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著者	Zhang Jie, Furushima Hinako, Nakato Teruyuki, Mouri Emiko
journal or publication title	Chemistry Letters
volume	50
number	2
page range	240-243
year	2020-11-11
その他のタイトル	Preparation of Cellulose Nanocrystals based Core-Shell Particles with Tunable Component Location
URL	<a href="http://hdl.handle.net/10228/00008046">http://hdl.handle.net/10228/00008046</a>

doi: <https://doi.org/10.1246/cl.200702>

# Preparation of Cellulose Nanocrystals based Core-Shell Particles with Tunable Component Location

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**Abstract:** We report a versatile method for preparing a particulate composite based on cellulose nanocrystals (CNCs) and polyethylene glycol (PEG) via the self-organized precipitation method. The particulate composite had a core-shell structure, and depending on the molecular weight of the PEG, two types of particulates could form: one with CNCs as the core and the other with CNCs as the shell.

**Keywords:** cellulose nanocrystals, particle, polymer

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Cellulose nanocrystals (CNCs), derived from wood and other natural sources, are anisotropic, rod-shaped nanoparticles<sup>1-3</sup>. CNCs are regarded as one of the most promising sustainable and nontoxic materials, having versatile, attractive characteristics such as high mechanical strength, high gas barrier, and unique optical properties.

Incorporating CNCs with general polymer can exploit the attractive characteristics of CNCs. Especially, particulate composite fabrication of CNCs with polymer would be worth developed. One of the reasons is that the surface of CNCs is so hydrophilic that CNCs cannot be easily dispersed in a non-polar matrix simply by mixing. Thus, stable-composite fabrication using polymers is a practical way of imparting amphiphilic properties to CNCs<sup>4,5</sup>. In addition, the particulate composite can be used as a secondary building block to fabricate higher-order materials with more sophisticated architecture, an application that cannot be achieved with film-based CNC materials.

Among the various forms of CNC-polymer particles, core-shell particles with regulated CNC locations are a target for achieving controlled characteristics of CNCs. CNC particulates coated with other components can be dispersed in various media by controlling the affinity between the polymer component and the matrix. On the other hand, polymer particulates having a CNC crust can yield stable micro-spaces with cellulose walls similar to those of plant cells, resulting in a bio-inspired material with high mechanical strength.

In this study, we propose a fabrication method for the particulate composite of CNCs and polymer with a tunable component location. Confinement of CNCs in particles has been challenged by some groups, who chose to fabricate core-shell particles with CNC core by utilizing microfluidic emulsification<sup>6,7</sup>. Wang et al. also reported the synthesis of core-shell particles with CNC cores by emulsion polymerization, which yielded particles with 30–200 μm diameters<sup>8</sup>. On the other hand, Jatava et al. also reported

CNC capsules, in which CNCs are in the shell of a core-shell particle<sup>9</sup>. However, no previous studies have reported a particulate-composite fabrication method that can create core-shell particles that contain CNCs either in the core or the shell; developing a widely applicable method is a challenge. To widen the selection of possible counterpart components, the fabrication method should be simple, with few restrictions.

To create a core-shell-like composite featuring CNCs with tunable component locations, we used the self-organized precipitation (SORP) method proposed by Yabu<sup>10,11</sup>. Unlike other methods such as dispersion polymerization<sup>12</sup> or emulsion polymerization<sup>13</sup>, the SORP method does not require strict polymerization control or additional surfactant. The SORP method is known to be a facile method for preparing particles composed of two components. It usually involves two solutes and two miscible solvents (one solvent is good at dissolving solutes, while the other is poor). When the good solvent is evaporated, the solubility of the solutes decreases, causing core-shell particles to form. The particle architecture, i.e., the component location, is controlled by the difference in affinity between the two solutes and the poor solvent. Thus, by controlling the affinities between the CNCs and polymer components, this method can be applied to produce particles with a tunable location.

