Preparation of Functional Materials from Cellulose/Lithium Bromide Solution by Emulsion-Gelation Method

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Chapter 1.

General Introduction

1.1. Cellulose

Cellulose is the most abundant natural polymer on earth. Plants mainly produce it through photosynthesis, but some bacteria and ascidians also synthesize it. About 1.5 trillion tones of cellulose are produced annually [1–2]. In 1842, the French chemist Payen first isolated cellulose from green plants and reported its elemental composition. Cellulose is a linear homopolymer composed of D-anhydro glucopyranose units (AGUs) connected by β -1,4 glycosidic bonds (**Fig. 1-1a**). Its formula is (C₆H₁₀O₅)_n, where n is the degree of polymerization (DP). The DP values vary depending on the raw material of cellulose, but they usually range from 10,000 to 15,000 [3–4].



Fig. 1-1. (a) The cellulose molecule structure (b) Hydrophilic and hydrophobic parts

Cellulose contains a significant amount of hydroxyl groups. The three hydroxyl groups per AGU form a network of intra- and intermolecular hydrogen bonds, giving the chain its rigidity. Therefore, these hydrogen bonds were considered the basis of cohesion between cellulose molecules [5]. A more recent perspective emphasizes that cellulose molecules can be hydrophilic and hydrophobic. The glucopyranose ring is hydrophilic because of the three hydroxyl groups in the equatorial direction of the ring. However, the axial direction of the ring is hydrophobic due to the location of the hydrogen atoms of the C-H bonds (**Fig. 1-1a**). Thus, the cellulose molecule has an intrinsic structural anisotropy. This structural anisotropy is expected to have a significant impact on both the microscopic (e.g., interactions) and macroscopic (e.g., solubility) properties of cellulose [6–7].

Cellulose has the advantage of abundant source, renewability, biodegradability, and biocompatibility. For this reason, various forms of cellulose materials, like fibers, films and

membranes, hydrogel and aerogel, cellulose microsphere, and beads, have been successfully fabricated and employed in various fields [8-13]. Several technologies have been used to manufacture these materials, such as cellulose nanotechnology and cellulose dissolution and regeneration technology. Unlike cellulose nanotechnology, the cellulose dissolution and regeneration technology (developed for over 100 years) is mature [10].

1.2. Cellulose dissolution and regeneration

1.2.1. Cellulose dissolution

Cellulose is not soluble in common aqueous solvents and typical organic solvents. A widely accepted factor for this is the intra- and intermolecular hydrogen bonds formed in cellulose. However, as cellulose is an amphiphilic molecule, its solubility is strongly influenced by hydrophobic interactions between cellulose molecular chains. Therefore, cellulose solvents need to be polar solvents to break hydrogen bonds and overcome hydrophobic interactions [5, 7, 14]. Many solvents have been discovered so far, and they can be classified into the following six main groups.

Acid system. Concentrated mineral acid can dissolve cellulose. However, the protonation of cellulose causes the hydrolysis of β -1,4-glycosidic bonds, resulting in a drastically reduced degree of polymerization (DP) [15–16]. For this reason, cellulose dissolution in mineral acid has been extensively used as cellulose degradation pretreatment and cellulose nanocrystal production. Furthermore, to overcome the problems of cellulose hydrolysis, researchers developed the low-temperature mineral acid-cellulose dissolution system. This system's cellulose hydrolysis rate became very slow due to the low dissolution temperature [17–19].

Alkali system. The first study on the capacity of alkaline (NaOH) systems to dissolve cellulose was reported in 1930 [20–21]. Then, other alkaline systems, such as LiOH and quaternary ammonium hydroxides, were successfully found [22–23]. The addition of additives such as urea, thiourea, ZnO, and polyethylene glycol can increase the dissolution performance of these alkaline systems [24–27].

Metal complex system. A metal complex system consists of transition metal ions and nitrous ligands. In 1857, Schweizer discovered that cotton could be dissolved in a complex solution of copper salts and concentrated ammonia [28]. Since then, other complexing agents, such as amine or ammonium and ferric sodium tartrate, have been reported [29–32]. The most well-known are cuprammonium hydroxide (Cuam) and cupriethylenediamine hydroxide (Cuen) [33–34]. It is worth noting that the Cupra process, which uses Cuam as a solvent, has been

commercialized in Japan.

Organic solvent system. There are many types of organic solvent systems, which are typically divided into two categories: single-component and multi-component. Single-component systems include hydrazine, *N*-alkylpyridinium halides, and *N*-oxides of tertiary amines [35–37]. Multi-component systems include polar organic liquid/SO₂/amine and polar organic liquid containing amino component/ethanolamine or inorganic salt [38–40]. It's worth noting that LiCl/DMAc has been used for cellulose analysis and for preparing cellulose derivatives, while NMMO has been commercialized in Europe.

Ionic liquid. The ionic liquid is composed of a large organic cation and a smaller inorganic or organic anion. In 1934, Graenacher first used *N*-alkylpyridium salts to dissolve cellulose and as mediums for homogeneous chemical reactions [41]. Seventy years later, in 2002, a research group led by Swatloski reported ionic liquids with low melting points as cellulose solvents for both physical cellulose dissolution and regeneration [42]. This work opened up a new and exciting field of cellulose research, and since then, a massive variety of ionic liquids has been created. The number of potential ion combinations available is approximately a thousand ionic liquids. This combination with halide, phosphonate, formate, or acetate as anion and imidazolium, pyridinium, choline, or phosphonium as cation is considered the most efficient for cellulose dissolution [43–47].

Inorganic salt system. In 1932, Letters et al. found that cellulose can dissolve in 63% aqueous zinc chloride (ZnCl₂) [48]. Since then, many pure and mixtures of inorganic salts system has been reported for cellulose dissolution. Compared to other solvent systems with limitations such as high cost, long dissolution period, toxicity, and environmental issues, inorganic salt systems exhibiting the advantages of low price, high efficiency, easy preparation process, and environmental friendliness have drawn increasing attention [49–52].

1.2.2. Cellulose regeneration

Cellulose regeneration is a mandatory step for cellulose shaping and manufacture of novel cellulose materials. The cellulose regeneration process is a phase separation of cellulose from a soluble state to an insoluble state. This process is a counter-diffusion process, where the cellulose solvent diffuses from solution to bath, and the anti-solvent or non-solvent diffuses from bath to solution, leading to the isolation of cellulose molecules and recombination of intra- and intermolecular hydrogen bonds [5, 7]. However, regenerating bulk cellulose material is problematic because it relies on the diffusion of non-solvents (liquids that coagulate) into the

cellulose solution. In addition, the structure differs between the surface and the interior of the regenerated cellulose. Utilizing cellulose solvents such as calcium thiocyanate (Ca(SCN)₂) and lithium bromide (LiBr) can resolve this issue. These solvents can fully dissolve cellulose by heating. Interestingly, the cellulose solution can be directly regenerated by cooling without using non-solvents. Consequently, these solvents are deserved for producing bulk cellulose materials [53–56].

1.3. Emulsion techniques for preparation cellulose material

1.3.1. Emulsion

The emulsion is a heterogeneous mixture of two or more immiscible liquid phases stabilized by surfactant, one immiscible liquid phase in the form of microscopic spherical drops (dispersed phase) dispersing in the other immiscible liquid phase (continuous phase) [57–59]. The mixture/emulsification process, a mandatory process of emulsion formation, needs a significant amount of mechanical energy. These methods include high-pressure homogenizers, ultrasound generators, liquid injection through porous membranes, and simple shaking, mixing with rotor-stator systems [58]. In general, emulsions are divided into two types: water-in-oil (W/O) and oil-in-water (O/W) (**Fig. 1-2**). The former is a hydrophobic liquid phase, such as oil as the continuous phase, and a hydrophilic liquid phase as the dispersed phase. In contrast, the latter type is a hydrophilic liquid phase as the dispersed phase and a hydrophobic liquid phase as the continuous phase.



Fig. 1-2. Schematic diagram of water in oil (W/O) and oil in water (O/W) emulsions.

The emulsion is thermodynamically unstable because emulsion droplets tend to aggregate and return to an initially phase-separated state [60–61]. Surfactant is generally added to prevent the aggregation of emulsion droplets. Surfactants contain lipophilic and hydrophilic groups and can be adsorbed at the oil-water interface [62]. Various types of surfactants, such as Tween and Span, have been utilized to stabilize emulsion. The hydrophile-lipophile balance (HLB) value of surfactant is an essential factor in emulsion stability, wherein HLB value in the range of 4– 6 is suitable for W/O emulsions, HLB value in the range of 8–16 is ideal for O/W emulsions. Moreover, surfactant concentration, density, viscosity, and the fraction of two phases are crucial factors [63–64]. The industrial applications of emulsions are numerous, mainly in industrial processes related to food, cosmetics, pharmacy, enhanced oil recovery, and synthesis of macroporous materials.

1.3.2. W/O emulsion technique for preparation of cellulose material

As mentioned, W/O emulsion is a water phase in the form of globules dispersing in the oil phase. W/O emulsion techniques have been employed to prepare cellulose beads. Typically, the production process of cellulose beads through utilizing this technique is stated as follows: cellulose solution is mixed with an immiscible oil phase liquid in the presence of surfactants, subsequently forming a stable W/O emulsion containing cellulose droplets under sequential agitation, and finally inducing the gelation or solidification of these cellulose droplets [9, 65–67]. The mixing speed, W/O ratio, cellulose concentration, surfactant concentration, and HLB values can regulate the size distribution and diameter of beads. Because of their distinctive features, such as nontoxic, spherical shape, large specific surface area, and porous network structure, cellulose beads have gained much interest in many advanced applications, ranging from chromatography over solid-supported synthesis and protein immobilization to retarded drug release [9, 65–67].

1.3.3. O/W emulsion technique for preparation of cellulose material

Utilizing the O/W emulsion technique, commonly known as highly internal phase emulsions (an emulsion with over 74% oil phase by volume) template, cellulose material with micrometer pores can be created. The production process of such material through utilizing this technique is as follows [68–70]:

1. Oil phase liquid (disperse phase) and cellulose solution (continuous phase) are mixed to form O/W emulsions.

- 2. The cellulose solution in this emulsion is cured to form a solid network.
- 3. The oil phase is removed and will create pores.

Based on its high biocompatibility and pore structure of the order of micrometers, this material offers a new substrate for separation, oil spill recovery, scaffolds in tissue engineering, and catalysis.

In addition, nanocellulose can replace traditional surfactants to adsorb on the water-oil interface, forming stable O/W emulsions (also known as O/W Picker emulsions) in which oil is encapsulated in a nanocellulose shell. Based on this property, a nanocellulose-stabilized O/W emulsion opens possibilities for designing an encapsulation technique [71–72].

1.4. Outline of this thesis

LiBr aqueous solution dissolves cellulose at 120 °C and coagulates by cooling the solution to room temperature without any non-solvents. The solvent will offer a simple, environmentfriendly, and low-cost process for preparing cellulose materials. The emulsion–gelation method is an important technique that helps to prepare cellulose material with unique structure and performance. This dissertation entitled "Fabrication of cellulose materials under cellulose/LiBr system via emulsion–gelation method" consists of five chapters. The emulsion-gelation method is used to fabricate cellulose materials with unique performance and structures using cellulose/LiBr aqueous solution. This dissertation may provide a simple, environment-friendly, low-cost process for preparing cellulose material with unique structure and performance. The outline of the present thesis is described below and illustrated schematically in **Fig. 1-3**.

In Chapter 2, we successfully manufactured cellulose beads using a simple cellulose/LiBr solution-in-oil emulsion-gelation method. Subsequently, we evaluated the dye adsorption capacity of the resultant cellulose beads. The effects of the ratio of the cellulose solution to oil, surfactant concentration, stirring speed, cellulose concentration, and type of surfactant on the size of the beads were investigated. The cellulose beads exhibited a highly porous structure, with a high specific surface area and high adsorption performance for the anionic dye Congo red. In addition, carboxyl groups were introduced into the cellulose beads by oxidation while retaining their highly porous structure. The adsorption capacity of the cationic dye methylene blue on the oxidized cellulose beads significantly increased with increasing oxidation time and carboxyl group content. In contrast, the adsorption of the anionic dye, Congo red, was inhibited. Cellulose beads with a high carboxyl group content maintained a high adsorption capacity even after repeated adsorption-desorption cycles, demonstrating

their potential as reusable adsorbent materials.

In Chapter 3, an environment-friendly method was developed for producing cellulose beads, which were used as a supporting material for Cu-based nanocatalysts. The cellulose beads were synthesized from a water-in-oil emulsion, using cellulose dissolved in a LiBr solution as the water phase and vegetable oil as the oil phase. In contrast to Chapter 2, the process is entirely eco-friendly because of the use of vegetable oil. Upon cooling, gelation of the cellulose solution produced spherical cellulose beads, which were then oxidized to introduce surface carboxyl groups. These beads (diameter: 95–105 μ m; specific surface area: 165–225 m² g⁻¹) have a three-dimensional network of nanofibers (width: 20–30 nm). Furthermore, Cu₂O nanoparticles were loaded onto the oxidized cellulose beads before testing their catalytic activity in reducing 4-nitrophenol using NaBH₄. The apparent reaction rate constant increased with the amount of loaded Cu₂O nanoparticles, and the conversion efficiency was > 90%. The turnover frequency was 376.2 h⁻¹ for the oxidized cellulose beads with the lowest Cu₂O loading, indicating higher catalytic activity than other Cu-based nanoparticle-loaded materials. In addition to their high catalytic activity, the cellulose beads are reusable and exhibit excellent stability.

