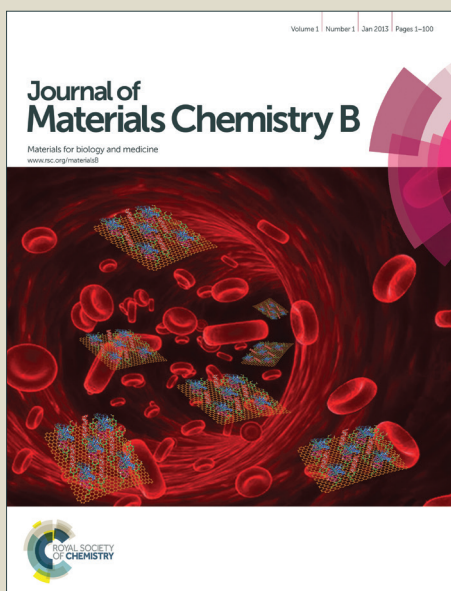


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COMMUNICATION

Highly stretchable and super tough nanocomposite physical hydrogels facilitated by coupling of intermolecular hydrogen bond and analogous chemical crosslinking of nanoparticle

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Highly stretchable and super tough nanocomposite physical hydrogels (NCP gels) are fabricated by a facile and one-pot process. NCP gels show superior mechanical properties with tensile strength of 73 kPa - 313 kPa and elongation at break of 1210 % - 3420 %. This is due to the effective strengthening mechanism: under stretching, the intermolecular hydrogen bonds can dynamically break and recombine to dissipate energy and homogenize the gel network simultaneously. And vinyl hybrid silica nanoparticles (VSNPs) can work as stress transfer centres to transfer the stress to the grafted polymer chains.

Hydrogel is a three dimensional polymeric network containing a large amount of water, and has attracted much attention over the past two decades due to their promising applications in tissue engineering and regenerative medicine^[1-2], drug and cell delivery^[3-4], and cosmetics. However, the mechanical properties of conventional chemically crosslinked hydrogels (C gel) are inherently weak (e.g. < 100 kPa) due to their inhomogeneous network structure and the lack of energy dissipation mechanism.^[5-6] To date, many attempts have been made to prepare hydrogels with enhanced mechanical properties, by optimizing network structures^[7-9], or introducing multifunctional crosslinker^[5, 10-12, 21-23]. Outstanding representatives include double network gels^[13-17], topological gels^[18], nanocomposite gels^[19-22] and hybrid gels^[23-24]. Okay et al^[25] prepared a physical hydrogel with extremely stretchability which is crosslinked by hydrophobic interaction. And the tensile strength of this hydrogel is a few dozen kPa. Haraguchi^[5, 19] and Gong^[26] reported physical hydrogels with high tensile strength. And the elongation at break of them is with an approximate value of 1000 %. Here, we fabricate nanocomposite physical hydrogels (NCP gels) by a facile process, which shows a great balanced performance on both the tensile strength and the elongation at break.

In our previous works^[27-30], we used Stöber procedure^[31] to prepare silica nanoparticles and modified them with γ -methacryloxypropyltrimethoxysilane. Then, the monomer, acrylic acid (AA), in situ grafting polymerized from the surface of silica nanoparticles to form a physical gel, which is crosslinked by intermolecular hydrogen bonds among the grafted poly (acrylic acid)

(PAA) chains. The physical gel demonstrated excellent mechanical properties. However, its strengthening mechanism is still elusive.

In order to understand the strengthening mechanism of the gels, and further improve the mechanical properties of NCP gels, in this study we synthesized three vinyl hybrid silica nanoparticles (VSNPs) of varying diameters to replace the silica nanoparticles in the NCP gels, and developed a series of highly stretchable and tough NCP gels. We found that the tensile strength and the elongation at break of these physical gels can be modulated within a wide range of 73 kPa - 313 kPa and 1210 % - 3420 %, respectively, by simply varying the mass fraction and/or diameters of VSNPs. Based on these results, we propose a mechanism to explain the superior mechanical properties of NCP gels.

