Electronic Supplementary Material (ESI) for RSC Advances

Nanocomposite Hydrogels with High Strength Cross-linked by Titania

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Experimental

***Materials*:**

Acrylic acid (98%, Bodi Co., China), N,N-dimethylacrylamide (99%, Kohjin Co., Japan) were purified by reduced pressure distillation and filtering through activated alumina, respectively. Colloidal titania (anatase; size=15~20nm in diameter; Wanjing Co., China) and other reagents, *e.g.*, Potassium persulfate (KPS) (99.5%, Bodi Co., 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 including swelling measurements was purified by a Millipore Direct-Q purification system and bubbled with N_2 for 3h before use.

Preparation of hydrogels:

11.5g TiO_2 colloidal solution (15%, W_{TiO2}/W_{water}) was firstly bubbled with N_2 for 1h to remove any soluble O_2. Then, an appropriate amount of AA and DMAA were added into the former solution under stirring. After stirring for another 15min, the solution was cooled to 0℃ before catalyst(TEMED,8 μ l) and initiator(0.01g in 0.5ml water) were added. Finally, the solution was transformed to different vessels, and free radical polymerization was allowed to carry out for 24h in a 20℃ water bath. The hydrogels obtained were washed thoroughly with distilled water to remove the unreacted monomer and other impurities, and the water on the surface of hydrogels was then swept by filter paper.

Heat-treatment of hydrogels:

The TNC10 gels with different shapes were placed into drying ovens without taking from glass vessels. After heating for certain time at different temperatures, the samples were cooled to room temperature and taken out. The obtained hydrogels were cleaned by the same way as that of as-prepared samples.

Measurements and characterizations:

The TEM images of TiO_2 NPs were taken by a Tecnai G20 (FEI) at an acceleration

voltage of 80 kV. FT-IR spectra were performed with a Nicolet 6700 instrument (Thermal Scientific, USA) by the KBr method in the range 500–4000 cm^{-1}. The mechanical properties of hydrogels were measured on an ASG-J electronic universal testing machine (Shimadzu Co., Japan) at room temperature. Clubbed samples with size of Φ6.3mm×40mm (gauge length, 20 mm) were used for tensile tests with a crosshead speed of 20mm min^{-1} . Cylindroid samples with size of Φ10mm×10mm were used for compressive tests with a crosshead speed of 5mm min^{-1}. The strength and modulus were calculated by the stress-strain curves based on the initial cross-section area of hydrogel samples. Swelling measurements were carried out with a gravitational method. Hydrogel samples with size of Φ6.3mm × 2mm were immersed in a water bath with temperature of 20℃, and weighed after certain interval before sweeping the water on surfaces. The swelling ratio (SR) was determined as: SR %= (swollen mass/initial mass).

Shpe memory behaviors of hydrogels:

Shape memory behaviors were conducted on TNC10 gels heat treated by 80℃ for 12h. Straight or U-shaped hydrogels(original shapes) were firstly immersed in water until swelling equilibrium. Then the swellon samples were hand-made into alternative shapes (straight to U-shape and U-shaped to straight) and fixed by special vessels. After that, hydrogels were placed in 60℃ drying oven for 30min. Next, the hydrogels were placed into distilled water at room temperature and observe the recovery behavors of hydrogels.

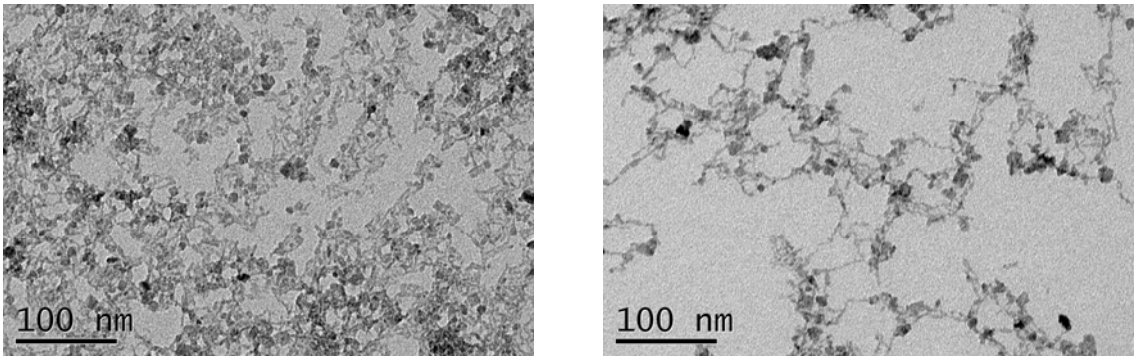

Figure S1 TEM images of TiO_2 nanoparticles.