In Chapter 4, large-scale, firm, no-leakage cellulose/paraffin composite foams were successfully fabricated via an emulsion–gelation method using cellulose/LiBr solution. SEM and FTIR analyses showed that spherical paraffin particles were embedded into the three-dimensional nanofibrillar network structure of regenerated cellulose material, with no chemical reaction between paraffin and cellulose. This cellulose/paraffin foam exhibited excellent mechanical properties, no leakage at 80 °C even for up to 80% paraffin content, relatively lower thermal conductivity, and high latent heat. Thus, the foams are promising potential materials for efficient and reliable thermal energy storage applications.

In Chapter 5, the conclusions obtained through the studies of this dissertation are summarized.



Fig. 1-3. The outline of the present thesis.

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Chapter 2.

Adsorption properties of cellulose beads

prepared by emulsion-gelation method and

subsequent oxidation

2.1. Background

Emulsion-gelation methods (generation of droplets by water-in-oil emulsion coupled with specific solidification/coagulation techniques) have attracted considerable interest in fabricating cellulose beads, obtaining a smaller diameter as well as stable and reproducible properties; moreover, no particular facility or equipment are required [1–6]. However, the fabrication of cellulose beads via emulsion-gelation faces challenges, such as high costs and the necessity of toxic solvents for dissolving cellulose and non-solvents for coagulation. In addition, high-quality cellulose beads have been prepared using cellulose derivatives as starting materials. However, this route requires the preparation of cellulose derivatives and their subsequent conversion back to cellulose [7, 8]. These processes are not straightforward and require high consumption of chemicals. Therefore, developing a synthetic route for directly converting cellulose solutions to cellulose beads with excellent properties is desirable [7, 9].

Recently, an inorganic salt-based cellulose solvent, LiBr solution, was reported [10, 11]. Here, cellulose was dissolved in a LiBr solution at 120 °C without pretreatment, and the cellulose solution was transformed into a gel upon cooling to room temperature. By washing the gel with water, a cellulose hydrogel with a three-dimensional (3D) network structure consisting of nanofibers with widths of tens of nanometers can be prepared. The resultant properties are a high specific surface area, water content, and toughness [10, 11]. The cellulose/LiBr solution undergoes coagulation upon cooling, eliminating the need for a separate coagulation bath, thereby offering a new pathway for cellulose bead production.

In this chapter, cellulose beads were prepared using the emulsion-gelation method, wherein a cellulose/LiBr solution was dispersed in an oil phase to form a water-in-oil (W/O) emulsion and subsequently cooled to obtain a solid product. The effects of preparation parameters on the cellulose bead diameter were investigated, such as the ratio of cellulose solution to oil, surfactant concentration, stirring speed, and cellulose concentration. The morphology and structure of the prepared cellulose beads were evaluated. Carboxyl groups were introduced on the surface of the cellulose beads by 4-acetamido-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation, and their applicability as a dye adsorbent was evaluated.

2.2. Experimental

2.2.1 Preparation of the cellulose beads

The experimental procedure for preparing cellulose beads is shown in Fig. 2-1.

Commercially available regenerated cellulose (Bemcot, Asahi Kasei Co. Ltd., Japan) was used as the starting material; the viscosity average molecular weight was measured as 91,000 at 25 °C using a 0.5M copper ethylenediamine solution (Aldrich); the α-cellulose content, which indicates the cellulose purity, was 94% [12, 13]. The regenerated cellulose was dissolved in a 60 wt% LiBr (Fujifilm Wako Pure Chemical) solution by stirring at 120 °C for 15 min to obtain a transparent cellulose solution [11]. The cellulose/LiBr solution (water phase) was added to a solution of the surfactants Span 85 (sorbitan trioleate, Tokyo Chemical Industry), Span 80 (sorbitan monooleate, Tokyo Chemical Industry), Span 40 (sorbitan monopalmitate, Tokyo Chemical Industry), Span 20 (sorbitan monoleate, Tokyo Chemical Industry), and Tween 80 (polyoxyethylene sorbitan monooleate, Sigma-Aldrich) in decane (oil phase, Fujifilm Wako Pure Chemical) at 120 °C by stirring. After W/O emulsion formed in 10 min, the solution was cooled to room temperature under continuous stirring to gelatinize the micelles in the cellulose solution.



Fig. 2-1. Experimental scheme for the preparation of cellulose beads.

The suspension was allowed to stand until it separated into two layers. The upper layer containing the oil phase was removed, and the lower layer containing the cellulose beads was collected, washed with acetone, and then washed with deionized water using repeated centrifugation until no LiBr was detected with silver nitrate [14]. The weight ratio of cellulose solution to decane, surfactant concentration in decane, stirring speed, cellulose concentration, and types of surfactants with different hydrophilic-lipophilic balances (HLBs) in the 60 wt% LiBr solution were modulated according to the parameters listed in **Table 2-1**.

		Parameters					
Entry		Weight ratio of	Surfactant	Stirring	Cellulose		
EII	ſу	decane to cellulose	concentration	speed	concentration	Surfactant	
		solution	^a (wt%)	(rpm)	^b (wt%)		
	1	1					
٨	23	3	1	500	1	See. 90	
A		6	1	300	1	Span 80	
	4	9					
	1		0.05				
	2		0.1		1	C	
р	3	2	0.5	500			
В	4	3	1	300	1	Span 80	
	5		2				
	6		4				
	1			250			
C	2	2	2	500	1	Seen 80	
C	3	3	Z	750	1	Span 80	
_	4			1000			
	1			500	0.5		
Л	2	3 2	2		1	C	
D	3		Z		2	Span 80	
	4				3		
1 2 E 3 4 5	1					Span 85	
	2					Span 80	
	3	3	2	500	2	Span 40	
	4					Span 20	
	5					Tween 80	

Table 2-1. Parameters modified during the preparation of cellulose beads.

^a Concentration of surfactant in decane

^b Concentration of cellulose in 60 wt% LiBr solution

2.2.2 TEMPO-mediated oxidation of cellulose beads

Wet cellulose beads (0.3 g dry weight) were added to acetate buffer (30 mL, 0.2 M, pH 5.2) containing 80% NaClO₂ (0.51 g) and 4-acetamido-TEMPO (0.03 g). Subsequently, a NaClO solution (1.86 mL, 40 mM) was added dropwise to the suspension and stirred at 60 °C for 1, 4, and 24 h. The prepared cellulose beads were designated as CB-1h, CB-4h, and CB-24h. The carboxylate content in the cellulose beads was determined by conductometric titration. Freeze-dried cellulose beads (approximately 0.2g) were added to 40 mL of water; then 0.1 M HCl was added to adjust the pH to about 3.0. An automatic titrator (AT–710, Kyoto Electric Manufacturing, Japan) injected 50 mM NaOH solution at 180 s/mL until the pH was approximately 12. Subsequently, the electrical conductivity was measured every minute, and titration curves were generated [15]. The carboxylate content was calculated using the

following equation:

$$C_{COOH} = \frac{V}{M} \times C$$

where C_{COOH} is the carboxylate content of the cellulose beads (mmol/g), *C* is the NaOH concentration (mM), *V* is the amount of NaOH (L) required for the neutralization of the carboxylic acid (equivalent to the horizontal portion of the titration curve), and *M* is the dry weight of the cellulose beads (g).

2.2.3 Characterization of cellulose beads

Fourier-transform infrared spectroscopy (FTIR) was performed using the attenuated total reflectance method (PerkinElmer, USA). The absorbance FTIR spectra of the dried beads were recorded over a 400–4000 cm⁻¹ range with a resolution of 4 cm⁻¹. Images of the wet beads were captured using a light microscope (Eclipse LV100N, Nikon, Japan). Phase contrast images of the wet beads were captured using a light microscope (Olympus BX53, Japan). The mean diameters and diameter distributions were obtained by measuring the diameters of 1000 cellulose beads for each sample using ImageJ. The never-dried beads were immersed in 30% *t*-butyl alcohol/water and freeze-dried at -80 °C for 48 h. To observe their internal structures, the beads in *t*-butyl alcohol were frozen using liquid nitrogen, crushed in a mortar while frozen, and dried in vacuo. The microstructures of the freeze-dried and freeze-fractured beads were observed using scanning electron microscopy (SEM) (Hitachi S-4800, Japan). Brunauer–Emmett–Teller (BET) measurements were performed at a relative N₂ vapor pressure of 0.05–0.3 at 77 K (BELSORP MINI X, Japan), and the pore volume and average pore size were calculated from the adsorption branch using the Barrett–Joiner–Halenda (BJH) method.

2.2.4 Adsorption of methylene blue and congo red solution

The adsorption of methylene blue (MB) (Fujifilm Wako Pure Chemical) and congo red (CR) (Fujifilm Wako Pure Chemical) onto the beads was examined using batch adsorption experiments. Each dye was dissolved in a 50 mM sodium phosphate buffer at pH 7.0 at 100 and 1000 mg/L concentrations. Freeze-dried cellulose beads (approximately 20 mg) were immersed in a dye solution (10 mL) and gently shaken at 25 °C. Once the adsorption equilibrium was reached (after 48 h), the dye concentration in the supernatant was measured at 664 nm for MB and 485 nm for CR using a UV-Vis spectrophotometer (UV-2450, Shimadzu Corporation, Japan). The amount of dye adsorbed on the beads (q_e , mg/g) was defined as

follows:

$$q_e = \frac{C_0 - C_e}{m} \times V \,,$$

where C_0 and C_e are the initial and final concentrations (mg/L) of the dye solutions, respectively, V is the solution volume, and m is the dry weight of the beads.

The reusability of the beads as adsorbents was examined by performing successive adsorption-desorption cycles. Freeze-dried cellulose beads (approximately 20 mg) were immersed in a 100mg/L MB solution (10 mL) and shaken at 25 °C for 24 h. After measuring the amount of adsorbed MB, the MB-adsorbed beads were treated with HCl solution (0.01 M) at 25 °C and washed several times with deionized water. The adsorption-desorption cycle was then repeated five times [16].

2.3. Results and discussion

2.3.1. Effect of preparation conditions on the size and shape of cellulose beads

The size and shape of the cellulose beads were studied by modulating the preparation parameters listed in **Table 2-1**. Optical micrographs of cellulose beads prepared under different conditions are shown in **Fig. 2-S1**. The cellulose beads obtained were spherical under all preparation conditions (**Fig. 2-S1**), except for low cellulose concentrations (0.5 wt%) and Tween 80, in which they were dispersed and irregularly shaped (**Fig. 2-S1D1** and **2-S1E5**). The bead diameter frequency distribution and mean values were measured from the micrographs, and are shown in **Fig. 2-S2** and **2-2**, respectively.

As the weight ratio of decane to cellulose solution increased from 1 to 9, the average diameter of the cellulose beads decreased from 21.2 μ m to 9.4 μ m (**Fig. 2-2a**), and the distribution of their diameters became narrower. The result indicates that increasing the oil phase ratio while maintaining a constant surfactant content leads to tiny micelles of uniform size formation. A higher weight ratio of decane to cellulose solution corresponds to a higher ratio of surfactant to water; hence, more surfactant molecules cover the emulsion droplets formed, thus exhibiting higher resistance to the coalescence of the emulsion droplets [6, 17]. As the surfactant concentration increased from 0.05 to 2 wt%, the average diameter of the cellulose beads decreased significantly from 42 to 8.27 μ m with a simultaneous narrowing of their distribution. At surfactant concentrations higher than 2 wt%, the average diameter of the beads remained nearly constant at approximately 8 μ m (**Fig. 2-2b**). Hence, a high surfactant concentration facilitates complete coverage of the entire surface area of the emulsion droplets,

maximizing stability against coalescence and maintaining the emulsion droplet size at a minimum [6, 17]. Varying the stirring speed did not significantly alter the size of the cellulose beads obtained; the average diameter only changed from 11.0 to 8.5 μ m when the moving speed increased from 250 rpm to a range of 500–1000 rpm (**Fig. 2-2c**). However, at 250 rpm, the spherical cellulose beads agglomerated and formed clusters. Increasing the cellulose concentration, the average diameter of the cellulose beads slightly decreased from 8.3 μ m to 7.2 μ m at 1 wt% and 3 wt%, respectively. However, this difference was not considered significant (**Fig. 2-2d**).



Fig. 2-2. Average diameters of cellulose beads prepared by modulating parameters: (a) weight ratio of decane to cellulose solution, (b) surfactant (Span 80) concentration in decane, (c) stirring speed, (d) cellulose concentration in 60 wt% LiBr solution, and (e) types of surfactants. Error bars indicate \pm standard deviation from the average diameters. The numbers in the figure correspond to the conditions for preparing cellulose beads listed in **Table 2-1**.