Figure 1a shows the schematic illustration of the preparation process and structure model of NCP gel. To prepare the NCP gels, the VSNPs were first prepared with good dispersion and stability in aqueous solution using a general sol-gel process^[32-33]. Then acrylamide (AM) monomers and the ammonium persulfate initiator were introduced; the latter is known to be able to adsorb on the surface of VSNPs^[5]. It should be noted that no crosslinker was used in this study to promote the formation of NCP gels. Next, radical grafting polymerization was thermally initiated from the vinyl groups on the surface of VSNPs, leading to the formation of the grafted polymer chains, with one terminus attached to one VSNP and the other hanging freely in water to interact with other polymers to form a nanobrush gelator. Since the acrylamide repeat units are capable of forming strong hydrogen bonds^[34] with each other, a NCP gel can be achieved by intermolecular hydrogen bonds. Consequently the VSNP in the gelator could spontaneously serve as multifunctional chemical crosslinking point in the gels, i.e. an analogous crosslinking point (ACP)^[27]. Since the network of NCP gel is constructed by the intermolecular hydrogen bonds, they could undergo a gel-sol transition if these physical crosslinking points are disrupted by hydrogen bond dissociator, such as urea (see Figure S1).

In this study, NCP gels are designated as NCP-X-Y, where X denotes the diameter of VSNPs, and Y is the content of VSNPs expressed as a weight percentage with respect to the weight of monomer used in the preparation of NCP gels. For example, NCP-3-0.6 represents that the content of VSNPs with a diameter of 3 nm is 0.6 wt % relative to the weight of AM in NCP gel.

