Scalable synthesis of core-shell microgel particles using a 'dry water' method

(Supporting Information)

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Experimental

Materials

Acrylamide (AM, ≥99%), N,N'-Methylenebisacrylamide (MBA, 99%), potassium persulfate (KPS, ≥99%), Sodium bisulfite ($NaHSO_3$, ACS reagent), Sodium dodecyl sulfate (SDS, ≥98.5%), Tween 20 (≥97%), Hexadecyl trimethyl ammonium Bromide (CTAB, ≥98%), and Sodium chloride(NaCl, ≥99%) were obtained from Sigma-Aldrich. Cocamide diethanolamine (CDEA, 99%) was purchased from Shanghai Deyi Chemical Co., Ltd (China). Hydrophobic silica nanoparticles (H18) were kindly supplied by Wacker-Chemie.

Synthesis of CSMG

Typically, the dry-base reaction system was obtained by directly mixing 91 g aqueous solution of AM, MBA, KPS and $NaHSO_3$ with 9 g hydrophobic silica nanoparticles H18 in a blender at 22000 rpm for 90 s. The mass concentration of AM of the aqueous solution was 35 wt%. The mass of MBA, KPS, and $NaHSO_3$ were 0.3 wt%, 0.1 wt%, and 0.1 wt%, respectively, with respect to the mass of AM. Afterwards, the dry water

system in free-flowing powder state was poured into a flask and reacted at 38°C under N_2 protection for 4 hours. The produced wet CSMG sample was recovered and dried in a vacuum oven at 60 °C for 48 h before swelling tests.

For comparison, a conventional hydrogel was synthesized at the same conditions as CSMG. Briefly, 91 g aqueous solution of AM, MBA, KPS and $NaHSO_3$ reacted at 38°C under N_2 protection for 4 hours. The mass concentration of AM of the aqueous solution was 35 wt%. The mass of MBA, KPS, and NaHSO3 were 0.3 wt%, 0.1 wt%, and 0.1 wt%, respectively, with respect to the mass of AM. The produced wet hydrogel sample was cut into small particles and dried in a vacuum oven at 60 °C for 48 h before swelling tests.

Microstructure of CSMG

The microstructure of CSMG was observed using an ECLIPSE LV100N POL optical microscope (Nikon, Japan), an EVO 40XVP scanning electron microscope (Zeiss, Germany) and a JEM-2100F transmission electron microscope (JEOL, Japan). HYDRO2000 laser particle analyzer (Malvern, Britain) was used to measure the size distribution of CSMG particles.

Nitrogen adsorption

The Nitrogen sorption isotherms were measured using an F-Sorb 3400 surface area and porosity analyzer (Jinaipu, China) at a temperature of 77 K. The CSMG sample was heated to 110 °C under a 10^{-5} dynamic vacuum for 6 h before Nitrogen sorption measurement was performed.

Oil absorption experiments

1 g dry CSMG was soaked in oils or organic solvents for 10 min. Afterwards, the oil-absorption capacity was determined by the weight change of CSMG before and after soaking in using Eq.(1):

$$OAC = \frac{m_2 - m_1}{m_1} \quad (1)$$

Where *DAC* is the oil-absorption capacity; m_1 is the weight of dry CSMG sample before swelling, g; m_2 is the weight of the CSMG sample after soaking with excess oils or solvents removed, g.

Swelling ratio measurement

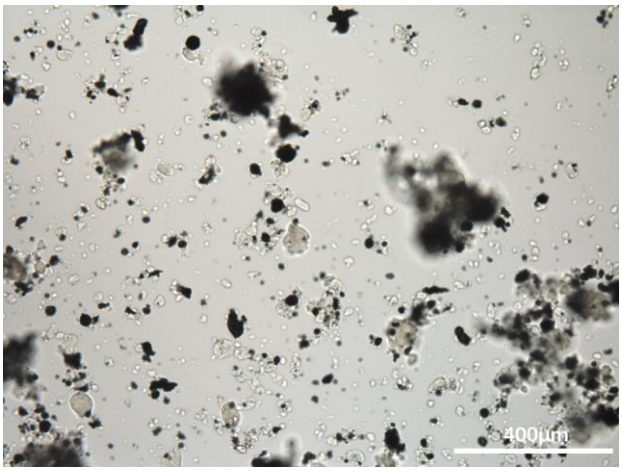
0.5 g dry CSMG was swollen in 100 ml water or surfactant solution for 48 h to reach the swelling equilibrium. Then, the swelling ratio was determined by the weight change of CSMG before and after swelling using Eq.(2):

