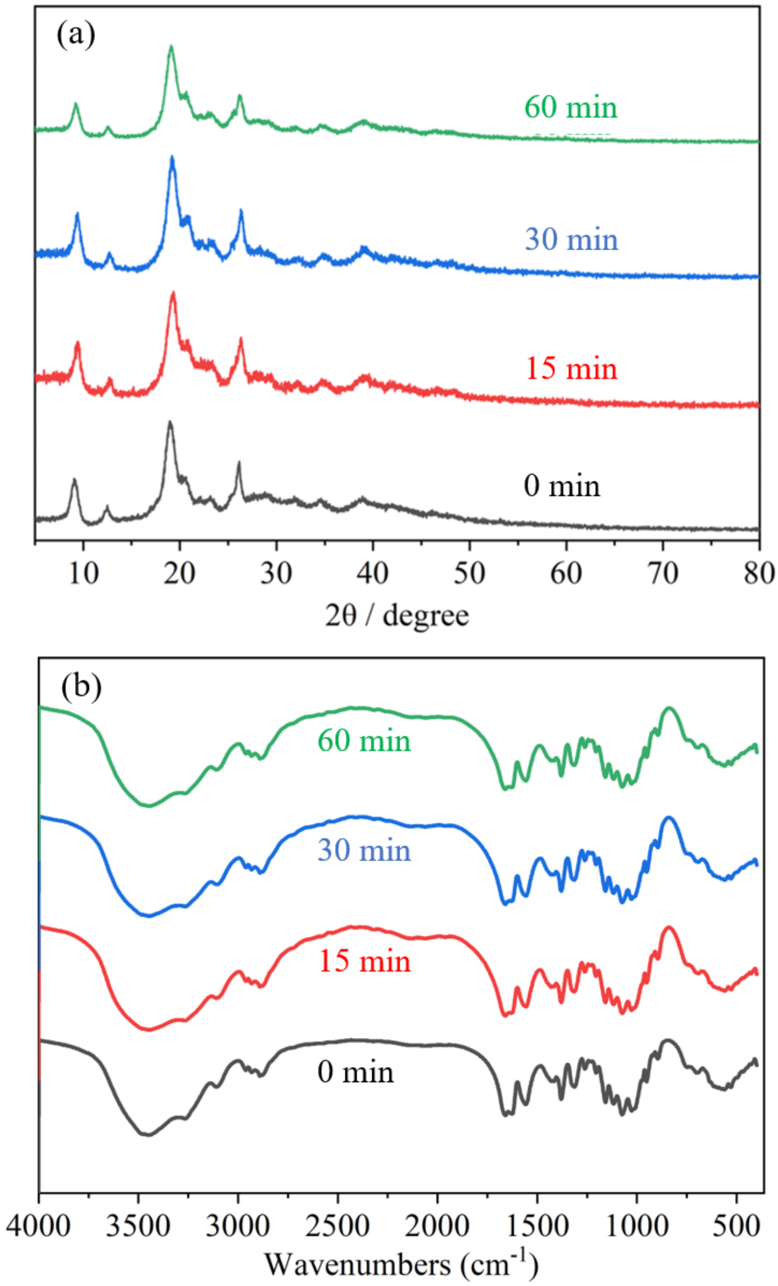

Fig. S9 (a) XRD and FTIR of solid residues after hydrolysis reaction for 0 min, 15 min, 30 min and 60 min. Reaction conditions: 0.2 g acid aged chitin (C/A ratio as 8/1) in 4 mL solvent was heated at 393 K for 1 h.