For surfactants with low HLB values, Span 85 (HLB 1.8) and Span 80 (HLB 4.3), the average diameter of the cellulose beads is about 8 μ m. On the other hand, for the surfactants with higher HLB values, Span 40 (HLB 6.7) and Span 20 (HLB 8.6), the average diameter of the cellulose beads is about 12 μ m, indicating a slight increase. For Tween 80 (HLB 15.0), which has a high HLB, spherical cellulose beads were not obtained (**Fig. 2-S1E5**). Surfactants with an HLB of 8.6 or lower should be used to prepare cellulose beads. These results show that with higher weight ratios of decane: cellulose solution and higher surfactant concentrations, cellulose beads with smaller average diameters and narrower diameter distributions are obtained. Cellulose beads of different diameters prepared using W/O emulsion have previously

been reported [1–6]. Notably, the method employed in this study for preparing cellulose beads is more straightforward, as it involves direct gelatinization of the beads by cooling them to room temperature without requiring a coagulation bath or cross-linking reagents. Higher amounts of decane and surfactant increased the chemicals used and the amount of acetone and deionized water needed for washing. Therefore, our optimized conditions for the TEMPO-mediated oxidation of cellulose beads were as follows: a decane: cellulose solution weight ratio of 3, surfactant concentration of 2 wt%, stirring speed of 500 rpm, cellulose solution concentration of 2 wt%, and surfactant of Span 80 (Entry D3 in **Table 2-1**).

2.3.2. Characterization of cellulose beads

The cellulose beads were predominantly spherical, with an average diameter of 7.95 μ m, smaller than other cellulose beads prepared using the emulsion-gelation method (**Table 2-S1**) [1–6]. A porous 3D network structure consisting of nanofibrils with widths of 20–50 nm was observed, similar to the cellulose hydrogels prepared in a 60 wt% LiBr solution [10, 11]. Furthermore, the average pore size of the cellulose beads was 14.1 nm, smaller than that previously reported for cellulose beads (**Table 2-S1**) [18–20].



Fig. 2-3. (a) Optical microscope and (b) SEM images of cellulose beads. Inset in (b) is the internal surface of a freeze-fractured bead.

The prepared beads exhibited a specific surface area of 230 m²/g and a pore volume of $1.41 \text{ cm}^3/\text{g}$, which are significantly higher than those previously reported for cellulose beads (**Table 2-S1**) [1, 3–6, 18–21], suggesting the formation of a porous cellulose bead structure. The high specific surface area was attributed to the 3D network structure of the nanofibrils [18]. In this study, we adopted a simple method to assess the mechanical stability by applying defined forces to cellulose beads through centrifugation and mechanical stirring [7]. As illustrated in **Fig. 2-S3a–b**, the cellulose beads maintained their spherical shape and did not collapse even after 50 centrifugations at 6,900 g and mechanical stirring at 500 rpm for 48 h. Thus, the cellulose beads prepared in this study have excellent mechanical stability, comparable to that of the cellulose hydrogels prepared by Isobe et al. [10].

2.3.3. Characterization of TEMPO-mediated oxidized cellulose beads

To introduce carboxyl groups into the cellulose beads, TEMPO-mediated oxidation was performed with durations of 1, 4, and 24 h. The carboxyl group content per gram of cellulose of the initial cellulose beads (CB-0h) was approximately 0, while those of the oxidized cellulose beads CB-1h, CB-4h, and CB-24h were 0.19, 0.61, and 1.47 mmol/g, respectively. This result shows that the carboxyl group content in cellulose can be modified by adjusting the duration of the TEMPO-mediated oxidation reaction. However, the amount of carboxyl groups in CB-24h, 1.47 mmol/g, is nearly the limit of the amount of carboxyl groups introduced that can maintain mechanical strength without causing dissolution. Confirming the stability of cellulose beads, their weight loss when immersed in a buffer solution with a pH of 7 for one week was revealed to be a mere 2% (**Fig. 2-S4**).

The FTIR spectra of the initial (CB-0h) and oxidized cellulose beads (CB-1h, CB-4h, and CB-24h) are shown in **Fig. 2-4**. Features indicative of regenerated cellulose, namely the crystal structure of cellulose II, were observed in all FTIR spectra: a broad O–H stretching band centered at 3358 cm⁻¹ with two small bands at 3488 and 3441 cm⁻¹; C–H stretching bands in the region of 2800–3000 cm⁻¹; an antisymmetric C–O–C stretching band at 1156 cm⁻¹; and the characteristic fingerprint region reported by Marchessault and Liang [22]. In the spectrum of the oxidized cellulose beads, an absorption band originating from the C=O stretching vibration appeared at 1602 cm⁻¹ [15], and the absorbance of this band increased with increasing oxidation time. This result is consistent with the carboxyl group content in oxidized cellulose beads calculated using the conductometric titration results.



Fig. 2-4. FTIR spectra of cellulose beads (CB-0h) and cellulose beads oxidized for 1, 4, and 24 h (CB-1h, CB-4h, and CB-24h, respectively).

The size, shape, and microstructure of the oxidized cellulose beads were investigated using optical and SEM microscopy. Optical micrographs (Fig. 2-5 upper) show that all oxidized cellulose beads retained their spherical shape in the wet state. The average diameters slightly increased with increasing oxidation time, with the value rising from 7.95 μ m to 8.80 µm for CB-0h and CB-24h, respectively. However, the distributions of the bead diameters remained relatively stable after oxidation (Fig. 2-S5). The oxidized cellulose beads in this study were smaller than previously reported beads (Table 2-S1) and, thus, were expected to have a high adsorption performance. The swelling of the cellulose beads can be attributed to the introduction of carboxyl groups. SEM micrographs obtained after freeze-drying the beads (Fig. 2-5 lower) show that CB-1h and CB-4h beads have spherical morphologies. Conversely, CB-24h beads are mostly spherical; however, they contain certain structural irregularities, leading to the assumption that introducing many carboxyl groups may cause the cellulose beads to become fragile [23]. The microstructure of the oxidized cellulose beads was almost identical to that of the initial cellulose beads, maintaining a 3D network structure consisting of nanofibers with widths of 20-50 nm. The average pore size and volume of the cellulose beads were maintained after oxidation (Table 2-S1). Thus, the specific surface areas of the cellulose beads were also maintained after oxidation: 246 m²/g for CB-1h, 255 m²/g for CB-4h, and 215 m^2/g for CB-24h, which are higher than those of previously reported cellulose beads (Table 2-S1), indicating that they can be used as adsorbents [7, 24].



Fig. 2-5. Optical microscope (upper) and SEM (lower) images of oxidized cellulose beads: (a) CB-1h, (b) CB-4h, and (c) CB-24h. Inset in the SEM image is an enlargement of the bead surface.

2.3.4. Adsorption of MB and CR onto oxidized cellulose beads

The adsorption behavior of the oxidized-cellulose beads was investigated using an anionic dye (CR) and a cationic dye (MB). When the beads were immersed in a CR solution (100 mg/L), the CB-0h beads absorbed the dye, turned red, and the supernatant solution became clear. The adsorption of CR onto CB-0h could be attributed to several possible factors: (i) electrostatic interactions between amino or azo groups of CR and the hydroxyl groups of the cellulose, (ii) hydrophobic interactions between aromatic groups of CR and the glucose rings of cellulose [25–27]. In contrast, using the oxidized beads (CB-4h), the color of the supernatant did not change and was almost the same as the color of the original CR solution (**Fig. 2-6a**). The adsorption capacity of CR onto the beads decreased with increasing oxidation time and carboxyl group content (**Fig. 2-6b**).

When the CB-0h and CB-4h beads were immersed in MB solution (100 mg/L), the CB-4h beads turned navy blue, and the supernatant lightened considerably. In the CB-0h adsorption experiment, the color of the supernatant remained identical to that of the original MB solution (**Fig. 2-6c**). The adsorption capacity of MB onto the beads increased with increasing oxidation time and carboxyl group content in the beads (**Fig. 2-6d**). The difference in MB adsorption capacity with carboxyl group content was more pronounced at a higher MB concentration of 1000 mg/L: 13 mg/g for CB-0h and 438 mg/L for CB-24h. This phenomenon can be explained

by the acid dissociation constants (pKa) of the carboxyl groups in the oxidized cellulose beads and the dye. At pH 7.0, the carboxyl groups are mostly dissociated, and the oxidized beads have a negative surface charge. The pKa of MB and CR are <1 and 4.0–4.1, respectively; thus, at pH 7.0, MB and CR are mostly dissociated and in cationic and anionic forms, respectively [28, 29]. The electrostatic interactions between the negatively charged carboxyl groups and the MB cations markedly enhanced the adsorption capacity of the oxidized beads. Conversely, the adsorption of anionic CR onto the oxidized beads was strongly inhibited by electrostatic repulsion.



Fig. 2-6. Photographs of (a) CR and (c) MB adsorption experiments on initial CB-0h and oxidized CB-4h cellulose beads. Adsorption of (b) CR and (d) MB by the beads. Dosage = 20 mg/10 mL, pH = 7.0, 25 °C, 48 h

The adsorption isotherms of CB-0h for CR and CB-24h for MB are shown in **Fig. 2-S6**; the experimental values were successfully fitted using Langmuir isotherm models, expressed in the form of the following linear equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}},\tag{2}$$

where q_e is the amount of adsorbate (mg/g) at equilibrium, q_{max} is the theoretical maximum adsorption capacity (mg/g), K_L is the Langmuir equilibrium constant (L/mg), and C_e is the

equilibrium concentration (mg/L). The refined parameters are listed in **Table 2-S2**. The maximum adsorption capacity (q_{max}) of CR on CB-0h and MB on CB-24h was 238.1 mg/g and 526.3 mg/g, respectively, higher than that of cellulose-based beads previously reported in the literature [16, 18, 30–33] (**Table 2-2**).

Table 2-2. Comparison of the maximum adsorption capacity of CR on cellulose beads and MB on oxidized cellulose beads in this study and other cellulose-based beads in the literature.

Adsorbent	$q_{\rm max}$ (CR, mg/g)	$q_{\rm max}$ (MB, mg/g)	Ref.
Recyclable carboxylated cellulose beads	_	288	[16]
Reed-based beads	40.1	45.9	[18]
Carboxymethyl cellulose/graphene composite aerogel beads	_	222.7	[30]
Molybdenum disulfide/cellulose microspheres	76.1	90	[31]
Cellulose-graphene nanoplatelets beads	98–139	_	[32]
Hollow cellulose-carbon nanotubes composite beads	_	285.7	[33]
CB-0h	238.1	—	This work
CB-24h	—	526.3	This work

The adsorption kinetics of CR on CB-0h and MB cellulose beads on CB-24h are shown in **Fig. 2-S7**. The experimental kinetic data were fitted with pseudo-first-order, pseudo-second-order, and intraparticle diffusion models expressed in the form of the following equations:

$$\ln(q_e - q_t) = \ln q_e - k_1 t,$$
(3)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e},$$
(4)

$$q_t = k_{di} t^{1/2} + C_i, (5)$$

where q_e is the amount of adsorbate (mg/g) at equilibrium; q_t is the adsorption capacity (mg/g) at a given time t; k_1 (min⁻¹), k_2 (g mg⁻¹ min⁻¹), and k_{di} (g mg⁻¹ min^{-1/2}) are the rate constant of pseudo-first-order, pseudo-second-order, and intraparticle diffusion, respectively; and C (mg/g) is the adsorption constant [34, 35]. The refined parameters are presented in **Table 2-3** and **Table 2-4**. The correlation coefficient R² of the pseudo-second-order model was higher than that of the pseudo-first-order model, indicating that the adsorption process for CR on CB-0h and MB on CB-24h followed that of the pseudo-second-order model. These results suggest that

chemisorption controls the adsorption kinetics [35–37]. The plots of q_t versus $t^{1/2}$ analyzed using the intraparticle diffusion model were nonlinear and exhibited two stages for CR and MB (**Fig. 2-S7c** and (**Fig. 2-S7f**). The adsorption rate (k_{d1}) during the first stage was higher than that during the second stage. The first rapid adsorption phase was attributed to boundary layer diffusion effects, and the second slow adsorption phase was attributed to intraparticle diffusion effects [35–37]. The CR and MB dyes were rapidly adsorbed on the outer surface of the CB-0h and CB-24h particles and then gradually adsorbed by subsequent diffusion into the interior.

Table 2-3. Kinetic parameters of the pseudo-first-order and pseudo-second-order models forCR on cellulose beads (CB-0h) and MB on oxidized cellulose beads (CB-24h).

	Pseudo-first-order			Pseudo-second-order		
Adsorbate	$q_{ m e,cal} \ (m mg/g)$	k_1 (min ⁻¹)	\mathbb{R}^2	$q_{ m e,cal}$ (mg/g)	k_2 (g mg ⁻¹ min ⁻¹)	\mathbb{R}^2
CR	177.3	0.169	0.979	200.0	0.0014	0.995
MB	13.3	0.313	0.936	253.5	0.0714	0.999

Table 2-4. Intra-particle diffusion model constants and correlation coefficients for CR on cellulose beads (CB-0h) and MB on oxidized cellulose beads (CB-24h).

