

Electronic Supplementary Information (ESI)

Copper on responsive polymer microgels: a recyclable catalyst of tunable catalytic activity

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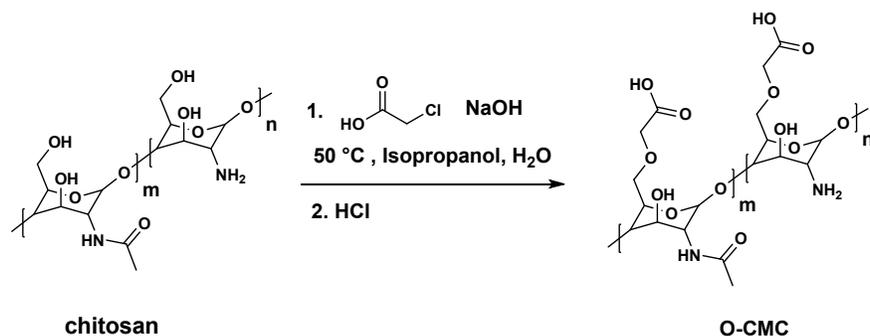
SI 1. Experimental Procedures

1.1. Materials

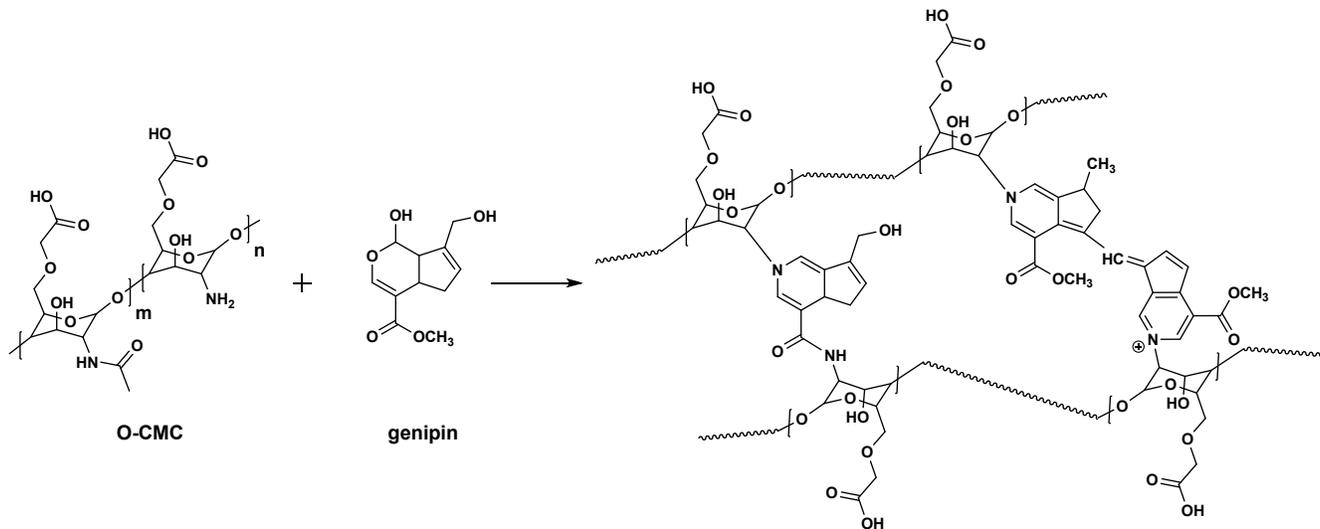
Chitosan (deacetylation degree 75-85%) was purchased from Sigma-Aldrich, and other chemicals were purchased from Alfa Aesar. All chemicals were used as received without further purification. The water used in all experiments was of Millipore Milli-Q grade.