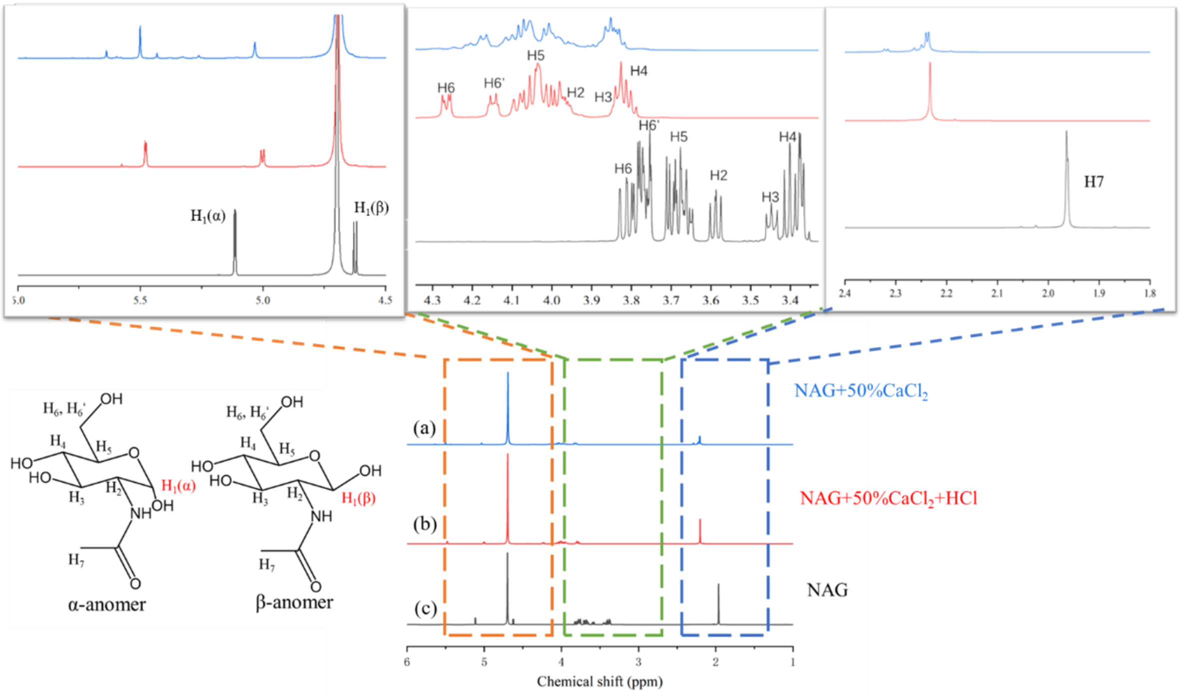

Fig. S10 [1]H NMR of (a) NAG, (b) NAG with HCl (30 mM HCl) and 50% $CaCl_2$ and (c) NAG with 50% $CaCl_2$. The solutions were prepared using D_2O.

Table S6 The chemical shift of NAG, NAG-$CaCl_2$ and NAG-$CaCl_2$-HCl in [1]H NMR.

H numbers	NAG ppm	NAG-$CaCl_2$ ppm	NAG-$CaCl_2$-HCl ppm	NAG-$MgCl_2$-HCl ppm
H1-Alpha	5.12-5.11 (d)	5.53	5.51	5.21
H1-Beta	4.63-4.62 (d)	5.06	5.04-5.03 (d)	4.77-4.76 (d)
H6	3.83-3.79 (m)	4.41-4.35 (m)	4.28-4.25 (m)	3.93-3.83 (m)
H6'	3.78-3.75 (m)	4.21-4.17 (m)	4.16-4.14 (m)	3.82-3.79 (m)
H5	3.71--3.65 (m)	4.12-3.95 (m)	4.10-3.98 (m)	3.78-3.72 (m)
H2	3.60-3.58 (m)	4.12-3.95 (m)	3.97-3.96 (m)	3.71-3.64 (m)
H3	3.46-3.43 (m)	3.86-3.83 (m)	3.84-3.79 (m)	3.64-3.59 (m)
H4	3.42-3.37 (m)	3.86-3.83 (m)	3.84-3.79 (m)	3.51-3.45 (m)
H7	1.96 (d)	2.24 (d)	2.23	2.07 (m)

Table S7 The chemical shift of NAG, NAG-$CaCl_2$ and NAG-$CaCl_2$-HCl in ^{13}C NMR.

