Supplementary Material (ESI) for Chemical Communications

Designable synthesis of nanocomposite hydrogels with excellent mechanical properties based on chemical cross-linked interactions

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Supplementary Information for Chemical Communications

Experimental

***Materials*:**

Styrene (99%, Sinopharm Chemical Reagent, China), Acrylic acid (98%, Sinopharm Chemical Reagent, China) and N-vinyl pyrrolidone (99%, J&K Chemical, China) were distilled under reduced pressure to remove the inhibitor before used. All the other reagents, *e.g.*, 2-Hydroxy-4'-hydroxyethoxy-2-ethylpropiophenone (98%, Sigma Aldrich Chemicals, USA), Methacryloyl chloride (97%, Aladdin Reagent, China), Dodecyl sodium sulfate (SDS) (86%, Sinopharm Chemical Reagent, China), Acrylamide (AAm) (98.5%, Sinopharm Chemical Reagent, China), N,N'-methylenebis-acrylamide (NMBA) (98%, Sinopharm Chemical Reagent, China), Potassium persulfate (KPS) (99.5%, Sinopharm Chemical Reagent, China) and N,N,N',N'-tetramethyldiamine (TEMED) (99%, Sinopharm Chemical Reagent, China) were used as received without further purification. The water used in all experiments was passed through a Millipore Milli-Q Plus 185 purification system and had a resistivity exceeding 18.2 MΩ cm.

***Synthesis of photoactive PS nanoparticles*:**

The photoactive PS nanoparticles were prepared in a similar manner to that reported by Prof. Ballauff previously. The polymerizable photoinitiator 2-[p-(2-hydroxy-2-methylpropiophenone)]-ethylene glycol-methacrylate (HMEM) was used to fabricate photoactive PS nanoparticles. HMEM was prepared by a Schotten-Baumann reaction of 2-hydroxy-4'-hydroxyethoxy-2-methylpropiophenone and methacryloyl chloride in acetone with pyridine as base. The resulting product was carefully washed with water and purified chromatographically. The chemical structure of HMEM is shown in Scheme S1.

^{1}H NMR δ_H(400 MHz; CD_3COCD_3; Me_4Si) 1.52 (3 H, s, -C(C*H*$_3$)$_2$-), 1.91 (3 H, s, =C(C*H*$_3$)-), 4.40 (2 H, t, *J* 4.6, CH_2CH_2-O-), 4.53 (2 H, t, *J* 4.6, -(COO)-C*H*$_2$CH$_2$), 4.75 (1 H, s, OH), 5.63, 6.09 (2 H, t, *J* 1.6, C*H*$_2$=C), 7.02, 8.26 (4 H, m, C_6H_4).

The photoactive PS nanoparticles were synthesized using a seeded emulsion polymerization. Hence, 15 g St was polymerized in 45 ml water in the presence of

0.188 g SDS and 0.03 g KPS. After 1 h, 0.8 g HMEM dissolved in 6 ml acetone was added in the polymerizing PS emulsion under starved conditions (1.5 ml. h^{-1}). Then the latex was cooled to room temperature and dialysed in pure water for 72 h.

***Preparation of hydrogel samples*:**

The CNC gels were fabricated using *in-situ* free-radical polymerization. The initial reaction solution consisted of water-soluble monomer and dialysed photoactive PS latex. The nanoparticle content (w/w) of dialysed PS latex is 20%. After being bubbled with nitrogen gas for 30 min, the initial reaction solution was transferred into silicone mould (150mm length, 12 mm width and 2.5 mm depth) and illuminated by UV radiation (Omnicure S1500, EXFO, range of wavelengths: 250-450 nm) for 5 min in ice-water bath. For measurements of mechanical properties and swelling ratio, CNC gels were used as-prepared with the same size. OR gels are prepared as described previously, namely the NMBA is used as the cross-linking agent and KPS/TEMED is used as the redox initiator. In order to compare the mechanical properties with CNC gels, the monomer concentration and cross-linking agent content (NMBA) for OR gels (PAAm OR gel, PAA OR gel and PVP OR gel) are fixed at 4.2 mol L^{-1} and 20% (the same content as in CNC gels).

***Preparation of magnetic CNC PAAm gels*:**

Hydrophilic Fe_3O_4 nanoparticles coated with oleic acid with a diameter between 15-30 nm (as shown in Fig. S2) were synthesized by chemical coprecipitation. Then the ferrites were incorporated into the photoactive PS nanoparticles by a modified emulsion polymerization to prepare magnetic PS nanoparticles (Fig. S3). These magnetic PS nanoparticles were used as the cross-linking agent to fabricate magnetic CNC gels as described above.