1.2. Synthesis of the CPM

The partly *O*-carboxymethylated chitosan (*O*-CMC) was firstly prepared from chitosan. Typically, chitosan (20.0 g), sodium hydroxide (27.0 g) and water (200.0 mL) were stirred in a flask in an ice bath for 7 h. Monochloroacetic acid (30.0 g) dissolved in isopropanol (40.0 mL) was added into the mixture dropwisely. After stirring at 50 °C for another 7 h, the reaction was stopped by adding 70% ethanol to the mixture. The product was separated by filtration, rinsed by 70% ethanol for three times, and dehydrated with absolute alcohol. This primary product was the sodium salt of *O*-CMC. The sodium salt of *O*-CMC was converted to *O*-CMC via immersing in 70% ethanol and adding 32% HCl, and precipitating by adding ethanol. The sample was further rinsed in 70–90% ethyl alcohol to neutral, and dried in vacuum. The substitution degree of carboxymethyl groups determined from ¹H NMR spectra was ca. 73%.



Then, *O*-CMC (200.0 mg) was dissolved in water (70.0 mL) in a 250 ml round-bottom flask equipped with a stirrer, a N₂ gas inlet, and a condenser. After adjusting the solution pH value to about 6.0 using HCl solution, SDS (10.0 mg) was added. After stirring for 30 min, the crosslinking reaction was started by adding genipin (10.0 mg, dissolved in 1.0 mL water). The reaction was allowed to proceed for 36 h at 28.0 °C. The reaction mixture was centrifuged twice (3500 rpm, 30 min, 30 °C) with the supernatant discarded and the precipitate redispersed in water. The polymer microgels were further purified by 3 days of dialysis against very frequently changed water at room temperature. The concentration of the polymer microgels was adjusted to 6.2×10^{-1} mg/mL for further use.



To synthesize the CPM, the polymer microgels (10.0 mL, 6.2×10^{-1} mg/mL) were suspended in an aqueous solution of CuSO₄ (90.0 mL, 1.0 mg/mL) for 12 h under neutral conditions. The microgel catalyst was separated using a centrifuge (3500 rpm, 30 min, 30 °C), followed by 2.5 h of dialysis against water (changed per 0.5 h) at room temperature.

1.3. Catalytic Reduction

The model chemical reaction was conducted in a quartz cuvette, which was placed inside a UV-vis spectrophotometer equipped with a temperature controller (± 0.1 °C). Benzyl azide (5.3×10^{-3} mol/L) was added into an CPM dispersion (2.7×10^{-4} mol/L) in a DMF-H₂O (3:1 volume ratio) mixture in quartz cuvette, and the mixture was stirred for 5 min at room temperature. Phenyl acetylene (8.0×10^{-3} mol/L), and NaVc (6.7×10^{-4} mol/L) as well if necessary, was then added into the mixture, which was stirred. During the course of reaction, the reaction progress was monitored by measuring UV-vis absorption spectra of the mixture. After the completion of the reaction, the product was separated using ethyl acetate extraction and the CPM by centrifugation (3500 rpm, 30 min, 30 °C). The products were purified by re-crystallization or column chromatography. The recovered CPM was dried and reused at least five times.

1.4. Characterization

XPS measurements were carried out by using a Omicron photoelectron spectrometer (Al K α with 148 6.6eV operating at 15kV, 30W and 600 μ m spot size) and an Omicron Sphera II hemispherical electron energy analyzer. The base pressure of the systems was 1.0×10^{-9} mbar. FTIR spectra were recorded with a Thermo Electron Corporation Nicolet 380 Fourier transform infrared spectrometer. TEM images were taken on a JEOL JEM-1400 transmission electron microscope at an accelerating voltage of 100 kV. TECNAI F-30 high resolution transmission electron microscopy operating at 300 kV, and JEM-2100 high resolution transmission electron microscopy operating at 200 kV. Scanning electron microscopy (SEM) images were obtained on Hitachi S4800 scanning electron microscope with a field emission electron gun. UV-vis absorption spectra were recorded on a Shimadzu UV-2550 UV-Vis spectrometer. The pH value was measured on a EUTECH PH 700 instruments. Dynamic light scattering (DLS) was performed on a 90Plus multi angle particle sizing analyzer equipped with a BI-9000AT digital autocorrelator (Brookhaven Instruments, Inc.). A He-Ne laser (35 mW, 659 nm) was used as the light source. All samples were passed through Millipore Millex-HV filters with a pore size of 0.80 μ m to remove dust before the DLS measurements.