Carbon Numbers	NAG ppm	NAG-$CaCl_2$ ppm	NAG-$CaCl_2$-HCl ppm	NAG-$MgCl_2$-HCl ppm
C9	174.72	176.21	176.10	174.93
C1	174.49	175.57	175.50	174.65
C10	94.91	94.66	94.62	94.67
C2	90.81	91.27	91.22	90.72
C11	75.93	74.92	75.01	75.67
C12	73.88	73.15	73.24	73.67
C3	71.53	71.15	71.17	71.42
C4	70.66	70.95	71.00	70.57
C5	70.04	70.03(merged)	70.01(merged)	69.90
C13	69.81	70.03(merged)	70.01(merged)	69.71
C14	60.72	61.19	61.19	60.70
C6	60.55	60.52	60.56	60.56
C15	56.67	55.92	56.25	56.55
C7	54.06	52.99	53.36	53.96
C16	22.16	24.46	24.32	22.44
C8	21.88	24.3	24.14	22.19

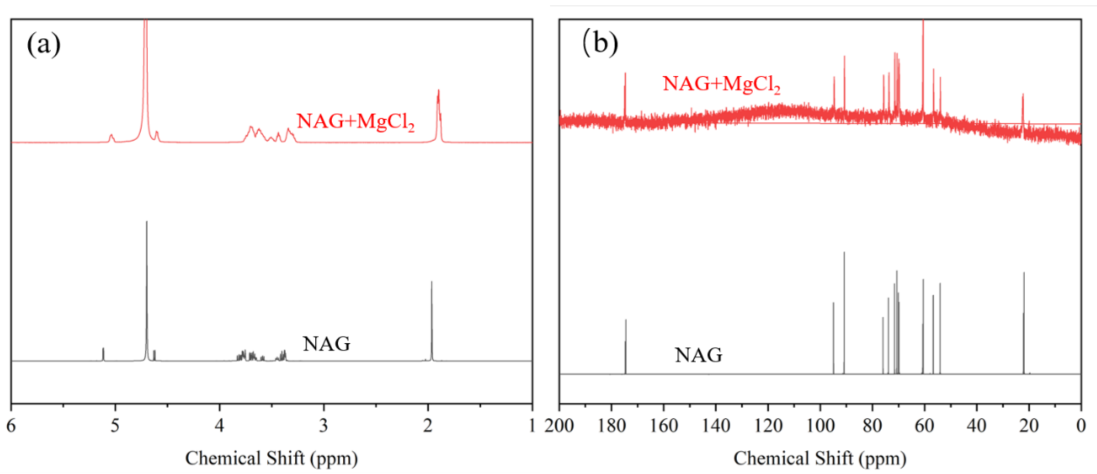

Fig. S11 (a) ^{1}H and (b) ^{13}C NMR of NAG and NAG with HCl (30 mM HCl) and 50% $MgCl_2$

