Supporting Information for

A multi-responsive shape memory hydrogel with triple shape memory effect based on reversible switches

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Materials and Instruments: Chitosan (deacetylation: 80%~95%, viscosity: 50~800mPa.s), Dextran(M_w=40000), acrylamide (AAm), sodium m-periodate, acetic acid, sulfuric acid (H_2SO4), oxalic acid dehydrate, boric acid, sodium acetate trihydrate, potassium chloride, potassium bromide were obtained from Sinopharm Chemical Reagent Co., Ltd.Ammonium persulfate (APS), *N,N′*-Methylene bis(acrylamide) (Bis), sodium tetraborate, ethylenediaminetetraacetic acid disodium salt (EDTA·2Na), silver nitrate, nickel(II) acetate tetrahydrate, cobalt(II) acetate tetrahydrate, iron chloride hexahydrate, zinc nitrate hexahydrate, vitamin B6 hydrochloride, D-alanine, tert-butyl carbazate rhodamine B(red dye), methyl violet (purple dye), tartrazine (yellow dye) and erioglaucine disodium salt(blue dye) were purchased from Aladdin. APS and AAm were used after recrystallization, and the other chemicals were used without further purification. ^{1}H NMR spectra were recorded on a Bruker Advance AMX-400 spectrometer.

Preparation of oxidized dextran (Odex):[1] The oxidized dextran was prepared according to previous reports. The aqueous solution of dextran was prepared by dissolve 5 g dextran in 200 mL deionized water, then 4 g $NaIO_4$ (dissolved in 100 mL water) was dropwise added to the solution of dextran, protected with the N_2 atmosphere, shielded from light, with stirring at room temperature for 24 h. Then, the equal stoichiometric ratio of glycol was added to quench the unreacted $NaIO_4$ for 12 h. The resulting solution was dialyze for 3 days against deionized water (M_w cut off=3500Da). The pure oxidized dextran was obtained by reduced pressure distillation. The degree of the oxidation was determined by quantifying the aldehyde groups react with tert-butylcarbazate (tBC) via carbazone formation. The content of aldehyde groups was determined to be 30% by ^{1}H NMR spectrum.

Preparation of the hydrogel: The oxidized dextran (Odex) solution was obtained by dissolving 100 mg of Odex in 1 mL deionized water. The chitosan (CS) solution 4% (w/v) was prepared by dissolving certain amount of chitosan in acetic acid 2.1% (w/v) aqueous solution and stirred for about 8 h. Typical CS-Odex/AAm hydrogel was prepared by thoroughly mixing the Odex aqueous solution, CS aqueous solution, AAm, Bis (crosslinker) and APS (initiator) with deionized water. After heating at 60 ^{o}C for about 3 h, the mixture was polymerized.

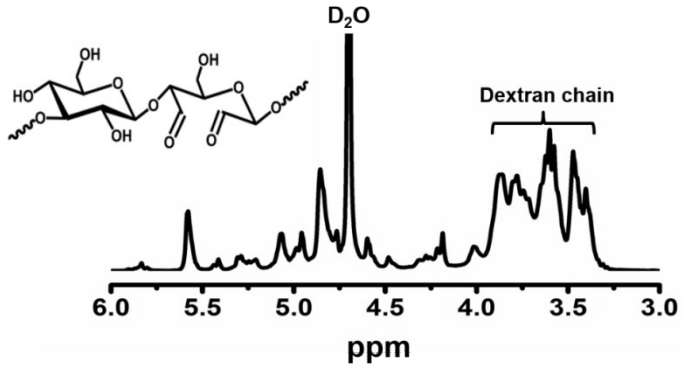

Figure S1. ^{1}H NMR spectrum of the oxidized dextran (Odex) in D_2O.

