Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information for

One-step Mechanochemical Conversion of Chitin and Shrimp Shells into Low Molecular Weight Chitosan

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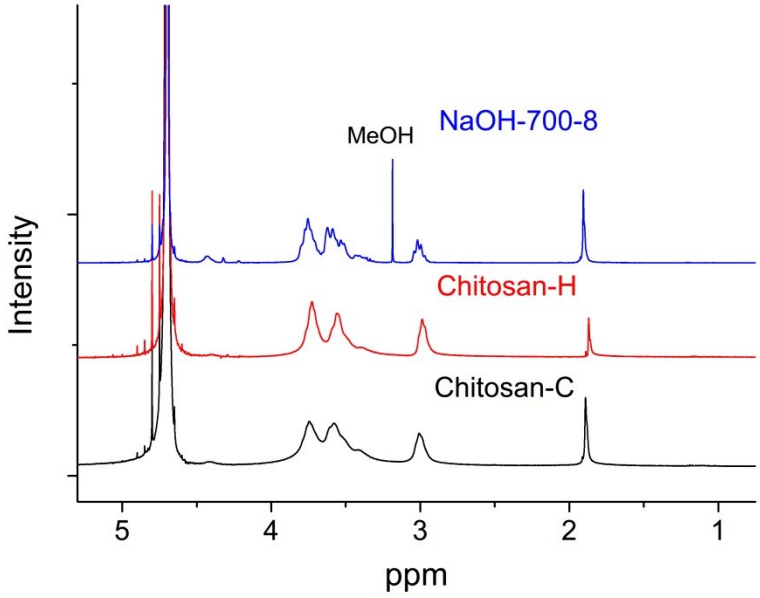

Figure S1 ^{1}H NMR spectra of Chitosan-C, Chitosan-H and NaOH-700-8 dissolved in acidified D_2O solution.

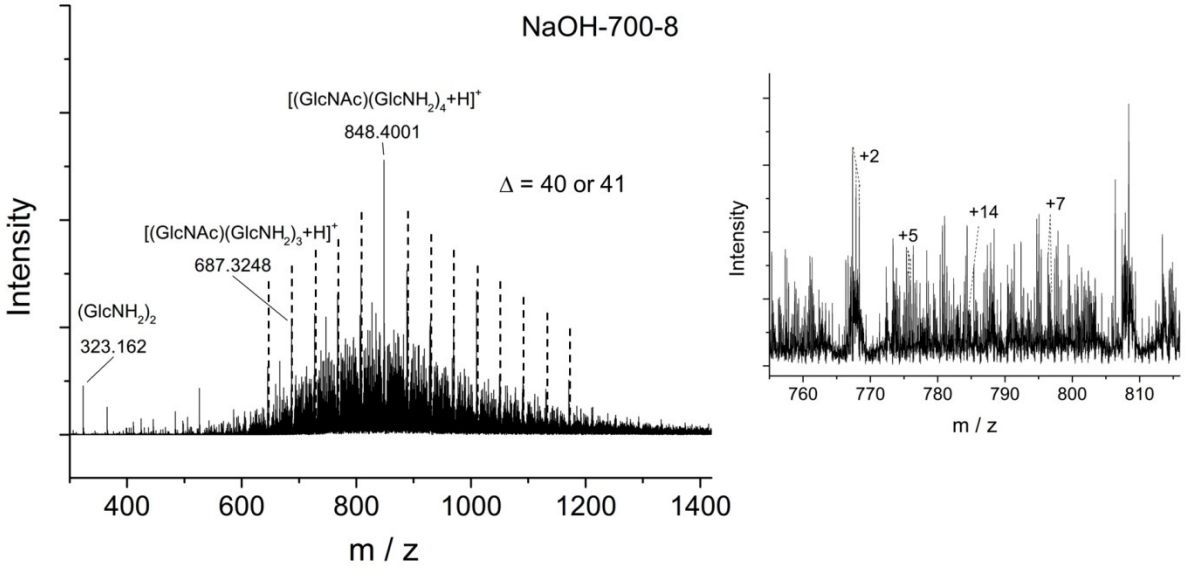

Figure S2 (a) the ESI signal of NaOH-700-8 sample (positive mode); (b) magnification of one of the signals to show the multi-charged status.

