

1 Electronic Supplementary Information

2

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

6 *Fu-Kuan Shi, Xi-Ping Wang, Ruo-Hai Guo, Ming Zhong and Xu-Ming Xie **

7

8 **1. Experimental Section**

9 *Materials:* Acrylamide (AM), N,N'-methylenebis(acrylamide) (BIS), Ammonium

10 persulfate (APS) were purchased from Xilong Chemical Co., Ltd. Vinyl triethoxy

11 silane (VTES) and sodium dodecyl sulfate (SDS) were purchased from Alfa Aesar.

12 All reagents were used as received.

13 *Synthesis of VSNPs:* Vinyltriethoxysilane (VTES, 3.8 g) was added into water (30 g)

14 under vigorous stirring until the oil (VTES) droplets completely (about 12 h)

15 disappeared and a transparent dispersion of VSNPs with a diameter of 3 nm was

16 obtained. If a certain amount of SDS was added into the aqueous dispersion of 3 nm

17 VSNP, after reacting for about 12h, a light blue dispersion of VSNPs with a diameter

18 of 52 nm was obtained with SDS aqueous solution of 6.9 mmol/L. If the concentration

19 of SDS aqueous solution was 20.8 mmol/L, a milky dispersion of VSNPs with a

20 diameter of 247 nm was obtained.

21 *Synthesis of NCP gels:* The aqueous dispersion of VSNP was firstly diluted with

22 deionized water to a desired concentration. AM (9 g), and ammonium persulfate

23 (0.045 g, 0.5 wt% of AM) were then added into the diluted aqueous dispersion of

24 VSNP (30 mL). The solution was added into a tube. After three degassing cycles, the

1 tube was sealed under N₂. Next, free-radical polymerization was allowed to proceed
2 in a water bath at 28 ± 2 °C for 20 h. All of the gel samples were synthesized in
3 plastic tubes (the internal diameter is 5 mm, and the length is 60 mm).
4 *Synthesis of LP gel:* AM (9 g), and ammonium persulfate (0.045 g, 0.5 wt% of AM)
5 were added into water (30 mL). The mixture was stirred to form a homogeneous
6 solution. And then the solution was added into a tube. After three degassing cycles,
7 the tube was sealed under N₂. Next, free-radical polymerization was allowed to
8 proceed in a water bath at 28 ± 2 °C for 20 h.

9 **2. Characterizations and measurements**

10 *TEM observations.* One drop of VSNP aqueous dispersion was placed on the
11 copper mesh grid. Then, the copper mesh grid was rapidly plunged into liquid
12 nitrogen for about 5 min to avoid the damage of the morphology of VSNPs, and
13 lyophilized until all the water was removed. The sample was measured with a Hitachi
14 H7700 transmitting electron microscope operated at an accelerating voltage of 100 kV.
15 We obtained the average size of VSNP and its standard deviation, according to the
16 statistical result of two hundred nanoparticles.

17 *FTIR measurements.* A Fourier transform infrared (FTIR) spectrometer Nicolet
18 6700 was used for the infrared analysis, spectra were obtained by signal averaging 32
19 scans at the resolution of 4 cm⁻¹ in the range of 4000–650 cm⁻¹.

20 *Mechanical properties test.* Tensile mechanical measurements were performed
21 on hydrogels of the same size (5 mm Φ × 60 mm length) using an electromechanical

1 testing machine (Zwick-Roell Z005, Zwick-Roell, Ulm, Germany). Data were
2 recorded with dedicated software (Textexpert 8.1, Zwick-Roell). The testing
3 conditions were as follows: temperature 25 °C; gauge length of 15 mm; crosshead
4 speed of 100 mm/min. The strain under stress is calculated on the basis of the change
5 in length relative to the initial length of the specimen. The strength was calculated on
6 the basis of the initial cross section. The initial tensile modulus was calculated from
7 the initial slope of the stress-strain curves of NCP gels.