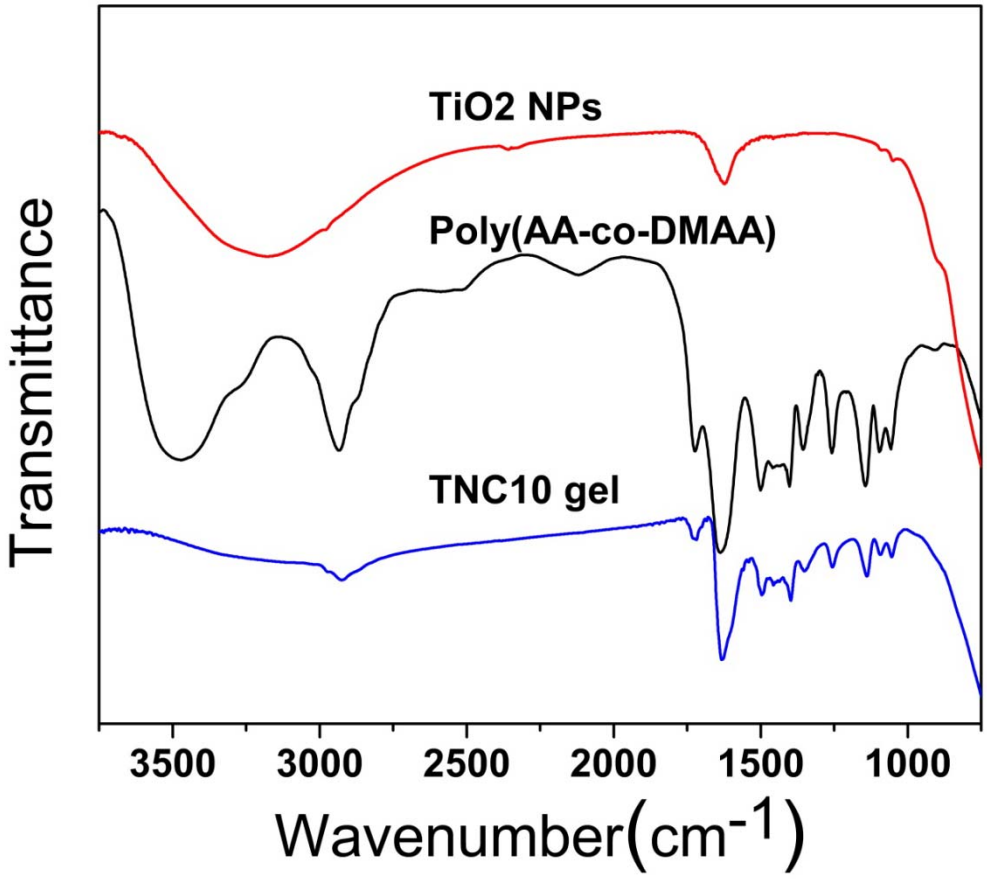

Figure S2 FT-IR spectra of TiO_2 NPs, Poly(AA-co-DMAA)(1:9) and dried TNC10 gel. The broad absorption peak of TiO_2 NPs at 3177 cm^{-1} is attributed to –OH on TiO_2 surface. The absorption peak of Poly(AA-co-DMAA) at 3465 $cm^{-1,}$ 2927 cm^{-1} , 1631 cm^{-1} are attributed to –OH, -CH_3 and C=O, respectively. However, the broad absorption peak at 3177 cm^{-1} and 3465 $cm^{-1,}$ are disappeared, indicating the strong interactions between hydroxy groups on TiO_2 and carboxyl groups on polymer chains.

