Thermal and water dual-responsive shape memory poly(vinyl alcohol)/Al_2O_3 nanocomposite

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Experimental

Materials:

Polyvinyl alcohol (PVA) was obtained from Kermel Chemical reagent plant (Tianjin, China). Average degree of polymerization of PVA was 1700 with 98.5%-100% hydrolyzed and used as received. Colloidal alumina sols (size=5~20 nm in diameter; 17 wt% ($W_{Al_2O_3}/W_{H_2O}$); Hangzhou Wanjing Co. China) was used as received without further purification. The water needed in all experiments was purified by a Millipore Direct-Q purification system.

Synthesis of PVA -Al_2O_3 nanocomposites

PVA and PVA–A films were prepared by freezing and thawing technique. In a typical experiment, the aqueous solution (8 wt%) was prepared by dissolving PVA in deionized water at 95 °C for at least 3 hours. After cooled to room temperature overnight, the solution was injected into a customized Teflon model. The sample on vessel was kept in the sealed vial and then frozen at -20 °C for 24 h and thawed at 25 °C for 3 h. Then it was dried for 72 h at room temperature (25 °C) in air with the humidity at 40%. All the sealed samples were kept in the refrigerator.

Characterization

The TEM image of Al_2O_3 NPs was took by a Tecnai G20 (FEI) at an acceleration voltage of 80 kV. FT-IR spectra were performed with a Nicolet 6700 instrument (Thermal Scientific, USA) by the KBr method in the range 500–4000 cm^{-1}. The thermal characteristics of pristine PVA and nanocomposite films were determined by TGA and DSC. The thermo-gravimetric analysis was carried out using a TG-DTA

6200 LAB SYS analyzer under Nitrogen, at a flow rate 200 ml min^{-1}.The heating rate in both cases was 10 °C min^{-1}. DSC measurements of pristine PVA films and PVA–Al_2O_3 nanocomposite films were performed on a Seiko instrument (DSC 6200) in the temperature range -10–240 °C. The heating rate was 10 °C min^{-1}. The wide-angle X-ray diffraction (WXRD) pattern of the samples was obtained on a Rigaku D25 X-ray diffractometer with Cu-Kα radiation (λ=1.5406Å). Mechanical properties were investigated using an ASG-J electronic universal testing machine (Shimadzu Co., Japan) in an atmosphere of 40% relative humidity with a strain rate of 100 mm/min (as per ASTM D882-12). Swelling measurement was carried out by immersing samples with the size of 40mm×3mm×0.1mm in a large excess of water at a temperature of 25 °C, and the weight of the samples were measured at specific times after removing excess water from the surface. The swelling ratio (SR) was defined as: SR = (swollen mass/initial mass).

Shape memory behavior

Shape memory behaviors were conducted on PVA-3, PVA-A10-1, PVA-A10-3 and PVA-A10-5 nanocomposites. Straight and circle specimen (original shapes) were firstly transformed into spiral and straight ones respectively at 90 °C, when cooled down to room temperature, the samples maintain the deformation under the external force. Lastly, the treated samples were immersed into water at room temperature or placed in the oven at the temperature of 90 °C. The transformation of shape and the change of the angle with time were recorded. The shape fixity ratio (R_f) and shape recovery ratio (R_r) was defined as $R_f = (360° - \theta_t)/360°$, $R_r = (\theta_f - \theta_t)/(180° - \theta_t)$, where θ_t is the temporarily fixed angle and θ_f is the change of the angle.

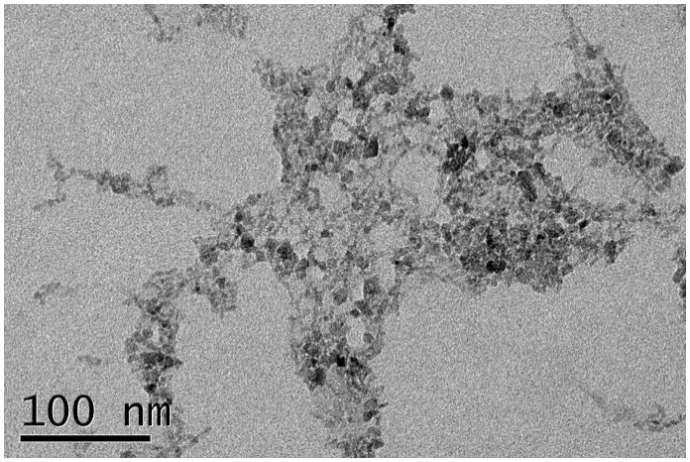

Fig.S1 TEM image of the Al_2O_3 NPs.