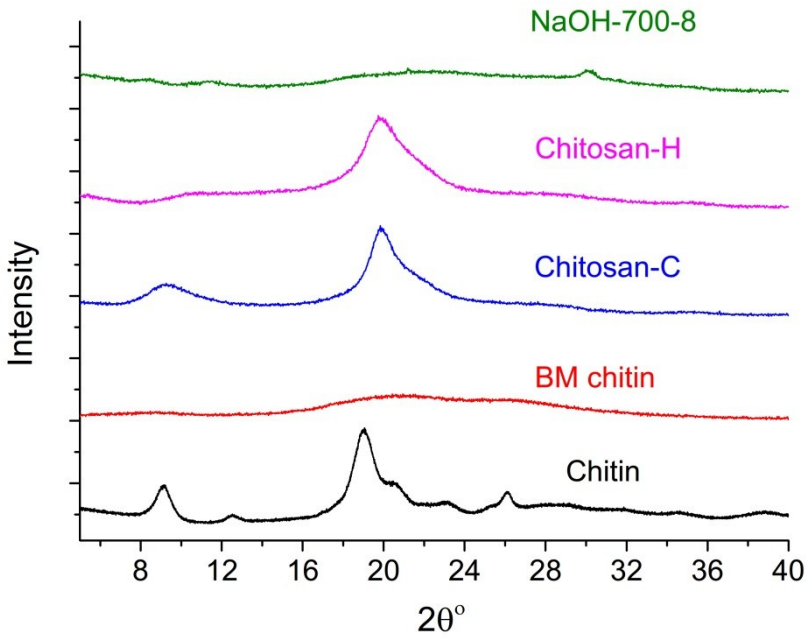

Figure S3 XRD patterns of chitin, BM-chitin, Chitosan-C, Chitosan-H and NaOH-700-8. The small peak at around 2θ = 30 ° in the spectrum of NaOH-700-8 was assigned to ZrO_2.

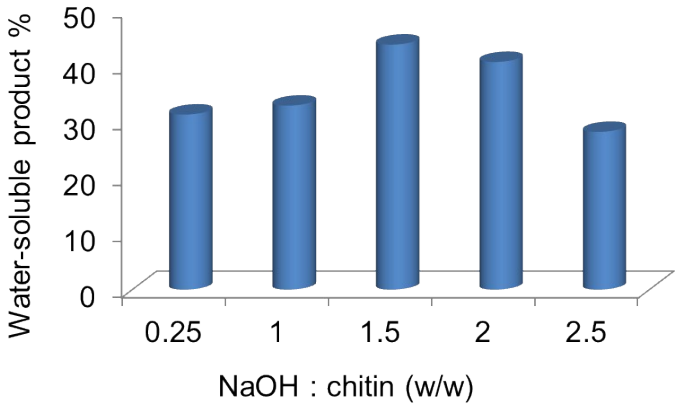

Figure S4 Yields of water-soluble product with varied NaOH to chitin ratio (weight percentage). Number of balls: 100; milling speed: 700 rpm; two cycles.

