

Supporting Information

1. Experiments

1.1 SEM observation

In a case of SEM image of swollen PAA/PAMPS/CNS gel, the sample for SEM observation was prepared as the following procedure: Firstly, hydrogel was put into water to acquire its' swelling equilibrium. Then, this saturated hydrogel was put into liquid nitrogen for several minutes, taken out from liquid nitrogen, and finally dried in a vacuum freeze dryer at $-50\text{ }^{\circ}\text{C}$. This freeze-dried sample was used for SEM observation.

As for SEM image of not swollen gel, the sample was prepared as the following procedure: Hydrogel was directly put into liquid nitrogen for several minutes, taken out from liquid nitrogen, and finally dried in a vacuum freeze dryer at $-50\text{ }^{\circ}\text{C}$. This freeze-dried sample was used for SEM observation.

1.2 Swelling experiments

Nowadays, many methods have been used to measure swelling ratio of water absorbing materials including natural filtration method (nylon mesh: 10-400 mesh), tea bag method (nylon mesh: 250 mesh) and suction filtration method (weighting unabsorbed water), and so on [1]. Natural filtration method is one the most commonly used method to measure swelling ratio of water absorbing materials. The procedure is as the following: Firstly, the gel is immersed into adequate water to absorb water. After a predetermined time interval, the swollen gel is taken out from water by using nylon mesh to calculate the swelling ratio. If the swelling ratio shows a small change (like 5%), then we can conclude that the saturated water absorption is gained. In this work, we use natural filtration method to calculate the swelling ratio of the gel. Firstly, the villi-like gel is put into adequate water to absorb water. After a predetermined time interval, the swollen villi-like gel is taken out from water by using nylon mesh (mesh number: 20) to calculate the swelling ratio.

2. Results and discussions

NaOH is mainly used to neutralize or buffer carboxylic acid ($-\text{COOH}$) group to carboxylic sodium ($-\text{COONa}$) group. Because $-\text{COOH}$ group is difficulty to be dissociated, leading to a low swelling ratio. However, $-\text{COONa}$ group is easily to be dissociated into $-\text{COO}^-$ and Na^+ . On the one hand, $-\text{COO}^-$ group shows high affinity to water. On the other hand, Na^+ can increase osmotic pressure of ions. These two factors contributed to the significantly increase of water absorbing capability of the hydrogels.

Herein, XRD pattern is used to confirm the formation of $\text{Ca}(\text{OH})_2$ in the hydration product of Ca_3SiO_5 (Fig. S1 a), while TEM image illustrates the size of $\text{Ca}(\text{OH})_2$ particles (Fig. S1 b). It is clear that the hydration product of Ca_3SiO_5 particles shows four sharp peaks at $2\theta=17.9^\circ$, 33.7° , 46.9° and 54.5° belonged to the characteristic diffraction peak of $\text{Ca}(\text{OH})_2$ particles, indicating the

existence of Ca(OH)_2 in the hydration product (Fig. S1 a) [2]. TEM image shows that Ca(OH)_2 particles have spherical morphology and regular shapes with homogeneous size (Fig. S1 b). Histogram of TEM image implies that the frequency of the size of CNS $< 5 \text{ nm}$ is about 100% (Fig. S1 c). At the same time, Ca(OH)_2 particles with size large than $3 \mu\text{m}$ (Fig. S1 d) at the same concentration were also applied to prepare hydrogel. Such as-prepared hydrogel would dissolve in water in less than 10 minutes, indicating that Ca(OH)_2 with large size cannot effectively cross-link polymer chains to obtain a stable hydrogel, because the cross-linking density (the number of particles) of the larger Ca(OH)_2 is much smaller. Size effect can be used to explain this different phenomenon. Surface area of small-sized Ca(OH)_2 particles (CNS) was larger than that of large-scaled Ca(OH)_2 particles, which was favorable for the exposure of binding sites to polymeric chains. Thereby, CNS could provide more cross-linking points to bind and tough polymeric chains under the same content of Ca(OH)_2 particles, leading to a stable hydrogel.

