# Methods and materials

**2.1 Chemicals and reagents**

Polyvinyl alcohol (PVA124) (average degree of polymerization=2400, 99% hydrolyzed) and tannic acid (TA) were obtained from Aladdin. 1,1-diphenyl-2-picrylhydrazyl (DPPH) was purchased from AlfaAesar. Anhydrous methanol (AR) was purchased from Sinopac Chemical Reagent Co., LTD. Deionized water was obtained from a Milli-Q system (Merck Millipore, USA) in our lab.

**2.2 Preparation of PVA124-TA hydrogels**

PVA124-TA hydrogels were prepared by freezing-thawing cycle according to the reported procedure (Hong, K. H., 2017). Briefly, 2.0 g PVA124was fully swelled in 20ml deionized water. The fully swollen PVA124 was stirred in an oil bath at 95℃ for 2 h. Finally, a clear and transparent hydrogel precursor fluid was formed. TA (0%, 0.625%, 1.25% and 2.5%, respectively) was added into the hydrogel precursor fluid and stirred for 3 h. The obtained precursor fluid of hydrogel was ultrasonicated for 15 min to remove the bubbles. Proper amounts of the precursor fluid of hydrogel were poured in a mold, followed by freezing at -20℃ for 18 h and thawing at room temperature for 6 h for different freeze-thaw cycles (Once, twice and three times).

**2.3 Determination of antioxidant activity of the PVA124-TA hydrogels.**

The antioxidant activity of the hydrogels was determined by DPPH free radicals using a previously reported method (Hong, K. H., 2017). DPPH is a very stable nitrogen-centered free radical whose stability is mainly due to the co-yoke effect of the three benzene rings and the space barrier, which prevents the unpaired electrons of the nitrogen atoms trapped in the middle from exerting their proper electron pairing. Therefore, adding DPPH to observe whether the rate of a certain chemical reaction slows down as an indicator of the radical nature of that reaction. Briefly, 50 mg of lyophilized hydrogel was immersed in a container containing 3 ml 0.15 mM MMDPPH/methanol solution. The solution was left in the dark for 1 h and then the absorbance at 517 nm was determined by UV-Vis spectrophotometer. The following formula is used to calculate the scavenging activity of DPPH:

DPPH scavenging rate (%) = (C-S) /C×100

In the equation, S and C are the absorbance of the sample and the reference, respectively.

**2.4 Determination of mechanical properties of the PVA124-TA hydrogels.**

Tensile test: Dumbbell hydrogels with the size of 50 mm×15 mm (inner length of 30 mm×3 mm) and thickness of 2 mm were prepared by a mold. HP-200 Edberg digital push-pull tension meter was used for tensile test. The fracture tensile rate is calculated by the following formula:

Fracture tensile rate (%) = (L-L0) /L0×100

In the equation, L is the tensile length and L0 is the initial length of hydrogel.

The tensile stress is calculated by the following formula:

Tensile stress =F/ AB

In the equation, F is the maximum force generated during stretching, A is the tensile thickness of hydrogel, and B is the tensile width of hydrogel.