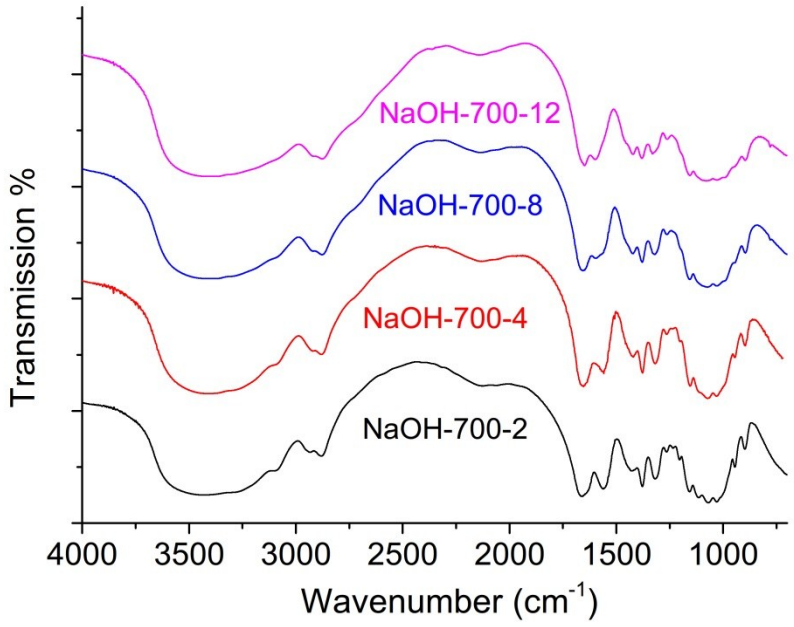

Figure S5 FTIR spectra of NaOH-700-2, NaOH-700-4, NaOH-700-8 and NaOH-700-12.

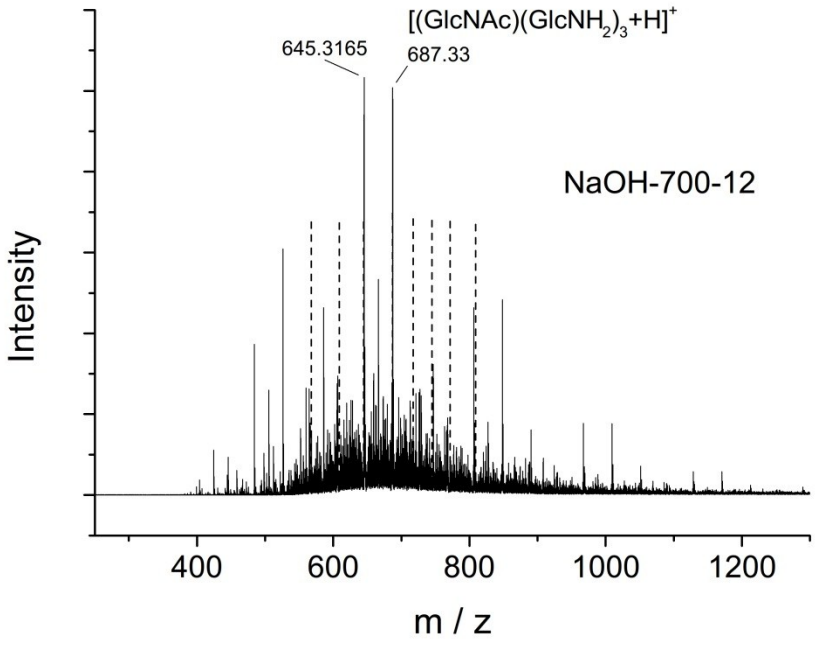

Figure S6 ESI-MS signal of NaOH-700-12 sample (positive mode).

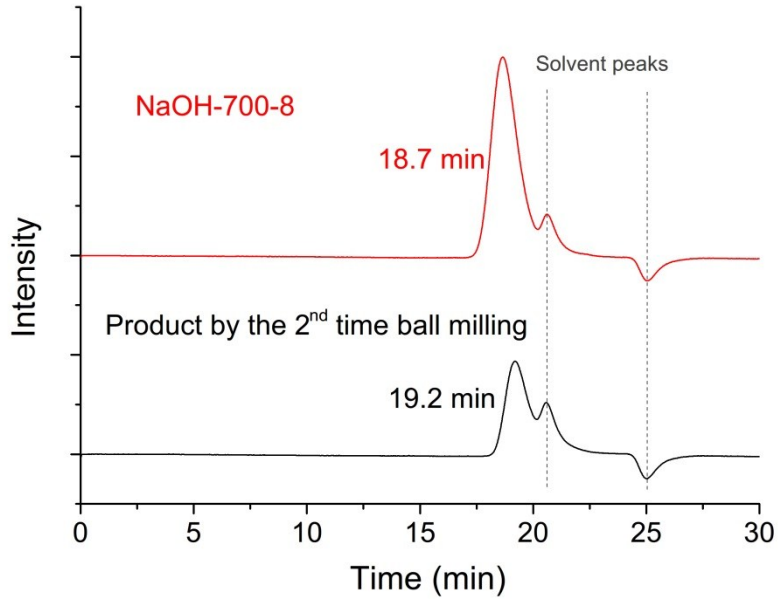

Figure S7 GPC spectra of the product obtained by a 2nd time ball milling and NaoH-700-8 product. The 2nd time ball milling is using NaOH-700-8 (0.4 g) as the starting material, and ball milled for 6 cycles at 700 rpm in the presence of 0.4 g NaOH.