SI2. Figures.

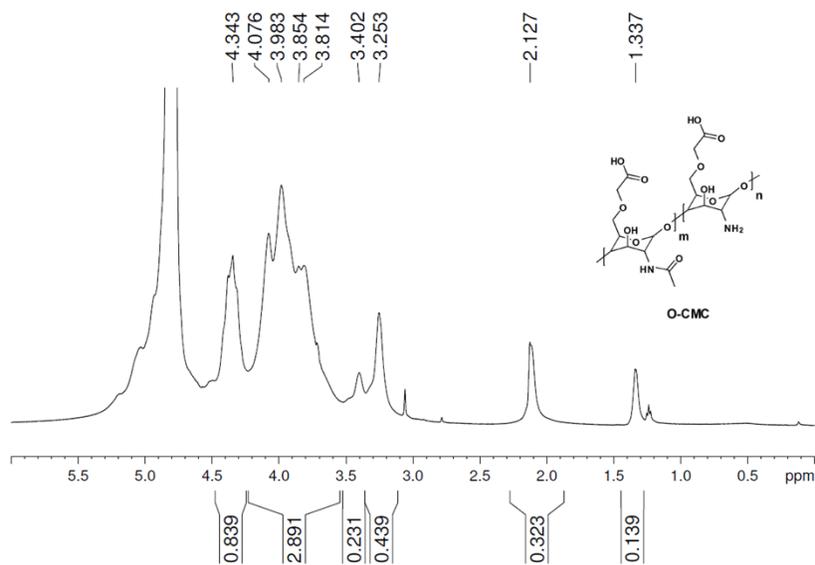


Fig. S1 ¹H NMR spectrum of the partly *O*-carboxymethylated chitosan (O-CMC) in D₂O.

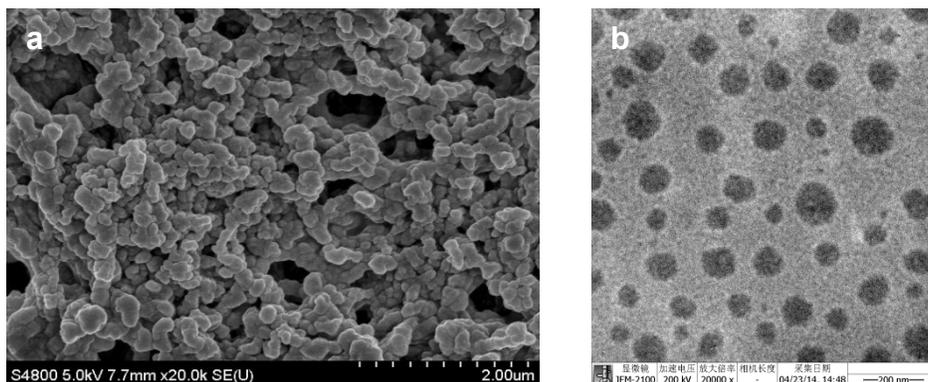


Fig. S2 (a) Typical SEM and (b) TEM images of the polymer microgels without adding CuSO₄.