In this paper, we report the fabrication of core-shell-like particles via the SORP method. Two types of CNC/polyethylene glycol (PEG) particles with different CNC locations were obtained simply by changing the molecular weight of PEG. In the experiment, CNCs and PEG were used as the two solutes, and water and ethylene glycol (EG) were used as the two miscible solvents. In this

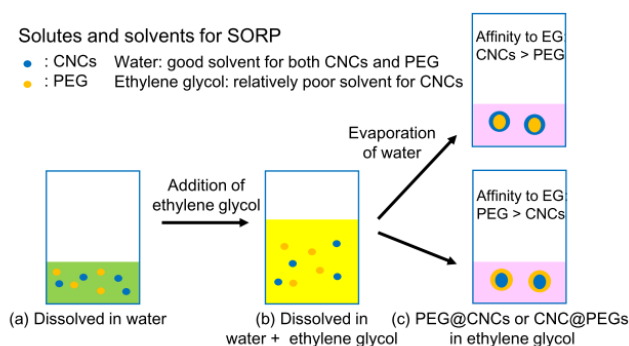


Figure 1 Schematic concept of CNCs/PEG particle fabrication with tunable CNCs locations *via* SORP method.

1 system, water is a good solvent for both CNCs and PEG,  
 2 and EG has a higher boiling point than water. We chose  
 3 PEG as the polymer component because the affinity  
 4 between PEG and solvent can be varied through the  
 5 molecular weight<sup>14</sup>. Furthermore, PEG has been widely  
 6 applied in biomedical materials because of its non-toxicity  
 7 and bio-degradability, characteristics that could make the  
 8 combination of CNCs and PEG a sustainable material.

9 Figure 1 shows a schematic of the SORP method  
 10 applied to the CNC-PEG solute in the water-EG system.  
 11 First, CNC and PEG are dissolved in water (Fig. 1a), and  
 12 EG is added to the solution (Fig. 1b). Water then evaporates,  
 13 while EG remains unevaporated (Fig. 1c). In this process,  
 14 CNCs and PEG tend to deposit because of their decreased  
 15 solubility in EG. The resultant core-shell particles depend  
 16 on the relative affinities of CNC and PEG to EG, as shown  
 17 in Fig. 1c. If the CNC-EG affinity is greater than that of  
 18 PEG-EG, then CNCs form a shell around the PEG core  
 19 because the CNC-EG interaction is favored, and vice versa.  
 20 Using PEG solubility differences, we aimed to fabricate two  
 21 types of core-shell particles with tunable CNC locations, as  
 22 shown in Fig. 1c.

23 We used two types of PEG with average molecular  
 24 weights of 2,000 and 20,000, denoted hereafter as  
 25 PEG2,000 and PEG20,000, respectively. CNCs having a  
 26 length of around 40–100 nm and a width of 2–5 nm CNCs  
 27 were purchased from CelluForce, Canada. CNC has sulfonic  
 28 acid groups with sulfate content of ca. 250 mmol kg<sup>-1</sup>.  
 29 PEG20,000 and PEG2,000 were purchased from Wako  
 30 Chemical Industry, Japan, and their molecular weight ranges  
 31 claimed by the supplier are 15,000~25,000 and 1,800~2,200,  
 32 respectively. The sample preparation procedure is  
 33 represented in Fig. 1. CNCs and PEG were separately  
 34 dispersed in Mill-Q water completely to a concentration of  
 35 8 g L<sup>-1</sup>. For the preparation of the CNC/PEG sample, the  
 36 CNC dispersion was mixed with the PEG dispersion and  
 37 water to prepare 4  
 38 mL of 2 g L<sup>-1</sup> of  
 39 CNCs and PEG.  
 40 The same volume  
 41 (4 mL) of ethylene  
 42 glycol  
 43 was gradually added to  
 44 form an aqueous  
 45 mixture. The  
 46 solution was stirred  
 47 for 24 hours to  
 48 prepare a mixture  
 49 of CNCs (1 g L<sup>-1</sup>)  
 50 and PEG (1 g L<sup>-1</sup>)  
 51 in the  
 52 water/ethylene  
 53 glycol solvent  
 54 mixture. The  
 55 solutions for both  
 56 systems were  
 57 transparent at this  
 58 stage, as shown in  
 59 Fig. 2a, b.