$$SW = \frac{m_4 - m_3}{m_3} \quad (2)$$

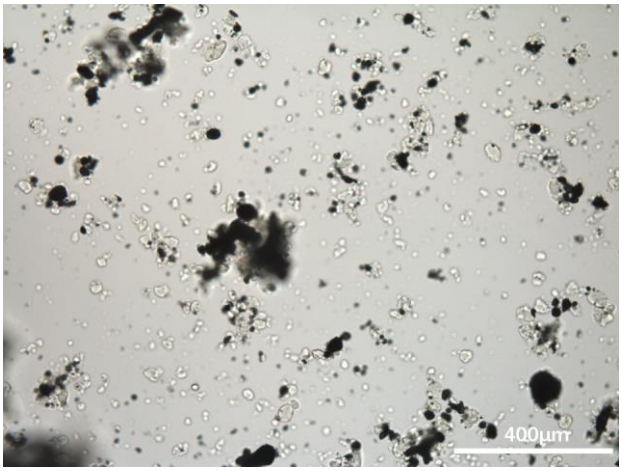
Where *SW* is the swelling ratio; m_3 is the weight of dry CSMG sample before swelling, g; m_4 is the weight of the CSMG sample after swelling with excess water removed, g.

Contact angle measurement

Prior to each test, CSMG sample was glued on a glass slide. After that, the contact angle of an oil droplet on the surface of CSMG was determined at 25 ^{o}C using a Drop Shape Analyzer 25 (Kruss) with acquisition software.



(a)



(b)

Figure S1. Microscope images of the dry water system (a) before and (b) after polymerization