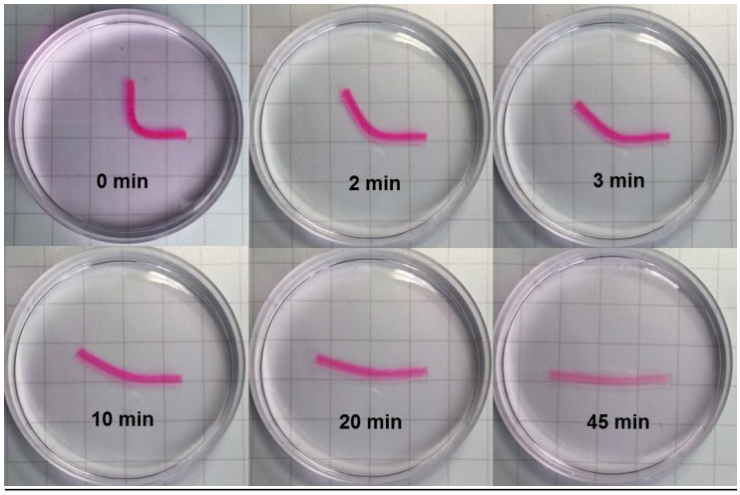

Figure S2: The recovery procedure of the PAAm/CS-Odex hydrogel in buffered solution (pH=3, 0.1 M HCl-$C_6H_8O_7$-NaOH).

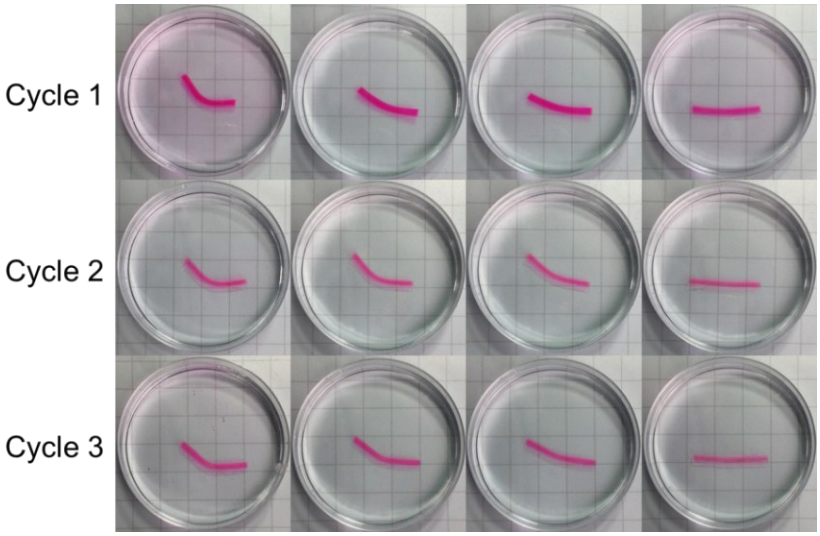

Figure S3: Cycled shape memory behavior of the PAAm/CS-Odex hydrogel *via* dynamic Schiff base bonds. Buffered solution (pH=10) and buffered solution (pH=3) were used for shape memory and shape recovery procedures, respectively.

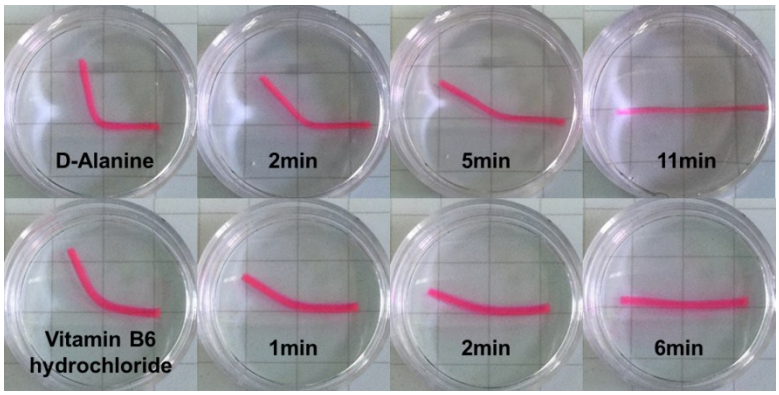

Figure S4: The recovery procedure of the PAAm/CS-Odex hydrogel in D-Alanine (0.1 M) and Vitamin B6 hydrochloride (0.1 M).