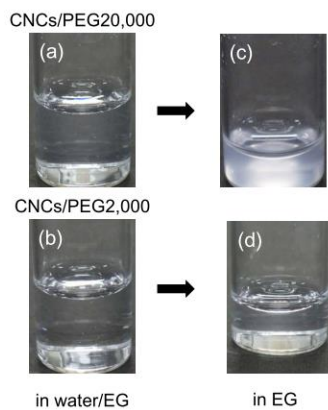


Figure 2 Appearances of CNCs/PEG20,000 ((a),(c)) and CNCs/PEG2,000((b),(d)) solutions in the process of SORP method: Before EG evaporation dispersed in water/EG ((a),(b)) and after the evaporation of EG ((c), (d))

60 Core-shell particles with CNC shell were obtained when  
 61 using PEG20,000. The CNC/PEG20,000 solution in water  
 62 and EG was transparent at room temperature. The mixtures  
 63 were heated at 45 °C to evaporate to half the volume in  
 64 order to remove the water and obtain the EG solution. The  
 65 evaporation of ca. 2 ml of water out of 4 ml mixture solution  
 66 takes three days. At this stage, the CNC/PEG20,000 solution  
 67 turned turbid, as shown in Fig. 2c. However, we could not  
 68 observe the particle formation clearly by optical  
 69 microscopy; we confirmed the fluctuation in the contrast of  
 70 the optical microscopy image for the CNC/PEG20,000  
 71 solution.

72 Subsequently, we took small amounts of the  
 73 dispersions and kept in a 40 °C vacuum oven for two days to  
 74 dry completely, and characterized the dried state. We  
 75 observed the dried samples using an optical microscope  
 76 (Olympus Bx-51, Tokyo, Japan). Figure S1a is a  
 77 representative microscope image for the CNCs/PEG20,000  
 78 sample. The image indicates the formation of numerous  
 79 particles with irregular shapes. We observed particles  
 80 ranging in size from 2 μm to several micrometers. In the  
 81 case of the larger particles, core-shell-like contrast could be  
 82 observed in the images, with dark, irregular shells  
 83 surrounding brighter cores. These results suggest that the  
 84 SORP process formed core-shell particles of CNCs and  
 85 PEG.

86 To identify the core-shell components, we observed  
 87 the dried particles using fluorescence microscopy.  
 88 Rhodamine 6G (R6G) dye was used as the fluorescent probe.  
 89 To identify the location of the CNCs and PEGs in the  
 90 composite, samples containing R6G were also prepared  
 91 besides CNC/PEG. R6G was added to the CNC/PEG  
 92 aqueous mixture to a concentration of  $2.46 \times 10^{-5}$  mol L<sup>-1</sup>  
 93 before EG addition. The final concentration of R6G in the  
 94 solvent was  $1.23 \times 10^{-5}$  mol L<sup>-1</sup>.