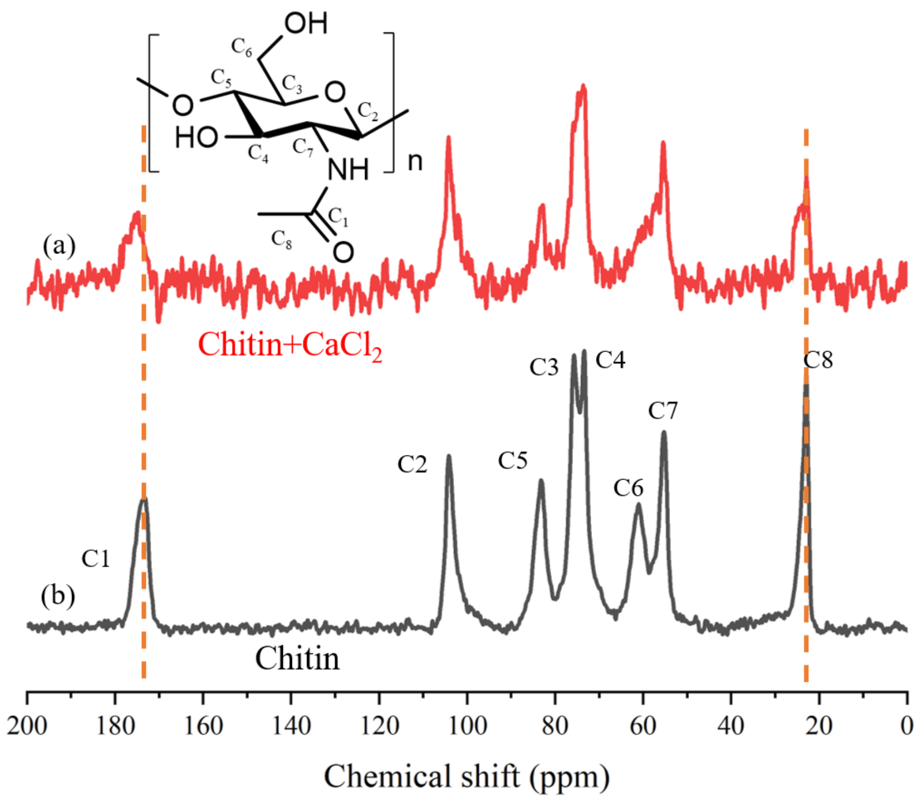

Fig. S12 Solid-state ^{13}C NMR of (a) Chitin+$CaCl_2$, (b) Chitin.

Table S8 The chemical shift of chitin, chitin-$CaCl_2$ in solid-state ^{13}C NMR.

Numbers	Chitin ppm	Chitin-$CaCl_2$ ppm
C1	173.31	175.55
C2	104.30	104.30
C5	83.20	83.20
C3	75.81	74.53(merged)
C4	73.47	74.53(merged)
C6	61.22	55.49(merged)
C7	55.39	55.49(merged)
C8	23.05	24.18

Table S9 Percentage of chitin and Chitin-$CaCl_2$ of chemical elements in XPS

Sample	C			O		N	
	C=O (%)	C-O-C/C-OH (%)	C-C/C-H (%)	C=O (%)	C-O-C (%)	-NH (%)	NH-Ca (%)
Chitin	18.6	50.3	31.1	92.4	7.6	100	-
Chitin-$CaCl_2$	18.3	26.9	54.9	80.3	19.7	73.9	26.1

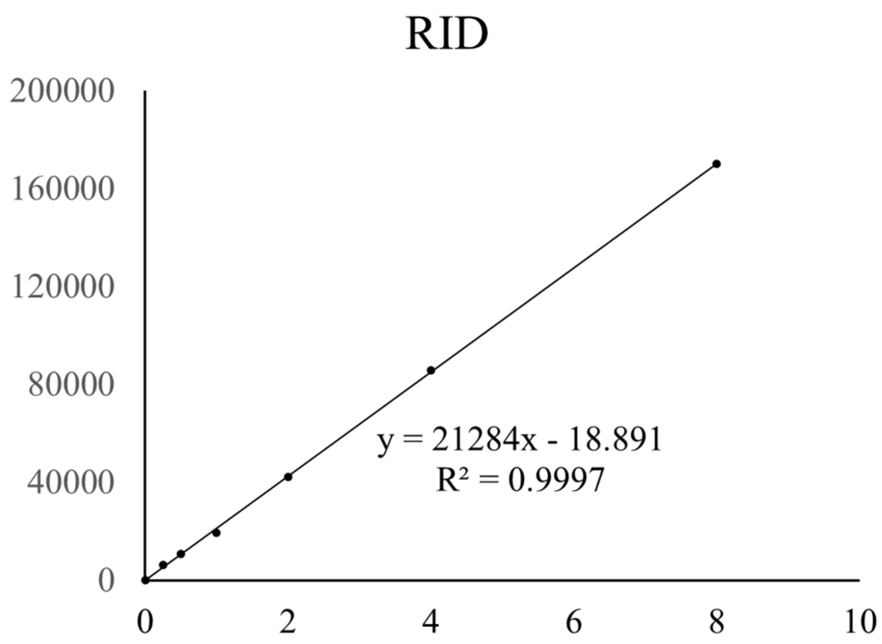

Fig. S13 Calibration curve of NAG detected by RID.