***Interior Morphology (SEM) of CNC gels*:**

The SEM analysis of CNC gels were studied on JSM-5600LV scanning electron microscope (JEOL, Japan). The swollen gel samples, reaching equilibrium-swollen in water at room temperature, were quickly frozen in liquid nitrogen and freeze-dried under vacuum at -48 ℃ for 48 h. Then the freeze-dried gels were fractured carefully and coated with gold on the cross-section of the samples before observation of SEM.

***Measurements of Mechanical Properties*:**

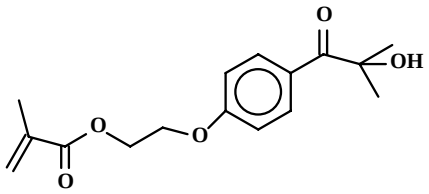
Mechanical properties were measured using WDW3020 electronic universal testing machine (Changchnun Kexin, China). Tensile strength measurements were performed on the same size (12 mm width, 2.5 mm thickness, 150 mm length) and under the following conditions: temperature, 25 ℃; gauge length, 15 mm; crosshead speed, 100 $mm.min^{-1}$. The strain under stress is defined as the change in length relative to the initial length of the specimen. The initial cross section of the gel samples is used to calculate the tensile and compression strength.

***Measurement of Swelling Ratio*:**

Swelling ratio of CNC gels were measured by immersing as-prepared hydrogels (sample size: 12 mm width, 2.5 mm thickness and 12 mm length) in a large excess of pure water at room temperature and the water was replaced every 8 h. On reaching swelling equilibrium, the gels were gently wiped with filter paper and weighed, then dried in an oven at 60 ℃ until reaching constant weights and weighed. The swelling ratio (Q) was calculated as follows:

$$Q= (W_s-W_d)/W_d$$

Where W_s is the weight of the swollen gel and W_d is the weight of the dry gel.



Scheme S1 The structures of HMEM.

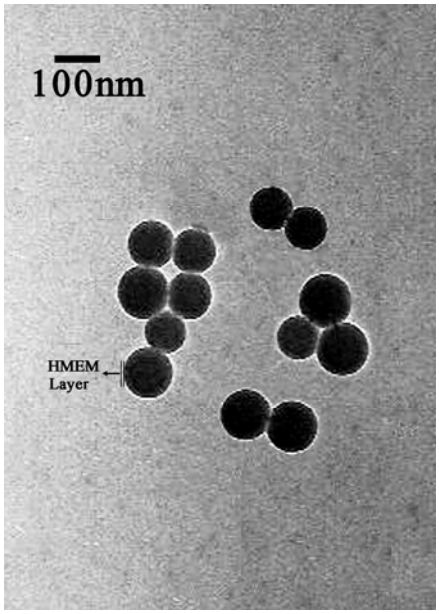


Fig. S1 TEM micrograph for the morphology of photoactive PS nanoparticles with the diameter between 96 to 105nm. The HMEM is grafted on the nanoparticle surface with the thickness at 2-3nm.

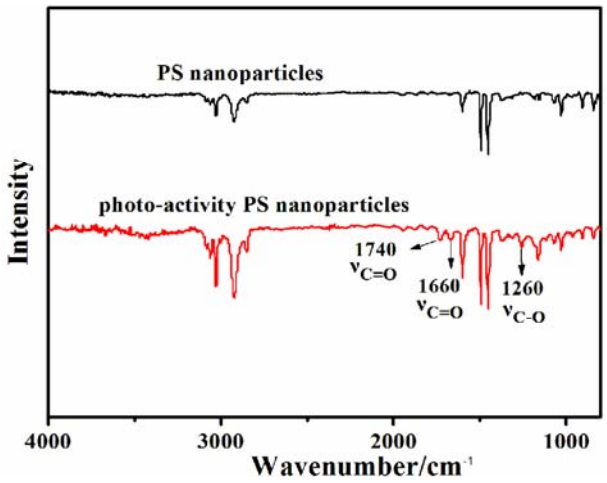


Fig. S2 FTIR spectra of conventional PS nanoparticles and photo-active PS nanopartices which are grafted HMEM on the surface. (These samples have been extracted in acetone for 72h before measurement.)