95 The optical microscope was equipped with a Bx2-FL-  
 96 1 fluorescent unit, and the fluorescent optical microscopic  
 97 (FOM) images were taken with an Olympus U-MSWB-3

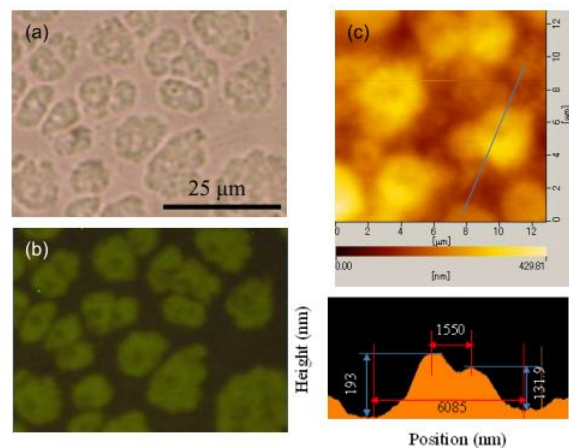


Figure 3 Observed images of dried CNCs/PEG20,000/R6G. (a) Bright field microscope image, (b) fluorescent optical microscope image, and (c) AFM topological image with cross-section.

1 filter. In a preliminary test using fluorescent measurements,  
 2 we confirmed that R6G selectively adsorbed to CNCs in  
 3 water (Fig. S2, S3). Thus, we concluded that we could  
 4 identify the location of the CNCs using R6G fluorescence  
 5 and FOM.

6 We observed the CNCs/PEG20,000 particles  
 7 containing R6G (CNCs/PEG/R6G). Figures 3a, and b show  
 8 images of dried CNC/PEG20,000/R6G by bright-field and  
 9 FOM, respectively. In Fig. 3a, we can see similar images  
 10 without R6G, as shown in Fig. S1, which indicate that the  
 11 addition of R6G did not change the morphology of the core-  
 12 shell particulates. In the fluorescent images (Fig. 3b), we  
 13 could locate the position on CNCs to which R6G adsorbed.  
 14 Figure 3b shows bright-green shells (rims) and darker  
 15 particulate centers. The results of FOM suggest that the  
 16 CNCs are located in the shell. The core-shell structure can  
 17 be visualized more clearly in Fig. S4, which shows color-  
 18 modified images with specific color assignments for each  
 19 measurement. Thus, we confirmed that in the  
 20 CNC/PEG20,000 system the structures were core-shell-like  
 21 particulates with CNC shell components.

22 To further identify the particulate structure, we  
 23 performed AFM observation using the Nanonavi IIs station  
 24 and a Nanocute unit (Hitachi High-Tech Science Corp.  
 25 Tokyo, Japan) in dynamic force mode with a PRC-DF40P  
 26 cantilever (SII Nanotechnology, Tokyo, Japan). The  
 27 location of PEG is confirmed by the AFM images shown in  
 28 Fig. 3c. AFM topological observations can reveal the exact  
 29 particle morphology. The particulates observed by AFM  
 30 were donut-shaped, with a small cavity in the center. This  
 31 shape also confirms the core-shell-like structure visualized  
 32 by optical microscopy in Fig. 3a. The particle diameter was  
 33 found to be about 6  $\mu\text{m}$ , which is comparable to the  
 34 diameter obtained from the optical microscope image. The  
 35 cross-sectional view indicates that the height was 100–200  
 36 nm. The cavity had a depth of several tens of nanometers,  
 37 but it had a certain height relative to the background, which  
 38 suggests that this is not a simple hole but it is filled with a  
 39 PEG component.

40 On the other hand, the same procedure using  
 41 CNC/PEG2,000 yielded core-shell particles with a CNC  
 42 core and PEG shell, structures that were distinctively  
 43 different from the CNC/PEG20,000 particles. The  
 44 difference was confirmed by the appearance of the sample  
 45 after the water evaporation process represented in Fig. 2d.  
 46 At this stage, the sample liquid was transparent, while for  
 47 the CNC/PEG20,000 sample, the liquid was turbid. We also  
 48 dried and observed this sample. A representative optical  
 49 microscopy image is shown in Fig. S1. It indicates the  
 50 formation of numerous monodisperse spherical particles  
 51 around 1  $\mu\text{m}$  in diameter with clear core-shell contours:  
 52 shells were brighter than the cores, which were dark gray.  
 53 The particle size was an order of magnitude smaller than the  
 54 CNC/PEG20,000 particles. Therefore, the particles obtained  
 55 from the CNC/PEG20,000 and CNC/PEG2,000 samples  
 56 were clearly different: the contrast was inverted, and there  
 57 was a difference in particle size and shape.