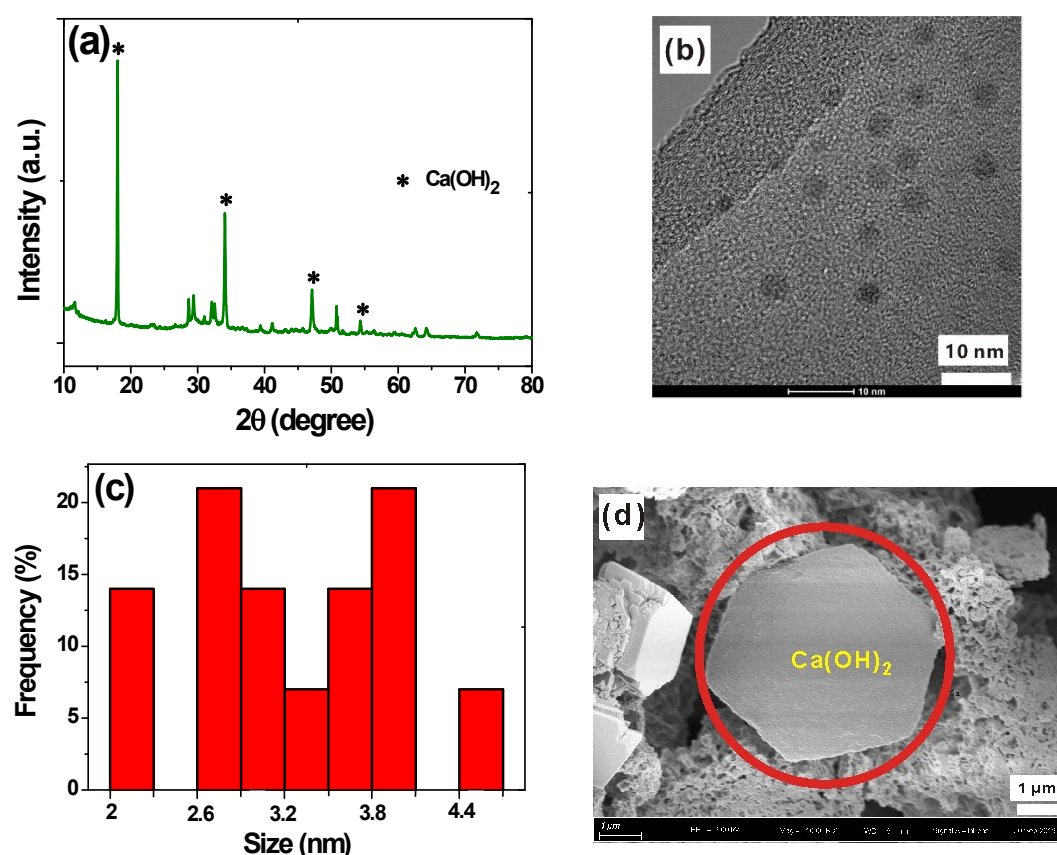


Fig. S1 (a) XRD pattern of hydration products of Ca_3SiO_5 particles; (b) TEM image of CNS released from Ca_3SiO_5 particles at 0°C ; (c) Corresponding histogram of TEM image; (d) SEM image of Ca(OH)_2 particles with size $> 3 \mu\text{m}$.

FTIR spectrum is used to determine the copolymerization of AA monomer and AMPS monomer in pure PAA/PAMPS hydrogel and villi-like PAA/PAMPS/CNS hydrogel (Fig. S2 a). It is found that the peaks of C=O , $-\text{COO}^-$ and O-H belonging to PAA polymeric chains and the peaks of C=O , C-N , N-H and S-O belonging to PAMPS polymeric chains can be found in both PAA/PAMPS gel and villi-like PAA/PAMPS/CNS gel, implying the successful copolymerization of AA monomer

and AMPS monomer [2]. However, there are no obvious peak shifts in FTIR spectra between pure PAA/PAMPS gel and cross-linked PAA/PAMPS/CNS gel, which is due to the low content of CNS. The concentration of CNS is only 200 mg/L (0.004 g), while the weight of AA/AMPS/NaOH reaches up to 9.8 g. The mass ratio of CNS versus AA/AMPS/NaOH is <0.01 wt%. Thereby, no obvious peak shifts are observed in FTIR spectra.