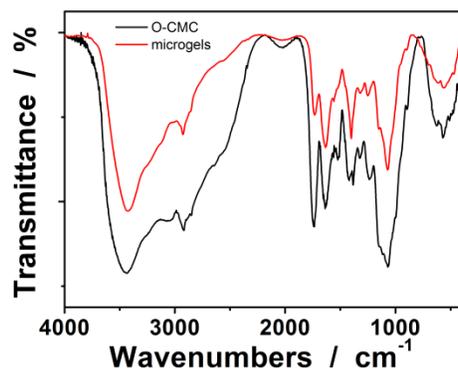


Fig. S3 FTIR spectra of the partly *O*-carboxymethylated chitosan (O-CMC) and the polymer microgels.

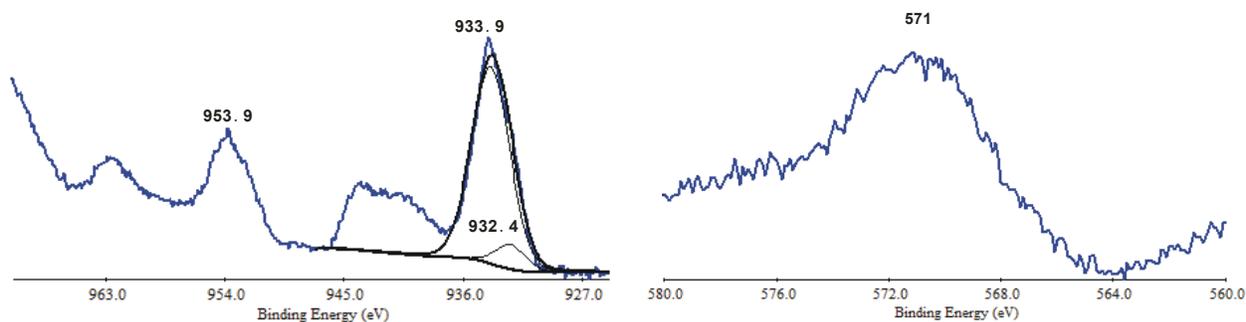


Fig. S4 XPS spectra of the CPM.

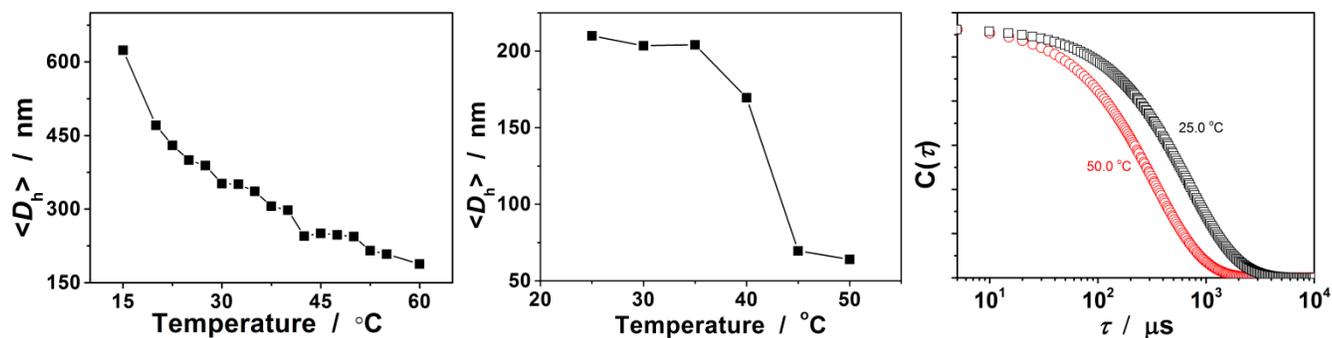


Fig. S5 Temperature-dependent $\langle D_h \rangle$ values for the polymer microgels dispersed in (a) a DMF-H₂O (3:1 volume ratio) mixture, or (b) water. (c) DLS intensity autocorrelation function ($C(\tau)$) for the polymer microgels dispersed in water at 25.0 °C (\square) and 50.0 °C (\circ).