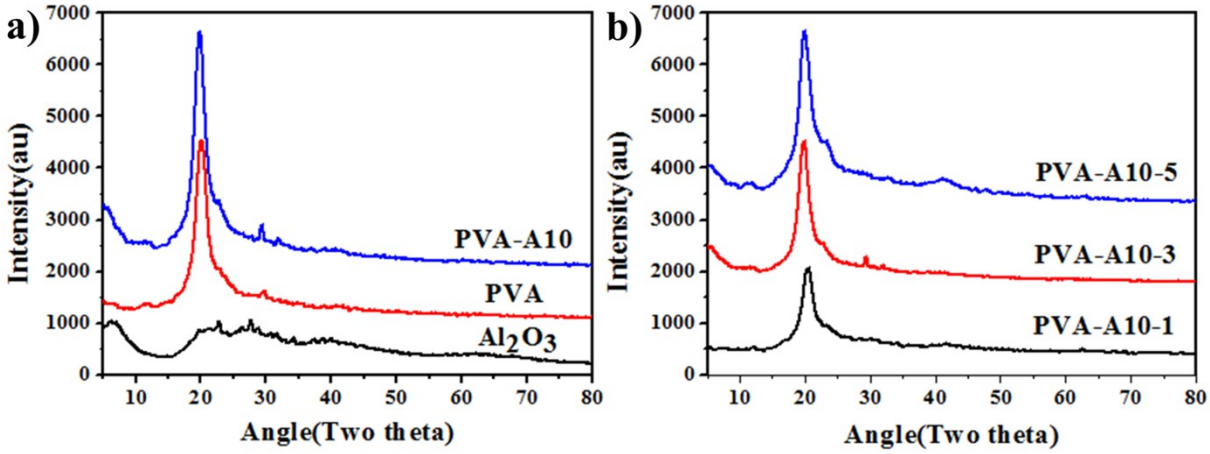

Fig.S2 XRD patterns of a) Al_2O_3 NPs, pristine PVA and PVA-A10 and b) PVA-A10 with different freezing/thawing cycle number.

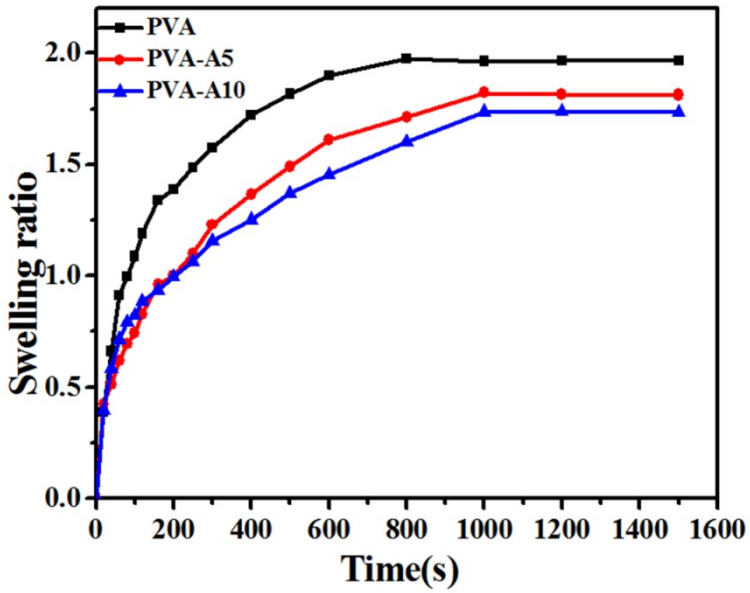

Fig.S3 Swelling behaviors of PVA, PVA-A5 and PVA-A10 samples.

