Facile Preparation and Functionalization of Cellulose Microgels and their Properties and Application in Stabilizing O/W Emulsions

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The preparation and functionalization of cellulose microgels (CMGs) has been presented. Only a trace concentration of CMGs (< 0.2 wt.%) stabilized oil-in-water (O/W) emulsions and produced high internal phase emulsions (HIPE). The size and morphology of the CMGs were characterized with dynamic light scattering (DLS) and atomic force microscopy (AFM), and the structural properties were discussed. Based on the experimental results, the correlation between the amphiphilicity, and adsorption of the CMGs, and their capability to stabilize the emulsions, which are closely related to the cross-linking density of the CMGs, were elaborated. Having a porous percolating structure and being rich in free hydroxyl groups, the CMGs were functionalized by Fe_3O_4. The unique dispersibility of the Fe_3O_4-CMGs and their ability to stabilize the emulsions were investigated in detail. The results pave the way to a deeper understanding of Pickering emulsions stabilized by soft solvent-swollen materials and are expected to further expand the application of cellulose.

Keywords: Cellulose microgels; Pickering emulsions; Composite; Functionalization

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INTRODUCTION

Emulsions are dynamically stable colloidal systems stabilized by surfactants and/or amphiphilic polymers (Lovell and El-Aasser 1997; Binks 1998). In recent years, a variety of colloidal particles have been used as stabilizers for emulsions (Binks 2002; Aveyard *et al.* 2003). Examples include silica nanoparticles (Vignati *et al.* 2003; Simovic and Prestidge 2004; Huo *et al.* 2014), clay (Yang *et al.* 2006), and latex particles (Giermanska-Kahn *et al.* 2002; Walther *et al.* 2008). Recently, Wei *et al.* used a natural polymer, *i.e.*, alkaline lignin extracted from furfural residues, to prepare Pickering emulsions, which can further be used as a template to fabricate composite capsules (Wei *et al*. 2012; Yi *et al*. 2015). Over the past decade, this new type of emulsion, *i.e.*, Pickering emulsions, have received increasing attention both in fundamental research and practical applications due to their unique properties such as greater stabilization, relatively well controlled size, lower toxicity, and a reduced rate and extent of creaming/sedimentation owing to the enhanced viscosity of the continuous phase (Liu *et al.* 2012).

A big task and challenge in the study of Pickering emulsions is further optimizing their properties and expanding their applications by engineering colloidal stabilizers. In this case, soft stabilizers such as microgels are more advantageous over rigid stabilizers due to their high flexibility and stimuli responsiveness (Nayak *et al.* 2005; Brugger *et al.* 2008; Berger *et al.* 2009; Shah *et al.* 2009; Monteux *et al.* 2010; Geisel *et al.* 2012; Liu *et al.* 2012; Destribats *et al.* 2013; Agrawal *et al.* 2014; Massé *et al.* 2014). Microgels have great water-absorbing (up to 99 wt%) and expansion properties, which can be easily regulated by tuning the solution parameters. In addition, the highly porous internal structure of microgels can potentially host a variety of substances with various functionalities that can make the emulsion system multifunctional.

From an economical and environmental viewpoint, microgels are preferentially made of materials that are abundant and eco-friendly. Cellulose is an ideal candidate to fulfill these requirements. Though cellulose of different forms including nanocrystals (Capron and Cathala 2013; Kalashnikova *et al.* 2013), nanofibers (Andresen and Stenius 2007), and bacteria cellulose (Ougiya *et al.* 1997; Kalashnikova *et al.* 2011a, 2011b; Wongkongkatep *et al.* 2012) have been used to stabilize emulsions, there has been no report on Pickering emulsions stabilized by cellulose microgels. The current study reports for the first time a facile way to prepare Pickering emulsions stabilized by cellulose microgels (CMGs). The factors influencing the properties of the Pickering emulsions were investigated in detail, and the stabilizing mechanism was discussed. In addition, the Pickering emulsions were further modified *in situ* by magnetic nanoparticles, *i.e.*, Fe_3O_4, which made the emulsion responsive to an external magnetic field.

EXPERIMENTAL

Materials

Cellulose in the form of cotton linter pulp with an average polymerization degree of 525 was supplied by Yinying Chemical Fiber Co. Ltd. (Gaomi, China). NaOH, urea, paraffin oil, and styrene were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). N,N'-Methylenebisacrylamide (MBA) was a product of Fuchen Chemical Reagents Factory (Tianjin, China). The styrene was dried by CaH_2 and distilled before use to remove any stabilizers. Emulsion polymerization of the styrene was initiated by AIBN (2,2'-Azobis (2-methylpropionitrile)) purchased from Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Water-soluble Congo red was used as a fluorescent dye for the CMGs and was purchased from Tianjin Sixth Chemical Factory (Tianjin, China). Oil-soluble fluorescein green, which was used to stain the paraffin oil, was a gift from Jinan Fangda Chemical Sales Department (Jinan, China). With the exception of styrene, all chemicals were used without further purification. Double distilled water was used throughout the experiment.

Sample Preparations

Preparation of cellulose solutions

Cellulose was dissolved according to the method described by Cai *et al.* (Cai and Zhang 2005, 2006; Cai *et al.* 2008). In summary, an aqueous solution of 7 wt.% NaOH/12 wt.% urea was pre-cooled to -12 °C in a refrigerator for 20 min, and 3 wt.% cellulose was added under stirring. The solution was then degassed by centrifugation at 4000 rpm for 5 min to create a transparent cellulose solution.

Preparation of cellulose microgels (CMGs)

Cellulose hydrogels were prepared from the cellulose solution by cross-linkage of the dissolved cellulose with MBA. A mixture of MBA powder and the cellulose solution was stirred for 10 min and then left standing at room temperature for 4 h, during which the solution gradually became a hydrogel elastomer. The hydrogels were dialyzed in de-ionized water, during which the NaOH and urea were nearly completely removed and the pH reached 7. The resultant hydrogels with different MBA amount had different swelling behavior, which was determined by comparing their weight to their oven dry weight. CMGs of a constant concentration were produced by sonicating the cellulose hydrogels in pure water for 45 min using a probe sonicator (Scientz, Ningbo, China; 3 mm titanium probe, 3 s pulse on, alternating with 5 s pulse off at a 1.5 kW power level). The cross-linking density of the CMGs was regulated by the amount of added MBA. Consequently, three types of CMGs of different cross-linking densities, denoted as CMG-0.5, CMG-0.75, and CMG-0.90, were obtained according to the weight proportion of MBA and cellulose. The resulting concentrations of all of the CMG aqueous dispersions were fixed to 0.2 wt.% (oven dry weight).