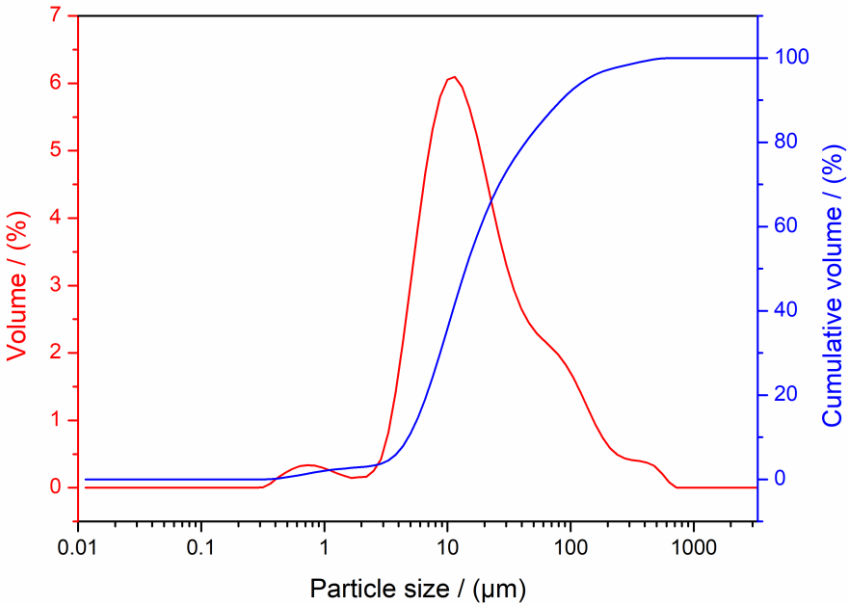


Figure S2. Particle size distribution of CSMG

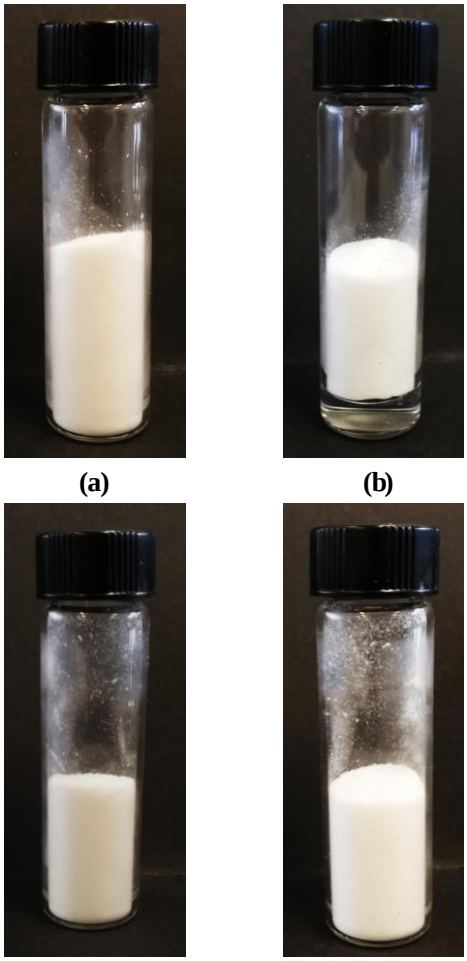
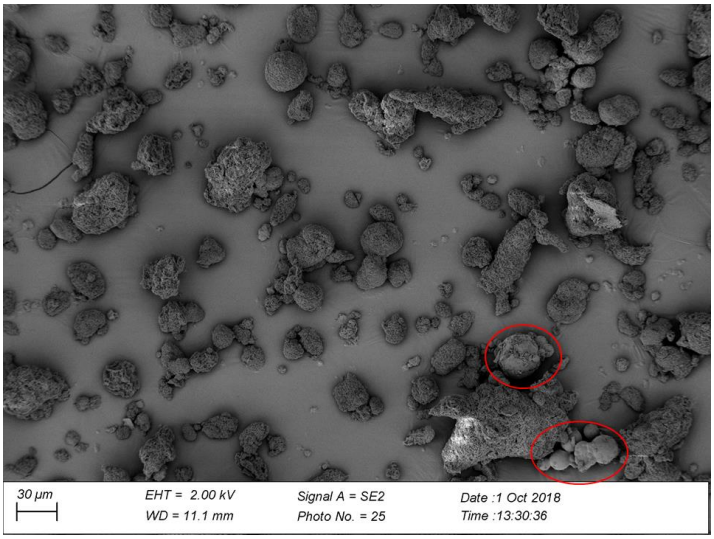
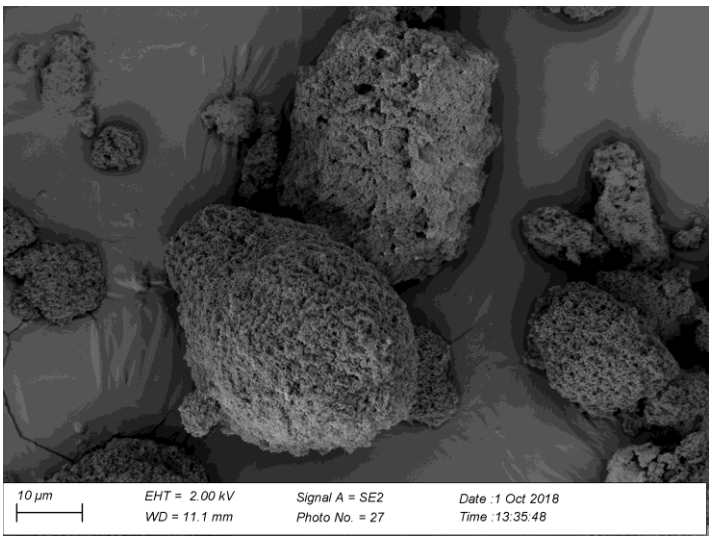


Figure S3. Stability of conventional dry water system (water + hydrophobic silica nanoparticles) and CSMG system: (a) conventional dry water system; (b) conventional dry water system after standing for 30 days; (c) CSMG system; (d) CSMG system after standing for 30 days.