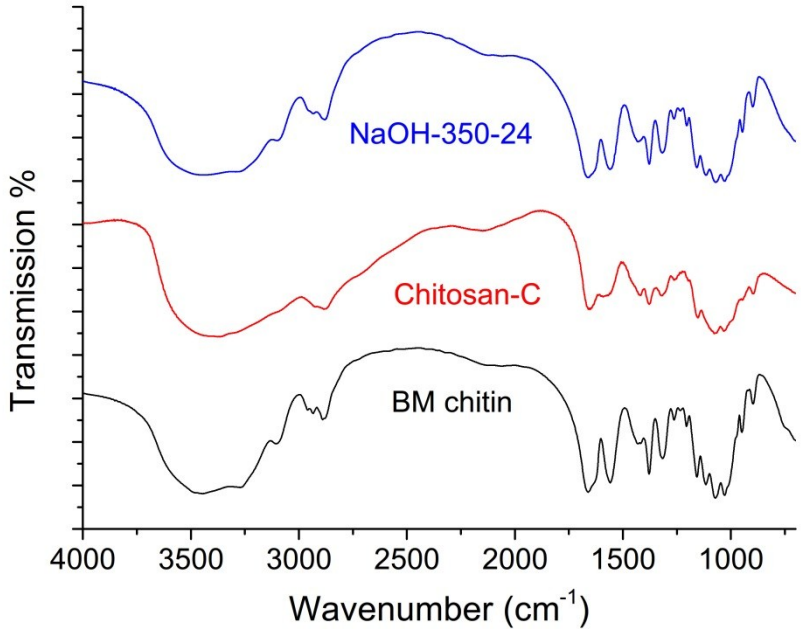

Figure S8 FTIR spectra of NaOH-350-24 and the comparison with BM chitin and Chitosan-C.

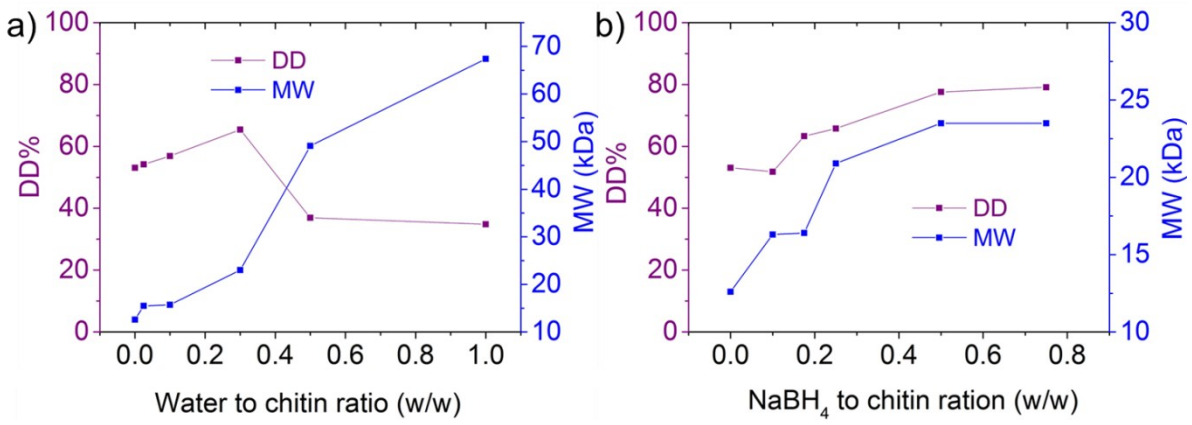

Figure S9 The influences of (a) water and (b) $NaBH_4$ on the DD and MW values of the products in the mechanochemcial process. Conditions: 0.4 g chitin, 0.4 g NaOH, a desired amount of water or $NaBH_4$, 100 ball, 700 rpm, 4 cycle.