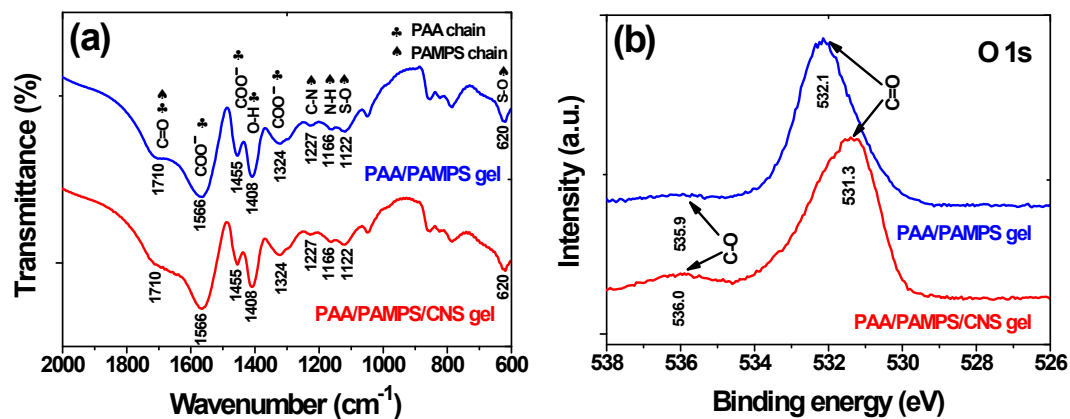


Fig. S2 (a) FTIR spectra and (b) XPS spectra of pure PAA/PAMPS gel and villi-like PAA/PAMPS/CNS gel.

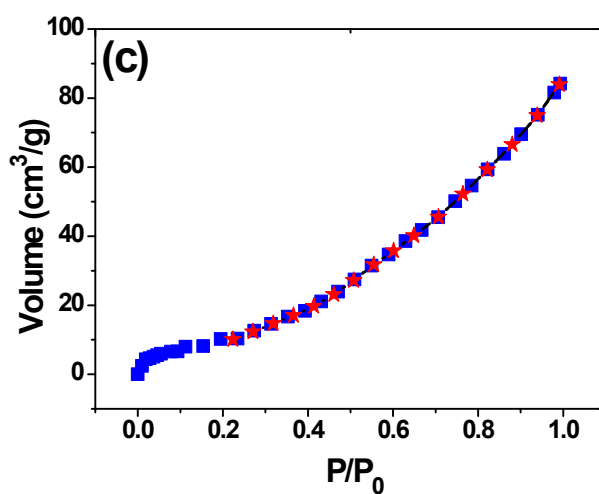
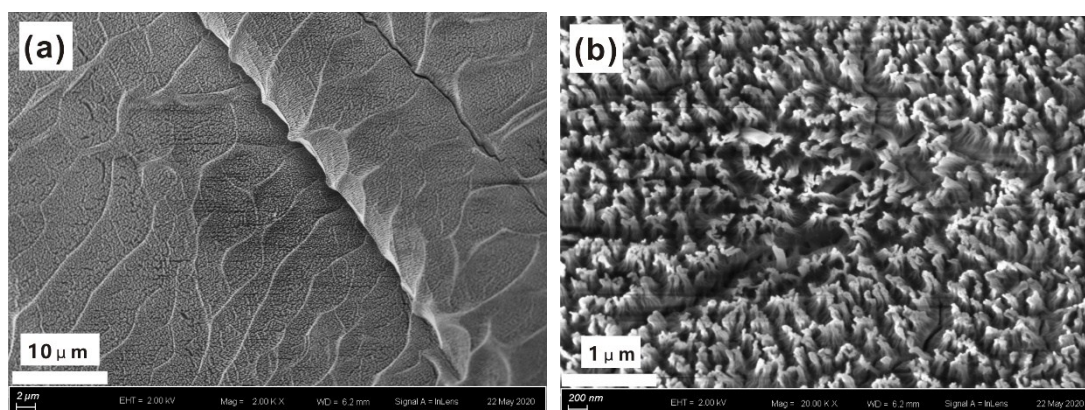


Fig. S3 (a-b) SEM images of not swollen villi-like PAMPS/PAA/CNS gel; (c) BET fitting curve of dried villi-like PAA/PAMPS/CNS gel.