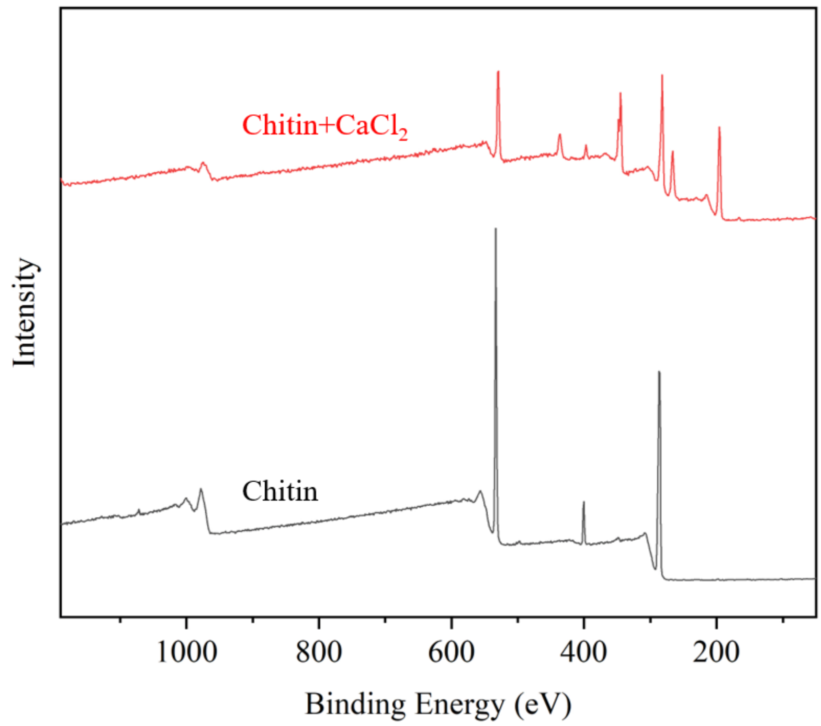

Fig. S14 XPS survey of the chitin and chitin-$CaCl_2$

Life cycle Analysis

LCAs were employed to tentatively assess and compare the potential environmental impacts of the as-established aging- hydrolysis (AH-Ca) method with the traditional method by using concentrated acid solutions. A Gate-to-Gate approach was set up and the energy consumption as well as various emissions of mainly the (aging and) hydrolysis stages were evaluated. Fig. S16 shows the boundary of the chitin-to-NAG preparation process. The inventory analysis and environmental impact analysis are provided in the Supporting Information. Based on the analyses, the AH-Ca method emits much less carbon dioxide (about 52% of the traditional method), and the fossil resource consumption index reduces to only 35.5%, which would be more advantageous to mitigate global warming (see Fig. S15). In addition, the fine particle formation index and water consumption index of the AH-Ca method drops to 71.1% and 53.4% as those for the traditional method, indicating the environmental friendliness of the AH-Ca method. Compared to the traditional method, much less H_2SO_4 was engaged in the AH-Ca method. The unit primary energy in H_2SO_4 production was 8.2 times higher than that of $CaCl_2$, owing to the additional carbon emissions from process electricity and wastewater treatment during H_2SO_4 production. In this regard, although the AH-Ca method employed a higher reaction temperature of 393 K than the traditional method at 323 K, the total primary energy consumption is still lower. To sum up, chitin hydrolysis by the AH-Ca method is more environmentally benign with diminished carbon emissions compared to the traditional method.

