† Electronic Supplementary Information (ESI)

Super tough double network hydrogels reinforced by covalently compositing with silica-nanoparticles

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FTIR of Vinyl modified silica nanoparticles.

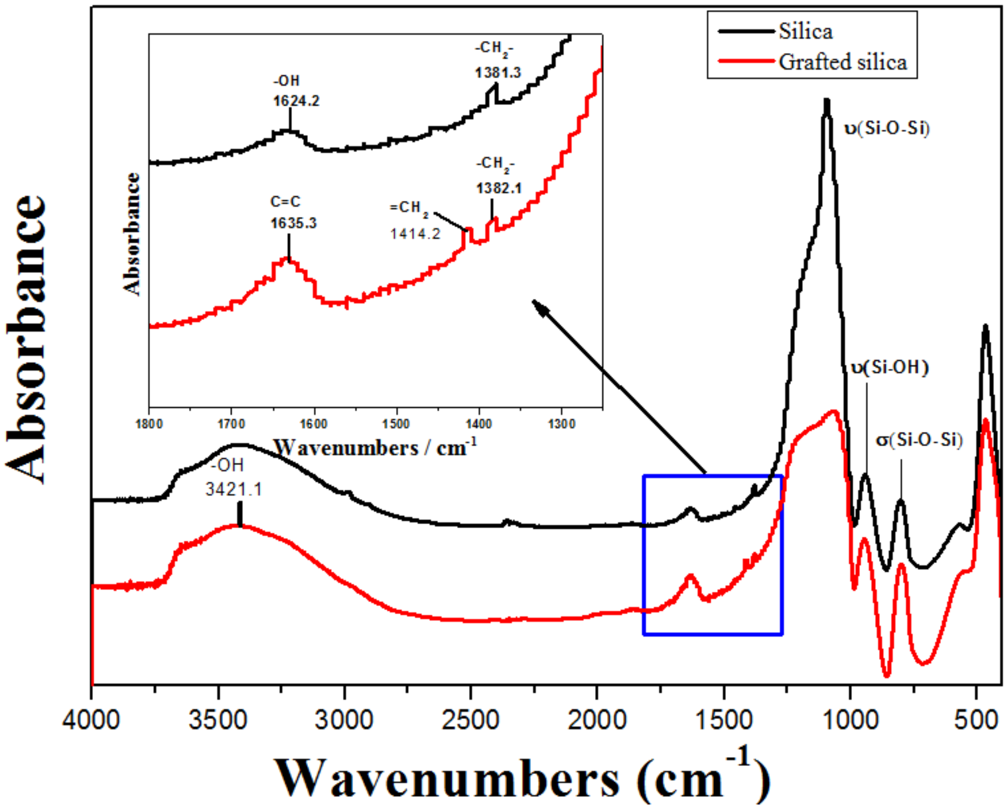

Fig. S1 FT-IR spectra of 300 nm silica nanoparticle before and after modification with VTEOS.

As shown in Fig. S1, the major characteristic peaks were assigned as follows(where, *ν* and *δ* represent stretching vibration and stretching vibration respectively): the peaks at 3421 cm^{-1} and 1624 cm^{-1} were ascribed to ν(O-H) of silica nanoparticles and H_2O. The absorbances at 1085, 937 and 801 cm^{-1} were attributable to ν(Si-O-Si), ν(Si-OH) and δ(Si-O-Si), respectively. ν_{max}/cm^{-1} 1635 (C=C), 1414 (=CH_2) and 1381 (-CH_2-) confirmed the successful grafting of VTEOS to silica nanoparticles (Fig. S1 inset, ESI†).[32,33,31] These features confirmed the successful grafting of VTEOS to silica nanoparticles.

Optimizing the formulation of the double network hydrogels

Gong and coworkers[7,18,34] have demonstrated that the strongest stress is achieved when the first network is highly cross-linked and the second network is slightly cross-linked, and the DN gels become very tough only when the molar ratio of the second network to the first network is in a range of several to a few decades. Therefore, the first network was synthesized with a high cross-linker agent concentration of 4 mol%, meanwhile the monomer and cross-linker content of the second network were adjusted for obtaining the highest compressive strength of DN gels.

Fig. S2 compares the dependence of the compressive stress at 0.90 strain ($\sigma_{c,0.90}$) on the AAm content (Fig. S2a) and the dependence of the fracture stress on the MBAA content (Fig. S2b). With a specific formulation of AMPS content, initiator, and crosslinking reagents, the content of AAm showed critical influence on the fracture strength of the DN gels and led to a maximum of fracture strength at about 3 mol L^{-1} (Fig. S2a). On the other hand, with a specific formulation of AMPS content, initiator, and AAm, a low cross-linker content (0.01 mol% MBAA) led to a dramatic increase in the compressive strength of DN gel (Fig. S2b).