Preparation of O/W emulsions

Oil-in-water (O/W) emulsions were prepared by sonicating the biphasic systems containing both paraffin oil and the CMG aqueous solutions. Several oil/water (here, water refers to the CMG solution) volume ratios ($\mathrm{R}_{\mathrm{O/W}}$), *i.e.*, 10:90, 20:80, 30:70, 40:60, 50:50, and 60:40, were investigated, and the stability of these emulsions was determined. For instance, a biphasic system containing 1 mL of paraffin oil and 9 mL of CMG solution was sonicated for 5 min using a probe sonicator to obtain an O/W emulsion denoted as $R_{\mathrm{O/W}}$ = 1/9. The emulsions were stored at 25 °C for six months to observe the relative volume ratio of the separated upper phase (O/W emulsion) to the lower phase (water phase).

Preparation of magnetic CMGs and emulsions

The prepared cellulose hydrogels were immersed in a mixed solution of equimolar ratios of $Fe_2(SO_4)_3$ and $FeSO_4{\cdot}7H_2O$ under a N_2 atmosphere for 48 h. The cellulose hydrogel with Fe^{3+} and Fe^{2+} inside was then moved into a 2 M ammonia solution for another 48 h, during which a magnetic hydrogel was formed. Afterwards, the stabilized magnetic CMGs (Fe_3O_4-CMGs) were prepared in the same way as the previous CMGs and were centrifuged at 4000 rpm for 5 min to eliminate the uncoated Fe_3O_4 particles. Magnetic emulsions of the stabilized Fe_3O_4-CMGs were prepared using the same method used for the previous CMG emulsions.

Methods

The size distribution of the CMGs was measured using a dynamic light scattering (DLS) method with a BI-200SM instrument (Brookhaven Instruments, Austin, USA) at a constant scattering angle of 90°. Before measurement, the mother aqueous dispersion of the CMGs was diluted 10 times and then passed through 1 µm-pore syringe filters. The DLS data were analyzed by CONTIN software (Austin, USA). The zeta-potential of the CMG dispersions was measured using a particle electrophoresis instrument (Zetasizer Nano ZS, Malvern Instruments, UK).

To investigate the change in the amphiphilicity of the CMGs with varying cross-linking densities, the cellulose hydrogel films were first prepared using a template method (Yuan *et al.* 2015). The cellulose films were then dried on a glass plate at a constant temperature (30 °C) and humidity (65%) for 24 h, resulting in dried films with a flat surface. A 3 mL drop of deionized water was placed on the cellulose film surface, and the static contact angle was measured using a K100 tensiometer (Kruss Optronic, Germany).

Fourier-transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) spectra were obtained using a Thermo Nicolet NEXUS 670 infrared spectrometer (Thermo Scientific, Germany) and an X-ray diffractometer using a Cu Kα target at 40 kV and 30 mA, respectively. X-ray photoelectron spectroscopy (XPS) was conducted using a VG MicroTech ESCA 3000 X-ray photoelectron spectrometer (VG MicroTech Co., West Sussex, UK) with monochromatized Al Kα radiation (1200 eV).

Atomic force microscopy (AFM) was performed to capture the CMGs with a NanoScope IIIa (Veeco, USA). A mother aqueous dispersion of the CMGs was diluted with 10 volumes of absolute ethyl alcohol to reduce aggregation or crystallization of the CMGs. A drop of the diluted CMG dispersion was deposited onto a clean silicon wafer, and then dried at 30 °C for 30 min. AFM images were obtained with a tapping mode and analyzed with the Nanoscope software (version 5.30r3sr3).

The morphology of the emulsions and the distribution of CMGs around the emulsion droplets were visualized with an inverted Leica DMI 3000 fluorescence microscope (Leica, Germany). Paraffin oil was stained with 0.0085% fluorescein green and the CMGs were stained with 0.01% Congo red.

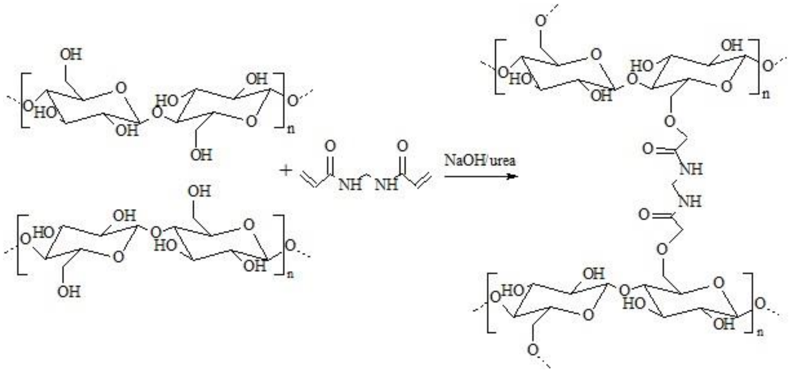
To ensure that complete adsorption of Congo red was only by the CMG particles, the stained CMG dispersions were dialyzed by de-ionized water using a dialysis bag with a 8000 to 14000 molecular weight cut-off for 48 h, and the de-ionized water was proved to show no alteration in color. Blue and green lasers were adopted to image the oil droplets and the CMGs, respectively. Scanning electron microscopy (SEM) was used to indirectly determine the morphology of the emulsions. To prepare the samples for SEM observation, the paraffin oil phase was replaced by styrene containing 0.826 wt% AIBN. Then, the emulsions containing styrene and the CMGs were initiated to polymerize in a water bath of 78 °C for 24 h. The dried samples were then coated with platinum and visualized by SEM (JEOL JMS-6700, Tokyo, Japan).

The magnetic properties of the magnetic CMGs were collected using a superconducting quantum interference device (SQUID; Quantum Design, USA) at room temperature. The hysteresis curves of the magnetization were collected by varying H between +7500 and −7500 Oe.

RESULTS AND DISCUSSION

Preparation and Properties of CMGs

An aqueous solution of 7.0 wt.% NaOH/12.0 wt.% urea is an appropriate solvent for cellulose, in which cellulose hydrogels can be slowly formed by adding a conventional cross-linking agent, *i.e.,* N,N'-methylene bisacrylamide (MBA). Formula 1 shows a possible reaction between cellulose and MBA in the solvent.



