Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

pH-Dependent and Self-Healing Properties of Mussel Modified Poly(vinyl alcohol) Hydrogels in a Metal-Free Environment

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The chemical structure of the PVA-DOPA polymer was confirmed by FTIR spectrum. Compared to PVA, a new peak at 1730 cm^{-1} appeared in FTIR of PVA-DOPA12 (as an example, Figure S1b), which assigned to the ester groups (Figure S1). Besides, peaks at 1568, 1498, 1654 and 3230 cm^{-1} belonged to C=C of the benzene groups and N-H in DOPA, respectively. These new peaks indicated the successful preparation of the PVA-DOPA polymer.

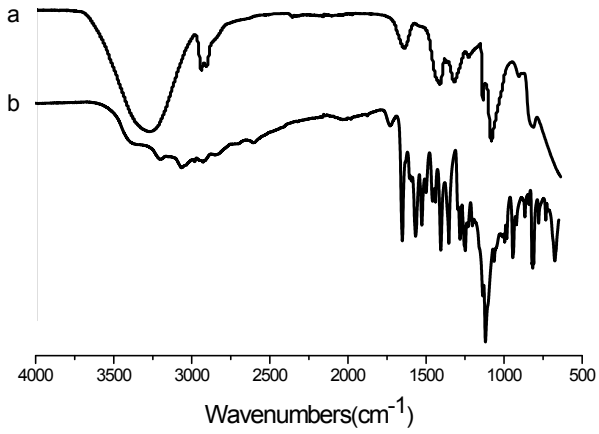

Figure S1. FTIR spectra of PVA (a) and PVA-DOPA12 (b).

DOPA had an absorption at λ_{max} = 280 nm in UV-vis spectra, as shown in Figure S2. PVA-DOPA polymer also showed the adsorption at 280 nm, indicating the successful conjugation of DOPA onto the PVA chains. The absorbance value of various PVA-DOPA polymers at 280 nm were measured, and the composition of DOPA was calculated based on the standard curve of DOPA (Table 1).

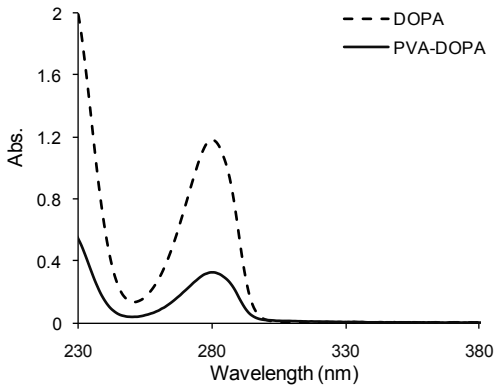

Figure S2. UV-vis spectra of DOPA and PVA-DOPA12

The hydrogel of the PVA-DOPA polymer and Fe ion was also prepared at pH 9. After adding Fe^{3+} into the PVA-DOPA polymer, a dark hydrogel was formed (Figure S3a), due to DOPA could strongly bind to Fe ions to form crosslinking-like structure. Raman spectroscopy (Inria, Co., Ltd.) is used to investigate the interaction between polymer and metal ions. Herein, resonance Raman spectroscopy was performed to detect the interaction between PVA-DOPA polymer and Fe ions, which was obtained with 532 nm excitation (Figure S3b). Peaks at 1100~1600 cm^{-1} region were arised from the catechol ring vibrations. Peaks at 550, 600, and 635 cm^{-1} assigned specifically to chelation of the metal ion by the phenolic oxygens of DOPA. The result form the Raman spectrum suggested the formation of the PVA-DOPA/Fe^{3+} hydrogels by the interaction of the Fe ions and the phenolic oxygens. The dynamic modulus of the complex hydrogel was investigated by changing frequency from 0.1~100 rad/s and fixing the strain at 1%, and the result is shown in Figure S3c. All the PVA-DOPA polymers with various compositions of DOPA (even for PVA-DOPA12) could form the hydrogels in the present of Fe^{3+}. G′ of the PVA-DOPA3/Fe^{3+} hydrogel was around 21000 Pa at 6.28 rad/s, which was higher than the

PVA-DOPA3 (~10000 Pa). For the PVA-DOPA hydrogels with other DOPA compositions, G′ was also higher than the PVA-DOPA hydrogels without Fe^{3+}. Since Fe ions could react with two or three DOPA molecules to form the network. For PVA-DOPA with the low DOPA composition, the crosslinking degree increased by introducing Fe ions, compared to the case of the free Fe ions. While for PVA-DOPA with higher DOPA composition, the intra-molecular interactions in PVA-DOPA polymer were broken by catechol-Fe^{3+} interaction, and the inter-molecular interaction increased. Therefore, the PVA-DOPA/Fe^{3+} hydrogel showed higher storage moduli to form the higher density of crosslinking bonds.