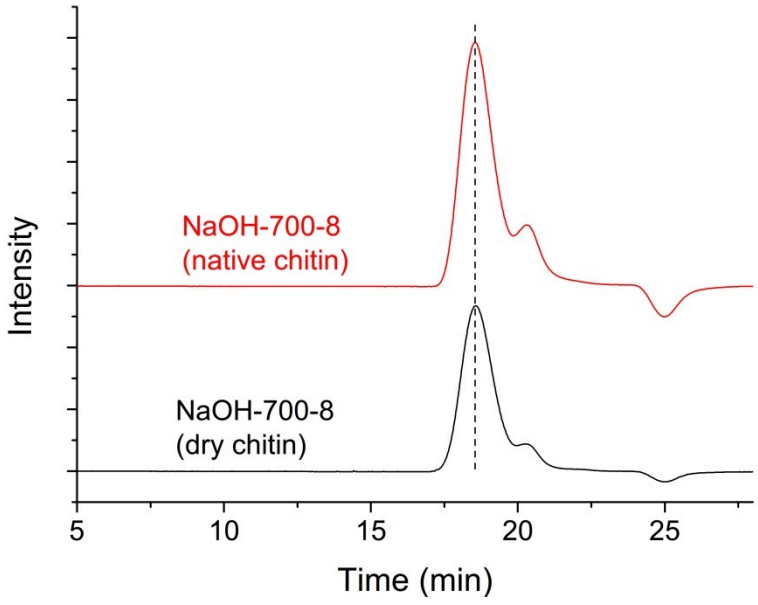

Figure S10 GPC analysis of NaOH-700-8 starting from native chitin and dried chitin.

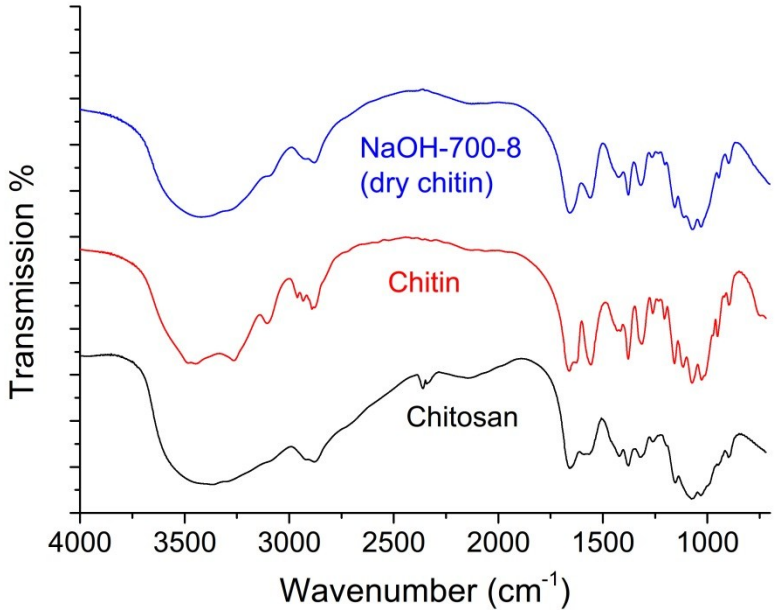

Figure S11 FTIR analysis of Chitosan-C, chitin and NaOH-700-8 starting from dried chitin.