(1)

Hydrogels can swell up to 100 times their initial absolute weight (Yuan *et al.* 2015). Hydrogel swelling allows CMGs to be prepared simply by powerful sonification of the hydrogels. The aqueous dispersion of the CMGs was clear and transparent to the naked eye, and it was stable for six months. In contrast, the dissolved cellulose without cross-linkage was unstable, with flocculated matter depositing at the bottom of the solution (Fig. 1a).

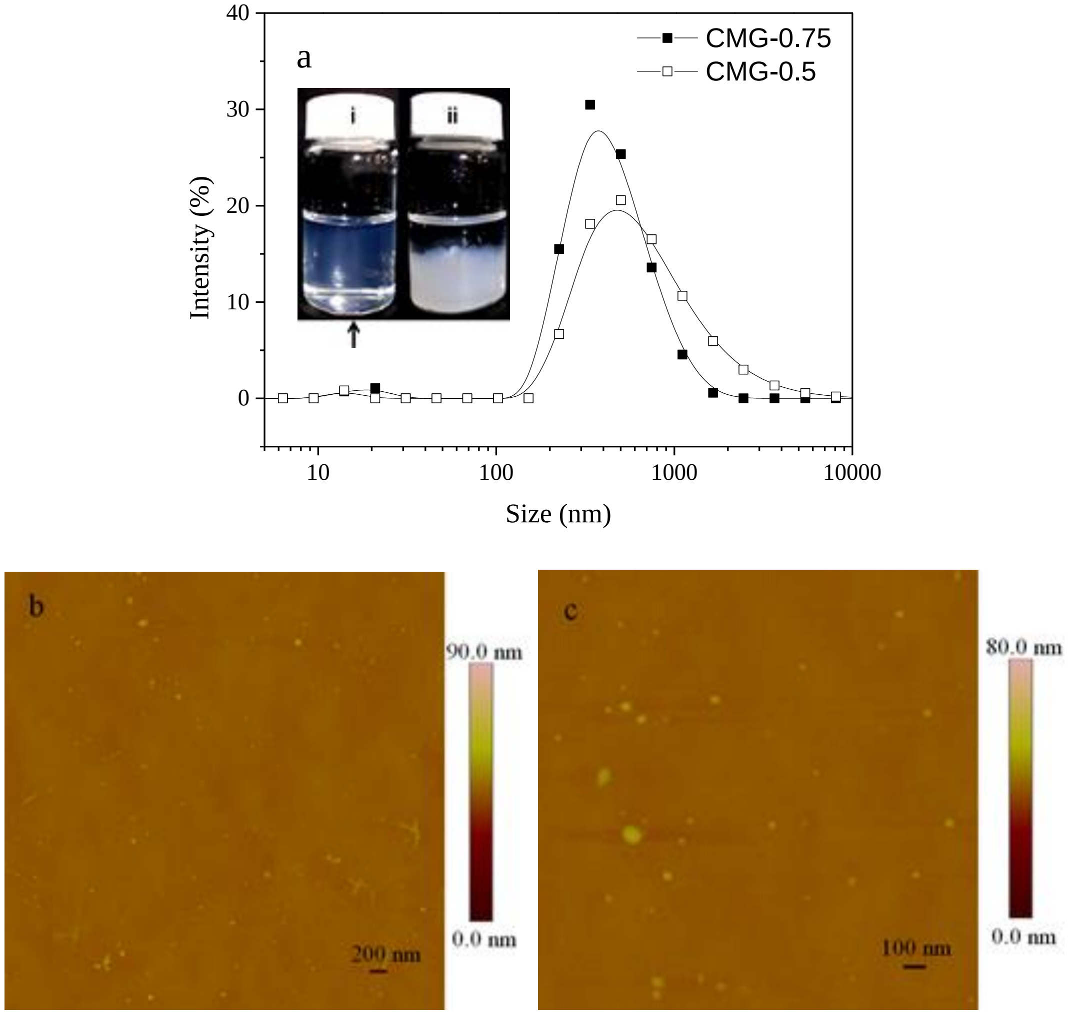


Fig. 1. (a) Distribution of hydrodynamic diameter of the CMGs in the aqueous solution. Insets are aqueous dispersions of the CMGs (i) and the cellulose without cross-linkage (ii). AFM images of the dried particles of CMG-0.75 at 16000x (b) and 40000x (c) magnification.

Dissolved cellulose without crosslinking did not stabilize the emulsions as the CMGs did in the subsequent emulsification experiments. The comparison in size distribution of the two typical samples, *i.e.*, CMG-0.5 and CMG-0.75, obtained from the DLS is shown in Fig. 1a. The CMG particles showed a comparatively broad size distribution with an average hydrodynamic diameter of 585 nm and 430 nm for CMG-0.5 and CMG-0.75, respectively. AFM pictures (Fig. 1b,c) showed that dried CMG particles were roughly spherical, having a polydisperse size, which is consistent with the DLS data. Due to drastic shrinkage during evaporation, the dried particles of the CMG-0.75 were comparatively smaller, with a size of only 30 to 80 nm.

Molecular simulations have indicated that cellulose is somewhat amphiphilic (Biermann *et al.* 2001; Mazeau 2011). The amphiphilicity of cellulose controls its adsorption behavior at the oil-water interface when used as a particle stabilizer (Kalashnikova *et al.* 2011a, 2013). With increases in the degree of cross-linkage, the total number of OH groups in the cellulose decreases. This is in agreement with the increasing contact angle of the water drop on the dried cellulose films (45.1°, 50.8°, and 54.5° for CMG-0.5, CMG-0.75, and CMG-0.9, respectively). Moreover, the zeta potentials of the CMGs of different cross-linking degrees were all nearly zero, indicating that the cross-linkage with MBA introduced few charges to the CMGs. These results imply that the high dispersibility and stability of the CMGs in the aqueous solution were not due to electrostatic repulsion between the CMGs. Thus, the perfect dispersibility of the CMGs in water should be ascribed to their strong hydration that originated from the numerous free hydroxyl groups. If the cross-linkage of cellulose with MBA consumed some of the hydroxyl groups, the hydration effect of the CMGs should decrease; however, the chemical cross-linkage of the dissolved cellulose by MBA would greatly lower the H-bonding interaction between cellulose molecules under a neutral pH, which would induce the liberation of more free hydroxyl groups to bind more water molecules. Having a lower cross-linking density, the water absorption of the CMG-0.5 was about 70 times that of its initial absolute weight; while for CMG-0.75, which had a relatively higher cross-linking density, this value was 180 times. The swelling of the hydrogels during immersion of cross-linked cellulose in water is promoted by a large osmotic pressure; thereafter, water is captured by the hydrophilic percolating network of cellulose containing numerous hydroxyl groups. Generally, the swelling of cellulose hydrogels can be closely related to the increasing number of free hydroxyl groups with hydrophilicity due to the expanding amorphous region of the cellulose with the increase in MBA (Yuan *et al*. 2015). The increase in hydration effect of the cellulose allowed the CMGs to adequately disperse in the water, leading to a subsequent high stability of the emulsions stabilized by the CMGs in the following experiments (see below).

