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An approach to enhanced redispersibility of cellulose nanocrystals *via* freeze-drying their Pickering emulsions

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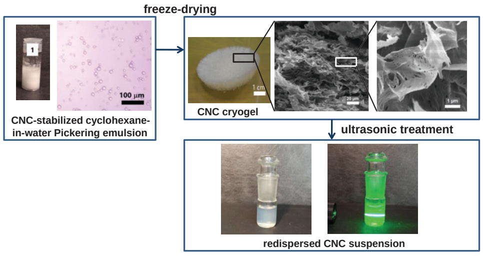
To enhance the redispersibility of dried nanocellulose, cellulose nanocrystal (CNC) cryogels were produced by freeze-drying CNC-stabilized cyclohexane-in-water Pickering emulsions. The CNC cryogels were easily redispersed in water and organic solvents; thus, the approach proposed made it possible to significantly improve CNC redispersibility in aqueous and nonaqueous media.



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Cellulose nanocrystals (CNCs) can be prepared by controlled hydrolysis of cellulose-containing materials.[1] CNC particles range from several dozens to several hundreds of nanometers in length and from 3 to 20 nm in diameter depending on the raw material and hydrolysis conditions.[2] The properties of CNCs (anisotropic particles, high mechanical strength, chemically modifiable surface hydroxyl groups, and the formation of a chiral nematic liquid crystal phase in aqueous suspensions and films) attract a lot of attention in terms of CNC application to the development of functional materials.[3–6] The use of CNCs in composite materials improved their mechanical, optical, and sorption properties or imparted new properties, such as biodegradability, to them.[7–9]

Operations with CNCs require solving the problem of CNC redispersion in aqueous and nonaqueous media. Redispersibility is important for restoring the unique properties of CNC suspensions after drying before storage or transportation. Commercial CNCs should be supplied in a dry form and redispersed on site to minimize the size and weight of the product and, hence, the transportation cost. Drying prevents the growth of bacteria and microorganisms in CNCs; it is often an essential stage of solvent exchange before CNC dispersion in organic solvents or polymers for nanocomposite production. The drying of aqueous CNC suspensions through free water evaporation leads to irreversible aggregation of CNC particles and makes their redispersion impossible.[10,11] This problem can be solved using special drying methods. Freeze-drying (lyophilization), spray-drying, spray freeze-drying, and supercritical drying of aqueous CNC suspensions make it possible to prepare CNC aero-, cryo-, and xerogels, foams, powders, and beads, which can be redispersed in water and organic solvents by ultrasonic treatment.[12–23] Furthermore, the drying technique influences the degree of CNC dispersion within polymer matrices in the fabrication of composites.[24]

Here, we propose an approach to the preparation of CNC cryogels using Pickering emulsions,[25,26] which considerably improvs the redispersibility of CNCs in water and nonaqueous solvents.[27]

The aqueous CNC suspensions were obtained by the sulfuric acid hydrolysis of microcrystalline cellulose in accordance with a published procedure.[28] Then, we have prepared a 1 : 1 mixture of an aqueous CNC suspension (a concentration of 2 g dm^{-3} without and with a KCl electrolyte additive) with cyclohexane. To obtain a stable Pickering emulsion, the cyclohexane mixture with the CNC suspension was treated using an ultrasonic homogenizer (Sonohuls HD 2070, Bandelin) in the pulse mode for 1 min and then immediately frozen. The average size of droplets in the CNC-stabilized emulsion was about 5–20 μm; an electrolyte additive reduced the average droplet size to 1–5 μm (see Online Supplementary Materials, Figures S1, S2) and considerably increased the emulsifying capacity and the emulsion stability in time.[29]

The Pickering emulsions were frozen and stored at –40 °C for two days and then freeze-dried at 6 Pa and –54 °C for 48 h. For comparison, porous cellulose materials were also prepared by conventional lyophilization of an aqueous CNC suspension (2 g dm^{-3}) and by drying a CNC organogel in ethanol[13] (with the above CNC concentration) in supercritical CO_2 using an experimental setup described elsewhere.[30]