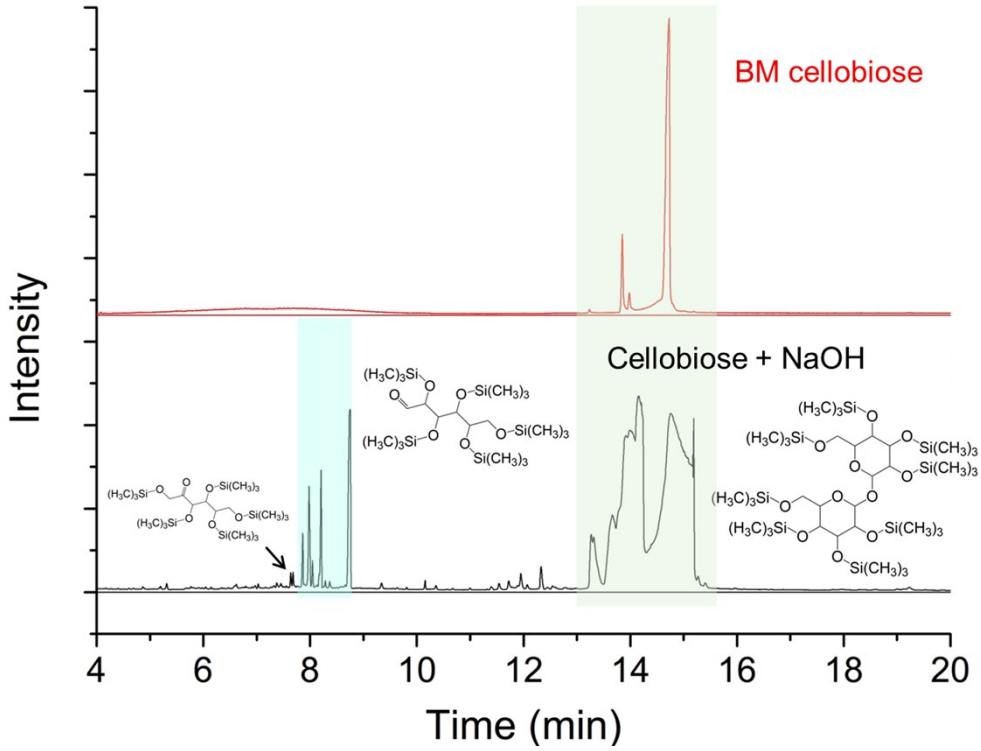

Figure S12 GC-MS spectra of the solid products after ball milling of cellobiose in the absence (top) and presence (down) of NaOH. Conditions: 0.4 g cellobiose, none or 0.1 g NaOH, 700 rpm, 5 min. The multiple peaks of the sugars ascribed to the isomers were induced by the silylation step.

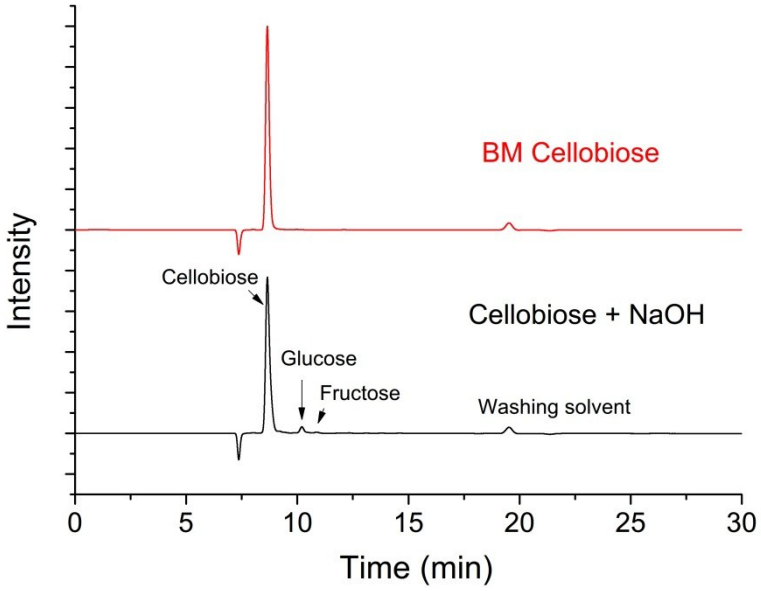

Figure S13 HPLC spectra of the products after ball milling of cellobiose in the absence (top) and presence (down) of NaOH. Conditions: 0.4 g cellobiose, none or 0.1 g NaOH, 700 rpm, 5 min.

