# Electronic Supplementary Information (ESI)

# Enhanced enzymatic hydrolysis of cellulose in microgels

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## SI 1. Experimental Procedures

### *1.1. Materials*

Native cotton fibers were picked directly from a farm. The cotton fibers were cut, size-selected to pass a 100-mesh screen (but retain by 120-mesh screen), and then extracted with benzene. To prepare cellulose, the fibers were further extracted with a benzene–alcohol mixture in a Soxhlet extractor to remove phytochromes, lipids, wax, and other contaminants on the fiber surface; finally, the fibers were washed by using water until neutral, and dried at 60.0 $^{o}$C in vacuum for at least 3 days. The obtained cellulose (0.5 g) was added into a NaOH/urea aqueous solution (200.0 g, containing 6.0 wt% NaOH and 4.0 wt% urea), which was stirred in an ethanol bath at -10 $^{o}$C for about 42 hours. The resultant solution was then centrifugated (8000 rpm, 30 min, 25 $^{o}$C), with the precipitate discarded and the supernatant (containing $1.3\times10^{-3}$ g mL cellulose) used for further experiments. To yield the RCe, a large amount of water was added into the supernatant. See below for the synthesis of the CeM by using the supernatant.

All other chemicals were purchased from Aldrich, and were used as received without further purification. The water used in all experiments was of Millipore Milli-Q grade.

### *1.2. Synthesis of the CeM*

The CeM microgels were prepared by polymerization of *N,N′*-methylenebisacrylamide (MBAAm) in a diluted cellulose solution (containing $3.3\times10^{-4}$ g mL cellulose). A mixture of MBAAm ($1.5\times10^{-4}$ mol) and cellulose (100.0 mL, containing $3.3\times10^{-4}$ g mL cellulose) was poured into a 250 mL three-neck round-bottom flask equipped with a stirrer, a $N_2$ gas inlet, and a condenser. The solution was stirred at

room temperature until it became clear. After 30 min, ammonium persulfate (5.0 mL, 1.5 M) and *N,N,N′,N′*-tetra-methylenediamine (10.0 mL, 0.2 wt%) was added one by one at 10 min interval to initiate the polymerization. The reaction was allowed to proceed for 5 h. The resultant microgels were purified by 3 days of dialysis (Spectra/Por® molecularporous membrane tubing, cutoff 12000-14000 Dalton) against very frequently changed water at room temperature.

### *1.3. Enzymatic hydrolysis*

In order to avoid the inhibition effect of cellobiose and glucose, a lower concentration of substrate was used. Typically, CeM microgels (containing 10.0 mg $mL^{-1}$ cellulose) were suspended in sodium acetate buffer (20.0 mL, 50.0 mM, and pH 5.0) in the presence of cellulase (its saccharifying capacity, as determined by filter paper activity, was 0.005 FPU per mg of cellulose, equivalent to 0.008 IU cellobiohydrolases, 0.104 IU endoglucanases, and 0.002 IU glucosidase per mg cellulose) in a 250 mL flask. A small amount of sodium azide (0.01 mg $mL^{-1}$) was also added to prevent contamination. Then, the hydrolysis reaction was performed at 45.0 $^{o}$C in a shaking bath at 30 rpm.

All sugar determinations were made on duplicate samples. Sugar yields were calculated as percent glucose produced based on the initial weight of the cellulose samples. Total reducing sugar (RS) yields were determined spectrophotometrically after different periods of enzyme hydrolysis using 3,5-dinitrosalicylic acid (DNSA) reagent according to the procedure of Miller (G.L. Miller, *Anal. Chem.*, 1959, **31**, 4426.). Glucose yields were determined by the oxygen rate method making use of a Beckman glucose analyzer.

### *1.4. Laser Light Scattering (LLS) studies*

A standard laser light scattering spectrometer (BI-200SM) equipped with a BI-9000 AT digital time correlator (Brookhaven Instruments, Inc.) and a Mini-L30 diode laser (30 mW, 637 nm) as the light source was used. The dilute microgel dispersions (10.0 μg $mL^{-1}$) were passed through Millipore Millex-HV filters with a pore size of 0.80 μm to remove dust before LLS measurements. In static LLS (SLS), we measured the weight-average molar mass ($M_w$) from the angular dependence of the excess absolute scattering intensity, known as Rayleigh ratio $R_{vv}(q)$, as

$$\frac{KC}{R_{VV}(q)} \approx \frac{1}{M_W}\left(1+\frac{1}{3}< R_g^2 > q^2\right)+2A_2C$$