Emulsions Stabilized by CMGs

An emulsion is a dispersion that is dynamically stable but thermodynamically unstable. This is true not only for surfactant-stabilized emulsions but also for particle-stabilized emulsions. For particle-stabilized emulsions, generally, the stability of an emulsion depends on the coverage or adsorption of the particles at the oil-water interface, as well as the repulsion interaction between emulsion droplets to resist flocculation and coalescence. The achievement of both points mainly depends on the intrinsic properties of the solid particles. Having numerous OH groups, cellulose mostly exhibits hydrophilicity; nevertheless, it simultaneously has lipophilicity to a certain extent due to the protruding

C(6)/O(6) units, and to a lesser extent, C(2)/O(2) moieties on the cellulose chains (Biermann *et al*. 2001). In the case of the cellulose in CMGs, the chemical cross-linkage of dissolved cellulose has two effects: (i) causing the total number of hydroxyl groups of CMGs to decrease; (ii) on the contrary, inducing the number of free hydroxyl groups to increase. However, the latter would dominate the former, giving rise to the strong hydration of CMGs. Therefore, the strong hydration repulsion among emulsion droplets would occur because of the adsorption of CMGs on their surface, thus preventing the emulsion droplets from aggregating and coalescing.

Pictures of the typical emulsion samples stabilized by the two CMGs (CMG-0.5 and CMG-0.75) are shown in Figs. 2a-f, which were taken after six months of equilibrium. Because of their tendency to disperse in water, there is no doubt they belong to the class of oil-in-water (O/W) emulsions, which was also demonstrated by traditional conductivity measurement (data not shown). Because the oil/water ratio (denoted as $R_{O/W}$) influences emulsion stability, the stability of the CMG-stabilized emulsions with varying $R_{O/W}$ was investigated. In Fig. 2h, a remarkable variation in emulsion volume fraction (denoted as EVF) was observed with increasing $R_{O/W}$ for the emulsions stabilized by both CMG-0.5 and CMG-0.75. When $R_{O/W}$ = 1:9, the EVF nearly reached 100%, and the EVF remained nearly constant when $R_{O/W}$ = 2:8.

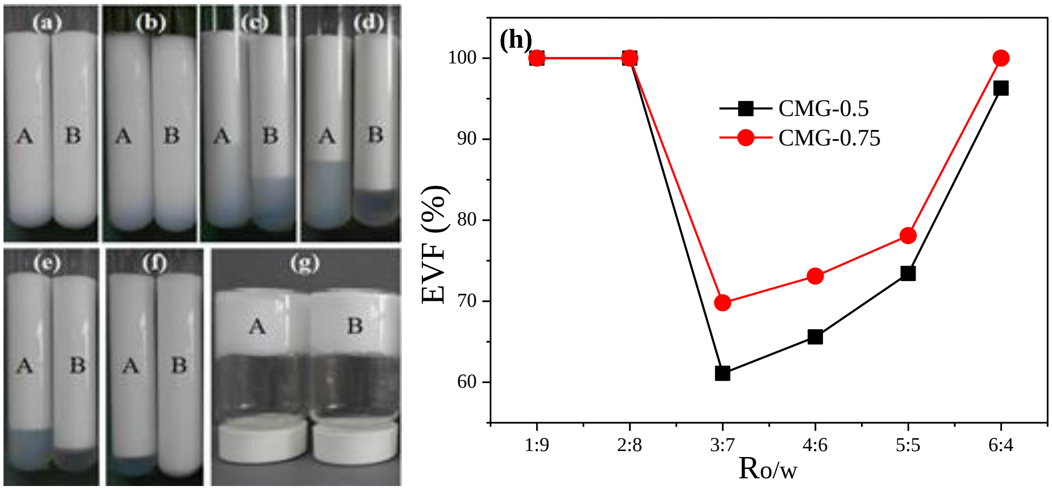


Fig. 2. (a-f) Pictures of the emulsions with increasing $R_{O/W}$: 1:9, 2:8, 3:7, 4:6, 5:5, and 6:4, respectively. (g) Emulsions in (f) held in inverted vessels with a large diameter. A and B denote the emulsions that were stabilized with CMG-0.5 and CMG-0.75, respectively. (h) EVF curves that are obtained according to the above pictures.

It was surprising that these emulsions were stable for up to six months without phase separation at such a small concentration of CMG (0.2 wt%). The EVF suddenly decreased when $R_{O/W}$ = 3:7, revealing that the emulsions were less stable and thus separated into two phases (including the upper O/W phase and the lower water phase). Phase separation was partly attributed to the coalescence of emulsion droplets. With increasing $R_{O/W}$, the number of CMGs becomes relatively low and does not completely cover the dispersive droplets, leading the droplets to coalesce. Afterwards, the EVF continued to increase with increasing $R_{O/W}$ and once again reached nearly 100% at a $R_{O/W}$ of 6:4. Here, the emulsion stability increased again with $R_{O/W}$. In fact, the viscosity of the emulsions noticeably increased at this $R_{O/W}$ because the emulsions were completely gelated in the vessels (Fig. 2g). This result reflects the formation of rather crowded droplets due to the high content of the oil phase at the higher $R_{O/W}$. In the emulsion gels, adjacent droplets tend to share the same interface composed of CMG layers; therefore, all droplets are bound together, forming a 3-dimensional network structure of closely packed high internal phase emulsions (HIPE). The solid-like property of the emulsion gels greatly reduces the collision between droplets, increasing the stability of the emulsions. In addition, the concentration of CMG particles undoubtedly influences the emulsion stability because EVF gradually increased with increasing number of CMG particles (data not shown).