Cyclohexane (mp 6.5 °C) made it possible to carry out freeze-drying efficiently and obtain CNC cryogels with a developed surface (Figures 1, 2). The CNC cryogels exhibited a cellular-like architecture, and their morphology was an arrangement of intersected thin plates consisting of very subtle CNC films. The CNC aerogel had a multiscale structure with a fine nanostructured fibrillated texture. The specific surface area of the cryogels obtained by the freeze-drying of CNC-stabilized Pickering emulsions was much higher than that of a CNC sample prepared by the freeze-drying of a CNC aqueous suspension and comparable to that of an aerogel obtained by the drying of organogel in supercritical CO_2 (Online Supplementary Materials, Table S1).[†]

[†] The cryogels were produced using an LS-500 freeze dryer (Russia). The CNC particle ζ-potential and size distribution (DLS method) were determined using a Zetasizer Nano ZS (Malvern Instruments Ltd.) device.

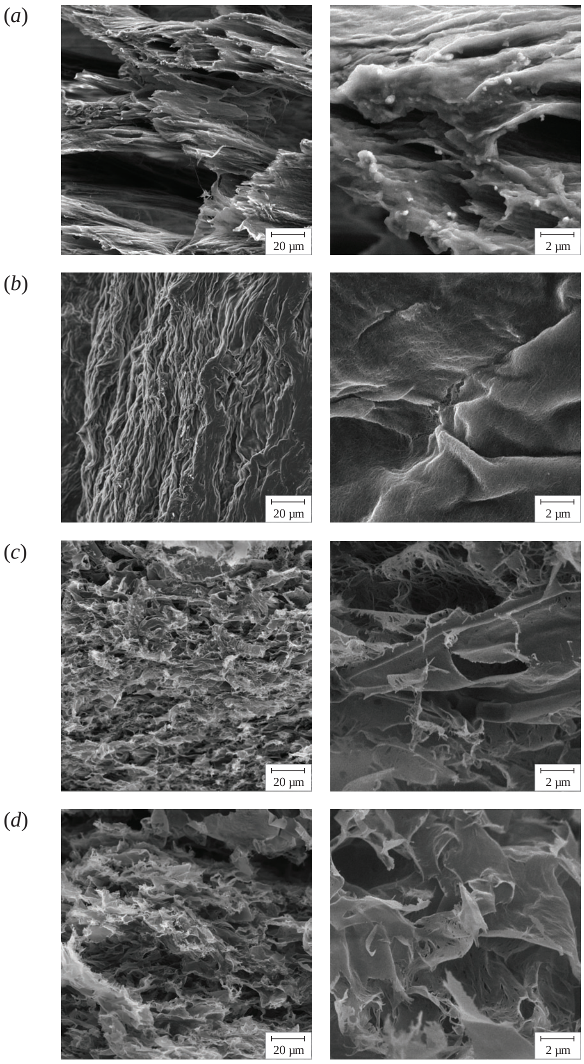

Figure 1 SEM images of CNC-based porous materials obtained by (*a*) conventional freeze-drying of an aqueous CNC suspension, (*b*) drying of a CNC ethanol organogel in supercritical CO_2, (*c*) freeze-drying of CNC-stabilized cyclohexane/water Pickering emulsion, and (*d*) freeze-drying of CNC-stabilized cyclohexane/water Pickering emulsion with a 0.02 M KCl additive at two magnifications (scale bars, 20 and 2 µm).

In the CNC-stabilized cyclohexane-in-water emulsions, the anisotropic amphiphilic CNC particles were distributed at the cyclohexane/water interface to produce a strong emulsifying effect. Thus, the cyclohexane droplets were stabilized in an aqueous solution, and contacts between the CNC particles were limited. We hypothesized that this circumstance enhanced the redispersibility of CNC cryogels produced using Pickering emulsions.

The CNC cryogels obtained using cyclohexane-in-water emulsions were completely redispersed in water and partially in organic solvents with moderate ultrasonic treatment (Sonorex DT100 Bandelin). The redispersibility of the cryogels can be evaluated in terms of particle-size distribution and colloidal stability of the suspensions. The particle-size distributions of redispersed cryogels did not demonstrate the appearance of CNC particle aggregates, and the particle sizes remained almost unchanged compared with that for a never-dried aqueous CNC suspension (Online Supplementary Materials, Figures S3). The redispersed aqueous suspensions demonstrated high colloidal stability after a month of holding, and the surface charge of the redispersed CNC particles was retained (the ζ potential was about –40 mV). Full CNC redispersion was accompanied by the Tyndall effect, which indicated a colloidal-like state and nanoscale sizes of CNCs in their suspensions.[31] In acetonitrile, dioxane, and chloroform, CNC particles aggregated and precipitated with time. Table 1 presents the results of visual control of the redispersibility of CNC cryogels in water, dimethyl formamide, acetonitrile, dioxane, and chloroform (for a CNC concentration of 2 g dm^{-3}).