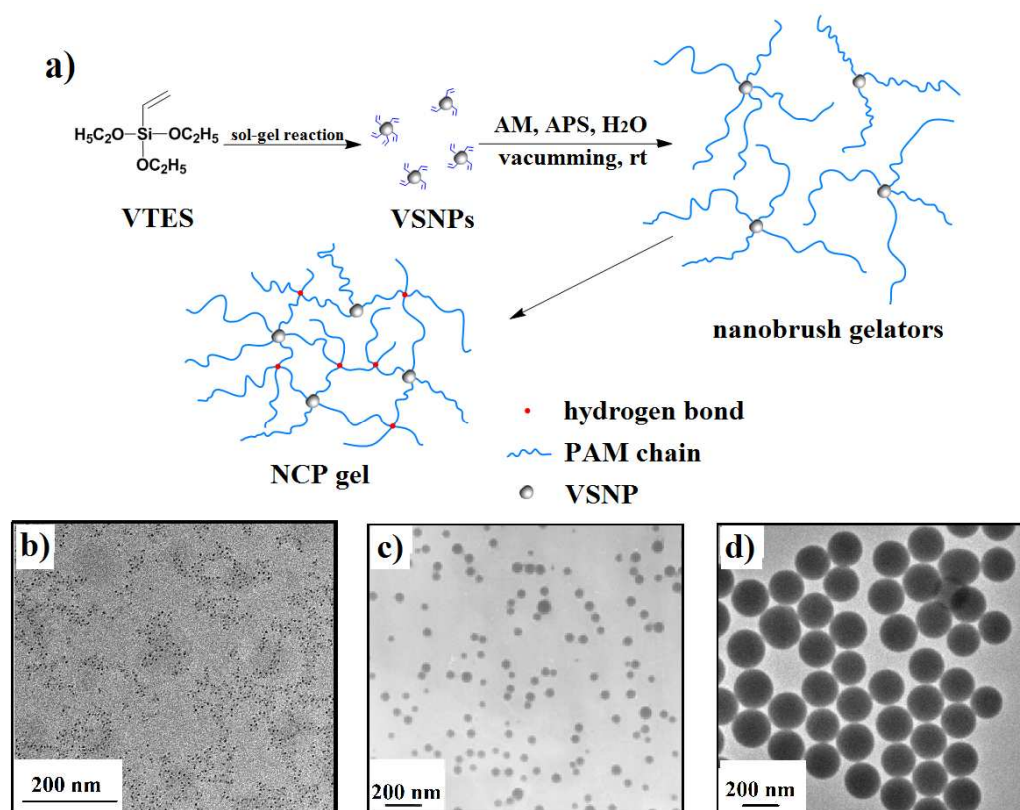


Figure 1. a) Schematic representation of the fabrication process of NCP gel and its network structure model. In the structure model, only a small number of polymer chains are depicted for simplicity. Transmission electron microscopy (TEM) images of highly monodisperse vinyl hybrid silica nanoparticles (VSNP) with a diameter of b) 3 nm, c) 52 nm, and d) 247 nm, synthesized by a sol-gel process.

Three VSNPs with different diameters were prepared as shown in Figure 1b-c. TEM observations reveal that VSNPs are nanometer-sized and highly monodisperse, which are synthesized using a general sol-gel process^[32-33] in aqueous solution. The average diameters of VSNPs are 3 nm, 52 nm and 247 nm, respectively. The aqueous dispersions of VSNPs are quite stable and no aggregates became visible even after 30 days (see Figure S2 and Figure S3). The FTIR studies confirm that a large amount of vinyl groups are displayed on the surface of VSNPs (see Figure S4), as evident by the appearance of $\nu_{\max}/\text{cm}^{-1}$ at 3062 and 2959 ($=\text{CH}^2$), 3024 ($=\text{CH}-$), 1602 ($\text{C}=\text{C}$), and 767 ($\text{Si}-\text{C}$).

Figure 2a shows the tensile stress-strain curves of NCP-X-0.6 gels. All of the NCP-gels are tough and highly stretchable (see Figure S5), with their high elongation at break of 2409 %, 2758 %, and 3420 % for NCP-3-0.6, NCP-52-0.6, and NCP-247-0.6, respectively, which are about one order of magnitude higher than that of C gel^[5, 16]. The tensile strength of NCP-3-0.6 gels is several times higher compared to that of C gel. Therefore, a great improvement in elongation at break and tensile strength have been achieved in NCP gel.

When the diameter of VSNPs was changed from 247 nm to 3 nm, the initial tensile modulus shows little change, which is approximately 40 kPa as shown in Figure 2b. This is due to the fact that the initial tensile modulus is mainly dependent on the density of

intermolecular hydrogen bonds, which serve as physical crosslinking points in NCP gels. At a fixed polymer concentration, the density of intermolecular hydrogen bonds should not be dramatically different. With the further tension, the NCP gel with smaller VSNPs can sustain much larger stress due to the analogous crosslinking effect of VSNPs. In the NCP-X-0.6 gels, the quantity of VSNPs and their specific surface area should increase with the decrease of their diameter, which leads to the increase of the density of ACPs. As a result, NCP-X-0.6 gel with smaller VSNPs can tolerate much larger stress at a fixed strain. The elongation at break of NCP-X-0.6 gels decreases in a small range in response to the decrease of the diameter of VSNPs, as shown in Figure 2c. This is possibly due to the increased number of grafting polymer chains on VSNPs and the simultaneous decrease of their average chain length. According to the structural model shown in Figure 1a, the longer the grafting polymer chains in the NCP gel, the longer elongation at break is. This is verified by determining the viscous average molecular weight of the grafting polymer chains separated from NCP-X-0.6 gels (see Table S1). The tensile strength of NCP-X-0.6 gels increases remarkably with decreasing the diameter of VSNPs, as shown in Figure 2d. This is possibly because VSNPs with smaller diameter can work as ACPs much more effectively to assure that the gel withstands much more stress at a fixed strain and the elongation at break only changes in a small range.