The cross-linking density of the CMGs induced by varying the quantity of added MBA had a dramatic influence on the emulsion properties. Figure 2h shows that the emulsions stabilized by CMG-0.75 had a higher EVF than those stabilized by CMG-0.5, indicating that the CMGs of higher cross-linking density had a relatively higher stabilizing ability. CMGs of higher cross-linking density could have higher lipophilicity, leading to a higher adsorption effect of CMG particles at the oil-water interface; however, the relatively higher hydration effect leads to stronger hydration repulsion between emulsion droplets, which also stabilizes the emulsions. In addition, for containing the same absolute amount of cellulose, CMG-0.75 had a comparatively larger swelling volume in the aqueous solution, which would give rise to the larger spreading area at the oil-water interface than the CMG-0.5, resulting in a higher stabilizing efficiency. The curves in Fig. 2h summarize the influence of $\mathrm{R}_{O/W}$ on EVF and reflect the influence of CMG cross-linking density on emulsion stability.

To further characterize the CMG-stabilized (CMG-0.75) emulsions, both fluorescence microscopy and SEM observations were performed. For this purpose, the emulsion with $R_{O/W}$ = 1:9 was selected, which was double labelled with the oil droplets stained by fluorescein green and CMGs by Congo red. The photograph of the emulsion droplets under ordinary white light is shown in Fig. 3a. When excited with a blue laser, solid spheres with green fluorescence appeared (Fig. 3b). These spheres represent paraffin droplets because the oil-soluble fluorescein green was preferentially excited. When subjected to green laser, bright red shells were observed around the corresponding paraffin droplets (Fig. 3c). The shells were composed of CMG layers because the CMGs were stained with Congo red, which prevented the oil droplets from flocculation and coalescence. Moreover, outside the droplets, plenty of dark red dots formed, indicating that a large number of CMGs were dispersed in the ambient aqueous phase.

In addition, at $R_{O/W}$ = 1:9, most spherical droplets were clearly identified, as shown in Fig. 3a-c. For the emulsion at $R_{O/W}$ = 6:4, however, the droplets were not as independently separated but rather densely packed (Fig. 3d). Nearly all of the oil droplets were entrapped in a network, thus forming a viscoelastic emulsion gel. It should be noted that this emulsion is a HIPE and only requires less than 0.2 wt% of CMGs.

To further visualize the morphologies of the CMG-stabilized emulsions, a method of emulsion polymerization was carried out, in which styrene was used as the oil phase instead of paraffin oil. The resulting flocculation and coalescence of the styrene emulsions were comparatively more serious than those of the paraffin oil emulsions (not shown); this is probably due to the stronger affinity between cellulose and styrene derived from the hydrophobic interactions and causes the size of the emulsion droplets to inevitably change to a certain extent when using styrene as the oil phase (Olivier *et al.* 2012).

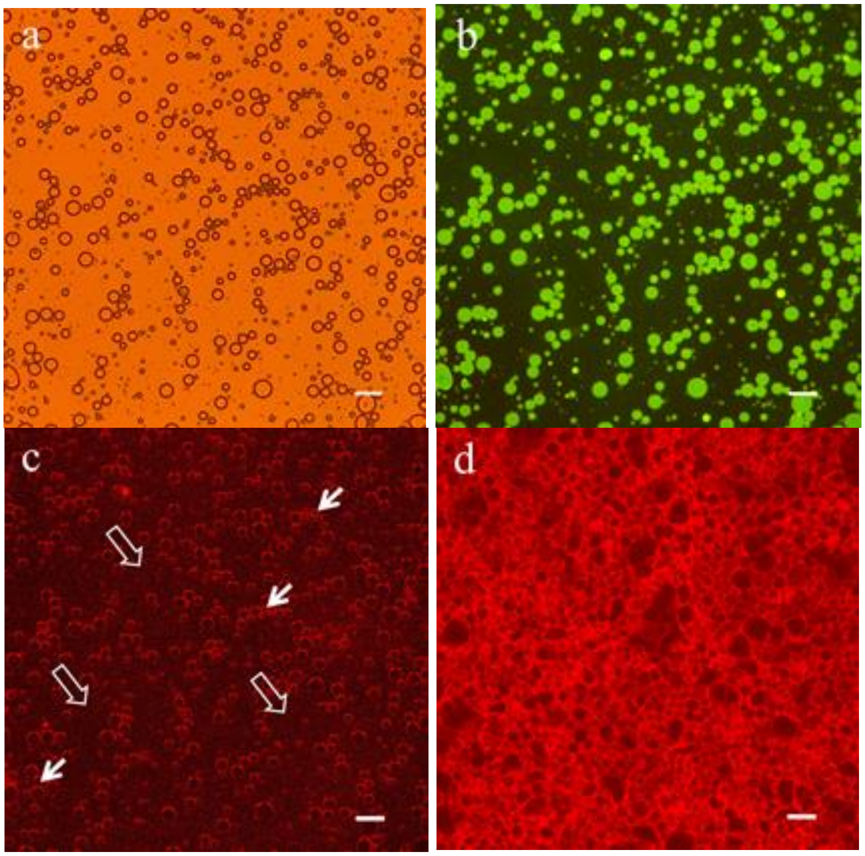


Fig. 3. Photographs of the emulsions ($R_{O/W}$ = 1:9) stabilized by CMG-0.75 observed with fluorescent microscopy under ordinary white light (a), blue (b), and green (c) lasers. The solid arrows denote the emulsion droplets and the hollow arrows denote the aqueous phase containing CMG particles. A fluorescent microscopy photograph of an emulsion at $R_{O/W}$ = 6:4 using a green laser (d). *The bars represent 20 µm.

The SEM images in Fig. 4 revealed a few relatively large spheres with a size distribution of around 3 to 5 µm, which were likely polystyrene (PS) microspheres and were regarded as the corresponding oil droplets in the emulsions.