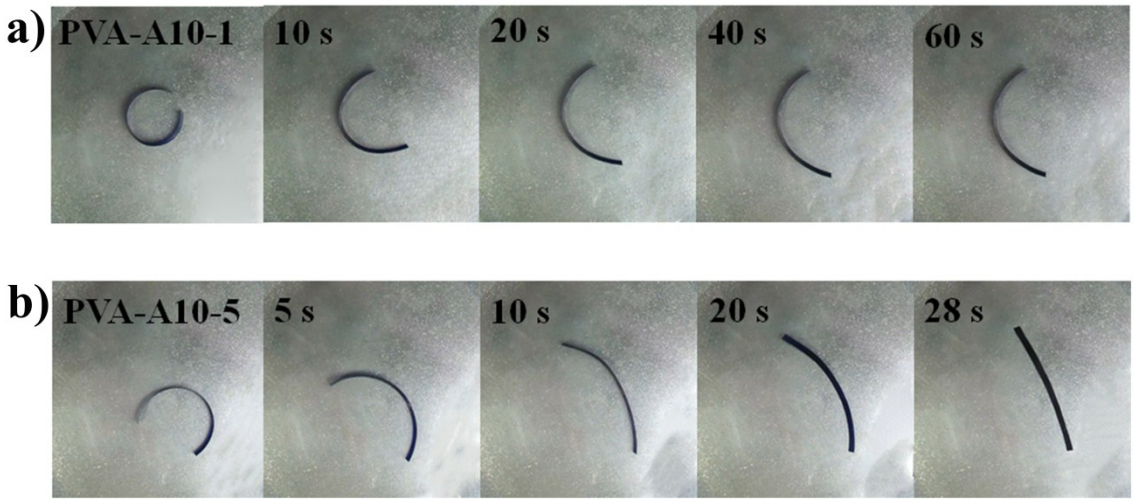

Fig.S4 Shape memory effect of temperature-induced PVA-A10 samples (bent into cycle shape) with different freezing/thawing cycle number. Permanent shape is straight shape.

Table S1. Shape fixity ratio and shape recovery ratio of temperature-activated PVA and PVA-A10 with different freezing/thawing cycle number.

Sample	Shape fixity ratio (%)	Shape recovery ratio (%)
PVA	94.4	47.5
PVA-A10-1	94.2	50.9
PVA-A10-3	91.9	94.7
PVA-A10-5	69.4	96.0

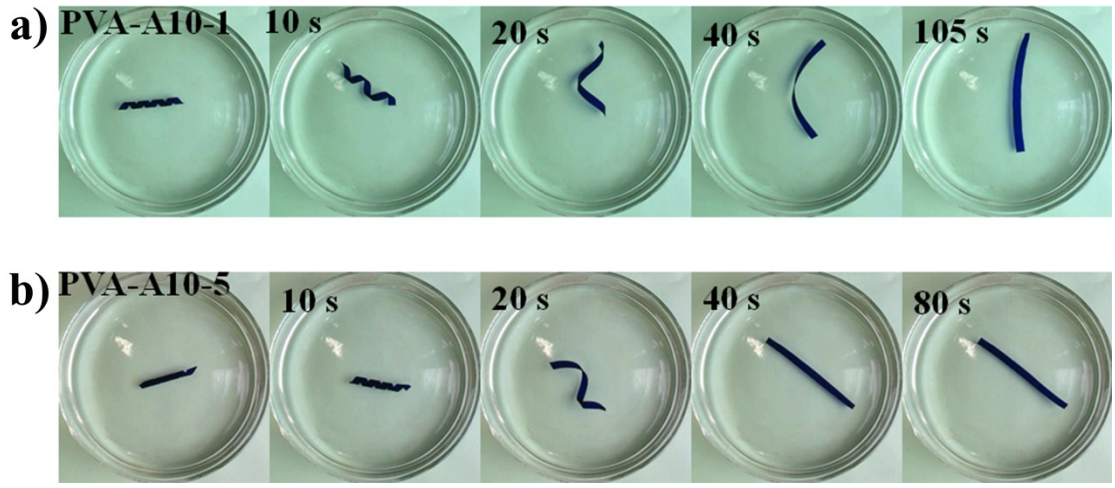

Fig.S5 Shape memory effect of PVA-A10 samples (bent into spiral shape) with

different freezing/thawing cycle number in water. Permanent shape is straight shape.