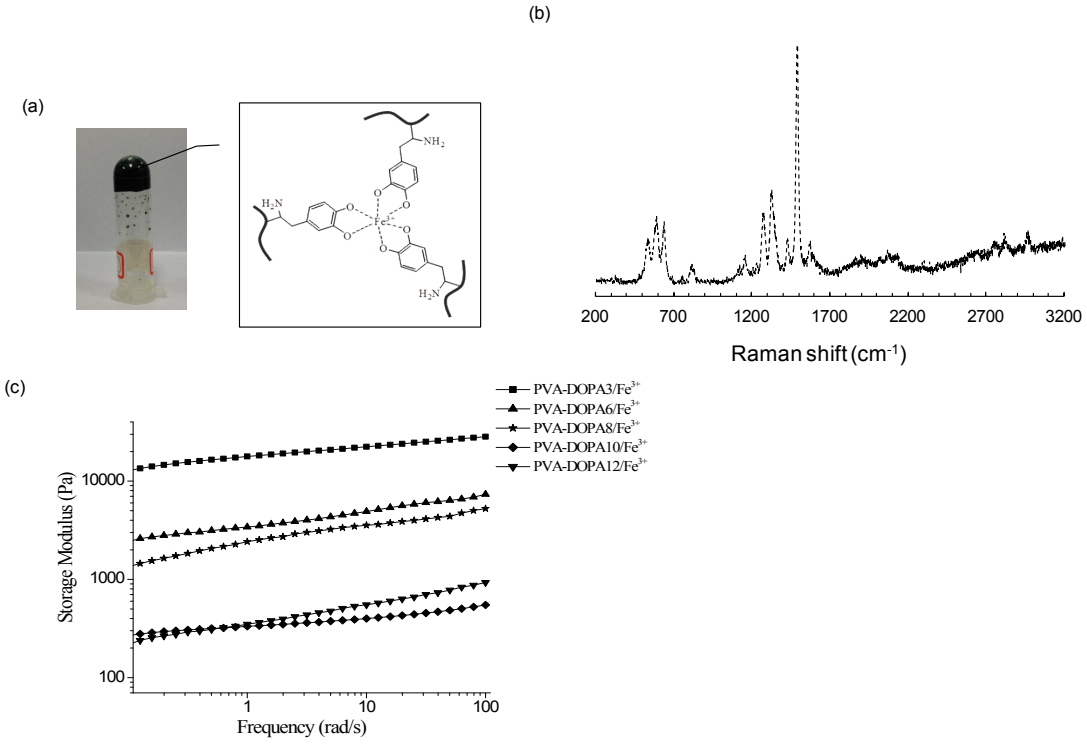

Figure S3. (a) Photo image of the PVA-DOPA/Fe^{3+} hydrogel in pH 9. (b) Resonance Raman spectrum of the PVA-DOPA3/Fe^{3+} complex hydrogel obtained with 532 nm excitation. (c) Frequency sweep of the PVA-DOPA/Fe^{3+} hydrogels in pH 9 (25 ^{o}C, strain = 1%).

The PVA-DOPA hydrogels in different pH solutions also showed the self-healing properties (Figure S4). For the PVA-DOPA hydrogel in pH 12, although the covalent bond interactions could not be healed, the hydrogen bond interactions might keep the self-healing property of the PVA-DOPA hydrogel. However, the storage moduli of the PVA-DOPA hydrogel in pH 12 decreased from 16000 Pa to 14700 Pa after self-healing for twice (Figure S4b). The seal-healing efficiency of the PVA-DOPA hydrogel in pH 12 was 92%, which was lower than other PVA-DOPA hydrogels in pH 3 and 9 (around 100%) after healing second time. This lower seal-healing property was possibly due to the existing less dynamically hydrogen bond interactions in the PVA-DOPA hydrogel in pH 12.

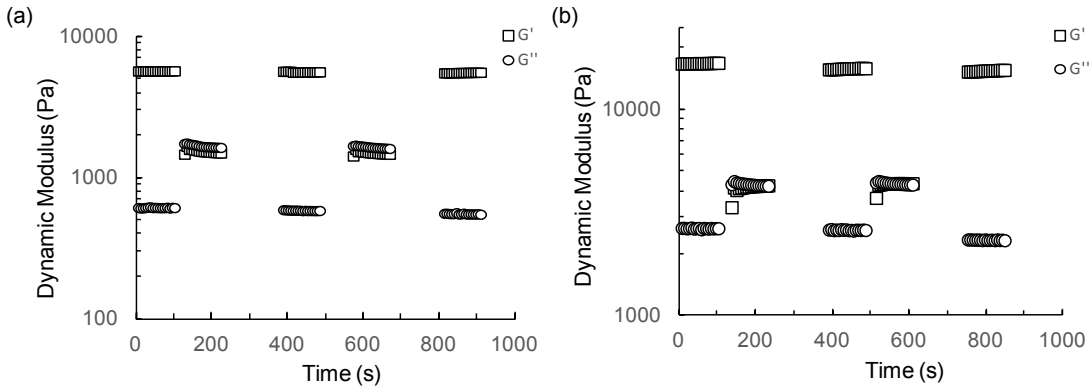

Figure S4. Storage moduli G′ and loss moduli G″ of the PVA-DOPA3 hydrogel in pH 3 (a) and pH 12 (b) from continuous strain sweep with alternate small oscillation force at 1% of strain and at 100% of strain.