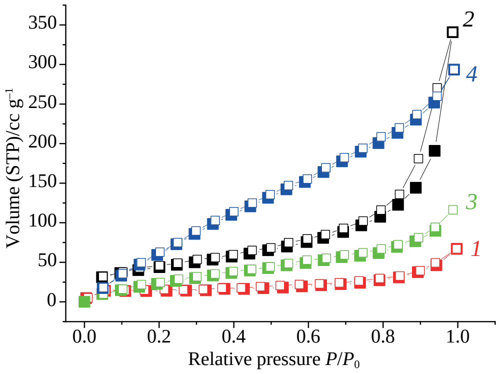

Figure 2 Low-temperature (77 K) nitrogen (solid symbols) adsorption and (open symbols) desorption isotherms for CNC-based porous materials obtained by (*1*) conventional freeze-drying of the CNC aqueous suspension, (*2*) drying of the CNC ethanol organogel in supercritical CO_2, (*3*) freeze-drying of the CNC-stabilized cyclohexane/water Pickering emulsion, and (*4*) freeze-drying of the CNC-stabilized cyclohexane/water Pickering emulsion with a 0.02 M KCl additive.

Table 1 Redispersibility of CNC cryogels in water and organic solvents.[a]

Pickering emulsions	Solvent				
	Water	DMF	Acetonitrile	Dioxane	Chloroform
Cyclohexane/ water/CNCs	++	++	+	+	–
Cyclohexane/ water/0.02 M KCl/ CNCs	++	++	+	+	+

[a] ++ complete redispersion; + partial redispersion; – no redispersion.

Thus, we were the first to use Pickering emulsions for producing CNC cryogels with improved redispersibility in water and nonaqueous media. This approach requires an additional study for its optimization (in terms of CNC concentration and the nature and concentration of an electrolyte).

The measurements were made with the use of equipment of the Upper Volga Region Centre of Physicochemical Research (Ivanovo, Russia). The authors are grateful to Dr. Dyshin for obtaining the CNC aerogel in supercritical CO_2.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.02.040.

References

1 L. Brinchi, F. Cotana, E. Fortunati and J. M. Kenny, *Carbohydr. Polym.*, 2013, **94**, 154.

2 K. J. Nagarajan, N. R. Ramanujam, M. R. Sanjay, S. Siengchin, B. S. Rajan, K. S. Basha, P. Madhu and G. R. Raghav, *Polym. Compos.*, 2021, **42**, 1588.

3 C. A. de Assis, C. Houtman, R. Phillips, E. M. Bilek, O. J. Rojas, L. Pal, M. S. Peresin, H. Jameel and R. Gonzalez, *Biofuels, Bioprod. Biorefin.*, 2017, **11**, 682.

The morphology of the samples was examined with the scanning electron microscopy (SEM) (VEGA 3 SBH TESCAM, Czech Republic). The Pickering emulsions were investigated using a Soptop CX40P polarization optical microscope (POM) (Sunny Instruments, China). A NOVAtouch NT LX Quantachrome (USA) automatic analyzer was employed to determine the specific surface area of the samples.