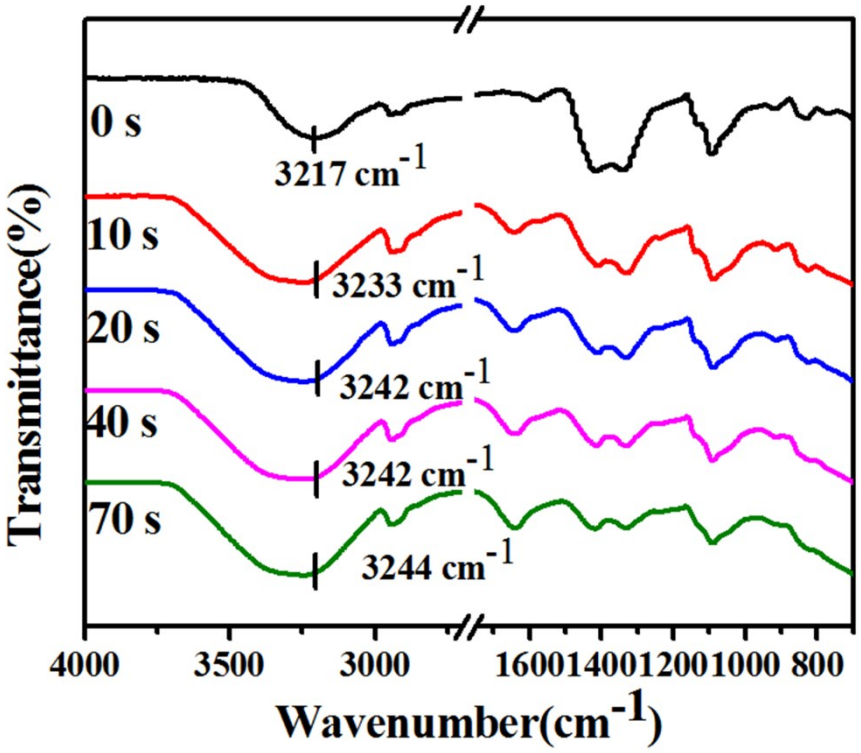

Fig.S6 FTIR spectra of PVA-A10 with different immersion time.

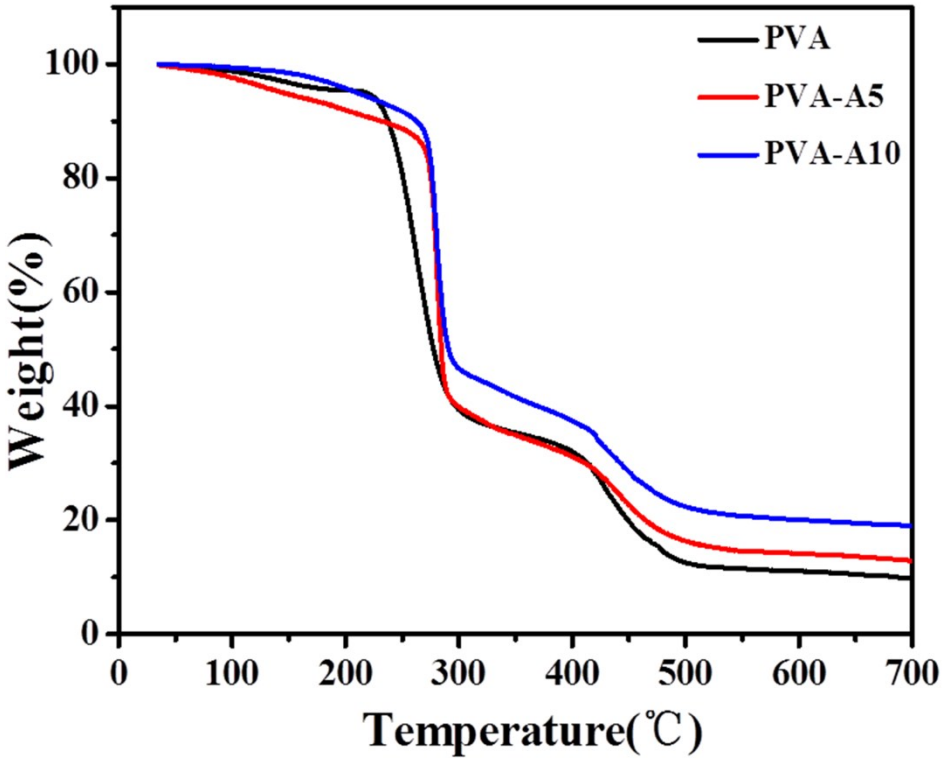

Fig.S7 TGA curves of pure PVA, PVA-A5 and PVA-A10 specimen obtained under nitrogen atmosphere and at a heating rate of 10 °C min^{-1}.