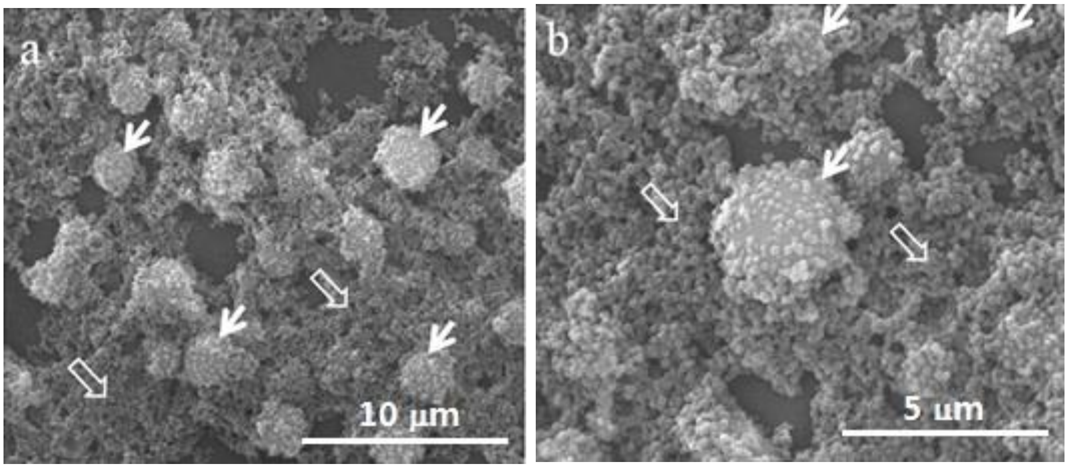


Fig. 4. SEM pictures at 5000x (a) and 10000x (b) magnifications of polymerized styrene-in-water emulsion stabilized by CMG-0.75 at $R_{O/W}$ = 1:9. The solid arrows denote PS microspheres and the hollow arrows denote CMG particles.

Around these PS microspheres were plenty of relatively small particles around 200 nm, some of which were distributed at the surface of the PS microspheres. These results were consistent with the confocal images, in which the CMG particles were distributed both at the surface of the emulsion droplets and in the surrounding aqueous phase; possibly, the small particles in the SEM pictures were derived from the CMGs. These particles were of medium size as compared with the dried CMGs shown in Fig. 1 and those in the swelling state. This can be explained by the fact that some styrene could have been adsorbed and polymerized in the porous CMGs; therefore, probably, both the water and oil were adsorbed inside the porous CMGs. This effect might ultimately be responsible for the dynamic stability of the oil-in-water emulsions.

Moreover, on the basis of the practical contents and characteristic sizes of the oil droplets and CMG spheres in the O/W emulsions, we estimated the relationship between the coverage of CMGs on droplet surface and the stability of the O/W emulsions. According to the calculation, the number of the oil droplets (typically 4 μm) is about 3×10^{10} for 1 mL of oil phase in the current O/W emulsions, while the number of CMGs is about 1.08×10^{13} in 1 mL of CMG-0.75 dispersions (with a typical diameter of 400 nm according to the DLS and SEM results). It was also calculated that around 400 of CMGs are needed to completely cover the surface of a droplet. When $R_{O/W}$ is 1:9, 2:8, 3:7, and 4:6, the number of CMGs is enough to cover all the droplet surface in the emulsions. For example, when $R_{O/W}$ = 2:8 for a 10 mL of emulsions, there are about 8.6×10^{13} of CMG spheres in 8 mL of aqueous dispersion, which could meet the needed number of CMGs (about 2.4×10^{13}) to stabilize 2 mL of oil droplets. When $R_{O/W}$ reaches 5:5, there would be 4.3×10^{13} of CMG spheres in 10 mL of emulsions, while the needed number of CMGs to stabilize 5 mL of oil droplets is 6.0×10^{13}. Because of the insufficient number of CMGs, the emulsion is unstable, until a droplet network (emulsion gel) tends to form when $R_{O/W}$ exceeds 5:5. Here, apparently, the rough estimation is fundamentally consistent with the observation of the emulsions in Fig. 2.

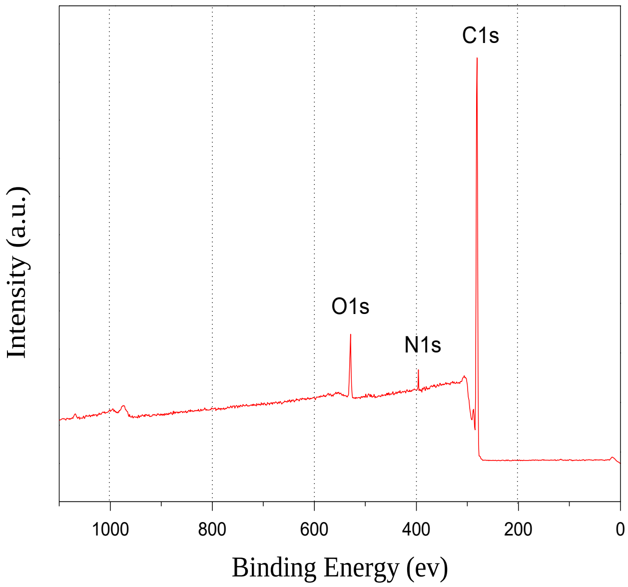


Fig. 5. XPS spectrum of the PS solid powder formed *via* the polymerization of the emulsion stabilized by the CMGs

XPS measurements validated the existence of CMGs in the powder samples (Fig. 5). Signals for carbon, oxygen, and nitrogen were found. Because there is no oxygen or nitrogen in PS, their respective signals were attributed to the existence of the CMGs and the remaining cross-linking agent contained in the CMGs.

Based on the results described, a possible mechanism by which CMGs stabilized emulsions was concluded (Fig. 6). Due to their amphiphilicity, CMGs have a tendency to adsorb at the oil-water interface of the emulsion droplets produced during external shearing. At the same time, the strong hydration of the CMGs leads to large hydration repulsion between droplets, thus enhancing the resistance of the emulsion against flocculation and coalescence. At a lower $R_{O/W}$, the CMGs were closely packed around the oil droplets. At an intermediate $R_{O/W}$, however, a relatively smaller number of CMGs caused inadequate coverage of the CMGs around the oil droplets, resulting in phase separation due to the coalescence of the droplets. At a higher $R_{O/W}$, a network of entrapped emulsion droplets was formed, leading to the gelation of an emulsion.