8 *Optical transparency of NCP gels.* Optical transparency of NCP gels was
9 quantitatively measured by using UV-vis spectrophotometer. The transmittance of
10 hydrogel sample prepared in a square columnar quartz vessel was recorded with a
11 TU-1810DPC UV-vis spectrophotometer at $\lambda = 520$ nm.

12 *Measurement of Gel swelling and gel -sol transition.* Lyophilized gel samples
13 were immersed in urea aqueous solutions at room temperature. ^[1-3] Gel samples were
14 taken out at certain time intervals, blotted with a filter paper to remove water on the
15 surface and weighted to obtain the mass m . The relative mass of gels R was calculated
16 as $R = m / m_0$, where m_0 is the initial mass of the gel sample. The initial mass of the
17 hydrogel sample and volume of urea aqueous solutions were fixed at ca. 0.1 g and 100
18 mL, respectively.

19 *Viscosity measurements of the grafted PAM seperated from VSNPs.* First, the
20 VSNPs of the nanobrush gelators were etched by HF aqueous solution to get the
21 grafted PAM. The grafted PAM seperated from the nanobrush gelator of NCP gel is

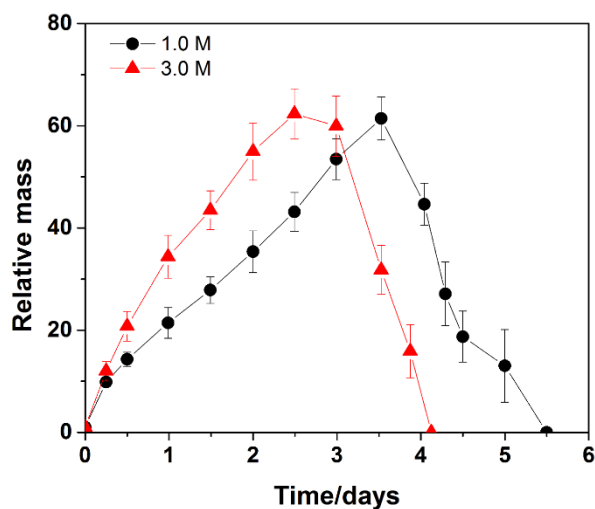
1 denoted as NCP-X-Y-VSNP. The viscosity measurements were performed on a standard
2 Ubbelohde viscometer, in 0.1 M NaCl solution, at 30 °C and pH = 7. The viscous
3 average molecular weights (M_η) of NCP-X-Y-VSNP and neat PAM from LP gel were
4 measured and calculated, according to the Mark-Houwink-Sakurada equation:

5
$$[\eta] = kM_\eta^\alpha,$$

6 we used Francois relation [4, 5]: $[\eta] = 9.33 \times 10^{-5} M_\eta^{0.75}$ (g/ml).

7 *DLS measurement of VSNPs:* A Zetasizer Nano-ZS instrument (Malvern
8 Instruments Ltd., Malvern, UK) was used to acquire the DLS diameter of VSNPs. The
9 particle solutions were measured by diluting the initial aqueous dispersion of VSNPs
10 (after stocking for a week) to a proper concentration to ensure pure Brownian motion
11 of the particles. The sample viscosity was assumed to be that of water at 20 °C (the
12 temperature set for all measurements) and the refractive indices of the particles and
13 water were assumed to be 1.45 and 1.33, respectively (particle absorption at 633 nm,
14 $A = 0.01$).

1



2

3 **Figure S1.** The changes of the relative mass of NCP-3-0.4 gel in aqueous solutions of
 4 urea as a function of time. The concentration of urea in the external solutions are 1.0
 5 M (●), 3.0 M (▲).

6 The network of the NCP gel is crosslinked by intermolecular hydrogen bonds
 7 between the grafted PAM chains on the surface of VSNPs. These physical
 8 crosslinking points are easily disrupted by the hydrogen bond dissociator, such as urea.
 9 When the NCP-3-0.4 gel sample is immersed into a large amount of urea aqueous
 10 solution at 25 °C, its relative mass gradually increases with the increase of time and
 11 attains a maximum value after several days. With the further increase of swelling time,
 12 the gel sample is totally disrupted to a sol. And the gel-sol transition of the NCP-3-0.4
 13 gel sample is accelerated with the concentration increase of urea aqueous solution.