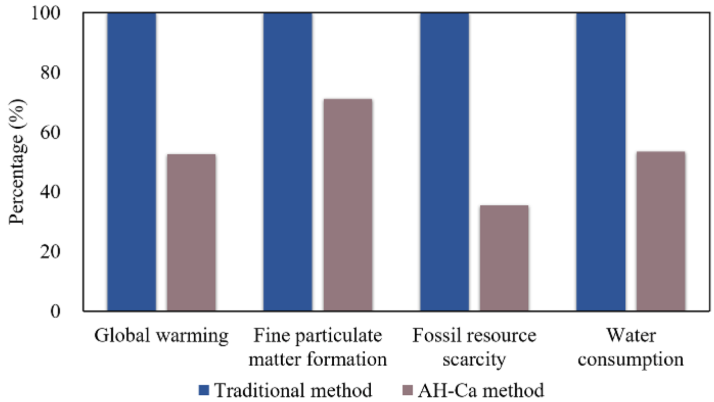

Fig. S15 Comparison of carbon footprint, particulate pollution, energy consumption and water consumption between traditional process and AH-Ca process.

The functional unit for this analysis is defined as 1 kg of chitin consumption, and all inventories assessed are converted to this functional unit. NAG subsequent life cycle stages (e.g., separation, transport, use and disposal of the product) were excluded because this analysis is mainly aimed at comparing different preparation processes. Typically, the analysis approach consists of four phases: (1) definition of objectives and scope, (2) inventory analysis, (3) environmental impact analysis, (4) interpretation of results.

1. Definition of objectives and scope

As shown in Fig. S16, the whole process is divided into 3 main parts. The conventional method uses hydrochloric acid at a concentration of 6.0 M for 5.5 h at 323 K. The NAG yield is 24.1%. The main differences between the two processes are in the treatment and hydrolysis stages.

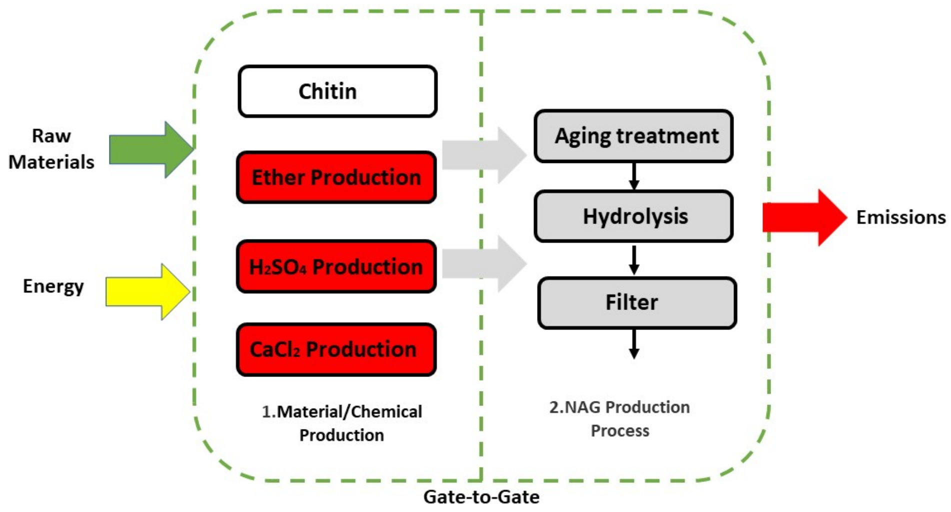

Fig. S16 Boundary of chitin-to-NAG process

2. Inventory Analysis

SimaPro is a professional LCA system analysis software and developed by the Center for Environmental Sciences at Leiden University in the Netherlands, and is widely recognized in more than 80 countries worldwide. The software and Environment database versions used in this paper are the latest version of the series, updated in March 2021, and the calculation results have good timeliness.

3. Life cycle impact analysis

According to ISO 14044 (2006b), LCIA has four stages: classification, characterization, standardization, and weighting. The following is an introduction to the classification, characterization and calculation methods.