Adsorbate	$k_{\rm d1} \ ({\rm mg \ g^{-1} \ min^{-1/2}})$	C_1	$(R_1)^2$	$k_{\rm d2} ({\rm mg \ g^{-1} \ min^{-1/2}})$	C_2	$(R_2)^2$
CR	42.717	12.903	0.862	2.010	173.9	0.593
MB	5.377	237.8	0.872	0.252	251.6	0.856
	ption capacity retention (%)	CB-1h		3-4h ⊠ CB-24h		

2 3 4 Number of cycles

5

Fig. 2-7. Adsorption capacity retention of oxidized cellulose beads CB-1h, CB-4h, and CB-24h for MB adsorption after five cycles.

Adso

1

To investigate the reusability of the oxidized cellulose beads as adsorbents, the adsorption-

desorption cycles were repeated five times after the initial adsorption of MB (**Fig. 2-7**). The adsorption capacity of the oxidized cellulose beads gradually decreased during each cycle. After five cycles, CB-24h still maintained 81.3% of its original adsorption capacity, while the adsorption capacities of CB-1h and CB-4h decreased by 72.7% and 80.1%, respectively. After repeated cycles, the oxidized-cellulose beads with a higher carboxyl group content maintained a high adsorption capacity. These results indicate that the oxidized cellulose beads have excellent regeneration properties and significant potential for repeated use as adsorbents.



2.4. Supporting information for Chapter 2

Fig. 2-S1. Optical microscopy images of the cellulose beads prepared by modulating various parameters (The figure numbers correspond to the conditions for preparing cellulose beads in **Table 1**)



Fig. 2-S2. Particle size distributions of the cellulose beads prepared by modulating various parameters (The figure numbers correspond to the conditions for preparing cellulose beads in **Table 1**)



Fig. 2-S3. Optical microscopic images of cellulose beads after (a) 50 repeat centrifugations at 6,900 g and (b) mechanical stirring at 500 rpm for 48 h.



Fig. 2-S4. Weight loss of cellulose beads immersed in 50 mM buffer solution at pH 7 for one week.



Fig. 2-S5. Particle size distributions of oxidized cellulose beads, (a) CB-1h, (b) CB-4h, and (c) CB-24h.



Fig. 2-S6. Adsorption isotherms of (a) CR on cellulose beads CB-0h and (b) MB on oxidized cellulose beads CB-24h fitted by linear equations of the Langmuir model.



Fig. 2-S7. Adsorption kinetics of CR on cellulose beads CB-0h (a-c) and MB on oxidized cellulose beads CB-24h (d-f) analyzed by pseudo-first-order (a, d), pseudo-second-order (b, e), and intraparticle diffusion models (c, f).
Method	Cellulose solvent	Gelation	Diam eter (µm)	Specific surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	Refer ence
	Ionic liquids	Lowering the temperature	66	34.6	_	_	[1]
	NaOH/CS ₂	Solidification at 90 °C	88	_	_	_	[2]
Emulsion- gelation	Ca(SCN) ₂	Cool to room temperature	over 10	200	_	_	[3]
	NaOH/thiourea	Chemical cross- linking/solidi fication in H ₂ SO ₄	15, 40	153, 142.9	_	_	[4, 5]
	NaOH/thiourea /urea	Coagulation in acetic acid	27.7	127	_	_	[6]
Dropping	Ionic liquids	Coagulation in H ₂ O	1200- 2000	4.45	21.3	0.013	[18]
	NaOH/urea	Coagulation	About 2000	64-99	16-20	_	[19]
		in H ₂ SO ₄ /Na ₂ S O ₄	3010	112.09	15.18	0.307	[20]
			2080- 2340	97.34	_	0.348	[21]
Emulsion- gelation	LiBr	Cool to room temperature	7.9–8. 8	215-255	9.9–1 4.1	1.04–1. 41	This study

Table 2-S1. Comparison of average diameter and the specific surface area of cellulose beads

 in this study and other regenerated cellulose beads.

Table 2-S2. Langmuir isotherm parameter for adsorption of CR on CB-0h and MB on CB-24h.

	Langmuir			
	$q_{\rm max}({\rm mg/g})$	$K_{ m L}$	\mathbb{R}^2	
CB-0h	238.1	0.036	0.939	
CB-24h	526.3	0.088	0.953	

2.5. Reference for Chapter 2

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Chapter 3.

Catalytic activity of Cu₂O nanoparticles supported on cellulose beads prepared by emulsion–gelation using cellulose/LiBr solution and vegetable oil

3.1. Background

Compared to bulk materials, metal nanoparticles (NPs) exhibit unique properties, specifically catalytic activity [1]. Copper (Cu) NPs are easily prepared and are preferred over precious metals such as Au, Ag, and Pt because Cu is naturally abundant and less expensive. Although Cu and Cu-based NPs are popular catalysts [2, 3], they tend to aggregate because of their high surface energy, which significantly reduces their catalytic activity. Several materials have been investigated as supports for Cu or Cu-based NPs to stabilize their catalytic activity, including carbon materials, metal oxides, silica/silicon, zeolites, and polymers [4-10].

Cellulose beads have also been studied as catalyst supports because of the abundance of modifiable hydroxyl groups on their surface, excellent mechanical strength and elasticity, and large surface area. For example, heteropoly acids have been incorporated into cellulose beads as catalysts for biodiesel production [19-21], and TiO₂ with various morphologies and polypyrene–TiO₂@WO₃ have been incorporated into cellulose beads to enable photocatalytic reactions [22, 23]. However, most studies used harmful or expensive solvents, such as the NaOH/CS₂ system or ionic liquids, petroleum-derived oils for emulsification, and coagulation baths for solidification. Therefore, the development of a sustainable method for synthesizing cellulose beads is highly desirable.

In the **Chapter 2**, we reported the successful preparation of cellulose beads using an innovative emulsion–gelation method. First, the cellulose was dissolved in a LiBr solution at 120 °C, droplets were created using water-in-oil (W/O) emulsions, and the droplets were solidified by cooling the emulsion suspension. The resulting cellulose beads are promising adsorbent materials owing to their three-dimensional network of cellulose nanofibers. These beads have a small diameter of ~10 μ m and a large specific surface area of 230 m² g⁻¹. Although this method offers advantages over the use of a coagulation bath or cross-linking agent, the process is not entirely ecofriendly because of the use of petroleum-based decane. Therefore, to achieve the goals of green chemistry, we attempted to synthesize cellulose beads with high specific surface areas using plant-derived oils instead of decane. We also investigated the ability of the beads to support metal catalysts by oxidizing their surfaces to introduce carboxyl groups and loading them with Cu₂O NPs to evaluate their catalytic activity.

3.2. Experimental

3.2.1. Preparation of cellulose beads

	Parameters						
En	ıtry	Oil	Surfactant (HLB)	Weight ratio of oil to cellulose solution	Surfactant concentratio n (wt.%) ^a	Stirring speed (rpm)	Cellulose concentrati on (wt.%) ^b
А	1 2 3 4 5 6	Decane Olive Palm Canola Rice MCT	Span 80 (4.3)	3	2	500	1
В	1 2 3 4	Canola	Span 85 (1.7) Span 80 (4.3) Span 40 (6.7) Span 20 (8.3)	3	2	500	1
С	1 2 3 4	Canola	Span 80 (4.3)	1 3 6 9	2	500	1
D	1 2 3 4 5 6	Canola	Span 80 (4.3)	3	0.1 0.5 1 2 6 12	500	1
Е	1 2 3 4	Canola	Span 80 (4.3)	3	2	250 500 750 1000	1
F	1 2 3 4	Canola	Span 80 (4.3)	3	2	500	0.5 1.0 1.5 2

^a Concentration of surfactant in edible oil

^b Concentration of cellulose in 60 wt.% LiBr solution

The regenerated cellulose was dissolved in a 60 wt.% LiBr (Fujifilm Wako Pure Chemical) solution by stirring for 15 min at 120 °C to obtain a transparent cellulose solution. The cellulose/LiBr solution (water phase) was added to a solution of surfactant (Sorbitan esters, also known as Spans, Tokyo Chemical Industry) in edible oil at 120 °C with stirring. A W/O emulsion was formed after 10 min and cooled to room temperature with continuous stirring to gelatinize the micelles in the cellulose solution. The suspension was allowed to stand until it

separated into two layers. The upper layer containing the oil phase was removed, and the lower layer containing cellulose beads was collected, washed with acetone, and washed with deionized water by repeated centrifugation until no LiBr was detected with silver nitrate. The effect of modulating the experimental parameters, such as the type of edible oil (olive, palm, canola, rice, medium chain triglyceride MCT from coconut, which were purchased at the local supermarket (Kyoto, Japan)), hydrophile–lipophile balance (HLB) value of the surfactant (Span 85, Span 80, Span 40, and Span 20), weight ratio of oil to cellulose solution, surfactant concentration in oil, stirring speed, and cellulose concentration in the 60 wt.% LiBr solution, on the diameter of the obtained cellulose beads was investigated (**Table 3-1**).

3.2.2. TEMPO-mediated oxidation of cellulose beads

The cellulose beads were oxidized using a 4-acetamido-TEMPO/NaClO/NaClO₂ system [24]. Briefly, wet cellulose beads (0.5 g dry weight) were dispersed in 50 mL of 0.2 M acetate buffer (pH 5.2) containing 80% NaClO₂ (0.85 g, 7.5 mmol) and 4-acetamido-2, 2, 6, 6-tetramethylpiperidine-1-oxyl (4-acetamido-TEMPO) (0.05 g, 0.225 mmol). A freshly prepared 1.6 M NaClO solution (0.32 mL, 0.5 mmol), which was diluted with water to 1% of its original concentration, was added to the above dispersion and gently stirred at 60 °C for 0.5, 3, or 9 h. The carboxylate contents of the cellulose beads were determined using a previously reported conductometric titration method [25].

3.2.3. Loading Cu-based NPs on cellulose beads

Approximately 5 g of wet cellulose beads (dry weight: 100 mg) was immersed in 50 mL of 500 mM CuSO₄ solution for 48 h at 25 °C under stirring. The Cu²⁺-loaded cellulose beads were washed with deionized water to remove unbound Cu²⁺ and dispersed in 50 mL of a 100 mM NaBH₄ solution. After stirring the suspension for 12 h, the Cu-NP-loaded cellulose beads were collected and thoroughly washed with deionized water. X-ray diffraction (XRD) was used to determine whether the prepared Cu-based NPs were Cu, Cu₂O, or CuO.

3.2.3. Characterization

Fourier-transform infrared (FTIR) spectra of the dried cellulose beads were recorded in the range of 500–4000 cm⁻¹ with a resolution of 4 cm⁻¹ using a attenuated total reflectance (ATR) attachment (PerkinElmer, USA). Images of the wet beads were recorded using an optical microscope (Olympus BX53, Japan), and the diameter and circularity of the cellulose beads

were evaluated using ImageJ software. Circularity is a value between zero and one, indicating how closely the shape of a particle resembles a circle, and is defined as follows:

$$Circularity = 4\pi \times \frac{A}{P^2}$$
(1)

where A and P are the area and perimeter of the cellulose beads, respectively, as measured using ImageJ software.

The beads were freeze-dried in 30% t-butyl alcohol/water, coated with osmium, and observed using scanning electron microscopy (SEM; Hitachi S-4800, Japan). The nanofiber widths of the beads were measured from SEM images using ImageJ software. Nitrogen adsorption measurements were performed using freeze-dried cellulose beads, and the specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method (BELSORP MINI X; Japan). Transmission electron microscopy (TEM) observations of the Cu-based NPloaded cellulose beads were performed using ultrathin sections prepared from the samples embedded in epoxy resin at an acceleration voltage of 120 kV. Electron micrographs were captured using a built-in charge-coupled device camera (JEM-1400, Jeol Co. Ltd., Tokyo, Japan). Elemental mapping of the Cu-based NP-loaded cellulose beads with SEM was performed using an energy-dispersive X-ray spectroscopy system (EDS; Genesis XM2, Japan) integrated with an SEM instrument (Hitachi S-4800, Japan). Thermogravimetric curves of the Cu-based NP-loaded cellulose beads were recorded at a heating rate of 10 °C min⁻¹ in air (TGA N-1000, Scinco, Republic of Korea). Freeze-dried cellulose beads were pressed into disks and their XRD patterns recorded using Cu K α radiation ($\lambda = 0.15418$ nm) and an imaging plate (R-AXIS Rapid II, Rigaku, Japan).

3.3.4. Catalytic performance test

The catalytic performance of the Cu-based NP-loaded cellulose beads was evaluated for the reduction of 4-nitrophenol to 4-aminophenol by NaBH₄. Wet Cu-based NP-loaded cellulose beads (125 mg) were dispersed in 50 mL of 1 mM 4-nitrophenol containing 50 mmol NaBH₄. At specific time intervals, 0.3 mL of the suspension was collected and diluted 10-fold, and the absorbance of the supernatant was measured at 400 nm (the wavelength of the maximum absorbance of 4-nitrophenol) using a UV–visible (UV–vis) spectrometer (UV-2450, Shimadzu, Japan). The reusability of the Cu-based NP-loaded cellulose beads was evaluated by repeating the reaction ten times. Once the reduction was completed (>90%), the catalyst beads were separated from the reaction solution using a sieve (mesh size: 63 µm). The recovered beads were washed with deionized water and used for absorbance measurements during subsequent

reaction cycles. After ten catalytic reaction cycles, the recovered beads were washed, vacuumdried, and weighed. The recovery efficiency of the catalyst beads was calculated as follows:

Recovery efficiency =
$$\frac{M}{m \times W} \times 100$$
 (2)

where m and W are the mass and solid content of the wet catalyst beads before the catalytic reaction, respectively, and M is the dried mass of the catalyst beads after ten catalytic reaction cycles. The stability of the Cu-based NP-loaded cellulose beads was also evaluated over 30 d. Freshly prepared Cu-based NP-loaded cellulose beads were stored in a refrigerator at 4 °C and their catalytic activity was measured every two days.