where $K = 4\pi n^2(dn/dC)^2/(N_A\lambda_0^4)$ and $q = (4\pi n/\lambda_0)\sin(\theta/2)$ with $N_A$, $dn/dC$, $n$, $\lambda_0$, and $\theta$ being Avogadro's constant, the specific refractive index increment, the solvent refractive index, the wavelength of the laser light in vacuo, and the scattering angle, respectively, and $A_2$ is the second virial coefficient. In Dynamic LLS (DLS), the Laplace inversion of each measured intensity-intensity time correlation function in a dilute dispersion can lead to a line-width distribution $G(\Gamma)$. For a purely diffusive relaxation, $\Gamma$ is related to the translational diffusion coefficient $D$ by $(\Gamma/q^2)_{C\to 0,q\to 0} = D$, so that $G(\Gamma)$ can be converted to a translational diffusion coefficient distribution and $<D_h>$ distribution by using the Stokes-Einstein equation, $<D_h> = (k_BT/3\pi\eta)/D$, where $k_B$, $T$, and $\eta$ are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively.

***1.5. Other characterizations***

XPS measurements were carried out by using an Omicron photoelectron spectrometer (Al Kα with 14 86.6eV operating at 15kV, 30W and 600μm spot size) and an Omicron Sphera II hemispherical electron nergy analyzer. The base pressrer of the systems was $1.0\times10^{-9}$ mbar. FTIR spectra were recorded with a Thermo Electron Corporation Nicolet 380 Fourier transform infrared spectrometer. NMR spectra were recorded on a Bruker AVIII 400MHz solid-state NMR spectrometer. TEM images were taken on a JEOL JEM-1400 transmission electron microscope at an accelerating voltage of 100 kV. UV-vis absorption spectra were recorded on a Shimadzu UV-2550 UV-Vis spectrometer. PL spectra were recorded on a JOBIN YVON Co. FluoroMax®-3 Spectrofluorometer equipped with a Hamamatsu R928P photomultiplier tube and a calibrated photodiode for excitation reference correction from 200 to 980 nm, with an integration time of 1 s. The pH value was measured on a EUTECH PH 700 instruments.

**SI2. Figures.**

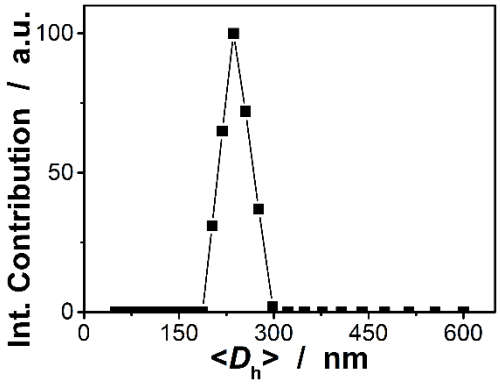


**Fig. S1** DLS size distribution of CeM microgels dispersed in a 50.0 mM sodium acetate buffer solution of pH = 5.0 at 25.0 °C.