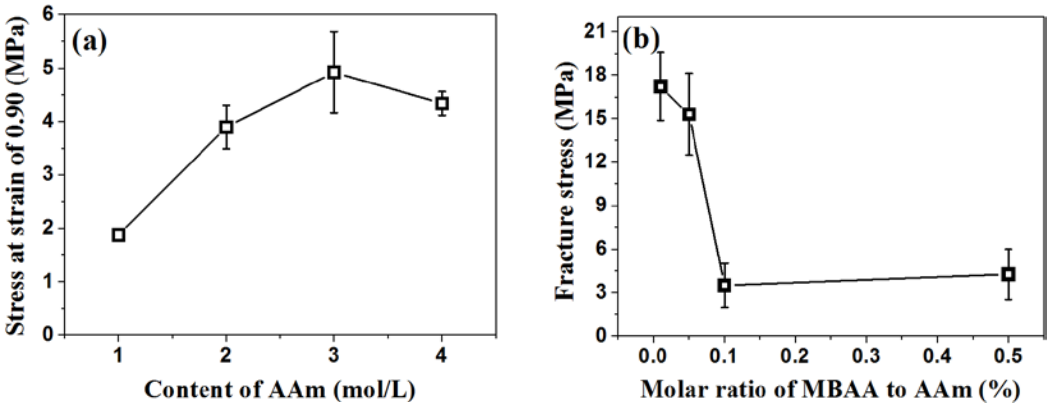

Fig. S2. Effect of the contents of AAm and MBAA on the mechanical strength of (a) PAMPS-1-4-0.01/PAAm-x_1-0.01-0.1 gel, (b) PAMPS-1-4-0.01/PAAm- 3-x_2-0.1 gel respectively.

SEM for microstructure of 300 nm silica-grafted DN gels.

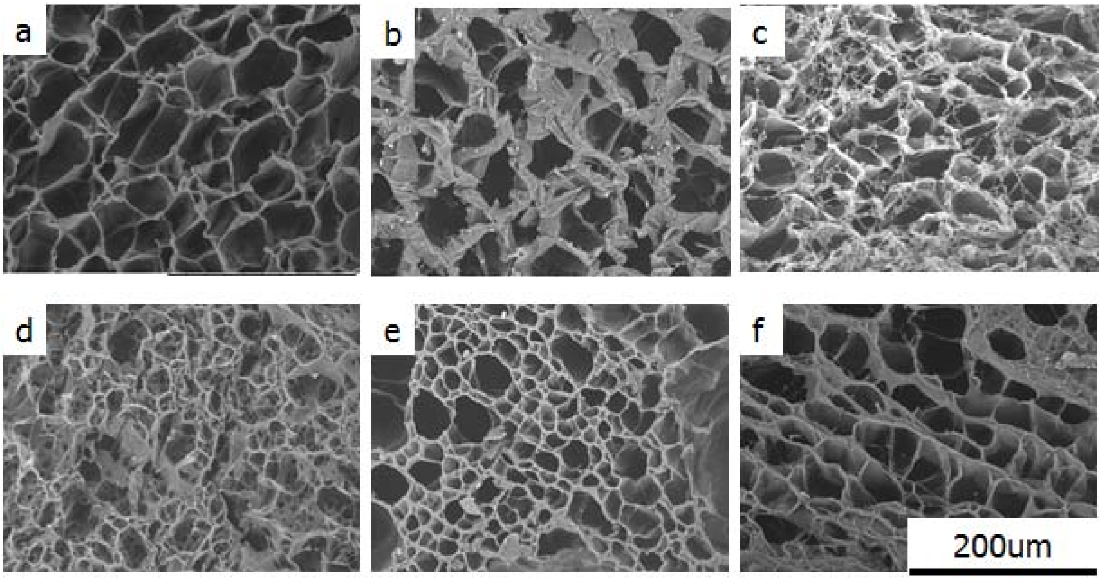

Fig. S3. SEM for microstructure of 300nm silica-grafted DN gels with silica particle content of (a) 0, (b) 0.5, (c) 1, (d) 2, (e) 3, and (f) 4 wt%.

Stress-strain curves.

The nanocomposite hydrogels exhibited very high mechanical strengths as measured by compression tests. For all samples, the compressive stress (σ_c) gradually increased with increasing strain until around ε=0.8, and after then abruptly increased. At this region (ε>0. 8), mostly stress of silica-grafted DN gel and silica-filled DN gel increased faster than DN gel, also the elastic modulus exhibited the same trend at low strain (ε<0. 1) (Table 2), here we took 1 wt% silica-grafted DN gel and 1 wt% silica-filled DN gel for example.

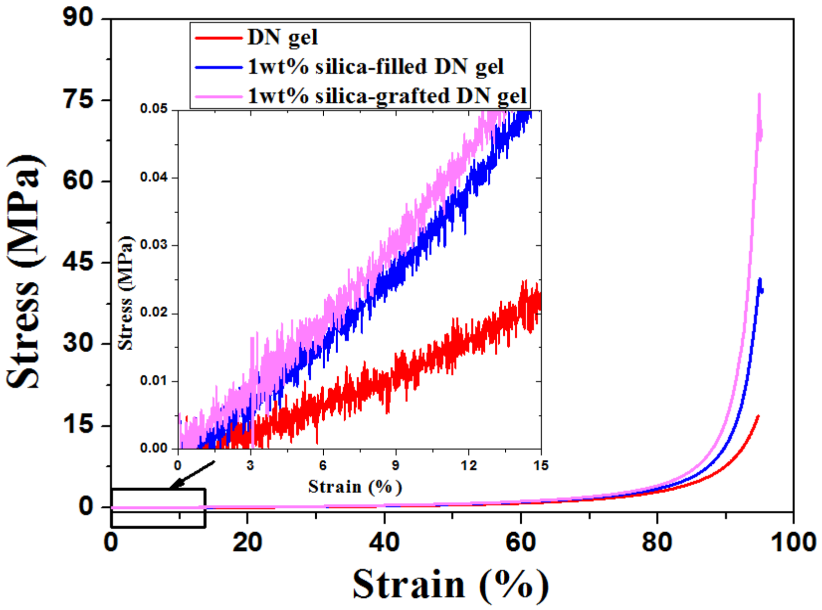

Fig. S4. Typical compressive stress-strain curves of hydrogels under uniaxial compression. The elastic modulus can be extracted as the slope of the stress-strain curves at a strain under 0.1.