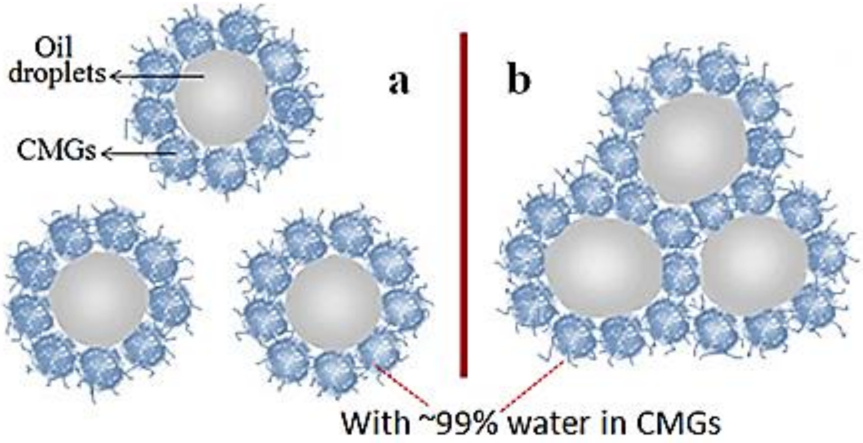


Fig. 6. Schematic representation of the oil-in-water emulsions stabilized by the CMGs: (a) separated emulsion droplets and (b) emulsion gels

Magnetic Functionalization of CMGs and Emulsions

Having a porous percolating internal structure, the CMGs were easily functionalized, and a high content of hydroxyl groups forced the CMGs to tightly bind with the introduced substances. To demonstrate this, a typical example of magnetic functionalization in the CMG matrix with Fe_3O_4 was carried out using a facile co-precipitation method. The photographs of a Fe_3O_4-CMGs aqueous dispersion with and without a permanent magnet and a TEM picture of the composite are shown in Fig. 7. Fe_3O_4 nanoparticles of a homogeneous size of less than 8 nm were formed in the CMG matrix, illustrating that the CMGs are of porous structure and could act as a microreactor for the synthesis of Fe_3O_4 nanoparticles. Regardless of vigorous agitation or long-term storage for more than six months, the aqueous dispersions of the Fe_3O_4-CMGs remained unchanged without precipitating any relatively heavy Fe_3O_4 nanoparticles, indicating the high stabilizing effect that the CMGs had on the Fe_3O_4 nanoparticles and the strong attraction between them. Therefore, the CMGs were a successful protective and dispersive agent for the Fe_3O_4 nanoparticles. Moreover, the flow of the Fe_3O_4-CMGs dispersion was easily controlled by a magnet (Fig. 7b), indicating that they were excellent magnetic fluids.

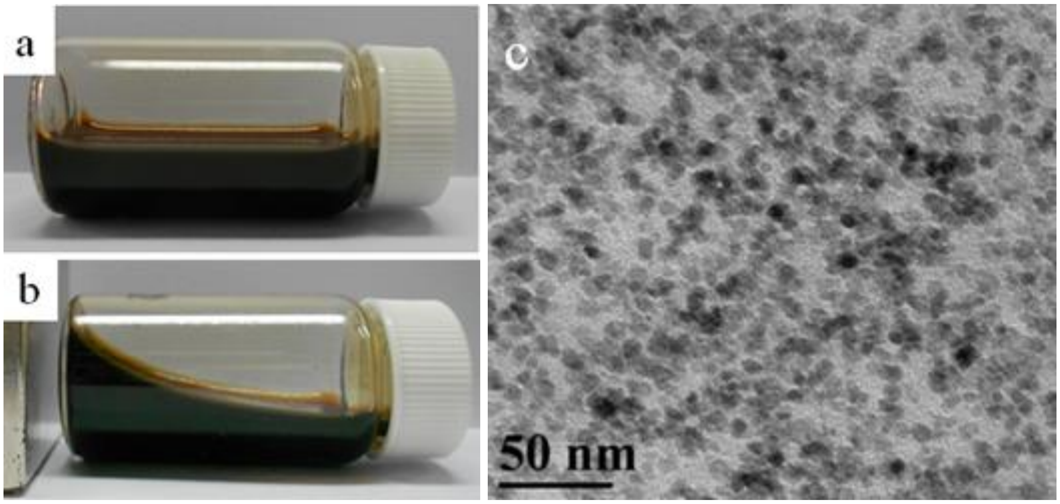


Fig. 7. (a,b) Photographs of the Fe_3O_4-CMG aqueous dispersion without (a) and with (b) a NdFeB magnet. (c) TEM image of the Fe_3O_4-CMGs layer showing that the Fe_3O_4 particles homogeneously deposited in the percolating network of the CMGs.

The high stability of the Fe_3O_4-CMGs originates from strong interaction between the Fe_3O_4 and the CMGs. Figure 8a shows the XRD spectrum of the Fe_3O_4-CMGs, where the individual characteristic diffraction peaks of both the Fe_3O_4 and the CMGs were found.