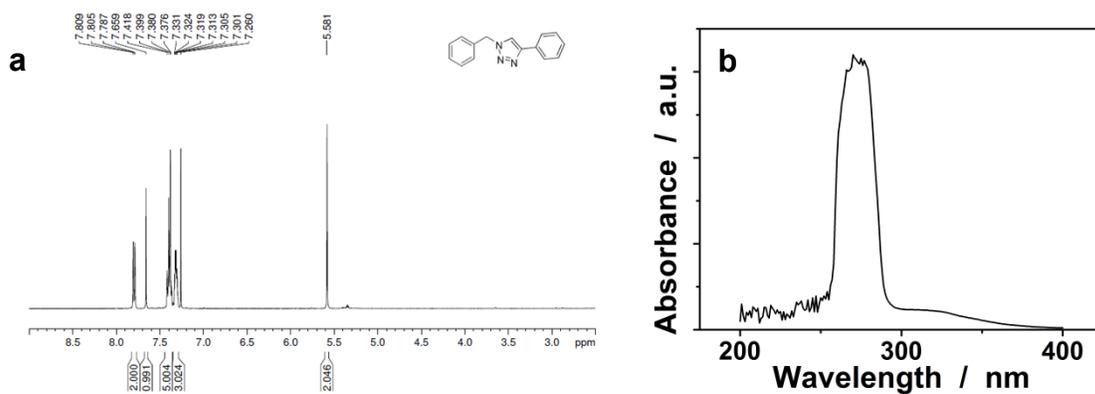


Fig. S6 (a) ¹H NMR and (b) UV-vis absorption spectra of 1,4-disubstituted triazole, which was yielded by the cycloaddition reaction of benzyl azide and phenyl acetylene as catalyzed by the CPM.

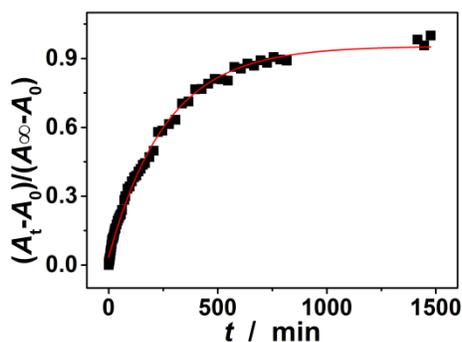


Fig. S7 Typical time trace of the triazole absorption at 325 nm during the reaction catalyzed by the CPM in the absence of NaVc at 27.5 °C. The solid line is exponential fit of the plot.

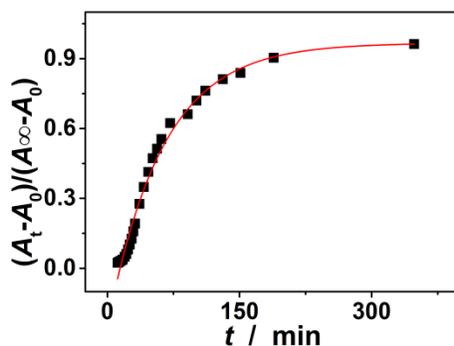


Fig. S8 Typical time trace of the triazole absorption at 325 nm during the reaction catalyzed by copper (adding CuSO₄ directly) in the presence of NaVc at 27.5 °C. The solid line is exponential fit of the plot.

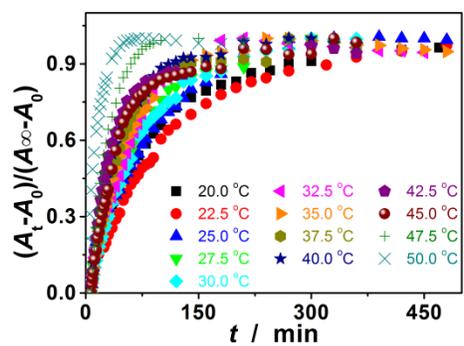


Fig. S9 The $(A_t - A_0) / (A_\infty - A_0) - t$ plots, showing influence of solution temperature on the kinetics of the reaction catalyzed by the CPM in the presence of NaVc.