

Supporting Information

High-Yield Preparation of Zwitterionically Charged Chitin Nanofiber and Its Application in Doubly pH-Responsive Pickering Emulsion

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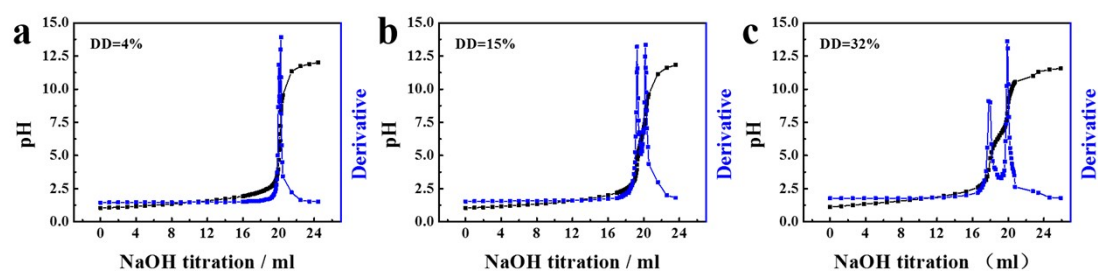


Figure S1. The titrimetric curves of (a) purified chitin (DD=4%) and DE-chitin with various degree of deacetylation (b) DD=15%, (c) DD=32%.

The DD values were calculated as follows¹:

$$DD = \frac{(V_2 - V_1) \times C \times 0.016}{0.0994 \times M} \quad \dots(1)$$

Where C is the accurate concentration of aqueous NaOH solution (mol L^{-1}), V_1 is the volume of aqueous NaOH solution (mL) at the first titration jump, V_2 is the volume of aqueous NaOH solution at the second titration jump, M is the sample weight (g), 0.016 is the molar mass weight of NH_2 (kg mol^{-1}), and 0.0994 is the theoretical NH_2 percentage in chitosan.

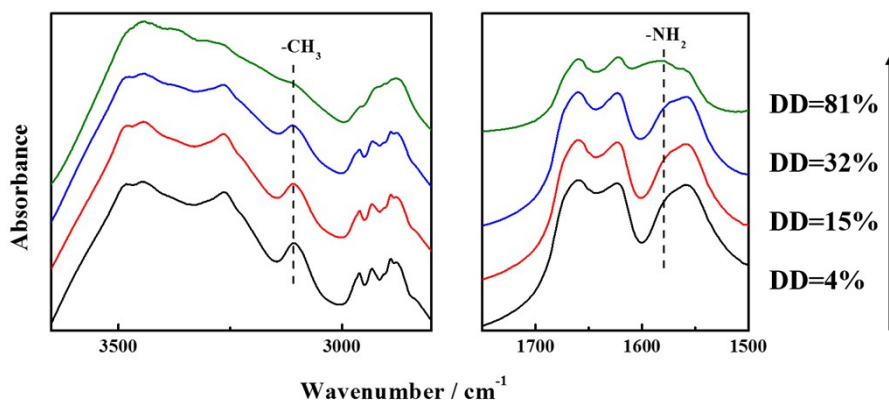


Figure S2. FT-IR spectra of purified chitin (DD=4%) and deacetylated chitin (DD=15%, 32%, 81%). The spectrum of chitosan (DD=81%) is also included for reference.

In Figure S2, the absent of the CH_3 stretching absorption peak at 3100 cm^{-1} and the relative enhancement of the new N-H bending absorption peak at 1596 cm^{-1} all demonstrate the successful deacetylation¹. After TEMPO-oxidation, the DD value is evaluated by IR (Fig. 1c). The two absorption intensities of the amide II and C-O band at 1560 cm^{-1} and 1030 cm^{-1} based on the baselines¹ from 1900 cm^{-1} to 1500 cm^{-1} and from 1220 cm^{-1} to 860 cm^{-1} are obtained, respectively. The DD is calculated according to equation (2).

$$y = -0.7x + 0.8 \quad \dots(2)$$

Where y is the intensity ratio of the IR band at 1560 cm^{-1} (amide II groups) and that at 1030 cm^{-1} (C-O stretching vibration), A_{1560}/A_{1030} , and x is the DD. The DD values of $11 \pm 2\%$ was deduced for DE-CO-ChNF.