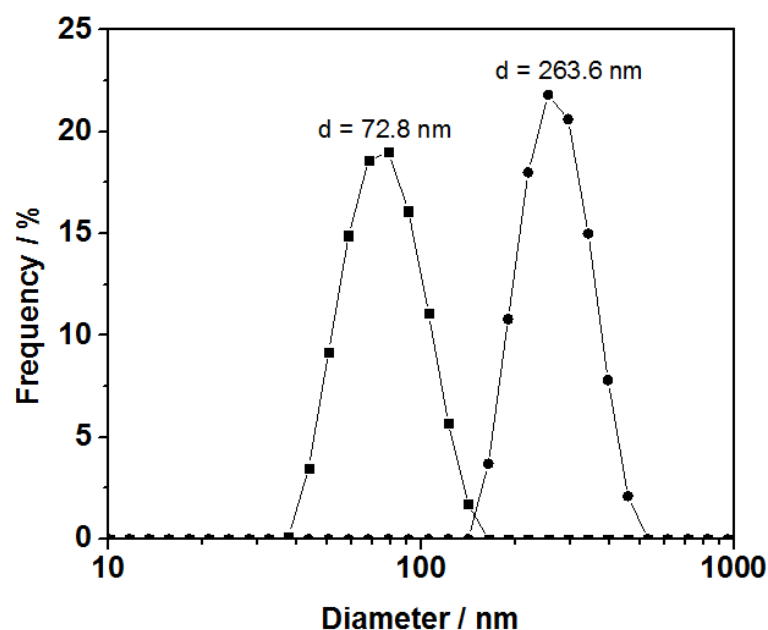


Figure S2. The number-weighted size distributions of VSNPs as measured by

DLS.

The diameter of VSNPs measured by DLS is a littler larger than that measured

by TEM, because DLS measure the hydrodynamic diameter and TEM measure the

inorganic core diameter of VSNPS. But the two different measuring methods verifiy

that the VSNPs are stable and monodisperse and no aggeregates of them exsit in the

aqueous solution. Due to the limitation of the characterization apparatus, we can not

get a DLS diameter of the VSNP which has a TEM diameter of 3 nm. But the 5 w/w %

aqueous solution of 3 nm VSNP is trasparent and stable for 1 month as shown in

Figure S3. So we believe that 3 nm VSNP is monodisperse and stable in the aqueous

solution.

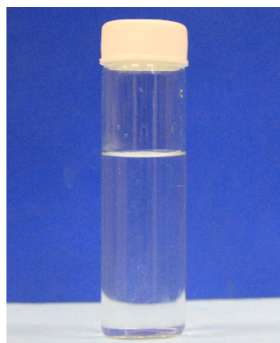


Figure S3. Digital photo of 5 w/w % aqueous solution of 3 nm VSNP after stocking for 1 month.