To begin with, in order to confirm whether hydrogen bonding interactions between CNS and $-\text{COO}^-$ groups play a key role in the formation of firm 3D framework for this villi-like PAA/PAMPS/CNS gel, the swelling experiments of such villi-like gel in urea solution are explored (urea is an efficient hydrogen-bonds-breaking reagent) (Fig. S4 a). SR of such villi-like gel in 0.05-10 wt% urea solution is 11000-5200 g/g after swelling for 3 days. High water absorbency capacity in urea solution can be achieved, indicating that hydrogen bonds between CNS and $-\text{COO}^-$ groups should be excluded in this work. Furthermore, high water absorbing capacity in urea solution also suggests the promising application of such villi-like gel in agriculture and horticulture.

The swelling behavior of such villi-like gel in 0.9 wt% of different salt solutions at pH=7 and 298 K is also investigated, as shown in Fig. S4 b. SR of this villi-like gel in NaCl and KCl solution are 310 g/g and 380 g/g, respectively, which are obviously lower than that in pure deionized water. The decreased osmotic pressure between the hydrogel network and the external salt solution, caused by the charge-screening effect, mainly contributes to this decreased SR. The charge-screening effect of Na^+ and K^+ can reduce the anion-anion repulsions among the $-\text{COO}^-$ group through the formation of $-\text{COONa}$ and $-\text{COOK}$, resulting in a lower osmotic pressure and furthering the shrinkage of the hydrogel network. Therefore, we found that SR declines in NaCl and KCl solution. Furthermore, we also found that water absorbency in 0.9 wt% of CaCl_2 , ZnCl_2 , FeCl_2 , and CuCl_2 solutions are all lower than 10 g/g. Compared with Na^+ and K^+ , the Ca^{2+} , Zn^{2+} , Fe^{2+} , and Cu^{2+} can easily combine with $-\text{COO}^-$ to generate much stronger complex effects, leading to a dramatic shrinkage of the hydrogel network followed by a lower SR [3, 4]. High SR of such villi-like gel in 0.9 wt% NaCl solution indicates its promising application as a hygienic product. Furthermore, the reduced SR in salt solution is mainly related with osmotic pressure between the inner and the outer networks of water absorbing materials. When the osmotic pressure increases, SR will decline; When the osmotic pressure decreases, SR would rise. In the salt solution, the osmotic pressure will decline, leading to a decreased SR.

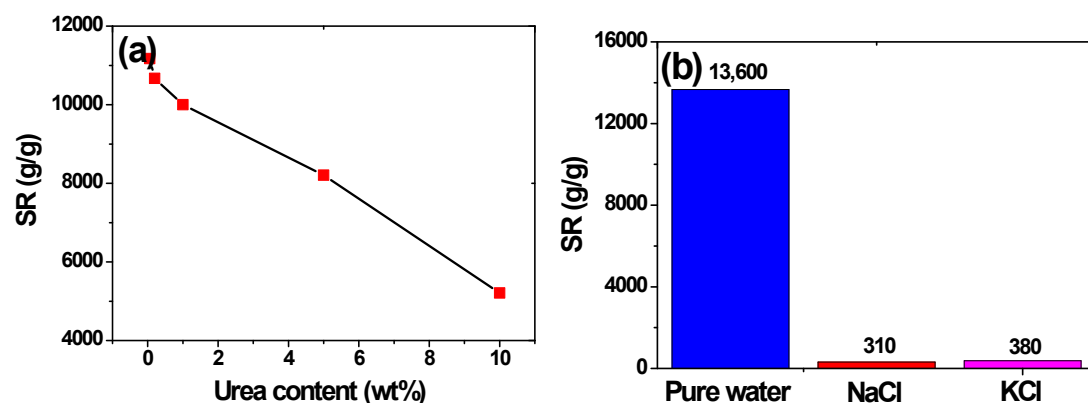


Fig. S4 Swelling capacity of villi-like PAA/PAMPS/CNS gel in (a) 0.05-10 wt% urea solution and (b) 0.9 wt% salt solutions (NaCl and KCl) at 298 K.

