

Electronic Supplementary Information (ESI) for:

**Reinforced conducting hydrogels prepared from in-situ polymerization of aniline
in an aqueous solution of sodium alginate**

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Fig. S1 shows FT-IR spectra of sodium alginate (SA), dedoped polyaniline (PANI) and a PANI/SA hydrogel. In the spectrum of SA (**Fig. S1a**), the peaks at 3468, 1616, 1418, and 1031 cm^{-1} are assigned to stretching vibrations of O–H, –COO^- (asymmetric), –COO^- (symmetric), and C–O–C, respectively.^[1,2] In the spectrum of dedoped PANI (**Fig. S1b**), the peaks at 1584 and 1494 cm^{-1} are assigned to C=C stretching vibrations of the quinonoid ring and benzenoid ring in the PANI, respectively. The peaks at 1308 and 1161 cm^{-1} are assigned to C–N and C=N stretching vibrations in the PANI, respectively. The peak at 829 cm^{-1} is assigned to bending vibrations of C–H (out-of-plane) in the benzene rings.^[3] In the spectrum of the PANI/SA xerogel (**Fig. S1c**), almost all characteristic peaks of SA and PANI can be found, but the wave numbers are shifted. For example, the characteristic peak of –COO^- in SA shifts to a higher wave number from 1616 to 1721 cm^{-1} ,^[1] and the intensity is decreased. The reason can be attributed to the formation of ionic bonds, namely the complex formation between the protonated amino groups ($\text{–NH}_2^+\text{–C}_6\text{H}_4\text{–}$) of PANI replacing the sodium ions of SA and SA chains. Thus, the charge density, radius and atomic weight of the cations were changed, resulting in a change of microenvironment around the –COO^- group and the consequent shifts of characteristic peaks.^[1] In addition, the characteristic peak of C=N in PANI/SA also exhibited a red shift from 1161 to 1137 cm^{-1} in comparison with dedoped PANI. It is also caused by the complex formation between PANI and SA, where C=N transforms to polarized C=N^+ .^[3] The FT-IR data confirm in-situ polymerization of An in the SA network and the complex formation between PANI and SA.

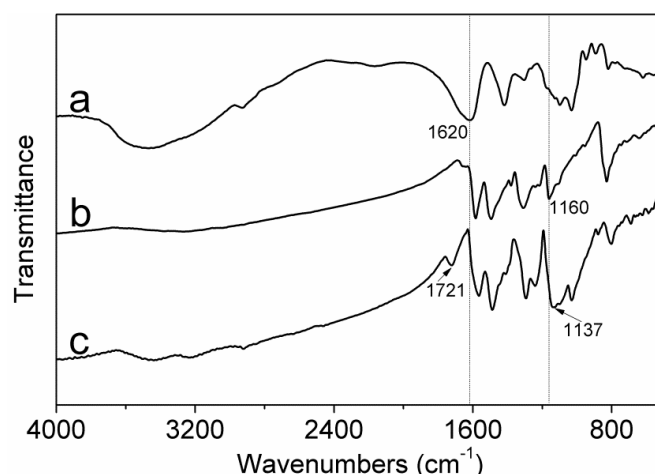


Fig. S1 FT-IR spectra of SA (a), dedoped PANI (b) and PANI/SA xerogel (c).

[Fig. S2](#) shows the UV-vis spectra of SA, PANI/SA hydrogel and PANI/SA hydrogel treated with 1 mol/L of ammonium hydroxide. The SA does not show any obvious absorption band in the range of the test wavelengths (spectrum a). In the spectrum of PANI/SA hydrogel (spectrum b), three absorption bands at 300, 425, and ~800 nm are observed. Here, the band at 300 nm can be assigned to the π - π^* transition of the benzene ring. The bands at 425 and 800 nm are assigned to the polaron band π - π^* transition and the π to the localized polaron band of doped PANI, respectively.^[2-4] When PANI/SA hydrogels were treated with ammonium hydroxide, the two bands at 425 and ~800 nm disappeared, but a new band appeared at 570 nm (spectrum c) which is a characteristic band of dedoped PANI.^[5] The inserted photographs in [Fig. S2](#) show the color changes of three samples. The aqueous solution of SA (photograph a) is the colorless. PANI/SA hydrogel is emerald, implying a doped state of PANI. The PANI/SA hydrogel treated with ammonium hydroxide is violet, implying a dedoped state of PANI. These results suggest that in-situ polymerization and doping of An has occurred in SA. The resultant PANI exists in the SA hydrogel as the form of a conducting emeraldine salt.