The kinetic rate constant (K, min⁻¹) and conversion (C, %) of 4-nitrophenol to 4-aminophenol were calculated using the following equations:

$$\ln\frac{A_t}{A_0} = -Kt \tag{3}$$

$$C = \frac{A_0 - A_t}{A_0} \times 100 \tag{4}$$

Here, A_0 and A_t are the initial absorbance values of the reaction solution and that at time *t*, respectively. The turnover frequency (TOF, h⁻¹), which is defined as the number of moles of reduced 4-nitrophenol per mole catalyst per hour for a conversion rate of >90% [7], was calculated using the following equation:

$$TOF = \frac{n_{4-NP} \times C}{t \times n_{Cu_2O}}$$
(5)

where n_{4-NP} is the initial moles of 4-NP, C is the conversion (>90%) of 4-nitrophenol to 4aminophenol at time t (h), and n_{Cu_2O} is the moles of Cu₂O on the cellulose beads.

3.3. Results and discussion

3.3.1. Effect of synthesis conditions on the size and shape of cellulose beads

The size and shape of the cellulose beads were examined by varying the preparation parameters listed in Table 1. Optical micrographs of the obtained cellulose beads are shown in **Fig. 3-1** and **3-S1**. All prepared beads were spherical, except those produced at a cellulose concentration of 0.5 wt.% and stirring speed of 250 rpm, which were dispersed and irregularly shaped (**Figs. 3-S1E1** and **3-S1F1**). The average diameter, circularity, and diameter frequency distribution of all beads, except the irregularly shaped ones, were measured from the micrographs (**Figs. 3-2 and 3-S2**). The average diameter of the cellulose beads prepared from edible oil was 100–200 µm, which is significantly larger than that of the beads prepared from

decane (average diameter: $10 \ \mu m$) in Chapter 2. The difference in bead size between decane and edible oils may be because decane is hydrophobic, whereas the edible oils are hydrophilic. Hydrophobic oils can interact more easily with the hydrophobic part of the surfactant, which helps prevent the coalescence of emulsion droplets and reduces the bead size [26].



Fig. 3-1. Optical microscopy images of cellulose beads prepared using various oils (A1: Decane, A2: Olive, A3: Palm, A4: Canola, A5: Rice, A6: MCT).

The average diameter of the beads was also greatly influenced by the type of edible oil used, with MCT oil having the largest effect, followed by rice, canola, palm, and olive oils (**Fig. 3-2a**). These differences are mainly attributed to variations in the chemical structure of the edible oils, such as the length of the fatty acid chains, number of unsaturations, and molecular configuration [26]. The average diameter of the cellulose beads was ~150 μ m when Span 85 (HLB 1.7) and Span 80 (HLB 4.3) surfactants were used and ~300 μ m when Span 40 (HLB 6.7) and Span 20 (HLB 8.3) surfactants were used (**Fig. 3-2b**). Low-HLB surfactants with strong lipophilic properties exhibit better compatibility with oil, resulting in more stable water droplets that are resistant to coalescence [26].

As the weight ratio of canola oil to cellulose solution increased from 1 to 9, the average diameter of the cellulose beads decreased from 161.5 to 109.6 μ m (**Fig. 3-2c**) and the distribution of their diameters also narrowed. This indicates that smaller micelles of uniform size were formed when the oil–water phase ratio increased while maintaining a constant surfactant content. A higher weight ratio of canola oil to cellulose leads to a higher surfactant to water ratio, implying that more surfactant molecules cover the emulsion droplets and resist coalescence [27, 28]. When the surfactant concentration increased from 0.01 to 12 wt.%, the average diameter of the cellulose beads decreased from 176.3 to 103.7 μ m, respectively, with a simultaneous narrowing of their distribution (**Fig. 3-2d**). This is because a high surfactant

concentration provides complete coverage of the entire surface area of the microemulsion droplets and avoids emulsion droplet coalescence, leading to smaller beads [28].

The average diameter also decreased from 142.1 to 98.8 μ m when the stirring speed increased from 500 to 1000 rpm, respectively (**Fig. 3-2e**). However, at 250 rpm, the spherical cellulose beads agglomerate and form clusters. Increasing the stirring speed enhances the shear force, reducing the droplet size of the generated microemulsion, resulting in a decrease in the average diameter of the beads [28].



Fig. 3-2. Average diameters and circularity of the cellulose beads prepared by using different (**a**) oils, (**b**) surfactants, (**c**) weight ratios of canola oil to cellulose solution, (**d**) surfactant (Span 80) concentrations in canola oil, (**e**) stirring speeds, and (**f**) cellulose concentrations in 60 wt.% LiBr solution. Error bars indicate the \pm standard deviation (SD) from the average diameters. The data labels correspond to the conditions for preparing cellulose beads in **Table 3-1**. The p-values for the average diameter and circularity of the beads were p < 0.0001 and p < 0.005, respectively, for (**a**–**f**), indicating that the differences between the various beads were statistically significant.

The average diameter of the cellulose beads increased from 142.1 to 277.1 μ m upon increasing the cellulose concentration from 1 to 2 wt.%, respectively (**Fig. 3-2f**). Higher cellulose concentrations result in higher viscosities and larger microemulsion droplets, forming beads with larger average diameters [28]. These results show that higher weight ratios of canola oil to cellulose solution, higher surfactant concentrations, and higher stirring speeds resulted in cellulose beads with smaller average diameters and narrower diameter distributions. However, higher cellulose concentrations yield cellulose beads with larger average diameters.

The circularity of all beads was >0.6, and the differences between the various beads was statistically significant (p < 0.005). Lower weight ratios of canola oil to the cellulose solution, lower surfactant concentrations, lower stirring speeds, and higher cellulose concentrations produced more circular beads (**Fig. 3-2**). Therefore, the optimal conditions for cellulose beads with a small diameter, narrow diameter distribution, and high circularity were as follows: canola oil-to-cellulose solution weight ratio of 3, surfactant concentration of 6 wt.%, stirring speed of 650 rpm, cellulose solution concentration of 1.5 wt.%, and selection of cellulose beads <250 µm through a sieve.

3.3.2 TEMPO-mediated oxidation of cellulose beads

The obtained cellulose beads were subjected to 4-acetamido-TEMPO-mediated oxidation to introduce surface carboxyl groups. Optical microscopy and SEM studies (**Fig. 3-3**) showed that all cellulose beads (before and after oxidation) were spherical in the wet state.



Fig. 3-3. Optical microscopy (above) and SEM (below) images of the cellulose beads: (a) CB-0h, (b) CB-0.5h, (c) CB-3h, and (d) CB-9h. Inset in the SEM images: lower magnification images.

The carboxyl group content of the initial cellulose beads (CB-0h) was negligible, while those of the oxidized cellulose beads CB-0.5h, CB-3h, and CB-9h were 0.115, 0.419, and 0.849 mmol g^{-1} , respectively (**Table 3-2**). The introduction of carboxyl groups caused the diameter of the beads to increase by ~10% (**Table 3-2**): 95.6 µm for the cellulose beads before oxidation (CB-0h) and 105.1 µm for the oxidized beads (CB-9h). The SEM micrographs (**Fig. 3-3**) show spherical beads with a three-dimensional network of nanofibers (width: 20–30 nm). Consequently, the specific surface area of the cellulose beads was very high and increased from 145 m² g⁻¹ (CB-0h) to 225 m² g⁻¹ (CB-9h) with increasing oxidation time (**Table 3-2**). Although this suggests that the nanofiber width decreased with increasing oxidation time, all SEM images revealed consistent nanofiber widths of 10–13 nm (**Table 3-2**). However, the bead diameter increased with oxidation time, indicating that the increase in the specific surface area was caused by the loosening of the nanofiber network as the cross-linked areas were loosened.

Sample	Average diameter (SD) (μm)	Nanofiber diameter (SD) (nm)	Specific surface area (m ² g^{-1})	Carboxyl group content (mmol g^{-1})	Amount of Cu ₂ O loaded (wt.%)
CB-0h	95.6 (28.3)	10.4 (3.9)	145	0	0.61
CB-0.5h	95.7 (28.9)	11.3 (4.1)	165	0.115	1.65
CB-3h	101.1 (30.4)	12.6 (4.6)	196	0.419	5.37
CB-9h	105.1 (32.2)	9.9 (3.7)	225	0.849	8.05

Table 3-2. Properties of the oxidized cellulose beads and amount of Cu₂O loaded on them.



Fig. 3-4. FTIR spectra of the unoxidized (CB-0h and oxidized beads (CB-0.5h, 3h, 9h).

The FTIR spectra of the unoxidized (CB-0h) and oxidized cellulose beads (CB-0.5h, CB-3h, and CB-9h) normalized by the absorbance of the antisymmetric glucoside C–O–C stretching band at 1156 cm⁻¹ are shown in **Fig. 3-4**. Because all beads were composed of cellulose nanofibers, their spectra were similar. The bands typical of cellulose type II are observed at 3488 and 3441 cm⁻¹ in the OH stretching region, and the patterns in the CH stretching and fingerprint regions are nearly identical [29]. However, the C=O stretching band at 1602 cm⁻¹ [30] was absent in the unoxidized cellulose beads (CB-0h) and became stronger with increasing oxidation time, consistent with the carboxyl group content measured by titration (**Table 3-2**).

3.3.3 Cu₂O NP-loaded cellulose beads

The XRD pattern of the unoxidized cellulose beads (CB-0h) is typical of cellulose II, exhibiting $1\overline{10}$, 110, and 020 diffraction peaks at $2\theta = 12.3$, 20.2, and 21.8° , respectively [31] (**Fig. 3-5**). The diffraction profiles after oxidation (**Fig. 3-5**) were similar, indicating that the oxidized cellulose beads were composed of cellulose II nanofibers, even when carboxyl groups were introduced on the surface.



Fig. 3-5. XRD profiles of unoxidized and oxidized cellulose beads (CB-0h, CB-0.5h, CB-3h, and CB-9h) and those loaded with Cu₂O NPs (Cu₂O@CB-0h, Cu₂O@CB-0.5h, Cu₂O@CB-3h, and Cu₂O@CB-9h).

The diffraction profiles of the unoxidized (Cu₂O@CB-0h) and oxidized cellulose beads (Cu₂O@CB-0.5h, Cu₂O@CB-3h, and Cu₂O@CB-9h) immersed in copper sulfate and then reduced were almost identical to those of the original oxidized cellulose beads (CB-0h). However, small but distinct peaks are observed at $2\theta = 36.2$ and 43.0° , corresponding to the 111 and 200 diffraction peaks of Cu₂O, respectively [32]. The Cu₂O peak intensity increased with increasing degree of oxidation, indicating that more Cu₂O was introduced onto the nanofiber surface. The formation mechanism of Cu₂O nanoparticles has been reported previously [33]. After the Cu²⁺ ions were adsorbed onto the carboxyl groups on the beads, they were reduced by NaBH₄ to form Cu nuclei. These generated Cu nuclei immediately interact with the dissolved oxygen molecules to oxidize and form either Cu₂O or CuO. Since the standard formation enthalpies for Cu₂O and CuO are -166.7 kJ mol⁻¹ and -155.2 kJ mol⁻¹, respectively, Cu₂O was formed as it is slightly more stable than CuO.



Fig. 3-6. (a) SEM images with low (upper) and high magnification (lower), (b) TEM image, (c) SEM-EDS maps, and (d) TGA curve of CB-9h and Cu₂O@CB-9h.

The SEM images of the freeze-dried Cu₂O-loaded cellulose beads (**Fig. 3-6a** and **3-S3**) reveal that the spherical shape and three-dimensional nanofiber network were maintained. The absence of Cu₂O nanoparticles at high magnification indicates a low particle size, consistent with the broad Cu₂O peaks observed in the XRD profiles (**Fig. 3-5**). The TEM image of Cu₂O@CB-9h (**Fig. 3-6b**) showed that the nanoparticles (4.9–21.6 nm, average size: 11.3 nm) are dispersed in the beads, although there is some aggregation. The introduction of Cu into the beads was confirmed by EDS Cu maps (**Fig. 3-6c** and **3-S4**). The amount of Cu₂O NPs loaded onto the cellulose beads was determined by thermogravimetric analysis (TGA) conducted in

air (Fig. 3-6d and 3-S5). When heated at 700 °C, Cu₂O is converted into CuO according to the reaction: Cu₂O + 1/2 O₂ \rightarrow 2 CuO [34]. Thus, the weight percentage of the Cu₂O NPs on the cellulose beads was calculated as follows:

$$W = \frac{W_1 \times 143.1}{W_2 \times 2 \times 79.5} \times 100,$$
(4)

where W is the weight percentage of Cu₂O, W_1 is the weight percentage of the CuO residue at 700 °C, W_2 is the weight percentage of the sample at 150 °C after the adsorbed moisture evaporated, and 143.1 and 79.5 are the molecular weights of Cu₂O and CuO, respectively. The Cu₂O loading increased from 0.61% for Cu₂O@CB-0h to 8.05% for Cu₂O@CB-9h (**Table 3-2**).



