Supporting Information

Temperature and CO₂ Dual-Responsive Pickering Emulsion using Jeffamine M2005-Modified Cellulose Nanocrystals

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Content

- S1. Conductimetric titration
- S2. Elemental analysis
- S3 TGA of CNCs-M2005 and CNCs
- S4. Emulsification ability study
- S5. Effect of temperature on the stability of Pickering emulsions
- S6. TEM Characterization of CNCs
- S7. Dissociation/reassociation cycles of CNCs-M2005
- S8. State distribution of CNCs-M2005
- S9. Emulsification ability of CNCs-M2005⁺

S1. Conductimetric titration of the CNCs-COOH



Figure S1. Conductimetric titration curve of the CNCs-COOH sample.

S2. Elemental analysis characterization

The amount of M2005 bound on the surface of CNCs-COOH was calculated using elemental analysis. The elemental analysis data are presented in Table S1.

Assuming that we have 1 g of CNCs-COOH powders and that n moles of M2005 (M_W =2000 g/mol) has been bound to the surface of the CNCs-COOH after modification with M2005, then the weight of the product (CNCs-M2005) we can obtain is (1+n×2000) g. The increased nitrogen content (M_W =14.0 g/mol) in the final product compared to starting and intermediate materials comes from the monomer; therefore, the final nitrogen content can be derived as follows:

$$\frac{1 \times 0.060\% + n \times 14}{1 + n \times 2000} = 0.473\%$$

n = 0.89 mmol

1 mmol M2005 = 1.78 g M2005

The amount of M2005 bound to the surface of the CNCs-COOH is 1.78 g M2005/g CNCs-COOH. As we know, 1 g of CNCs-COOH contain 0.89 mmol of -COOH groups, and 0.89 mmol -COOH groups can react with 0.89 mmol of -NH₂ groups, which correspond to approximately 1.78 g of M2005. Therefore, the molar ratio of -COO-: -NH₃⁺ in the CNCs-M2005 is 1:1.

	N (%)	C (%)	H (%)
CNCs	0.051	40.26	5.969
CNCs-COOH	0.060	39.34	5.737
CNCs-M2005	0.473	55.08	8.523

Table S1. Elemental Analysis Data for the CNCs, CNCs-COOH andCNCs-M2005.

S3. TGA of CNCs-M2005 and CNCs



Figure S2. TG (a) and DTG (b) of CNCs-M2005.



Figure S3. TG (a) and DTG (b) of CNCs.

S4. Emulsification ability of CNCs, CNCs-COOH, M2005, mixture of CNCs and M2005, and CNCs-M2005



Figure S4. Photographs of emulsions (immediately after emulsification) stabilized by 0.75 wt% CNCs (a), 0.75 wt% CNCs-COOH (b), 0.75 wt% M2005 (c), a mixture of 0.75 wt% CNCs and M2005 (d), and 0.75 wt% CNCs-M2005 (e) with equal volume of *n*-tetradecane and aqueous phases.

S5. Effect of temperature on the stability of Pickering emulsions

In the control experiment, the Pickering emulsifier CNCs-C18 (product of CNCs-COOH and $C_{18}H_{37}$ -NH₂) was prepared and used for Pickering emulsion formation. The Pickering emulsion stabilized by CNCs-C18 cannot be destabilized at 60 °C after 20 min of standing (Figure S5) because of the absence of thermosensitive groups, indicating that these Pickering emulsions cannot be simply destabilized by the temperature. Therefore, we speculated that the destabilization of the CNC-M2005 particle-stabilized Pickering emulsions could be ascribed to the thermosensitive behavior of the introduced M2005.



Figure S5. Photographs of Pickering emulsions stabilized by 0.75 wt% CNCs-C18 at 20 °C (left) and at 60 °C for 20 min (right). The volume ratio of *n*-tetradecane and aqueous phases is 1:1.

S6. TEM Characterization of CNCs



Figure S6. TEM image of the pristine CNCs.

S7. Dissociation/reassociation cycles of CNCs-M2005 by alternately bubbling CO_2 and N_2

The dissociation/reassociation of the CNCs-M2005 was proven by pH and conductivity measurements. The pH of the CNC-M2005 aqueous solution before and after CO₂ bubbling was approximately 7.3 and 4.2, respectively (Figure S5), and the conductivity of the CNC-M2005 aqueous solution before and after CO₂ bubbling was 80.2 μ S/cm and 145.9 μ S/cm, respectively (Figure S5). These results indicate that the CNCs-M2005 can alternately dissociate/reassociate for three cycles by alternately bubbling CO₂ and N₂ through the solution.



Figure S7. Changes in conductivity and pH induced by alternately bubbling CO_2 and N_2 through the solution.

S8. State distribution of CNCs-M2005

According to the pK_a of –COOH (4.5) in the CNCs-COOH and the pK_a of –NH₂ (9.2) in the M2005, state distribution of CNCs-COOH and M2005 with varying pH values was presented (Figure S6). From Figure S6, we can find that CNCs-COOH and M2005 would be completely reacted in the pH range of 6.0-8.0. In our experiment, the pH of the mixture of CNCs-COOH and M2005 is in the range of 6.0-8.0. In this pH range, electrostatic interactions occurred between CNCs-COOH and M2005, and CNCs-M2005 was obtained. After treatment of CNCs-M2005 aqueous solution with CO_2 , the pH was decreased from 6-8 to approximately 4.2. At pH 4.2, approximately 65% CNCs-M2005 was dissociated into CNCs-COOH and M2005⁺. The remained CNCs-M2005 (35%, approximately 0.25 wt% CNCs-M2005 relative to aqueous

phase) was not enough to stabilized the Pickering emulsions.



Figure S8. State distribution of the CNCs-COOH and M2005.

S9. Emulsification ability of CNCs-M2005⁺



Figure S9. Photograph of unstable emulsion (immediately after emulsification) stabilized by $0.75 \text{ wt\% M2005}^+$ with equal volume of *n*-tetradecane and aqueous phases.