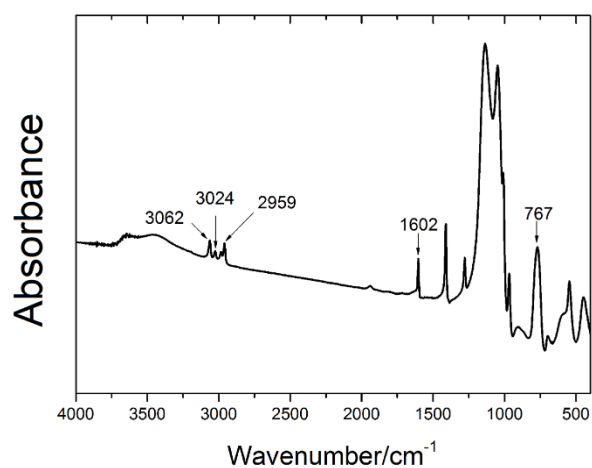
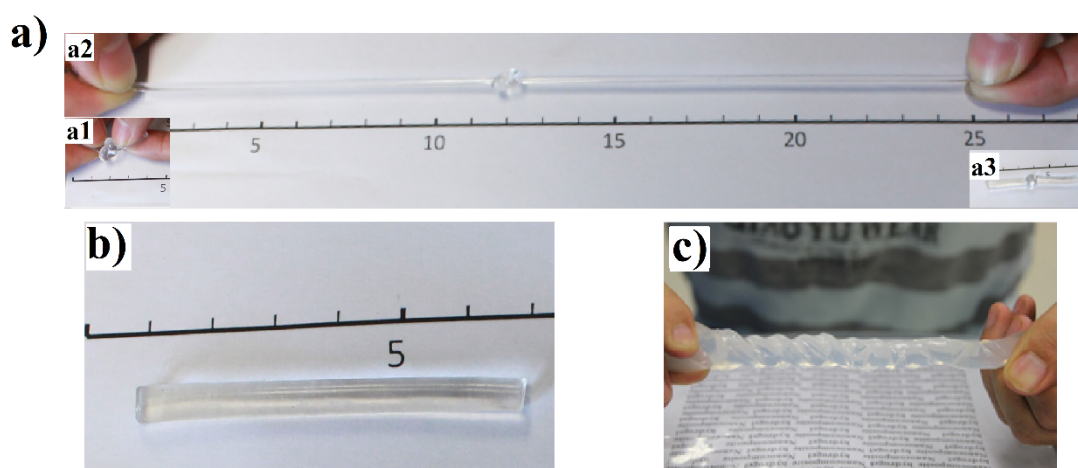


Figure S4. FTIR spectra of VSNP with a diameter of 52 nm.

