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.

![FTIR spectra of PVA (a) and PVA-DOPA12 (b).](image)

DOPA had an absorption at $\lambda_{\text{max}} = 280$ 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).
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 \( \text{Fe}^{3+} \). 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-\( \text{Fe}^{3+} \) interaction, and the inter-molecular interaction increased. Therefore, the PVA-DOPA/\( \text{Fe}^{3+} \) hydrogel showed higher storage moduli to form the higher density of crosslinking bonds.

![Figure S3](image)

**Figure S3.** (a) Photo image of the PVA-DOPA/\( \text{Fe}^{3+} \) hydrogel in pH 9. (b) Resonance Raman spectrum of the PVA-DOPA3/\( \text{Fe}^{3+} \) complex hydrogel obtained with 532 nm excitation. (c) Frequency sweep of the PVA-DOPA/\( \text{Fe}^{3+} \) hydrogels in pH 9 (25 °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.