3.3.4 Catalytic activity of Cu₂O NP-loaded cellulose beads

Fig. 3-7. Time-dependent UV–vis absorption spectra of 4-nitrophenol reduction by NaBH₄ in the (a) absence and (b–e) presence of Cu₂O-loaded cellulose beads: (b) Cu₂O@CB-0h, (c) Cu₂O@CB-0.5h, (d) Cu₂O@CB-3h, and (e) Cu₂O@CB-9h. (f) Color change of the solution upon the reduction of 4-nitrophenol to 4-aminophenol by NaBH₄ in the presence of Cu₂O@CB-3h.

The effectiveness of the Cu-based NP-loaded cellulose beads as catalysts for the reduction of 4-nitrophenol to 4-aminophenol using NaBH₄ was investigated (**Fig. 3-7**). Upon addition of NaBH₄, the 4-nitrophenol absorbance peak shifted from 317 to 400 nm, confirming the formation of 4-nitrophenolate ions [35]. However, the 4-nitrophenolate absorbance remained unchanged even after 210 min (**Fig. 3-7a**). When Cu₂O@CB-0h was added, the 4-nitrophenolate absorbance decreased gradually, and 25% conversion to 4-aminophenol was achieved in 180 min; the absorbance remained constant thereafter (**Fig. 3-7b**).

However, when Cu₂O@CB-0.5h was added, a conversion efficiency of >90% was attained over 25 min (**Fig. 3-7c**). The addition of Cu₂O@CB-3h and Cu₂O@CB-9h yielded even faster decreases in the 4-nitrophenolate absorbance (**Figs. 3-7d, e**); Cu₂O@CB-0.5h, Cu₂O@CB-3h, and Cu₂O@CB-9h had apparent kinetic rate constants of 0.103, 0.355, and 0.386 min⁻¹, respectively. Upon the addition of the Cu₂O-loaded cellulose beads, the yellow aqueous solution of 4-nitrophenol with NaBH₄ became colorless, visually confirming the catalytic reduction of 4-nitrophenol (**Fig. 3-7f**).

Sample	TOF (h^{-1})	Reference
Chitosan-silica nanocomposite fiber-supported Cu NPs	5.56	[4]
Cellulose acetate-ferric oxide NP-supported Cu NPs	0.45	[5]
Metal-organic framework MIL-101 (Cr)-supported Cu NPs	0.80	[6]
Biomass (Melia azedarach plant)-supported Cu NPs	4.98	[7]
Natural polymer (chitosan/cellulose microfiber)- supported Cu NPs	103.3	[8]
Cellulose nanocrystal-supported CuO NPs	1108.8	[9]
Spherical montmorillonite-supported Cu NPs	955.5	[10]
Cu ₂ O/MoS ₂	43.8	[36]
Cu ₂ O/Reduced graphene oxide (RGO)	52.8	[37]
Cu ₂ O/Cubic mesoporous carbon	35.8	[38]
Cu ₂ O@CB-0.5h	376.2	This work
Cu ₂ O@CB-3h	282.6	This work
Cu ₂ O@CB-9h	181.6	This work

Table 3-3. Comparison of TOFs of Cu-based NP-loaded support materials reported for the reduction of 4-nitrophenol by NaBH₄.

The conversion efficiencies for the reduction of 4-nitrophenol in the presence of $Cu_2O@CB-$ 0.5h, $Cu_2O@CB-3h$, and $Cu_2O@CB-9h$ were above 90%. We calculated the TOF values and compared their catalytic activities with those previously reported for Cu-based NP-supported materials (**Table 3-3**). $Cu_2O@CB-0.5h$ had a TOF value of 376.2 h⁻¹, which decreased to 181.6

 h^{-1} for Cu₂O@CB-9h. The TOF values were lower than those of cellulose nanocrystal-loaded CuO NPs [9] and spherical montmorillonite-loaded Cu NPs [10], but still higher than those of other Cu NP-loaded materials [4-7, 36-38]. Cellulose nanocrystals and montmorillonite, which exhibit high TOF values, are dispersions of nanosized particles that are not easily recovered by filtration or centrifugation. However, the Cu₂O-loaded cellulose beads developed in this study were larger and could be easily recovered by filtration, indicating their potential for practical applications.



Fig. 3-8. Conversion efficiency and kinetic rate constant for the reduction of 4-nitrophenol by NaBH₄ catalyzed by Cu₂O@CB-3h: (a) reusability evaluation over 10 cycles and (b) stability evaluation over 30 days (tested every other day).

The reusability of the developed catalysts was evaluated using Cu₂O@CB-3h for the 4nitrophenol reduction reaction over 10 cycles (**Fig. 3-8a**). After each cycle, the catalyst was washed with distilled water and reused for another cycle. Although the reaction rate constant decreased to 0.3 min⁻¹ after the first cycle and 0.111 min⁻¹ after the second cycle, it remained steady thereafter; the conversion efficiency remained above 90%, even after 10 cycles. The recovery efficiency of the catalyst beads after ten cycles was 96.8%. To test their long-term

stability, the Cu₂O NP-loaded cellulose beads were stored in a refrigerator at 4 °C and tested every other day; Cu₂O@CB-3h remained stable for 30 d (conversion efficiency > 90%, rate constant ~0.3 min⁻¹, **Fig. 3-8b**).



3.4 Supporting information for Chapter 3

Fig. 3-S1. Optical microscopy images of the cellulose beads prepared by modulating various parameters (The figure numbers correspond to the conditions for preparing cellulose beads in **Table 3-1**)



Fig. 3-S2. Particle size distributions of cellulose beads prepared by modulating various parameters (The figure numbers correspond to the conditions for preparing cellulose beads in Table 1)



Fig. 3-S3. SEM images of Cu₂O-loaded cellulose beads: (a) Cu₂O@CB-0h, (b) Cu₂O@CB-0.5h, and (c) Cu₂O@CB-3h; SEM image at low magnification (above) and high magnification (below).



Fig. 3-S4. SEM-EDX mapping images of Cu₂O NP-loaded cellulose beads: (a) Cu₂O@CB-0h, (b) Cu₂O@CB-0.5h, and (c) Cu₂O@CB-3h.



Fig. 3-S5. TGA curves of the cellulose beads before and after loading with Cu₂O NPs.

3.5. Reference for Chapter 3

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Chapter 4.

Preparation of cellulose/paraffin composite foams by an emulsion–gelation method using aqueous inorganic salt solution for thermal energy regulation

4.1. Background

Phase change materials (PCMs) have become popular in recent years due to their ability to absorb or release high latent heat within a particular temperature range during the phase transition process. These PCMs have been used for thermal storage and regulation in various fields, such as buildings, solar water heating, and thermos-regulating textiles [1–3]. Paraffin, a byproduct of crude oil refining, is considered the most promising PCMs due to its high latent heat, good chemical stability, low melting vapor pressure, and minimal supercooling [4,5]. However, paraffin leakage is a common issue during the phase transition process [6], and researchers have tried to solve this problem by encapsulating or impregnating paraffin in organic polymers such as poly(urea-urethane), polystyrene copolymers, acrylic copolymers, melamine-urea-formaldehyde, and poly(methyl methacrylate) [7–12]. Unfortunately, these polymers are derived from petrochemical sources and are not environmentally friendly.

Conversely, cellulose is an environmentally friendly material that has been gaining attention in recent years. Cellulose nanofibers (CNFs) are a form of cellulosic material that can be used as a Pickering stabilizer due to their amphiphilic surface chemistry [13,14]. In addition to providing good emulsion stability, CNFs have been studied as an encapsulation material for PCMs. Researchers have formed various forms of CNF-encapsulated PCMs, such as aerogels, foams [15–17], microparticles [18,19], paper [20] and hollow cellulose filaments [21]. Composites of PCMs encapsulated in CNF foams have attracted much attention due to their high thermal insulation and storage performance. However, preparing well-dispersed CNFs requires considerable technical expertise, time, and effort. Therefore, in this study, we proposed another system to encapsulate PCMs in cellulose foam.

Cellulose foams can be prepared by dissolution, regeneration, and drying processes using cellulose solvents without CNFs [22–24]. In a LiBr solution of inorganic salts, cellulose is dissolved at 120 °C and then regenerated to gel when the cellulose solution is allowed to cool to about 70 °C [25,26]. When washed with water, the regenerated gel becomes a cellulose hydrogel and a foam when further dried. The foam has a three-dimensional network structure consisting of nanofibers with a 20–30 nm width and a high specific surface area. This LiBr-based process allows for the preparation of foams on a large scale and the reuse of LiBr since it only uses a LiBr solution, in contrast to the usual method wherein the foam is regenerated in a poor solvent after dissolution. Therefore, composites of cellulose foams with proteins, polysaccharides, and inorganic materials have been prepared [27–30]. However, to the best of our knowledge, no examples of cellulose/paraffin composite foams have been reported.

In this study, we dispersed paraffin with an amphiphilic surfactant in an aqueous cellulose/LiBr solution to form an oil-in-water (O/W) emulsion with the cellulose/LiBr solution as the continuous phase of the emulsion and paraffin as the dispersed phase of the emulsion. This emulsion could be solidified without solvent by cooling to room temperature. The study reports on the structure, physical, and thermal properties of monolithic cellulose/paraffin composite foams prepared in a one-step emulsion–gelation process using LiBr solution and paraffin.

4.2. Experimental

4.2.1 Preparation of cellulose/paraffin composite foam

The experimental procedure for preparing cellulose/paraffin composite foams is shown in **Fig. 4-1**. Commercially available regenerated cellulose (Bemcot, Asahi Kasei Co. Ltd., Japan) was used as the starting material (viscosity average molecular weight: 91 000, α -cellulose content: 94%). The cellulose sample was dissolved in a 60 wt% LiBr (Fujifilm Wako Pure Chemical) solution by stirring at 120 °C for 15 min to obtain a transparent cellulose solution. Melted paraffin (120 °C, oil phase, Leica Biosystems Co. Ltd., Germany) and Tween 80 (polyethylene glycol sorbitan monooleate, 1.67 g/L, Sigma-Aldrich Co. Ltd., USA) were added to the above-mentioned transparent cellulose solution. This mixture was then stirred using high-speed blending (3,000 rpm, 5 min, Physcotron NS-51, Microtec Co., Ltd, Japan) to obtain an O/W emulsion. The O/W emulsion was cooled to room temperature to form a cellulose/paraffin composite gel.



Fig. 4-1. Schematic of the synthesis of cellulose-paraffin composite foams

The hybrid gels were washed with deionized water until no bromide ions could be detected. This was done by adding silver nitrate (FUJIFILM Wako Pure Chemical CO., Ltd, Japan)

solution to the wash water, verifying that no white precipitate had formed. The composite gels were treated via solvent exchange (30% *t*-butyl alcohol/water) and freeze-dried to obtain a cellulose/paraffin composite foam. For comparison, a cellulose foam without paraffin was also prepared using the same experimental procedure. Details of the mixtures of cellulose and paraffin used in this study are listed in **Table 4-1**.

Sample	Cellulose $(g/L)^{a}$	Paraffin (g/L) ^a	Weight ratio of cellulose to paraffin	Density (SD) (g/cm ³) ^b
C1/P0	10	0	_	0.014 (0.0003)
C2/P0	20	0	_	0.031 (0.002)
C3/P0	30	0	—	0.046 (0.001)
C3/P2	30	20	3:2	0.071 (0.004)
C2/P3	20	30	2:3	0.074 (0004)
C1/P4	10	40	1:4	0.075 (0.005)
C2/P8	20	80	1:4	0.163 (0.006)
C3/P12	30	120	1:4	0.190 (0.008)

Table 4-1. Cellulose-paraffin composite foam samples in this study

^a Concentration to the total volume of 60 wt% LiBr solution and paraffin.

^b SD is the standard deviation.