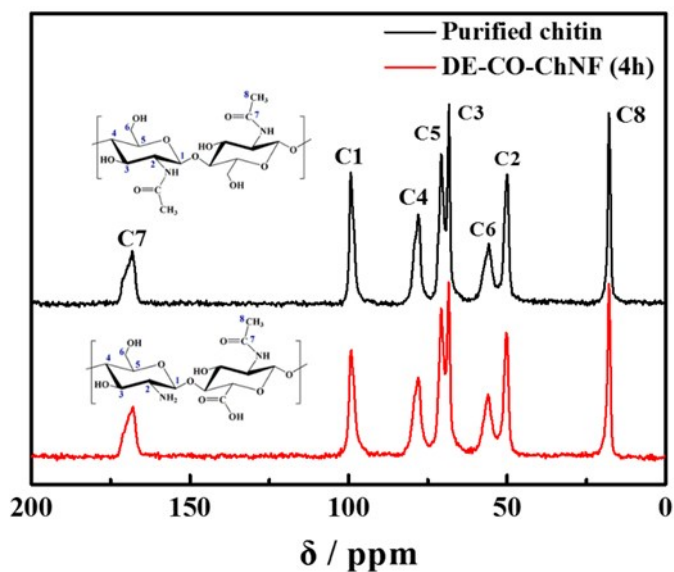


Figure S3. Solid-state ^{13}C NMR spectrum of purified chitin and DE-CO-ChNF (4h).

To confirm the degree of deacetylation (DD) of DE-CO-ChNF derived from IR spectra, solid state ^{13}C -NMR spectrum was also used to determine the DD value. In Figure S3, the patterns of the original solid-state ^{13}C -NMR spectra were essentially unchanged even after the deacetylation and TEMPO-oxidation. When the relative signal areas of C8 methyl around 18.1 ppm to those of C1 skeleton around 99.6 ppm are compared before and after the deacetylation and TEMPO-oxidation, there is obvious decrease due to the C8 methyl decreased by the deacetylation for chitin. The DD was calculated by the integral ratio of C8 and C1 based on the following equation²,

$$\text{DD} = \left(1 - \frac{\text{integral C8}}{1/6 \sum \text{integral}(C1 + C2 + C3 + C4 + C5 + C6)}\right) \times 100\% \quad \dots(3)$$

Where the integral of C8 corresponds to the methyl groups and the integral of C1, C2, C3, C4, C5 and C6 correspond to skeleton carbon in DE-CO-ChNF. Accordingly, the values of $11.4 \pm 2\%$ is obtained for DE-CO-ChNF which are consistent with the result calculated by the IR data.

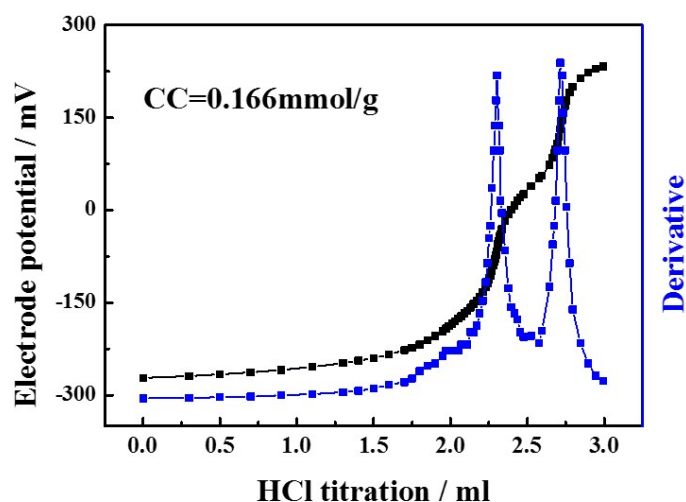


Figure S4. The titrimetric curve of carboxylic content (CC) of DE-CO-ChNF (DD=15%) by TEMPO-oxidization in 4h.

Note, the conductivity curve thus obtained reflected the content of both carboxylate and C2 amino groups in the DE-CO-ChNF because the carboxylic groups were apparently indistinguishable from the amino groups in the titration curves. Hence, the carboxylate content was obtained by subtracting the content of amino groups from the measured titration values for the DE-CO-ChNF³. The amino content (NC) was obtained by IR and NMR. The CC could be calculated by the equation (4):

$$CC = \frac{c \times (V_2 - V_1)}{M} - NC \quad \dots(4)$$

Where c is the accurate concentration of aqueous HCl solution (mol L^{-1}), V_1 is the volume of aqueous HCl solution (mL) at the first titration jump, V_2 is the volume of aqueous HCl solution at the second titration jump, M is the sample weight (g), NC could be transformed by the degree of deacetylation of DE-CO-ChNF, that is ca. 0.683 mmol/g.

References

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- 2 (a) M. R. Kasaai, *Carbohydr. Polym.*, 2010, **79**, 801; (b) L. Heux, J. Brugnerotto, J. Desbrières, M. F. Versali and M. Rinaudo, *Biomacromolecules*, 2000, **1**, 746.
- 3 (a) Y. Fan, T. Saito and A. Isogai, *Biomacromolecules*, 2008, **9**, 192; (b) S. Ifuku, T. Hori, H. Izawa, M. Morimoto and H. Saimoto, *Carbohydr. Polym.*, 2015, **122**, 1.