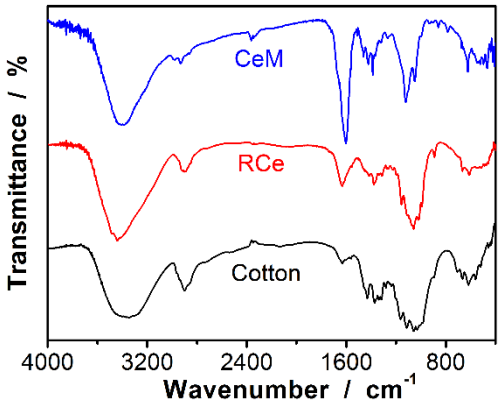


**Fig. S2** Typical FTIR spectrum of the CeM. The FTIR spectra of the RCe and cotton are also presented for comparison.

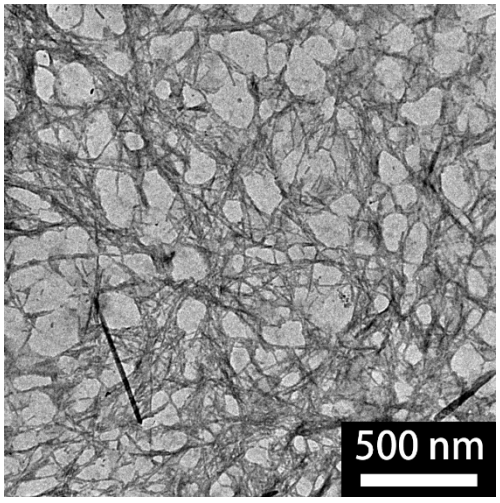


**Fig. S3** Typical TEM image of the RCe.

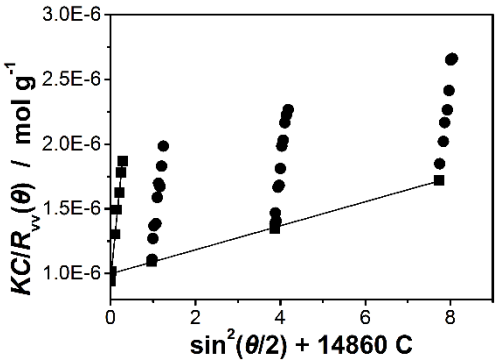


**Fig. S4** Typical Zimm plot of the dissolved cellulose, measured at 25.0 °C.

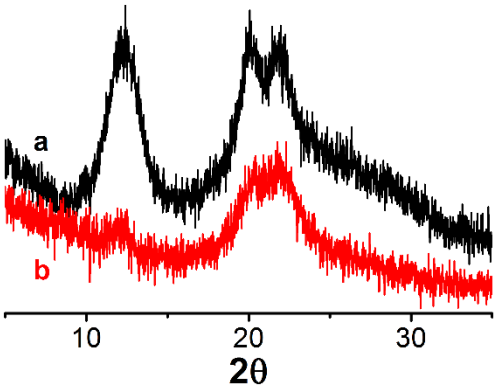


**Fig. S5** Typical XRD pattern of the RCe (a). The XRD pattern of CeM microgels (b) is also presented for comparison.

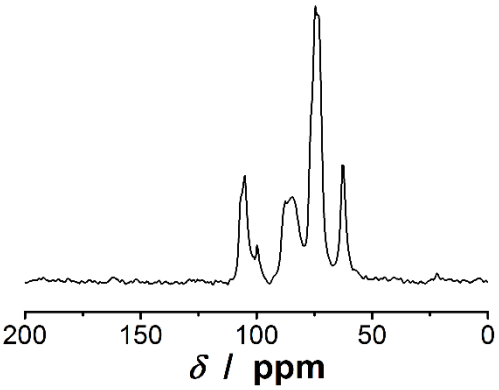


**Fig. S6** $^{13}C$ CP-MAS NMR spectrum of CeM microgels.

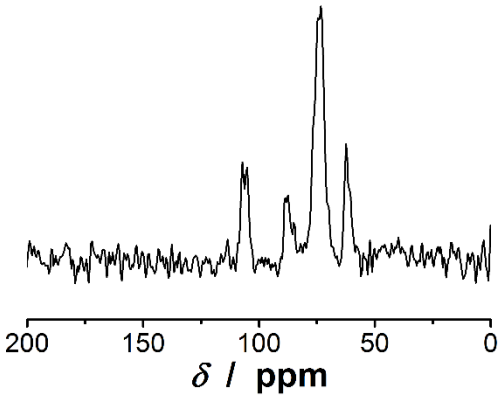


**Fig. S7** $^{13}C$ CP-MAS NMR spectrum of the RCe.

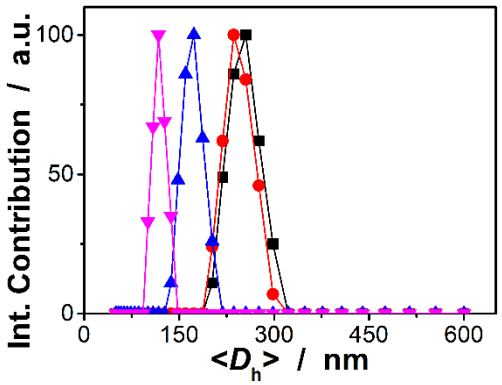


**Fig. S8** DLS size distribution of CeM microgels dispersed in a 50.0 mM sodium acetate buffer solution of pH = 5.0 at 20.0 °C (■), 25.0 °C (●), 35.0 °C (▲) and 50.0 °C (▼).

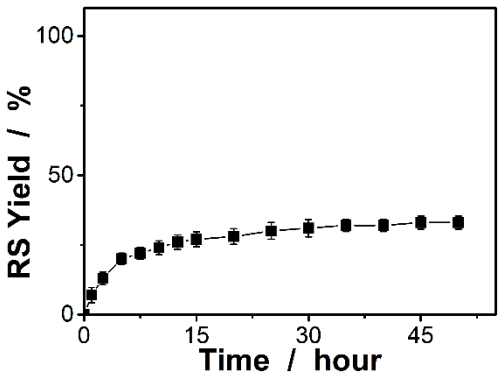


**Fig. S9** Reducing sugars yield during the hydrolysis of the RCe. Reaction conditions: cellulose, 10.0 mg $mL^{-1}$; cellulase, 0.005 FPU per mg of cellulose; sodium acetate buffer, 50.0 mM, 20.0 mL, pH 5.0; 45.0 °C.