(a)



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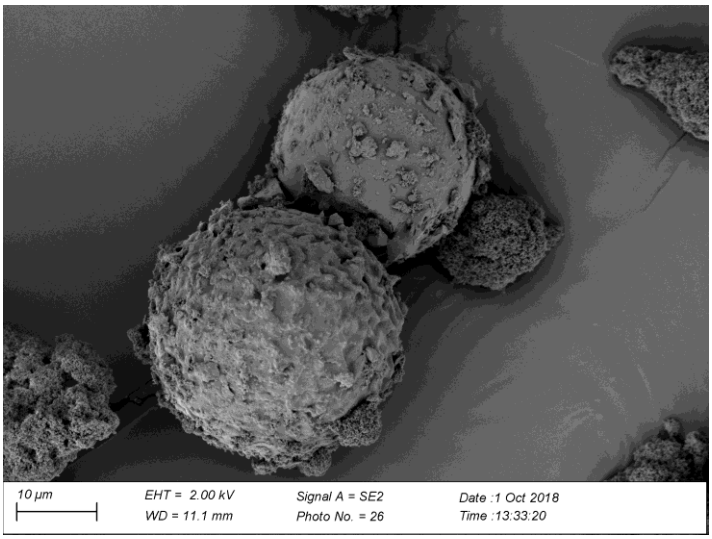
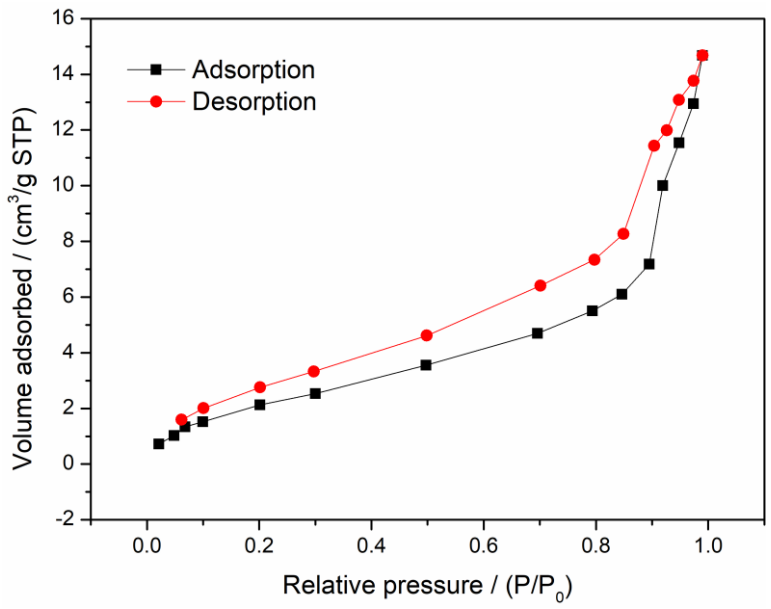
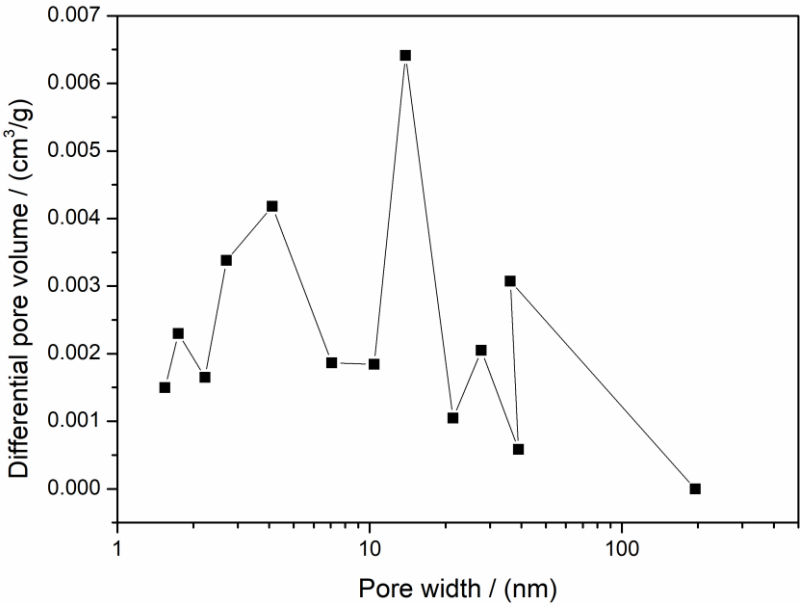