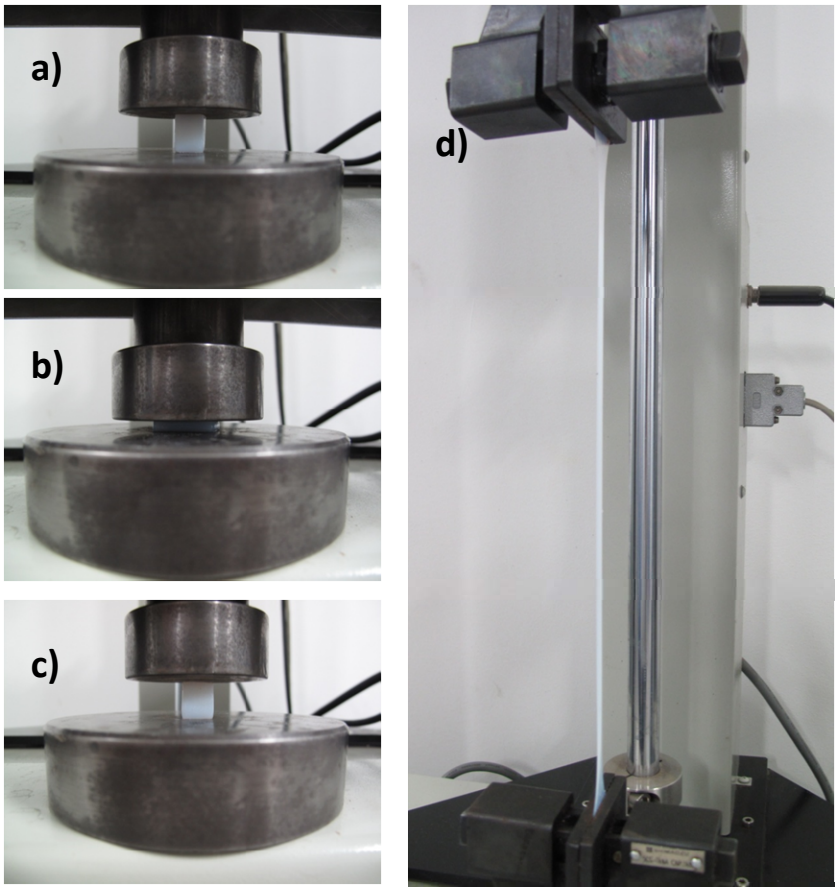

Fig. S3 Photographs of TNC10 gels a) before compression; b) compressed 95%; c) after compression; d) during tensile tests.

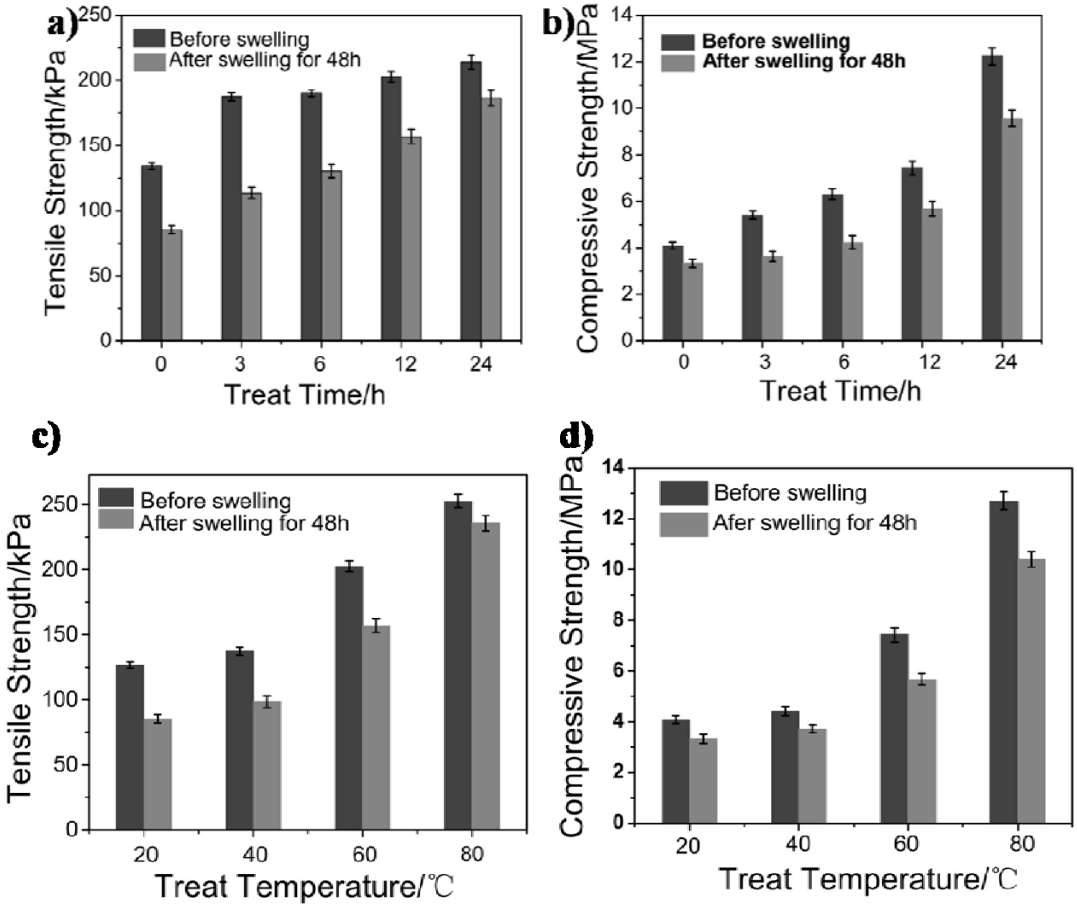

Fig. S4 The mechanical strength of heat treated TNC10 gels before and after swelling. **a)-b)** TNC10 gels treated for different time at 60℃； **c)-d)** TNC10 gels treated at different temperature for 12h.