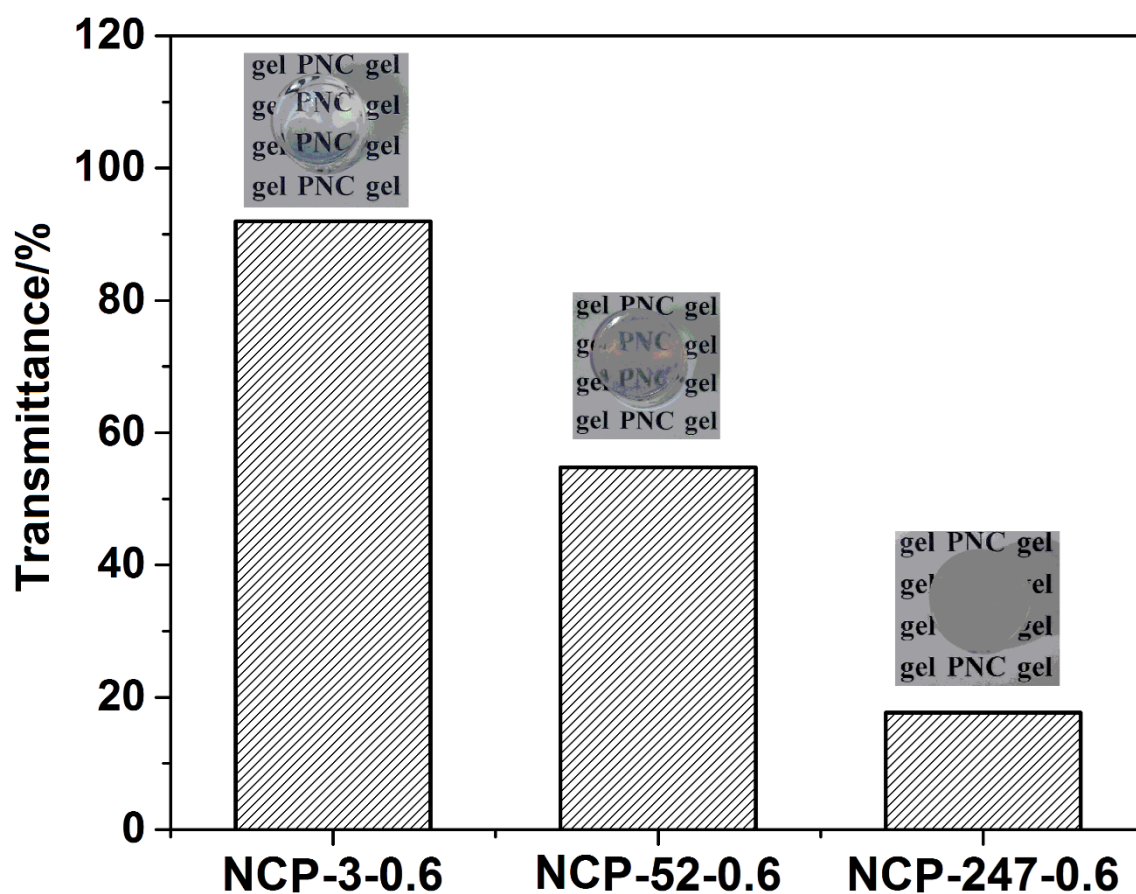


1 **Figure S5.** The mechanical performance of NCP gels. a) stretching of the knotted
2 NCP-3-0.6 gel sample; b) recovered and unknotted NCP-3-0.6 gel sample; c)
3 Stretching of the twisted NCP-52-0.6 gel sample.

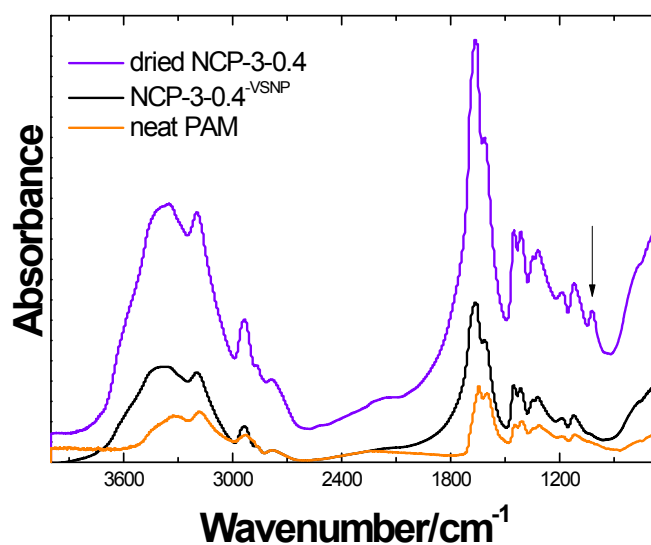
4 All NCP gels exhibit extraordinary mechanical toughness. NCP-3-0.6 can
5 withstand high level deformations, such as knotting and elongation (a1, the knotted
6 NCP-3-0.6 gel sample before being stretched. a2, the knotted NCP-3-0.6 gel sample
7 stretched to 25 times of its original length. a3, the knotted NCP-3-0.6 gel sample after
8 being stretched.). The knot of NCP-3-0.6 gel can be untied after being stretched as
9 shown in Figure S5b. And Figure S5c shows that the NCP-52-0.6 gel can be twisted
10 during uniaxial stretching.

11 **Table S1. M_n of the grafted PAM of the NCP-X-0.6 gels.**

Sample	$M_n/(10^6 \text{g} \cdot \text{mol}^{-1})$
NCP-3-0.6	0.56 ± 0.05
NCP-52-0.6	0.81 ± 0.10
NCP-247-0.6	1.82 ± 0.12