(c)

Figure S4. SEM images of dry CSMG samples: (a) CSMG particles (Red circles, particles with relatively smooth surfaces); (b) particles with rough surfaces; (c) particles with relatively smooth surfaces



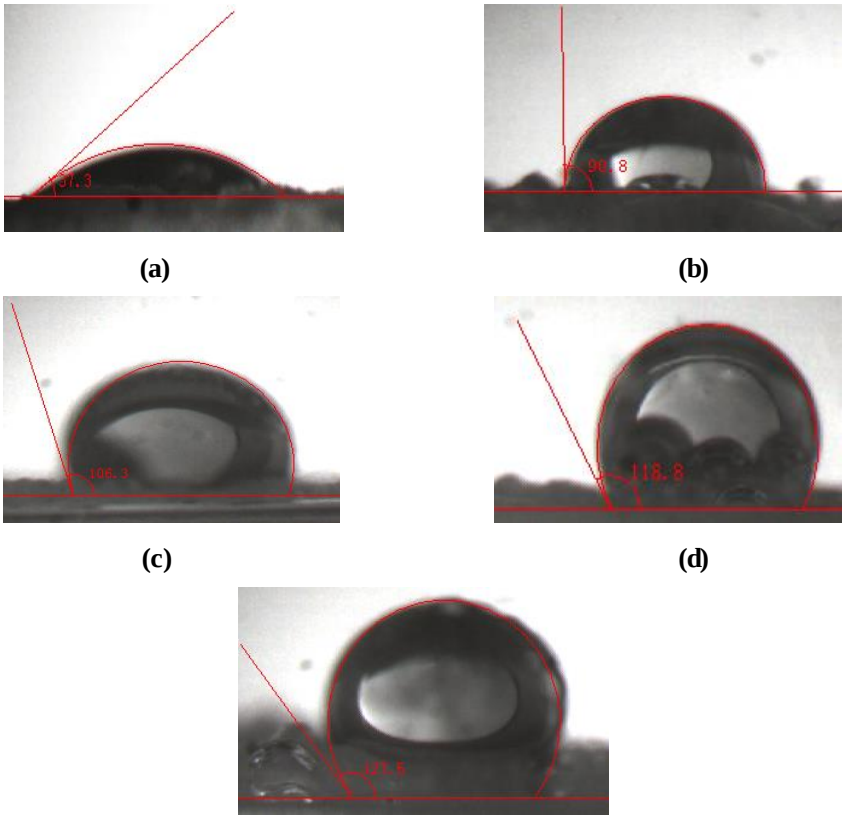
(a)



(b)

Figure S5. (a) Nitrogen sorption isotherms at 77 K; (b) pore size distribution.