For the FTIR spectrum of photo-active PS nanopartices, new adsorption peaks observed at 1260 cm^{-1}, 1660 cm^{-1} and 1740 cm^{-1}, corresponding to the C-O stretching vibration, C=O stretching vibration which connected with benzene ring and ester group, respectively. These new adsorption peaks are owing to the grafted HMEM on the particle surface. For a small amount of HMEM on PS particle, only weak peak can be observed.

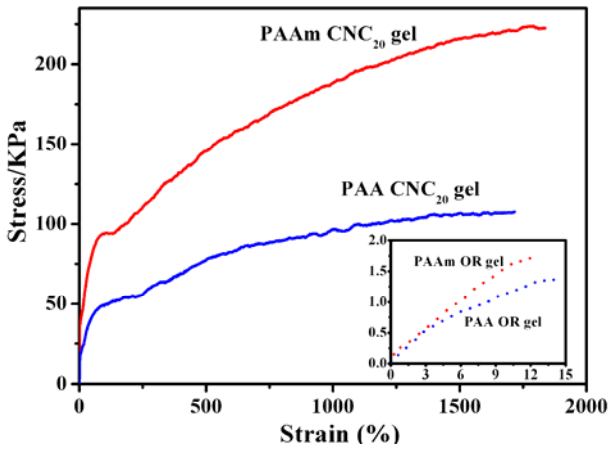


Fig. S3 Tensile properties of PAAm CNC gel, PAA CNC gel, PAAm OR gel and PAA OR gel with the same monomer concentration and cross-linking agent content.

The mechanical properties for CNC gels show significant improvement compared with OR gel, as revealed in Fig. S3. The tensile strength for PAAm CNC_{20} gels and PAA CNC_{20} gels can be attained 230.2 KPa and 110.1 KPa, while the elongation at break are 1837.2% and 1716.7%, respectively. However, the tensile strength for both PAAm OR gel and PAA OR gel are less than 2 KPa, and the elongation at break are less than 15%. For PVP OR gel, it shows poorer mechanical strength, and even can not afford the stress of crosshead in tensile strength measurement by a testing machine. We use load-bearing to measure the tensile strength, and the value is only 0.445 KPa, while the tensile strength for PVP CNC_{20} gel is 26.5 KPa.

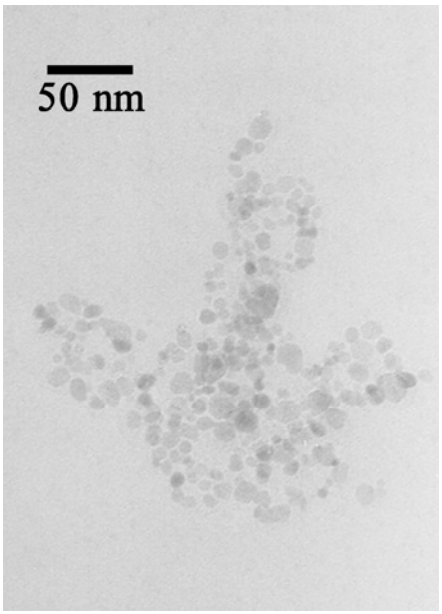


Fig. S4 TEM micrograph for the morphology of Fe3O4 nanoparticles with the diameter between 15 to 30nm.

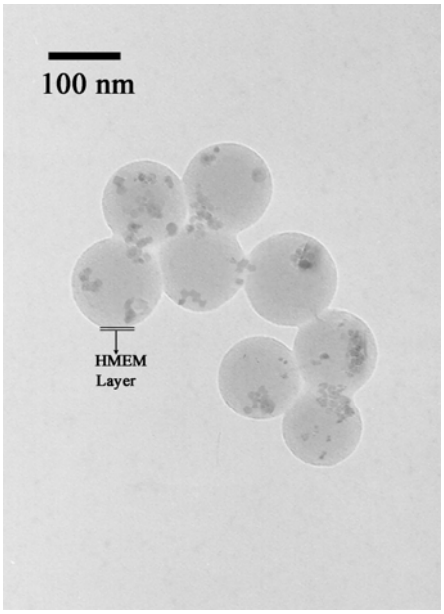


Fig. S5 TEM micrograph for the morphology of magnetic PS nanoparticles with an average diameter at about 120 nm. The HMEM is grafted on the nanoparticle surface with the thickness at 2-3nm.