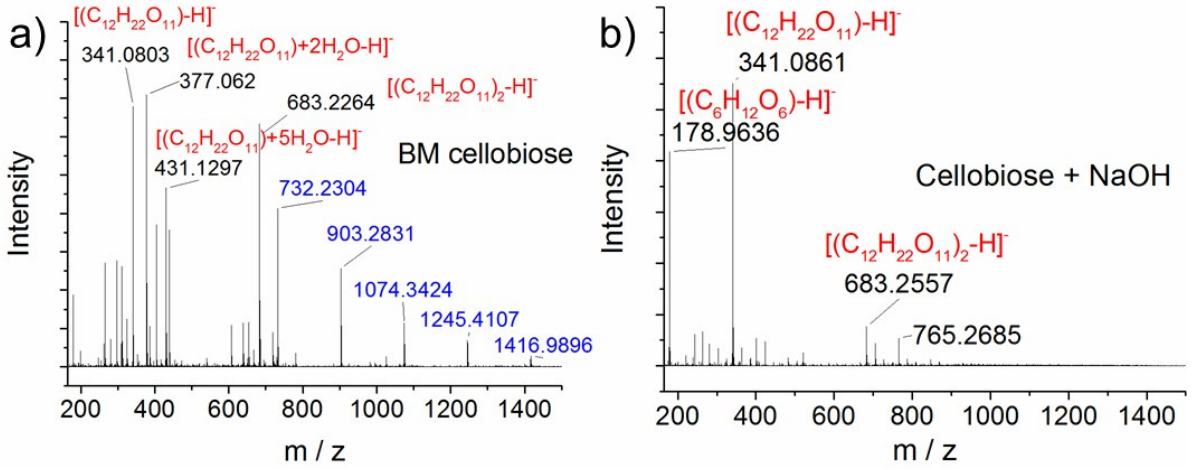

Figure S14 ESI-MS signals (negative mode) of (a) BM cellobiose; (b) Ball milled cellobiose in the presence of NaOH. Conditions: 0.4 g cellobiose, none or 0.1 g NaOH, 700 rpm, 5 min. The numbers in blue color indicate the charge to be -2. The proposed formulas are shown in red.