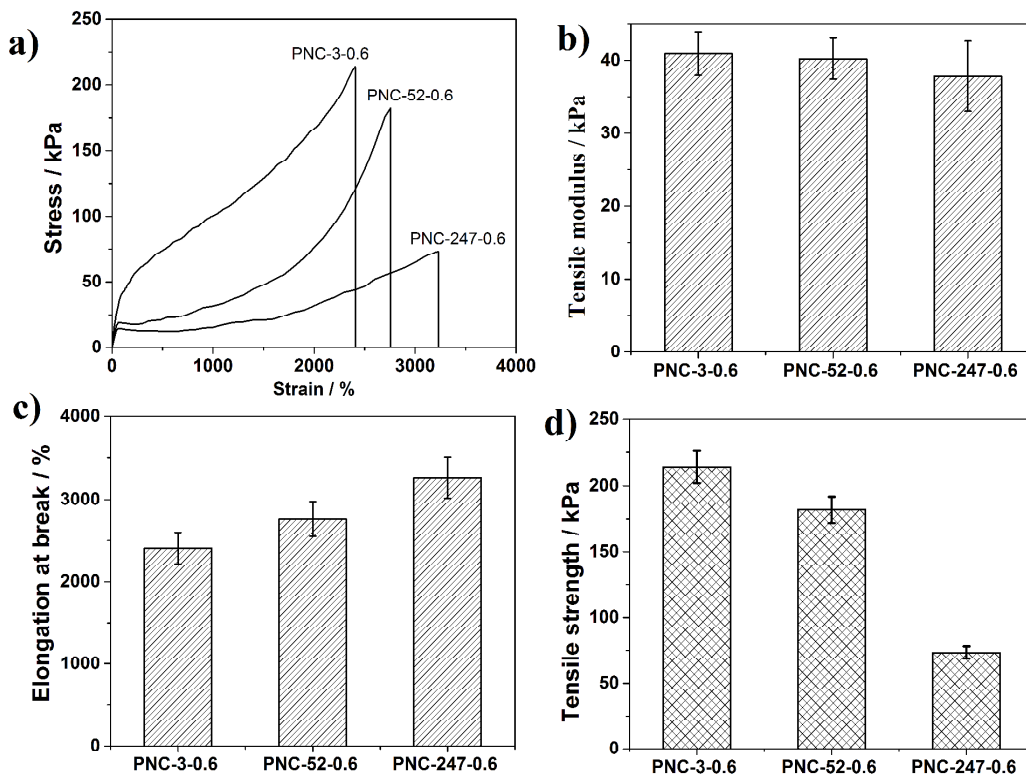


Figure 2. Mechanical properties of NCP-X-0.6 gels. a) Stress-strain curves of NCP-X-0.6 gels, b) tensile modulus, c) elongation at break, d) tensile strength. Here X denotes the diameter of VSNPs, and the content of VSNP is fixed to be 0.6 wt % with respect to the weight of monomer used in the preparation of NCP gels.

Furthermore, the effect of VSNPs on the mechanical properties of NCP-3-Y gels was investigated. Figure 3a shows the typical stress-strain curves for NCP-3-Y gels and linear PAM physical hydrogel (LP gel) [35-36] under stretching. Comprehensively, NCP gels exhibits a remarkably improvement in the mechanical properties, compared to LP gel. This result illustrates the important role of VSNPs on the toughening of NCP gels, which would be discussed later. At the strain smaller than 150%, NCP gels show almost identical stress-strain behavior with LP gel, suggesting that the intermolecular hydrogen bond among PAM chains is the primary contributing factor to withstand the stress. When the strain is higher than 150%, the stress tolerated by the NCP gel increases with the increase of the VSNP content. This observation indicates that VSNP acts as ACP in NCP gels to maintain the gel network even when the intermolecular hydrogen bonds start to break under the condition of tension. However, the stress of the LP gel decreases slowly with the sample necking above 150 % elongation ratio.

Figure 3b shows that the initial tensile moduli of NCP-3-Y gels are independent of the VSNP contents, which is about 40 kPa and close to the value of the LP gel. This unexpected observation can be possibly explained by the dependence of the tensile modulus on the density of crosslinking points in gel. At the initial stage of tension, intermolecular hydrogen bonds among PAM chains act as physical crosslinking points, and should have a similar crosslinking density for NCP-3-Y gels and LP gel with the same PAM concentration. So the initial tensile moduli of them are almost of the same value. With further stretching, the NCP-3-Y gel containing a higher VSNP content shows a higher value of modulus under the same strain, which can be attributed to the enhanced analogous crosslinking effect of VSNPs as shown in Figure 3a.