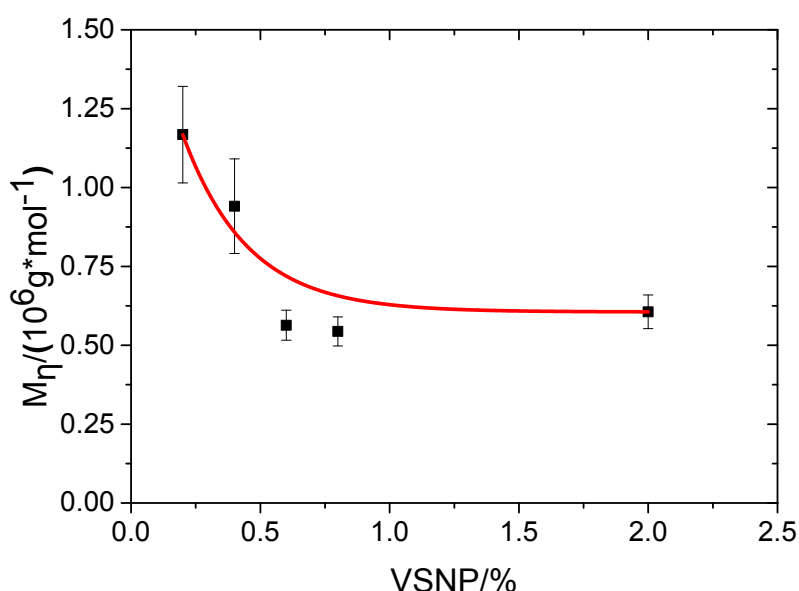


1
2 **Figure S6.** The transmittance of NCP-X-0.6 gels. The insets are the photo images of
3 the correspondent NCP-X-0.6 gels.



4
5 **Figure S7.** FTIR spectra of the dried NCP-3-0.4, NCP-3-0.4^{-VSNP}, and neat PAM.

1 By decomposing the Si-O bond of VSNP using HF aqueous solution, the grafted
 2 PAM is successfully separated from VSNPs. When the FTIR measurement of the
 3 three samples (Figure S7) are carried out, it is observed that the absorption at 1023cm^{-1}
 4 in the FTIR spectra that is ascribed to VSNP (Si-O) in dried NCP-3-0.4 disappeared
 5 in the case of NCP-3-0.4-VSNP. So the VSNP component is completely removed from
 6 the NCP-3-0.4 gel by HF etching. Since the FTIR spectra of neat PAM and NCP-3-
 7 0.4-VSNP are identical, it is also concluded that NCP-3-0.4 treated by HF does not
 8 undergo any chemical modification (e.g., hydrolysis of amide groups) during the HF
 9 treatment. And it was also reported that the molecular weights (M_w and M_n) and the
 10 molecular weight distribution (M_w/M_n) of the polymer were hardly changed by the HF
 11 treatment, regardless of their molecular weights.^[6]



12
 13 **Figure S8.** The dependence of M_η of the grafted PAM separated from VSNPs on the
 14 VSNP contents.

1 **Figure S8** shows the effect of VSNP contents on M_{η} of the grafted PAM which
2 were separated from VSNPs by aqueous HF solution etching. The M_{η} of the grafted
3 PAM separated from VSNPs decreases with the increase of VSNP contents and
4 reaches to an equilibrium value ca. $5.0 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$. For PAM in water, the critical
5 molecular weight M_c for entanglement between polymer chains was estimated to be
6 ca. $4.4 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$.^[7] For NCP gels, the molecular weights of the grafted PAM chains
7 are higher than this value. So physical crosslinking points can easily form among the
8 grafting polymer chains on the VSNPs.

9 **Reference:**

- 10 [1] J. Yang, X. P. Wang, X. M. Xie., *Soft Matter*, **2012**, 8, 1058.
11 [2] J. Yang, F. K. Shi, C. Gong, X. M. Xie., *J. Colloid Interf. Sci.*, **2012**, 381, 107.
12 [3] J. Yang, C. Gong, F. K. Shi, X. M. Xie., *J. Phys. Chem. B*, **2012**, 116, 12038.
13 [4] J. François, D. Sarazin, T. Schwartz., *Polymer*, **1979**, 20, 969.
14 [5] C. Chelaru, I. Diaconu, I. Simionescu., *Polym. Bull.*, **1988**, 40, 757.
15 [6] K. Haraguchi, Y. J. Xu, G. Li., *Macromol. Rapid Commun.*, 2010, 31, 718.
16 [7] W. M. Kulicke, R. Kniewske, J. Klein., *Prog. Polym. Sci.*, 1982, 8, 373.