4.2.2 Characterization

Fourier-transform infrared spectroscopy (FTIR) was performed using the attenuated total reflectance method (Spectrum 3, PerkinElmer, USA). The absorbance FTIR spectra of the sample were recorded in the $750-4000 \text{ cm}^{-1}$ range with a resolution of 4 cm⁻¹. The internal structures of the sample were observed using scanning electron microscopy (SEM) (Hitachi S-4800, Japan). Compression tests of these foams were conducted at constant temperature and humidity (23 °C, RH = 50%) using a testing machine (EZ-Test, Shimadzu Corporation, Japan) equipped with a 100 *N* load cell. Cylindrical foams were compressed at a 1 mm/min rate using a measuring plate, and eight samples of each foam were measured for the compression test. The elastic modulus was determined from the linear region of the stress-strain curve. The thermal energy storage capacity of samples (4–5 mg) was performed using differential scanning calorimetry (DSC, DSC7020, Hitachi high-technologies, Japan) at a rate of 10 °C/min under a nitrogen atmosphere. The samples were heated from -50 °C to 120 °C, kept at 120 °C for 1 min, cooled to -50 °C, held at -50 °C for 3 min, and then heated to 120 °C. Synchrotron X-ray diffraction (XRD) measurements of the samples were performed at the SPring-8 beamline BL40B2 (Hyogo, Japan) using X-rays with 0.075 nm wavelength. X-ray diffraction

patterns in the heating process were recorded on a PILATUS 2M detector (Dectris, Baden, Switzerland). The thermal conductivity of the sample (thickness: 10 mm, diameter: 30 mm) was measured using a thermal conductivity analyzer (Hot Disk TPS 2500 S, Hot Disk AB, Sweden), with three measurements for each sample. The surface temperature and the infrared image of the sample (thickness: 9 mm, diameter: 8.5 mm) placed on a hot plate or moved away from the hot plate were recorded using a thermal camera (FLIR, C2, FLIR C2, Teledyne FLIR LLC, USA) to evaluate its thermal regulation performance.

4.3. Results and discussion

4.3.1. Internal structure and chemical structure of cellulose/paraffin composite foams

A cellulose/paraffin composite foam was created using a new emulsion–gelation technique. The process involved adding paraffin and surfactant to a cellulose/LiBr solution, which was then stirred to create an O/W emulsion. Cooling the emulsion suspension caused it to solidify into a cellulose/paraffin composite foam, eliminating the need for regenerating solvents. This unique feature enabled the facile production of cellulose/paraffin composites in various shapes and sizes and with excellent formability (**Fig. 4-S1**).

The bulk density of the cellulose foams ranged from $0.071-0.190 \text{ g/cm}^3$ and increased with the initial cellulose concentration, C1/P0 < C2/P0 < C3/P0 (**Table 4-1**). The cellulose/paraffin composite foam had a higher bulk density ($0.071-0.190 \text{ g/cm}^3$) than the cellulose foams. Among the composite foams with the same total amount of cellulose and paraffin (C1/P4, C2/P3, C3/P2), the bulk density was almost the same at 0.07 g/cm^3 . When the cellulose and paraffin mixing ratio was the same (1:4) and the mixing amount increased from C1/P4 to C3/P12, the density increased from 0.071 g/cm^3 to 0.190 g/cm^3 .

An SEM study of freeze-fractured surfaces of the foam revealed the internal structure of the cellulose/paraffin composite foam (**Fig. 4-2**). The micrograph of cellulose foam showed a 3D network structure of interconnected, elongated cellulose nanofibrils, with a width of 20–30 nm and a porous structure with nanoscale pore sizes. This porous structure was similar to previously reported cellulose foams prepared by dissolution and gelation with aqueous LiBr solutions [25,26]. The cellulose/paraffin composite foam contained spherical paraffin particles with diameters ranging from 1 to 8 μ m (**Fig. 4-S2a-e**), embedded in the porous structure of the cellulose nanofibrils network. Paraffin, which was solubilized in micelles at high temperatures, solidified in the regenerated cellulose structure upon cooling to form spherical paraffin, with C3/P2

< C2/P3 < C1/P4. The number of particles also increased with increasing paraffin concentration for the samples of the same weight ratio of paraffin to cellulose (C1/P4 < C2/P8 < C3/P12). Since the surfactant concentration was constant in this study, the average particle size remained constant under all conditions (**Fig. 4-S2f**), because the amount of solubilization per micelle was constant. Moreover, as the amount of oil phase (paraffin) increased, the number of paraffin particles also increased. However, these spherical paraffin particles occur to aggregate to a certain degree in the foam with high paraffin content (**Fig 4-2**, the upper half contains Lowmagnification SEM images).



Fig. 4-2. SEM images of pure cellulose foams (a) and cellulose/paraffin composites foams (b– f): (a) C3/P0, (b) C1/P4, (c) C2/P3, (d) C3/P2, (e) C2/P8, and (f) C3/P12. For each image, the upper half contains low-magnification images, and the lower contains high-magnification images.

FTIR measurements were performed to evaluate the structure of the cellulose/paraffin composite foam. The recorded spectra are shown together with those of the paraffin and cellulose foams (**Fig. 4-3**). The spectrum of pure paraffin showed absorption peaks at 2915 cm⁻¹ and 2849 cm⁻¹ attributed to the stretching vibrations of the $-CH_3$ and $-CH_2$ groups. The adsorption peaks at 1471 cm⁻¹ and 1460 cm⁻¹ represent the deformation vibrations of the $-CH_3$ and $-CH_2$ groups, while the adsorption peak at 721 cm⁻¹ is attributed to the rocking vibration of the $-CH_2$ group [31]. The spectrum of cellulose foam was identical to that of low crystalline cellulose: a prominent absorption peak in the -CH stretching region at 3000–2800 cm⁻¹, and absorption peaks in a region called the fingerprint region below 1200 cm⁻¹ were present. Of the peaks in the fingerprint region, the absorption peak at 1155 cm⁻¹ is attributed to the C–O–C stretching vibration of the β -(1→4)-glucoside bond [27].



Fig. 4-3. FTIR spectra of paraffin, cellulose foam (C3/P0) and cellulose/paraffin composite foams (C1/P4, C2/P3, C3/P2, C2/P8, and C3/P12).

The FTIR spectra of the cellulose/paraffin composite foams are the sum of the cellulose and paraffin spectra. All cellulose and paraffin absorption peaks are included, and no other peaks

are present. The C=O stretching vibration at 1738 cm⁻¹, which originates from the surfactant [32], is absent, indicating that the composite foam is free from residual surfactant. As the weight ratio of cellulose to paraffin increased from C1/P4 to C2/P3 and then to C3/P2, the intensity of the characteristic absorption peak of paraffin decreased. No significant difference was observed in these absorption peak intensities for the same weight ratios of cellulose to paraffin (C1/P4, C2/P8, and C3/P12). This result means that paraffin is embedded in the cellulose foam without a chemical reaction with cellulose.

4.3.2. Mechanical property of cellulose/paraffin composite foams.

Cellulose and cellulose/paraffin composite foams underwent compression tests to study their mechanical properties. The stress-strain curves of all foams showed three stages: an initial linear elastic region, plastic deformation after the yield point, and a final densification region (**Fig. 4-4a**) [15].



Fig. 4-4. Stress-strain curves (a), elastic modulus (b), and yield stress (c) of cellulose foams and cellulose/paraffin composite foams from compression tests.

Fig. 4-4b and **Fig. 4-4c** show the elastic modulus and yield stress of the foams, respectively. The elastic modulus and yield stress of pure cellulose foams (C1/P0, C2/P0, and C3/P0) increased with increasing cellulose content, leading to increased sample density. Meanwhile, for cellulose/paraffin composite foams with nearly identical density (C1/P4, C2/P3, and C3/P2), both elastic modulus and yield stress increased as the weight ratio of cellulose to paraffin increased. For samples with the same weight ratio of paraffin to cellulose (C1/P4, C2/P8, and C3/P12), both elastic modulus and yield stress increased as the cellulose/paraffin composite foam density increased. C3/P12 had the highest elastic modulus of 7.08 MPa and yield strength of 241.9 kPa, which was about ten times that of the composite C1/P4 (elastic modulus of 0.62 MPa and yield stress of 25.3 kPa). The C1/P4 composite had the same weight ratio of cellulose to paraffin and one-third of the density. Changing the cellulose and paraffin composition allows for control over foam mechanical properties.



4.3.3. Thermal property and form stability of cellulose/paraffin composite foams

Fig. 4-5. DSC thermograms of paraffin and cellulose/paraffin composite foams during (a) heating and (b) cooling processes. (c) Wide-angle XRD profiles of C3/P12 composite foam during heating process.

DSC measurements were carried out to evaluate the thermal properties of the cellulose/paraffin composite foam. The DSC thermogram of the cellulose/paraffin composite foam (**Fig. 4-5**) showed two peaks in the temperature range of $30-70^{\circ}$ C during both heating and cooling processes, much like that of pure paraffin. Paraffin waxes consist of a mixture of n-alkanes (C_nH_{2n+2}) and exhibit a solid-solid phase transition below the melting point [33]. The small endothermic peak observed during the heating process represents the solid-solid phase transition, and the subsequent sharp peak corresponds to the solid-liquid phase change. During the cooling process, the sharp endothermic peak corresponds to the liquid-solid phase change, and the small endothermic peak corresponds to the solid-solid phase transition [34]. Since no peaks were seen in the temperature range of $30-70^{\circ}$ C in the pure cellulose foam (**Fig. 4-S3**), it can be concluded that the peaks observed in the cellulose/paraffin composite foams were of paraffin origin. As the weight ratio of paraffin to cellulose increased (C3/P2 < C2/P3 < C1/P4), the peak intensity also increased. The peak intensity varied very little for foams with the same mixing ratio of cellulose to paraffin (C1/P4, C2/P8, C3/P12).

Sampla	T_{m}	$\Delta H_{heating}$	Tc	$\Delta H_{cooling}$	Initial paraffin	Actual paraffin
Sample	(°C)	$(J g^{-1})$	(°C)	$(J g^{-1})$	content (%)	content (%)
Paraffin	48.7	192.4	54.6	197.8	—	—
C1/P4	49.3	158.4	53.9	150.4	80	82.3
C2/P3	48.9	122.4	53.3	125.3	60	63.6
C3/P2	47.9	63.4	53.1	71.6	40	32.9
C2/P8	49.2	166	54.6	173.2	80	86.3
C3/P12	49.0	148.5	54.7	150.4	80	77.2

Table 4-2. Thermal parameters of pure paraffin and cellulose/paraffin composite foams.

Table 4-2 shows the thermal parameters of pure paraffin and cellulose/paraffin composite foams calculated from the DSC thermograms. The melting (T_m) and crystallization (T_c) temperatures were determined by the onset temperatures of the solid-liquid and liquid-solid phase changes of the heating and cooling processes, respectively. The onset temperature of the DSC peak was determined by drawing a line at the point of maximum slope of the peak's leading edge and extrapolating to the baseline on that side of the peak (**Fig 4-S4**). The latent heat (Δ H) was calculated by numerical integration as the area under the paraffin peak (**Fig. 4-S4**) [35]. The pure paraffin had a melting point and crystallization temperature of 48.7 °C and 54.6 °C, respectively. The melting and crystallization temperatures of paraffin in the cellulose/paraffin composite foam were 47.9–49.3 °C and 53.1–54.7 °C, respectively, and did
not significantly differ from the melting and crystallization temperatures of pure paraffin. The latent heat of pure paraffin was 192.4 J g⁻¹ and 197.8 J g⁻¹ for the heating and cooling processes, respectively. For cellulose/paraffin composite foams of the same density (C1/P4, C2/P3, and C3/P2), those latent heats increased as the paraffin to cellulose weight ratio increased. Those latent heats remained almost the same for cellulose/paraffin composite foams with the same weight ratio of cellulose to paraffin (C1/P4, C2/P8, and C3/P12). The actual paraffin content determined from the ratio of the latent heat of cellulose/paraffin composite foams to that of pure paraffin is approximately equal to the initial paraffin content in the composite (**Table 4-2**) [16]. It is worth noting that the paraffin did not leak during sample preparation and is contained in the composite.



Fig. 4-6. (a) Volume shrinkage of cellulose/paraffin composite foams after heating at 80 °C for 24 h and (b) DSC thermograms of C3/P12 composite foams before and after heating.

The cellulose/paraffin composite foam underwent further investigation of its paraffin phase transition using wide-angle XRD. **Fig. 4-5c** shows the XRD profile of the C3/P12 composite foam during a temperature increase process. Before the temperature increase, at 30°C, two

sharp peaks at q = 15.1 and 16.7 nm^{-1} were observed, corresponding to the orthorhombic phase 110 and 020 of paraffin [36,37]. As the temperature increased to 40 °C, a broad peak ($q = 15.2 \text{ nm}^{-1}$) of the hexagonal rotator phase appeared, and the transition to the hexagonal rotator phase was complete at 42 °C. This temperature range of the orthorhombic to hexagonal rotator phase transition correlated with the results of the solid-solid phase transition of DSC. Therefore, the small endothermic peak of DSC (solid-solid transition) in the heating process matched with the orthorhombic to hexagonal rotator phase transition (**Fig. 4-5a**). When the temperature increased beyond the melting point of paraffin (**Table 4-2**), from 44 °C to 65 °C, the peak at $q = 15.2 \text{ nm}^{-1}$ disappeared, consistent with the peak of the solid-liquid phase transition in DSC thermogram (**Fig. 4-5c**). After the temperature increase, cooling to 30 °C resulted in the appearance of two distinct peaks in the orthorhombic phase, which returned to the profile before the temperature increase.

It is crucial to maintain the shape of PCMs after heating and prevent leakage for practical applications. To assess the stability of cellulose/paraffin composite foam, it was heated for 24 hours at 80 °C in an oven (**Fig. 4-6a** and **Fig. 4-S5**). The volume shrinkage of the cellulose foams was minimal, showing less than 3% shrinkage in all samples. Additionally, the shrinkage decreased as the density of cellulose increased. While the cellulose/paraffin composite foams had more significant shrinkage than the cellulose foams, it decreased as the cellulose content increased. For cellulose/paraffin composite foams with the same density (C1/P4, C2/P3, and C3/P2), volumetric shrinkage decreased significantly from 39.3% to 3.1% as the weight ratio of cellulose to paraffin increased. The shrinkage also decreased with increasing sample density for the foams of the same weight ratio of cellulose to paraffin (C1/P4, C2/P8, and C3/P12), reaching 6.3% for C3/P12.