4 Y. Sun, Y. Chu, W. Wu and H. Xiao, *Carbohydr. Polym.*, 2021, **255**, 117489.
5 B. L. Pelegrini, F. Ré, M. M. de Oliveira, T. Fernandes, J. H. de Oliveira, A. G. Oliveira, Jr., E. M. Girotto, C. V. Nakamura, A. R. Sampaio, A. Valim and M. M. de Souza Lima, *Macromol. Mater. Eng.*, 2019, **304**, 1900092.
6 M. A. Orlova, V. V. Spiridonov, G. A. Badun, T. P. Trofimova, A. P. Orlov, A. S. Zolotova, A. B. Priselkova, G. Yu. Aleshin, M. G. Chernysheva, A. A. Yaroslavov and S. N. Kalmykov, *Mendeleev Commun.*, 2022, **32**, 658.
7 S. Mondal, *Carbohydr. Polym.*, 2017, **163**, 301.
8 Z. Xiong, J. Lin, X. Li, F. Bian and J. Wang, *ACS Appl. Mater. Interfaces*, 2021, **13**, 12408.
9 I. V. Averianov, M. A. Stepanova, I. V. Gofman, A. Lavrentieva, V. A. Korzhikov-Vlakh and E. G. Korzhikova-Vlakh, *Mendeleev Commun.*, 2022, **32**, 810.
10 M. S. Reid, S. A. Kedzior, M. Villalobos and E. D. Cranston, *Langmuir*, 2017, **33**, 7403.
11 I. Déléris and J. Wallecan, *Adv. Colloid Inreface Sci.*, 2017, **246**, 1.
12 M. I. Voronova, A. G. Zakharov, O. Y. Kuznetsov and O. V. Surov, *Mater. Lett.*, 2012, **68**, 164.
13 M. I. Voronova, O. V. Surov, N. V. Rubleva, N. E. Kochkina and A. G. Zakharov, *Russ. J. Bioorg. Chem.*, 2020, **46**, 1295 (*Khimiya Rastitel’nogo Syr’ya*, 2019, no. 1, 39).
14 Q. Beuguel, J. R. Tavares, P. J. Carreau and M.-C. Heuzey, *J. Colloid Interface Sci.*, 2018, **516**, 23.
15 L. Di Giorgio, L. Martín, P. R. Salgado and A. N. Mauri, *Carbohydr. Polym.*, 2020, **238**, 116187.
16 E. Niinivaara and E. D. Cranston, *Carbohydr. Polym.*, 2020, **247**, 116664.
17 W. Abdallah and M. R. Kamal, *Cellulose*, 2018, **25**, 5711.
18 D. Wang, J. Li, J. Zhang, J. Yu and J. Zhang, *ChemNanoMat*, 2019, **5**, 163.
19 S. Sinquefield, P. N. Ciesielski, K. Li, D. J. Gardner and S. Ozcan, *ACS Sustainable Chem. Eng.*, 2020, **8**, 9601.
20 Q. Wang, Q. Yao, J. Liu, J. Sun, Q. Zhu and H. Chen, *Cellulose*, 2019, **26**, 7585.
21 D. Ciftci, A. Ubeyitogullari, R. R. Huerta, O. N. Ciftci and M. D. A. Saldaña, *J. Supercrit. Fluids*, 2017, **127**, 137.
22 M. V. G. Zimmermann, C. Borsoi, A. Lavoratti, M. Zanini, A. J. Zattera and R. M. C. Santana, *J. Reinf. Plast. Compos.*, 2016, **35**, 628.
23 N. Buchtová and T. Budtova, *Cellulose*, 2016, **23**, 2585.
24 V. Khoshkava and M. R. Kamal, *Powder Technol.*, 2014, **261**, 288.
25 S. A. Kedzior, V. A. Gabriel, M. A. Dubé and E. D. Cranston, *Adv. Mater.*, 2021, **33**, 2002404.
26 M. Yu. Koroleva and E. V. Yurtov, *Russ. Chem. Rev.*, 2022, **91**, RCR5024.
27 O. V. Surov, M. I. Voronova, A. V. Afineevskii and A. G. Zakharov, *The 6th International Conference of the CIS countries ‘Sol–gel synthesis and research of inorganic compounds, hybrid functional materials and disperse systems’ (‘Sol–Gel 2020’)*, Uzbekistan, Samarkand, 11–15 October 2021, p. 125.
28 D. Bondeson, A. Mathew and K. Oksman, *Cellulose*, 2006, **13**, 171.
29 O. V. Surov, M. I. Voronova and A. G. Zakharov, *Cellulose*, 2021, **28**, 6269.
30 Y. A. Vaksler, D. Benedis, A. A. Dyshin, R. D. Oparin, N. T. Correia, F. Capet, S. V. Shishkina, M. G. Kiselev and A. Idrissi, *J. Mol. Liq.*, 2021, **334**, 116117.
31 Z. Zhu, W. Wang, X. Wang, X. Zhao, N. Xia, F. Kong and S. Wang, *Cellulose*, 2021, **28**, 9661.

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