58 Our observations of the CNC/PEG2,000 sample are  
 59 summarized in Fig. 4. For the samples with added R6G

60 (CNC/PEG2,000/R6G), bright-field optical microscopy (Fig.  
 61 4a) and FOM (Fig. 4b) images are shown. Fig. 4a displays  
 62 core-shell particulates similar to those observed without  
 63 R6G, shown in Fig. S1b, which shows core-shell  
 64 particulates with darker centers and brighter surrounding  
 65 rims. In Fig. 4b, numerous small bright-green dots  
 66 corresponding to the cores are visible; this is also supported  
 67 by Fig. S4. This indicates that the cores of the  
 68 CNC/PEG2,000 particulates consist of CNCs, i.e., the CNC  
 69 locations are different from those in particulates made from  
 70 CNC/PEG20,000.

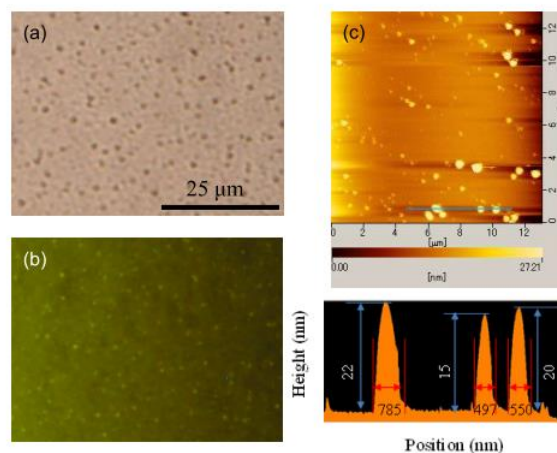


Figure 4 Observed images of dried CNCs/PEG2,000/R6G. (a) Bright field microscope image, (b) fluorescent optical microscope image, and (c) AFM topological image with cross-section.

71 In the AFM image (Fig. 4c), the particulates with  
 72 diameters of ca. 500 nm and heights of ca. 20 nm were  
 73 observed. We calculated particulate diameters from the  
 74 AFM images that are smaller than from optical microscopy;  
 75 this can be attributed to the higher resolution in detection by  
 76 AFM. As discussed above, CNC shells for CNC/PEG20,000  
 77 were detected to be higher than the centers. We can  
 78 conclude that CNC is the higher part because of their  
 79 stiffness in their dried state. However, in the AFM images  
 80 for the CNC/PEG2,000 system, smaller dots were detected.  
 81 In this case, only the CNC core could be visualized, since  
 82 the PEG2,000 shell could be detected as a lower height.  
 83 Furthermore, shells made of PEG2,000 could diffuse to the  
 84 exterior because of the smaller molecular weight of PEG  
 85 and because of the absence of constraints to PEG diffusion  
 86 in the shell. This interpretation can explain the smaller  
 87 diameters for CNC/PEG2,000 in AFM, although further  
 88 structural investigation, including an investigation in the wet  
 89 state, should be performed.

90 In order to confirm the effect of small content of water  
 91 which might have been left after 50% evaporation of solvent  
 92 from the initial mixed solution, we examined and compared  
 93 the results obtained from usual 50% evaporation (water) and  
 94 ca. 60% evaporation (water+EG). The obtained particle  
 95 morphology is quite similar, thus the small content of water  
 96 in the half volume evaporation process does not affect the  
 97 final morphology.