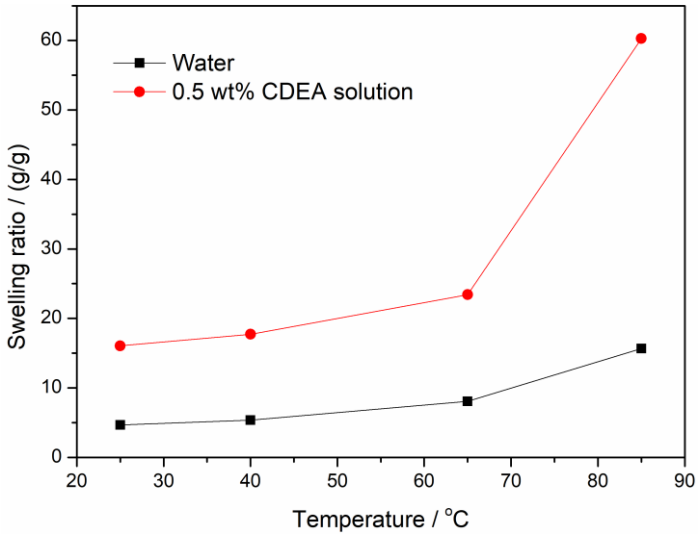
Figure S6. Appearance of CSMG in water



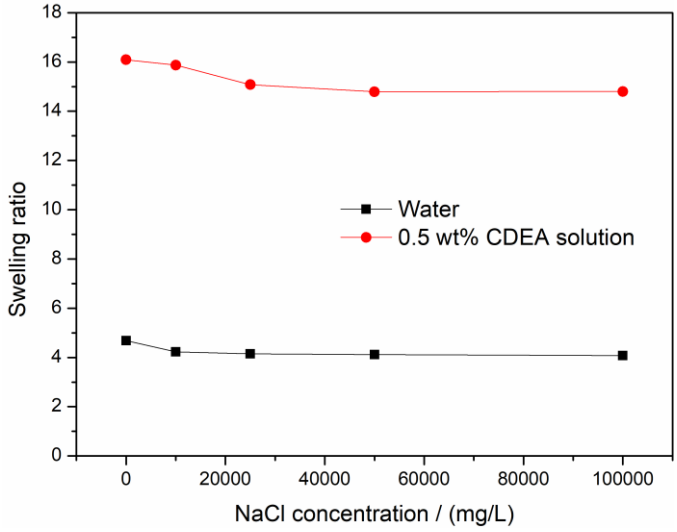
(a) **(b)** **(c)** **(d)** **(e)**

Figure S7. Contact angles of mineral oil on the surface of CSMG after CSMG was swelled in (a) water; (b) 0.01 wt% CDEA solution; (c) 0.05 wt% CDEA solution; (d) 0.25 wt% CDEA solution; (e) 0.50 wt% CDEA solution.

Figure S8. Appearance of CSMG after swelling in the CDEA solution.



(a)



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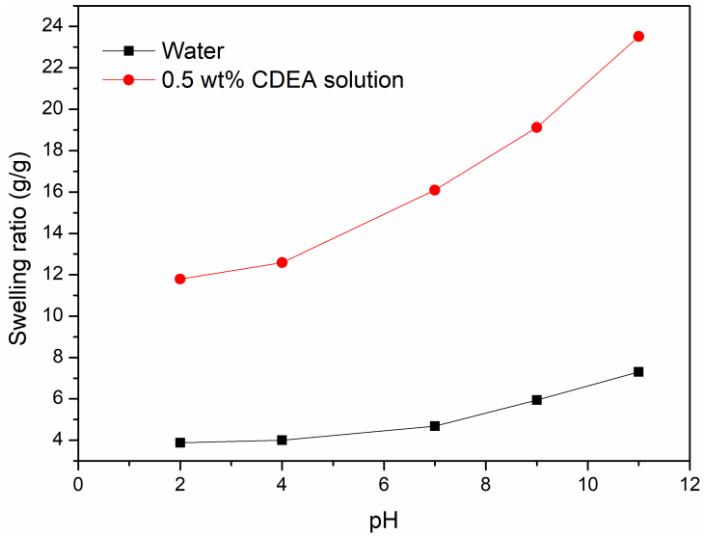

(c)

Figure S9. Swelling ratios of CSMG under different conditions: (a) different temperatures; (b) different salt concentrations; (c) different pH values