DSC measurements of cellulose/paraffin composite foams were performed after heating at 80 °C for 24 h to determine the paraffin leakage resistance of the foams. Identical DSC thermograms were observed before and after heating (**Fig. 4-6b** and **Fig 4-S6**), indicating that the thermal parameters of melting, crystallization, and latent heat changed minimally (**Table 4-S1**). In other words, the foam exhibited excellent paraffin retention capacity and high leakage resistance. The unique nanofibril structure of LiBr-based cellulose foams, namely the continuous 3D cellulose nanofibril network with nanoscale pore size, prevented paraffin leakage, contributing to the foam's high leakage resistance [15,16].

The cycle of heating the cellulose/paraffin composite foam C3/P12 at 80°C and cooling to room temperature was repeated 20 times. SEM images indicated that the paraffin particles

changed from spherical to plate-like after heating cycles, with significant anisotropy in shape after 20 (**Fig. 4-S7a-c**). This result suggests that the paraffin disrupted the internal structure of the cellulose nanofibril network during crystallization. However, the 3D network structure of cellulose still retained the paraffin particles after 20 heating cycles. The thermal parameters, melting and crystallization temperatures, and latent heat were calculated from DSC thermograms of the foams and remained almost unchanged after 20 heating cycles (**Table 4-S2**). The cellulose foam retained the paraffin after 20 heating cycles, indicating excellent leakage resistance.

4.3.4. Thermal regulation performance of cellulose/paraffin composite foams

The thermal conductivity of cellulose foam and cellulose/paraffin composite foam was measured to evaluate thermal insulation properties (Fig. 4-7a). Cellulose foam is a porous material with a high air content. Compared to common polymeric materials that have a thermal conductivity of 100–300 mW m⁻¹ K⁻¹ [38]. Cellulose foams (C1/P0, C2/P0, C3/P0) had lower thermal conductivity that ranged from 40.9 to 47.7 mW m⁻¹ K⁻¹. The introduction of paraffin slightly increased the thermal conductivities of cellulose/paraffin composite foams compared to cellulose foams. However, the values remained low, ranging from 46.5–77.2 mW m⁻¹ K⁻¹. The thermal conductivity also increased with increasing density of the composite foams. The densest C3/P12 foam had the highest thermal conductivity of 77.2 mW m⁻¹ K⁻¹.

The ratio of the thermal conductivity of the composite foam to that of pure paraffin ranged from 23 to 38% (**Fig. 4-S8**), with a higher ratio for higher paraffin content [39]. The thermal conductivity of the composite foams would be attributed to the presence of paraffin. However, paraffin did not form a continuum in the composite foam; instead, it was dispersed as spherical particles with a diameter of 1 to 8 μ m, which resulted in a relatively low thermal conductivity. The thermal conductivity of the composite foam after heating five times was almost unchanged from that before heating. However, the thermal conductivity of C3/P12 was 97.1 mW m⁻¹ K⁻¹, about 20% higher than before heating. This result may be due to the high paraffin content, which agglomerated and formed a plate-like structure during repeated heat treatment.

To evaluate the thermoregulatory properties of cellulose/paraffin composite foams, the surface temperatures of the foams were measured using an infrared camera while they were placed on a hot plate at 60 °C. The temperature-time graphs of the foams during the heating process showed that their surface temperatures increased and reached a plateau within the first 15 minutes and remained constant after that (**Fig. 4-S9a**). After being heated for 60 minutes,

the surface temperature of all the foams was below 60 °C (**Fig. 4-7**b), indicating that these foams have insulating properties. The surface temperature of cellulose foam reached 40–41 °C. In contrast, that of the cellulose/paraffin composite foam was lower after 60 minutes, indicating that the energy absorption by paraffin resulted in a lower surface temperature. For foams with the same sample density, a higher weight ratio of paraffin (C3/P2 < C2/P3 < C1/P4) resulted in a lower surface temperature.



Fig. 4-7. (a) Thermal conductivity of cellulose/paraffin composite foams before and after 5 times heating at 80 °C, (b) the top surface temperature of 9-mm thick foams on a hot plate set to 60 °C for 60 min, (c) infrared image of foams placed on a 60 °C hot plate for 60 min (left) and moved away from the heating source for 1 min (right).

After 60 minutes, the foams were moved away from the hot plate, and their surface temperatures were recorded. During the cooling process, the surface temperature of the foam dropped sharply and leveled off within the first 5 minutes (**Fig. 4-S9b**). Differences in surface temperature between samples were observed in the infrared image of the surface temperature one minute after the foam was moved away from the heat source (**Fig. 4-7**c). The surface

temperature of the cellulose foam had cooled to room temperature. In contrast, the cellulose/paraffin composite foam still had a high surface temperature; the higher the paraffin content, the higher the temperature. Moreover, this effect was more significant with a larger sample density, C1/P4 < C2/P8 < C3/P12. These results indicate that the cellulose/paraffin composite foam has an excellent thermal regulating performance based on the thermal energy absorption performance of the paraffin it contains.



4.4. Supporting information for Chapter 4

Fig. 4-S1. Images of emulsions containing paraffin in cellulose/LiBr solution and their gelation upon cooling (a), and large cellulose/paraffin composite foams of various shapes (b).



Fig. 4-S2. Diameter distribution (a-e) and average diameter (f) of spherical paraffin particles in the cellulose/paraffin composite foams (a: C1/P4, b: C2/P3, c: C3/P2, d: C2/P8, e: C3/P12).



Fig. 4-S3. DSC thermograms of pure cellulose foam (C3/P0).



Fig. 4-S4. Calculation of melting temperatures (a: T_m) and crystallization temperatures (b: T_c) latent heat (c: ΔH) of cellulose/paraffin composite foams.



Fig. 4-S5. Image of cellulose/paraffin composite foams before and after heating in an 80 °C oven for 24 h (left: before heating, right: after heating).



Fig. 4-S6. DSC thermograms of cellulose/paraffin composite foams before and after heating at 80 °C for 24 h, (a) C1/P4, (b) C2/P3, (c) C3/P2, (d) C2/P8.

Table 4-S1. Thermal parameters of cellulose/paraffin composite foams before and after heatingat 80 °C for 24 h.

Sample	heating	T_m (°C)	$\Delta H_{\text{Heating}} (J/g)$	T_{c} (°C)	$\Delta H_{Cooling} (J/g)$
C1/P4	Before	49.3	158.4	53.9	160.1
	After	49.4	158.4	54.3	160.2
C2/P3	Before	48.9	122.4	53.3	125.3
	After	48.5	120.5	54.6	122.8
C3/P2	Before	47.9	63.4	53.1	71.6
	After	47.1	62.8	53.0	66.3
C2/P8	Before	49.2	166.0	54.6	173.2
	After	48.5	168.9	54.6	171.2
C3/P12	Before	49.0	148.5	54.7	150.4
	After	48.2	147.9	54.8	155.6





Fig. 4-S7. SEM images (a-c) and DSC thermograms (d) of C3/P12 composite foams after repeated heating and cooling, (a) initial, (b) after 10 cycles, (c) after 20 cycles.

Table 4-S2. Thermal parameters of C3/P12 composite foams after repeated heating and cooling

Heating-Cooling cycles	T_m (°C)	$\Delta H_{\text{Heating}}$ (J/g)	T_{c} (°C)	$\Delta H_{Cooling} (J/g)$
Initial	49.0	148.5	54.7	150.4
10 cycles	49.2	147.0	55.3	147.0
20 cycles	49.6	144.0	54.8	146.0





Fig. 4-S8. The ratio of thermal conductivity of cellulose/paraffin composite foams to that of pure paraffin.

Fig. 4-S9. The top surface temperature versus time curves of cellulose/paraffin composite foams (thickness: about 9 mm) during heating on the hot plate of 60 $^{\circ}$ C (a) and during the cooling (b).

4.5. Reference for Chapter 4

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Chapter 5.

Summary and Conclusions

A series of experiments were conducted in this thesis to create cellulose materials using the emulsion-gelation method. The resulting cellulose materials were then explored for their functionality. The results of the studies in the individual chapters are summarized as follows.

In Chapter 2, spherical cellulose beads on a micrometer scale were successfully prepared from a cellulose/LiBr solution using the W/O emulsion-gelation method with a surfactant having an HLB lower than 8.6. In contrast to other reported methods that require cellulose derivatization or coagulation solvents to solidify droplets, our method enables the direct preparation of cellulose beads using commercially available cellulose. The diameter of the cellulose beads 8–42 µm could be easily controlled by modulating the preparation parameters, such as the ratio of cellulose solution to oil, surfactant concentration, stirring speed, cellulose concentration, and types of surfactants. The cellulose beads had a specific surface area of 230 m^2/g and a high anionic CR dye adsorption capacity of 238.1 mg/g. The oxidized cellulose beads with carboxyl groups formed by TEMPO-mediated oxidation were highly effective for the adsorption of cationic MB dyes, with an adsorption capacity of 526.8 mg/g. Repeated adsorption-desorption cycles showed that the adsorption capacity of the oxidized cellulose beads slightly decreased, retaining 73-82 % after five cycles. Therefore, the oxidized cellulose beads prepared in this study are suitable for application as high-performance dye adsorbents and are expected to exhibit excellent adsorption capacity for positively charged metals. The main limitation of this method is the use of decane, which is derived from fossil fuels, as the oil phase in the emulsion preparation. With a focus on green chemistry principles, we aim to enhance our method by substituting decane with oils sourced from renewable resources.

In **Chapter 3**, cellulose beads were successfully prepared using the emulsion–gelation method, wherein a W/O emulsion was prepared at 120 °C using a cellulose/LiBr solution for the water phase and plant-derived canola oil for the oil phase. The mixture was then cooled to room temperature to form beads that were used as supports for the Cu₂O NPs. Although emulsion–gelation methods have been used to prepare cellulose beads, our process is more environmentally friendly because it does not require a coagulation bath and uses plant-derived edible oils as the oil phase instead of petroleum-based oils. However, the diameter of cellulose beads, 95-105 μ m, was larger than those prepared using decane as the oil phase, and thus the surface area of the beads became small. The degree of surface oxidation of the cellulose beads affected the loading of Cu₂O NPs. The catalytic activity of the beads was evaluated for the reduction of 4-nitrophenol by NaBH₄. The apparent reaction rate constant increased with increasing loading of Cu₂O NPs and the conversion efficiency was above 90%. The TOF, which

indicates the intrinsic activity of the catalyst, was 376.2 h⁻¹, which is higher than most existing Cu or Cu-based NP-supported materials. Unlike cellulose nanocrystals-supported CuO NPs and spherical montmorillonite-loaded Cu NPs, which cannot be recovered easily owing to their high dispersibility, the developed cellulose beads (particle diameters: 95–105 μ m) can be quickly recovered by filtering. They are highly reusable and stable in water at 4 °C, making them promising catalysts.

In Chapter 4, Using the emulsion-gelation technique, we have developed a new method for preparing cellulose/paraffin composite foams. This method utilizes an environmentally friendly aqueous inorganic salt solution as the cellulose solvent. The cellulose solution is emulsified and cooled to form a gel, allowing a simple one-pot process to prepare composite foams. These foams can also be molded into various shapes and large sizes without regenerated solvent. These foams consist of spherical paraffin particles with a diameter distribution of 1-8 µm embedded in a three-dimensional network structure of cellulose nanofibers. The composite foams demonstrated excellent mechanical properties; the foam's elastic modulus and yield stress could reach 7.08 MPa and 241.9 kPa, respectively. Due to the stiffness of cellulose nanofibers, the volume shrinkage after heat treatment is minimal, and the paraffin is retained without any leakage even when paraffin content increases to 86.3%. The latent heat of foams is proportional to the paraffin content, reaching 173.2 J g^{-1} ; the latent heat of C3/P12 remained almost unchanged after 20 heating and cooling cycles. The thermal conductivity of the foams was low, ranging from 46.5–77.2 mW m⁻¹ K⁻¹, which is 23–38% of the thermal conductivity of pure paraffin. In conclusion, the composite foam exhibits good mechanical properties, thermal stability, high latent heat, and low thermal conductivity. It is an ideal candidate for thermal regulation in intelligent buildings, solar water heating, and thermal regulation textiles.

On account of the results summarized above, the author is convinced of considerable attainment of the initial purpose of this thesis. Cellulose functional material, including cellulose beads for dye adsorption and for catalyst supports, and cellulose/paraffin composite foams, were prepared from cellulose/LiBr solution using emulsion-gelation method, and this may provide references for potential application in dye adsorption, catalysis, and thermal regulation.

Finally, the author expects that the results of this thesis and further studies will facilitate the utilization of cellulose functional materials as renewable and eco-friendly resources for the development of functional materials. This may reduce the consumption of traditional oil-based polymer materials and contribute to a sustainable society.

Publications

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