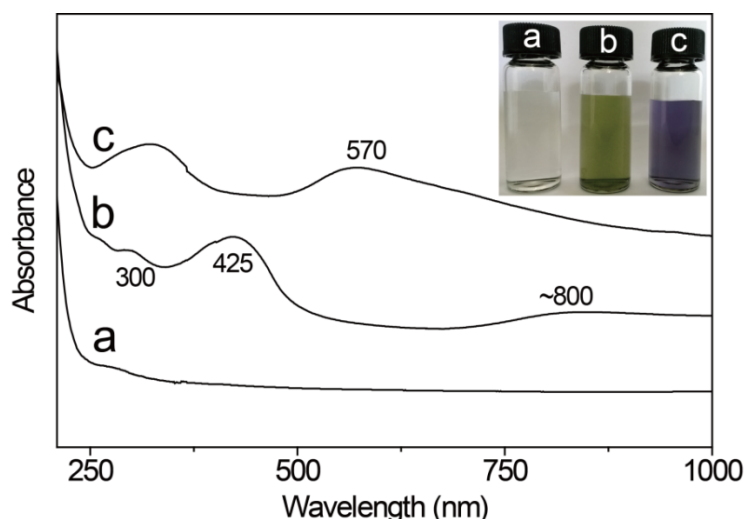


Fig. S2 UV-Vis spectra of SA aqueous solutions (curve a), PANI/SA hydrogel (curve b) and PANI/SA hydrogel treated with ammonium hydroxide. The inserted optical photographs show the color changes of three samples.

Fig. S3 shows XRD spectra of SA, PANI and PANI/SA xerogels. In the spectrum of SA (c), the peaks at $2\theta = 13.5^\circ$ and 21.4° are assigned to the typical diffraction of SA, and the peak at 31.8° is assigned to the by-product of NaCl.^[2] In the spectrum of PANI (a), the peaks at 14.7° and 25.5° are attributed to the periodicity perpendicular and parallel to the polymer chain, respectively. The peak at 20.5° is caused by the layers of the polymer chains at alternating distances.^[2] The XRD spectrum of the PANI/SA xerogel (spectrum b) is similar to that of PANI, but all characteristic peaks are broadened. The peak at 20.5° shifted to a lower position. These changes are likely a result from the intermolecular interactions between PANI and SA.

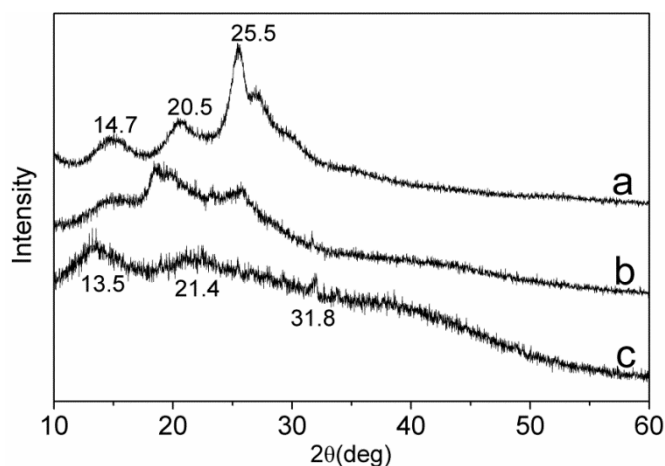


Fig. S3 X-ray diffraction patterns of PANI (a), PANI/SA xerogel (b), and SA (c).

References

- 1 Y. Yu, S. Zhihuai, S. Chen, C. Bian, W. Chen and G. Xue, *Langmuir*, 2006, **22**, 3899-3905.
- 2 Y. Li, X. Zhao, Q. Xu, Q. Zhang and D. Chen, *Langmuir*, 2011, **27**, 6458-6463.
- 3 S. Adhikari and P. Banerji, *Synthetic Met.*, 2009, **159**, 2519-2524.
- 4 T. Hino, T. Namiki and N. Kuramoto, *Synthetic Met.*, 2006, **156**, 1327-1332.
- 5 H. Fan, H. Wang, N. Zhao, X. Zhang and J. Xu, *J. Mater. Chem.*, **2012**, 22, 2774-2780.