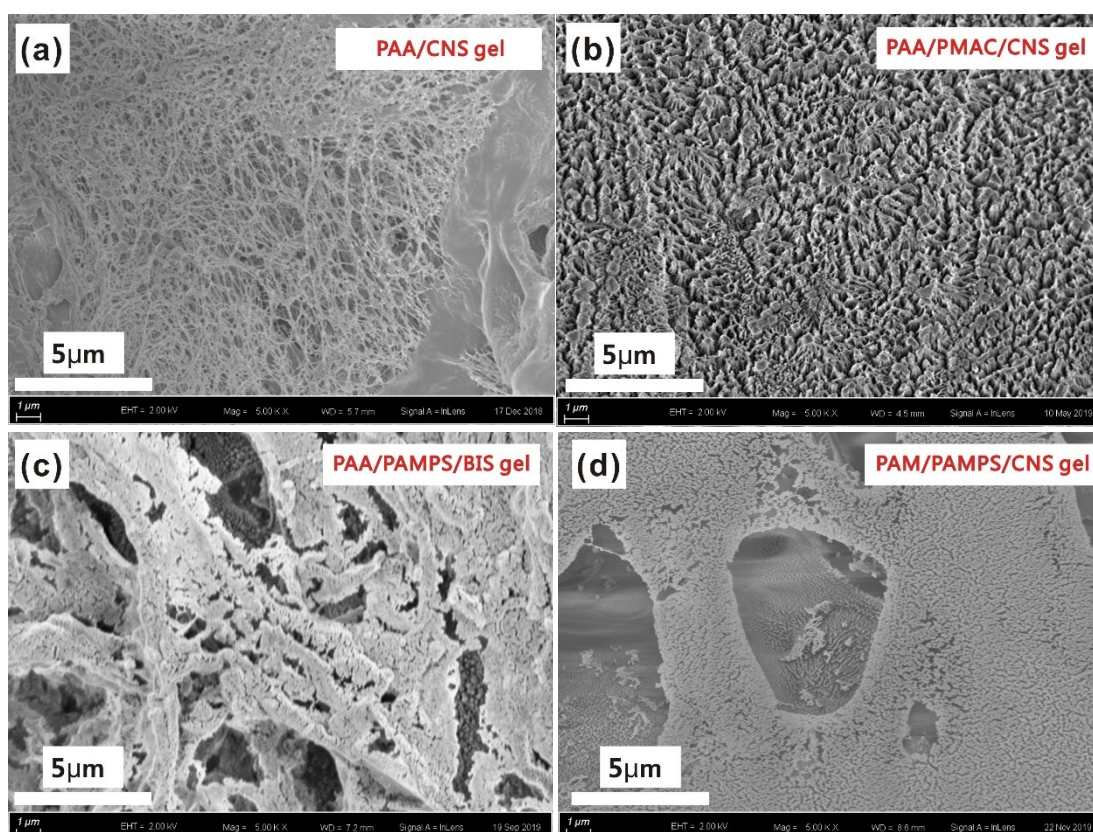


Fig. S5 SEM images of (a) mesh-like PAA/CNS gel, (b) villi-like PAA/PMAC/CNS gel, (c) porous PAA/PAMPS/BIS gel and (d) porous PAM/PAMPS/CNS gel.

Reference

- [1] J. Wu, M. Ling, L. Wei, B. Ling, High water absorbing and retaining materials [M]. Beijing (China): Chemical Industry Press, **2005**.
- [2] X. Hu, R. Liang, J. Li, Z. Liu and G. Sun, ES Mater. Manuf., **2018**, 2, 16—23.
- [3] N. Mohammad, Y. Atassi and M. Tally, Polym. Bull., **2017**, 74, 4453—4481.
- [4] M. Behrouzi and P. Moghadam, Carbohydr. Polym., **2018**, 202, 227—235.