1 As discussed above, we have successfully fabricated  
 2 core-shell particulates with tunable CNC locations by  
 3 changing the PEG molecular weight. We hypothesized that  
 4 the placement differences are due to slight differences in  
 5 affinity between CNC-EG and PEG-EG. All the  
 6 components are soluble in water, while the solubility of  
 7 PEG in EG is slightly different, depending on the molecular  
 8 weight. PEG20,000 is less soluble in EG as compared with  
 9 PEG2,000. This is evidenced by the appearance of EG  
 10 solutions of PEG2,000 and PEG20,000 (Figure S5). In the  
 11 CNC/PEG20,000 system, the PEG component is not  
 12 completely soluble in EG, and CNC has a higher affinity to  
 13 EG as compared with PEG20,000. In EG, this results in the  
 14 formation of a core-shell structure, with CNC forming the  
 15 shell. By contrast, PEG2,000 has a higher affinity to EG  
 16 than CNCs, which results in a core-shell structure with a  
 17 PEG2,000 shell. The difference in affinity to EG has a  
 18 significant effect on the morphology. The affinity between  
 19 the polymer and solvent can change drastically depending  
 20 on by the molecular weight as evidenced by Fig.S5. These  
 21 polymer characteristics can be applied to control the  
 22 morphology without changing the component itself.

23 In summary, we have reported a simple approach for  
 24 preparing CNC-based core-shell particles via modified  
 25 SORP method in which particle formation was carried out  
 26 by simply evaporation of solvent containing solutes with  
 27 different solubility. In this study, we showed that the molar  
 28 weight of the added PEG (2,000 vs 20,000) changes the  
 29 resultant particulate's morphology, CNC location, and shape  
 30 and size. On the basis of these findings, we expect that  
 31 core-shell particles with similar compositions can be  
 32 designed to include CNCs in different locations, which can  
 33 enrich the applications of this particulate composite system.

34 This work was partly supported by JSPS KAKENHI  
 35 (no. 18K04729 for E.M.). AFM apparatus used here belongs  
 36 to the laboratory of Prof. Shigeori Takenaka, we are  
 37 thankful to the resource supply. We would like to thank  
 38 Uni-edit (<https://uni-edit.net/>) for editing and proof reading  
 39 this manuscript. We appreciate financial support for English  
 40 editing of research paper from Kyushu Institute of  
 41 Technology.

42  
 43 Supporting Information is available on  
 44 [http://dx.doi.org/10.1246/cl.\\*\\*\\*\\*\\*](http://dx.doi.org/10.1246/cl.*****).

## 46 References and Notes

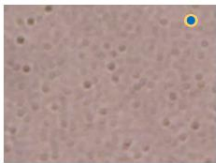
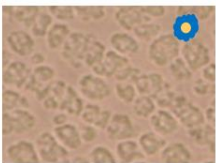
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**NOTE** The diagram is acceptable in a colored form. Publication of the colored G.A. is free of charge. For publication, electronic data of the colored G.A. should be submitted. Preferred data format is EPS, PS, CDX, PPT, and TIFF.

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Graphical Abstract	
Textual Information	
A brief abstract (required)	We report a versatile method for preparing a particulate composite based on cellulose nanocrystals (CNCs) and polyethylene glycol (PEG) via the self-organized precipitation method. The particulate composite had a core-shell structure, and depending on the PEG molecular weight, two types of particulates could form: one with CNCs as the core and the other with CNCs as the shell.
Title(required)	Preparation of Cellulose Nanocrystals based Core-Shell Particles with Tunable Component Location
Authors' Names(required)	Jie Zhang, Hinako Furushima, and Teruyuki Nakato, Emiko Mouri
Graphical Information	
<Please insert your Graphical Abstract: The size is limited within 100 mm width and 30 mm height, or 48 mm square>(required)	
<div style="display: flex; justify-content: space-around; align-items: flex-start;"> <div style="text-align: center;"> <p>CNCs @PEG</p>  </div> <div style="text-align: center;"> <p>PEG@CNCs</p>  </div> </div> <p style="text-align: center;">Tunable Core-Shell Particles</p>	