(1) Classification

Table S10 Classification of Life Cycle Inventory Factors

Impact type	**Inventory factor categorization**
Global warming	CO_2
Particle formation	Particulate matter, SO_2, NO_x
Fossil energy scarcity	Raw coal, crude oil
Water consumption	Water

The product life cycle inventory factors that contribute to the type of impact of the inventory factors according to their physicochemical properties. The product life cycle inventory factors that contribute to their impact types are grouped according to their physicochemical properties, as shown in Table S10.

(2) Characterization

The environmental impact characterization factors of pollutant emissions covered in this document adopt the ReCiPe2016Midpoint (H) method system, and the corresponding characterization models, type parameters and sources of environmental impact characterization types in the life cycle impact assessment are shown in Table S11.

Table S11 Characterization factor data

Environmental impact characterization	Unit	Parameter Indicator	Characterization Factor	Characterization Factor Unit
Global warming	kg CO_2eq	CO_2	1	kg CO_2eq/kg
Particulate matter	kg $PM_{2.5}$eq/kg	Particulate matter	1	kg $PM_{2.5}$eq
	kg $PM_{2.5}$eq/kg	SO_2	0.29	kg $PM_{2.5}$eq/kg
	kg $PM_{2.5}$eq/kg	NO_x	0	kg $PM_{2.5}$eq/kg
Fossil energy depletion	kg oileq	Raw coal	0.42	kg oileq/kg
	kg oileq	Crude oil	1	kg oileq/kg
Water consumption	m^3	Water	1	m/m^3

3) Calculation method

The calculation method uses the basic weighted summation as the following equation.

$$EP_i = \sum EP_{ij} = \sum Q_j \times EF_{ij}$$

Where EP_i is the ith impact type characteristic value

EP_{ij} is the contribution of the jth inventory factor in the ith impact type

Q_j is the j th inventory factor emissions

EF_{ij} is the characteristic factor of the jth inventory factor in the ith impact type

4. Interpretation of results

Fig. S17 shows the results of the characterization step. All impact scores are displayed using 100% scale. The color indicates different impact types.

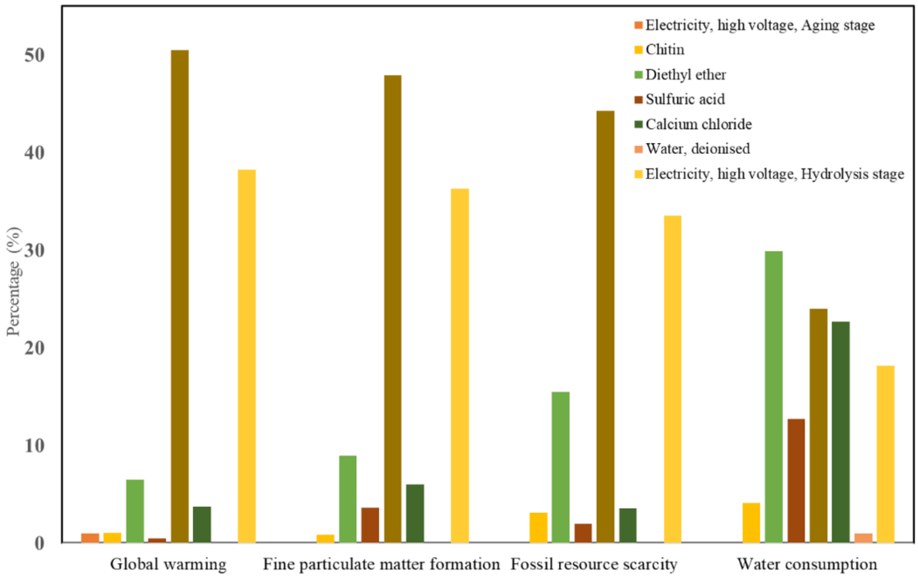

Fig. S17 Proportion of influence factors of different raw materials on AH-Ca method Life cycle analysis

The overall view of the complete life cycle network (showing the whole process) can analyze the whole process of extracting NAG from chitin. The thermometer (red bar on the right) shows the contribution to the environmental load, and the thickness of the line also indicates the total environmental load flow between processes. As shown in Fig. S18, the list of all processes, impact assessment results and process analysis are presented.