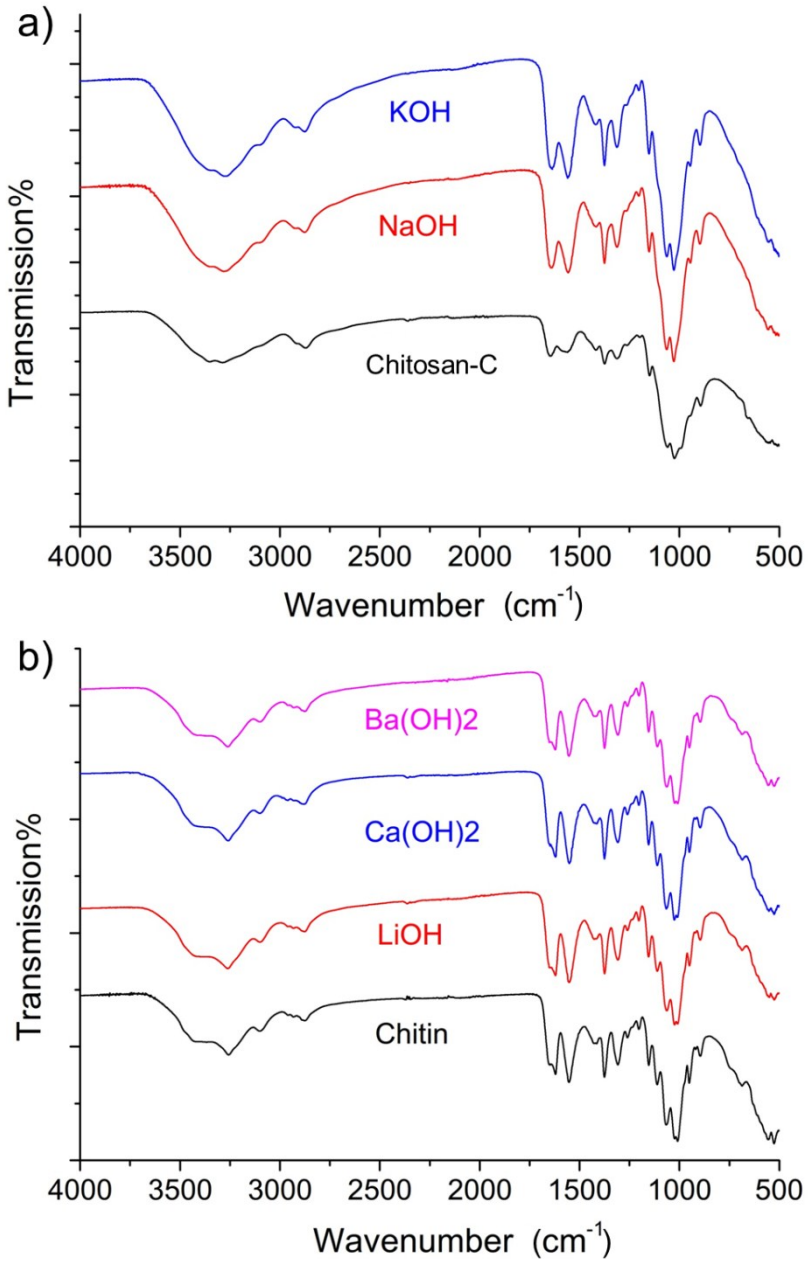

Figure S15 FTIR spectra of (a) Chitosan-C, NaOH-700-4 and KOH-700-4; (b) chitin, LiOH-700-4, $Ca(OH)_2$-700-4 and $Ba(OH)_2$-700-4.

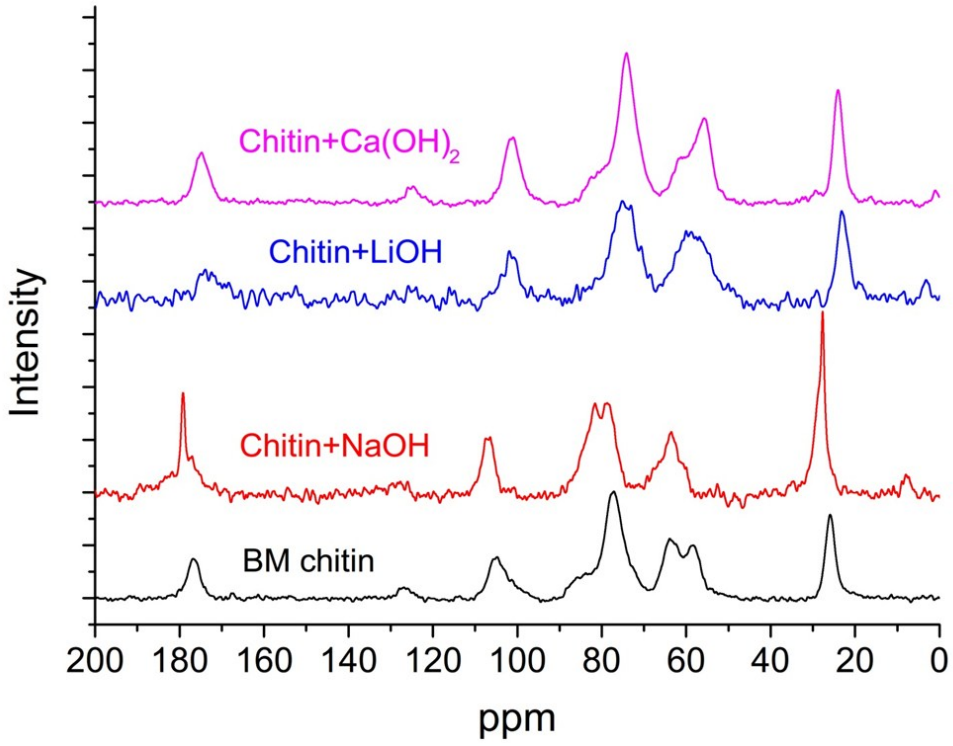

Figure S16 Solid-state NMR analysis of chitin without/with different base before and after ball mill. Conditions: 0.4 g chitin, 0.4 g base, 700 rpm, 4 cycles.

Table S1 The chemical shifts of the peaks of the base-promoted ball mill samples

	BM NAG	**NAG + LiOH**	**NAG + NaOH**	**NAG + $Ca(OH)_2$**
C7	0	-1.32	0	-0.42
C1	0	11.01	11.26	-0.20
C4	0	8.79	8.78	0
C5	0	3.96		-0.19
C3	0	3.30	4.62 (merged)	0.25
C6	0	1.07	1.32	0
C2	0	2.85	3.10	0
C8	0	-1.78	-0.31	0