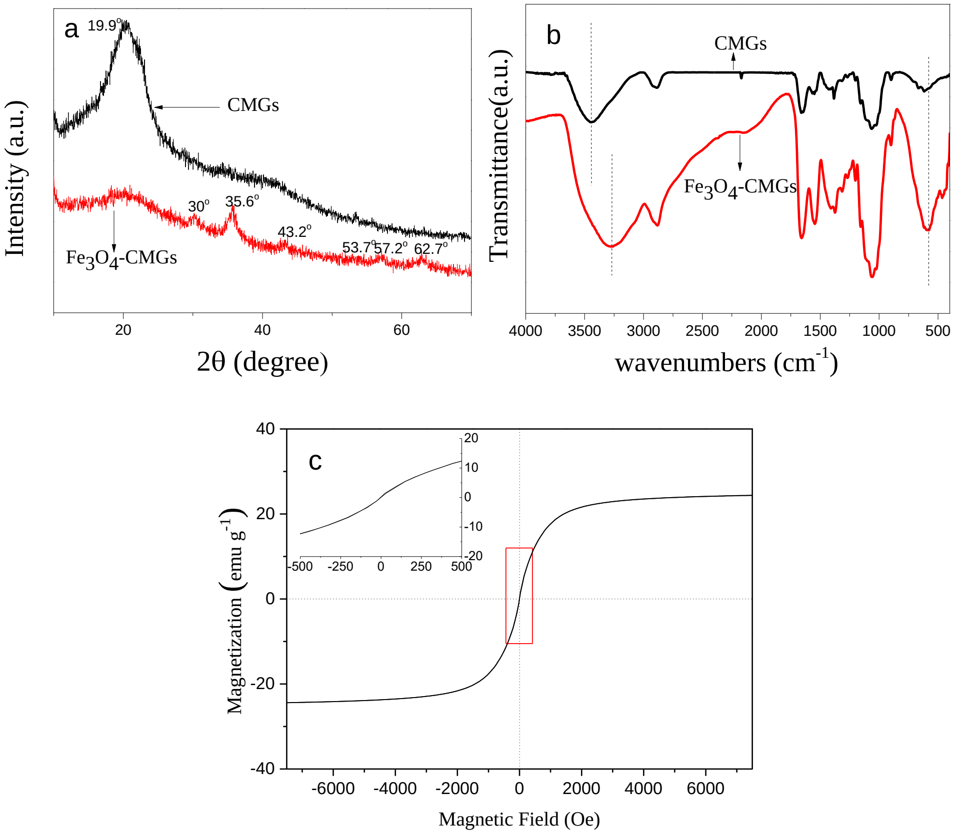


Fig. 8. (a) XRD and (b) FT-IR spectra of the CMGs and Fe_3O_4-CMGs. (c) Room temperature magnetization hysteresis loops of the Fe_3O_4-CMGs obtained with an applied magnetic field sweeping from -7500 to 7500 Oe. The inset is a partial enlargement of the magnetization hysteresis loops.

Moreover, the diffraction peaks of both the Fe_3O_4 and CMGs were broadened, which was possibly due to the combination of the Fe_3O_4 with CMGs. From the FT-IR spectra (Fig. 8b), a broader absorption and noticeable shift from 3445 cm^{-1} to 3273 cm^{-1} occurred for the stretching vibration peak of the hydroxyl groups in the Fe_3O_4-CMGs. Thus, a strong intermolecular association between the cellulose and the Fe_3O_4 was formed due to more negative charges from the oxygen atoms of Fe_3O_4 as compared with that of cellulose. Furthermore, the magnetic properties of the Fe_3O_4-CMGs are depicted in Fig. 8c. The Fe_3O_4-CMGs exhibited a superparamagnetic behavior with no coercivity and remanence. Because of the combination of the Fe_3O_4 and CMGs, the saturation magnetization (Ms) was about 23.4 $emu \cdot g^{-1}$, which is much lower than that of bulk Fe_3O_4 (Su *et al.* 2011).

Regardless of the combination of nanoparticles, the Fe_3O_4-CMGs provided excellent stability in O/W emulsions. Due to their magnetic functionalization, magnetic emulsions can be conveniently delivered to a target destination by an external magnetic field. Figures 9a and b show that the magnetic emulsion droplets were controlled by and moved with a magnet; oil droplets were transferred, enriched, and gathered. The magnetic emulsions had high stability, as no demulsification was observed even under an ultra-strong NdFeB magnet. Schematic drawings of the magnetic emulsions stabilized by the Fe_3O_4-CMGs and the intermolecular association between cellulose and Fe_3O_4 in the Fe_3O_4-CMGs are presented in Figs. 9c and d. The high stability of magnetic emulsions is important for targeting drug delivery and oil enrichment.

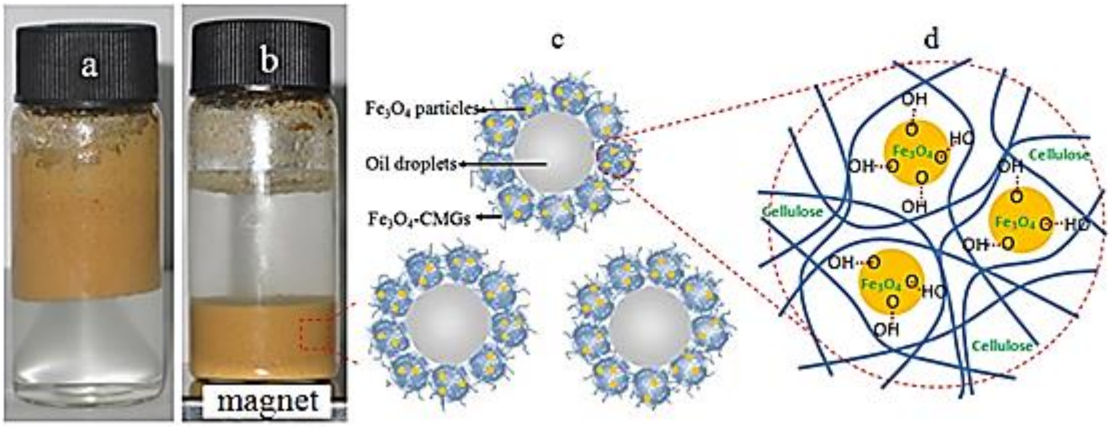


Fig. 9. (a) A photograph of the paraffin-water emulsion stabilized by the Fe_3O_4-CMGs. (b) The emulsion stabilized by the Fe_3O_4-CMGs was pulled down with a NdFeB magnet. (c) Schematic representation of the magnetic emulsions stabilized by the Fe_3O_4-CMGs and (d) a microschematic of the association between cellulose and Fe_3O_4 nanoparticles in Fe_3O_4-CMGs.

CONCLUSIONS

1. Oil-in-water (O/W) emulsions were stabilized effectively by cellulose microgels (CMGs) made from cellulose *via* a facile synthetic route. Having appropriate amphiphilicity, CMGs tended to adsorb at the oil-water interface.
2. The strong hydration of CMGs strengthened the steric hindrance and hydration repulsion between emulsion droplets and prevented them from flocculation and

coalescence. At the same time, the water-swollen character of CMGs increased the effective spreading area of the CMGs at the oil-water interface, thus improved the stability of the emulsion.

3. CMGs can be easily functionalized through tightly hosting objects such as magnetic nanoparticles in their percolating matrix to produce functional composites. Functionalized CMGs are stable because of the strong intermolecular association between cellulose and the objects and also dispersible due to a high content of hydroxyl groups inside the CMGs. As composites, CMGs were still able to stabilize emulsions.
4. Because of the facile preparation and functionalization of CMGs and their excellent ability in stabilizing O/W emulsions, this work expands the applications of natural cellulose.

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