Obviously, NCP-3-Y gels are highly stretchable, since their respective high elongation at break is greater than 3000 % for NCP-3-0.2 and NCP-3-0.4, and 2000 % for NCP-3-0.6 and NCP-3-0.8. It is also clear that VSNPs contribute significantly to the observed high stretchability because all the NCP-3-Y gels demonstrate much higher elongation at break than that of LP gel (843 %), as shown in Figure 3c. The fact that the elongation at break of NCP-3-Y gels decrease remarkably with the increase of VSNP content could be attributed to the decrease of the average chain length of grafting polymer chains on VSNPs with increasing the VSNP content (see Figure S8). These results correlate well with the result of NCP-X-0.6 gels with the change in the diameter of VSNPs.

Based on Figure 3d, the tensile strength of the NCP-3-Y gels ranges from 135 to 313 kPa, all much higher than that of the LP gel and C gel. With the increase of the VSNP content, it is apparent that the tensile strength of the NCP-3-Y gels first increases to the value of 313 kPa for NCP-3-0.4 gel and then decreases monotonically as shown in Figure 3b. This result is attributed to the effect of the VSNP content on the density of ACPs and the average chain length of grafted polymer chains in the NCP-3-Y gels. With VSNP content increasing to 0.4 wt % for NCP-3-0.4 gel, the density of ACPs increases remarkably and the average chain length decreases in a small range (see Figure S8), which leads to the increase of tensile strength of NCP-3-Y gels. With a further increase of VSNP content, the density of ACPs became too high and the average chain length decreases remarkably to a small value, which makes the NCP-3-Y gels brittle. So a decrease in the tensile strength of NCP-3-Y gels is exhibited.