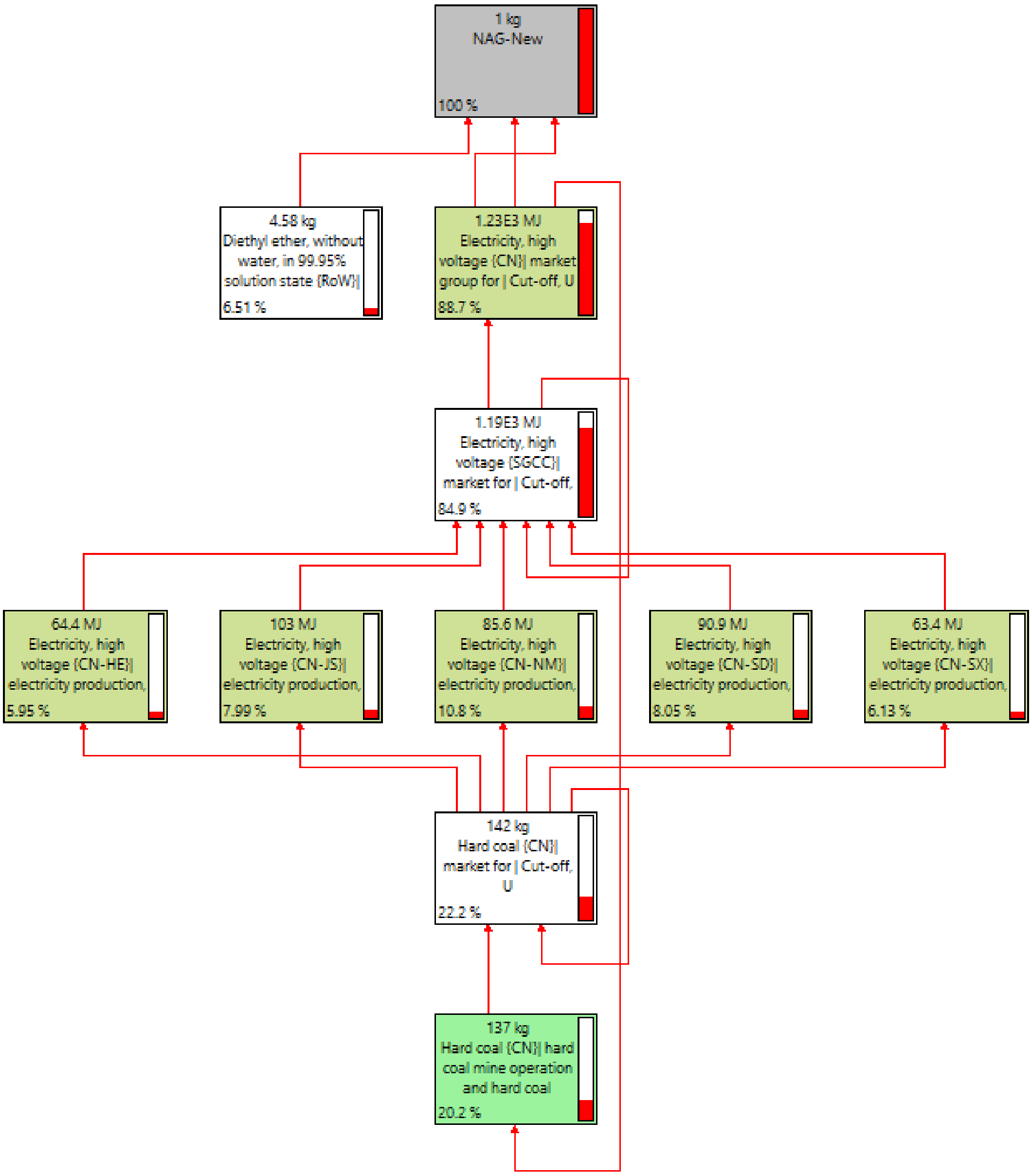

Fig. S18 General view of life cycle network.