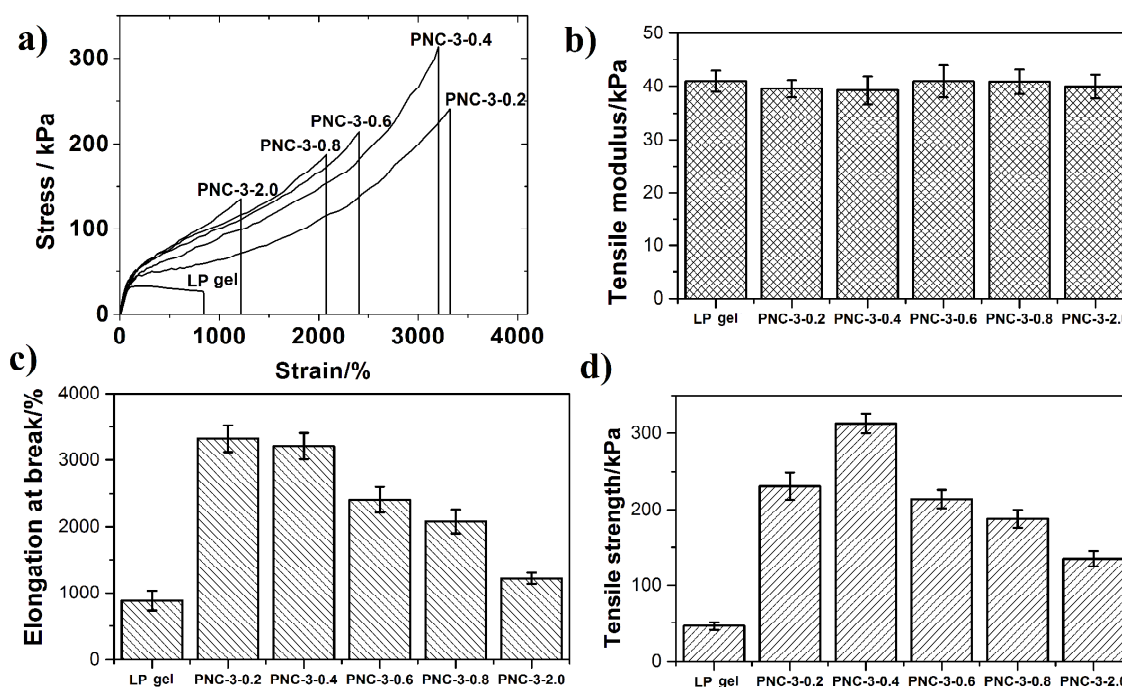


Figure 3. Mechanical properties of NCP-3-Y gels. a) Stress-strain curves of NCP-3-Y gels and LP gel, b) tensile modulus, c) elongation at break, d) tensile strength. Here Y is the content of VSNPs expressed as a weight percentage with respect to the weight of monomer used in the preparation of NCP gels, and the diameter of VSNP is fixed at 3 nm.

It is obvious that NCP gels show superior mechanical properties, especially toughness and high stretchability, both of which could be tuned by the change of the diameter of VSNPs and/or their content. The remarkable enhancement of the NCP gels could be explained in terms of their unique network structure and effective strengthening mechanism as shown in Figure 4. When a NCP gel is subjected to a tension force, the intermolecular hydrogen bonds as reversible physical crosslinking points could dynamically break and recombine to dissipate energy as shown in Figure 4b. This dynamic process

would reorganize the polymer chains to homogenize the gel network as shown in Figure 4c. It should be noted that the VSNPs maintain the gel network and tolerate stress even when part of the intermolecular hydrogen bonds start to break. After the gel network homogenization, the applied stress could be rapidly and uniformly distributed in the whole network, with the multifunctional VSNP as a transfer center. Thus, this highly effective strengthening mechanism assures NCP gels to show excellent mechanical performance.

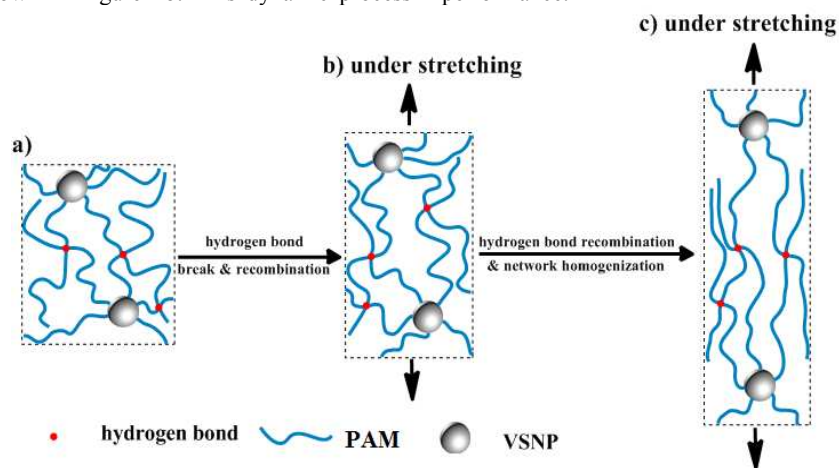


Figure 4. Schematic illustration of the structural change and the strengthening mechanism of the NCP gel under uniaxial stretching.

Conclusion

In summary, nanocomposite physical hydrogels (NCP gels) with superior toughness and high stretchability were prepared by taking advantage of the intermolecular hydrogen bond among the grafted polymer chains from VSNPs. Under

tension, the strengthening mechanism of NCP gels is based on three steps: 1) the break of intermolecular hydrogen bond could effectively dissipate energy; 2) the recombination of hydrogen bond could homogenize the gel network; 3) VSNP as a transfer centre of stress could effectively transfer stress to the network chains grafted on their surfaces. Thus, NCP gels exhibit superior mechanical properties, which could be tailored over a

wide range by varying the diameter and/or the contents of VSNPs.

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Nanocomposite physical hydrogels fabricated by a one-step polymerization shows ultra-extensibility and toughness due to an effective strengthening mechanism.