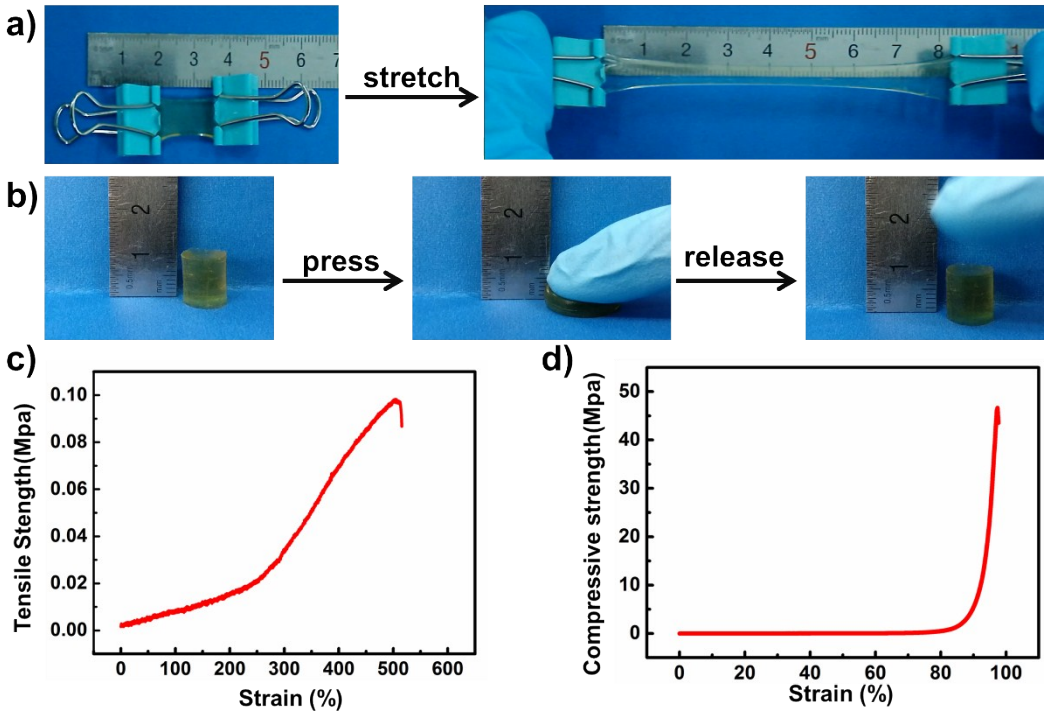

Figure S5. Images showing the tensile a) and compression b) properties of the developed hydrogels; c) tensile test measured at an extension rate of 50 mm/min and a temperature of 25°C; d) compression test measured at a compression rate of 10% original height/min and final compressive strain is 98%.

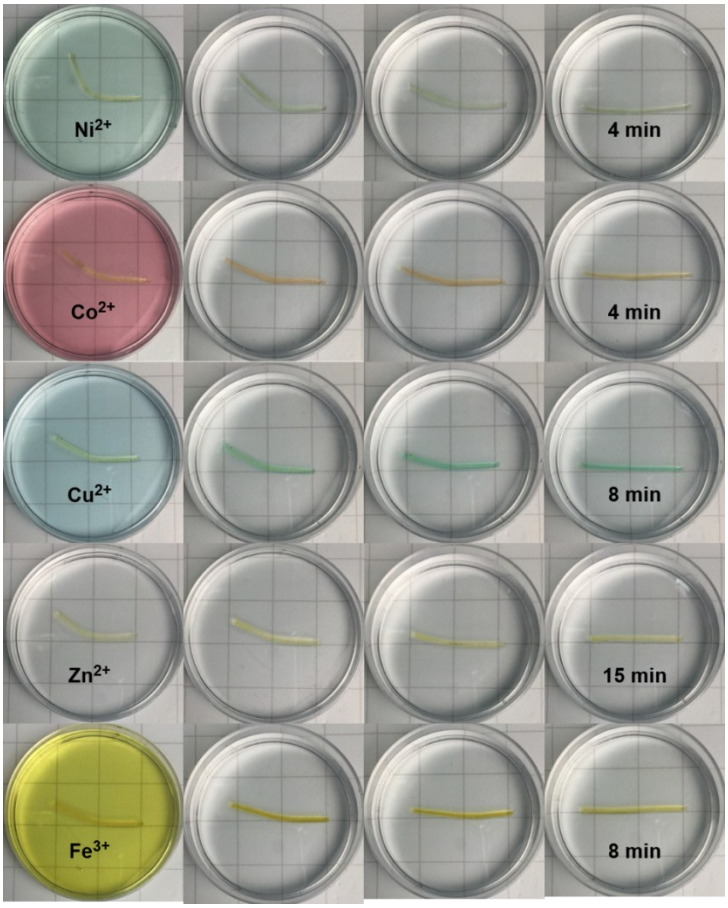

Figure S6: The shape recovery procedures of the PAAm/CS-Odex-M^{n+} hydrogel in aqueous solutions of EDTA (0.1 M).

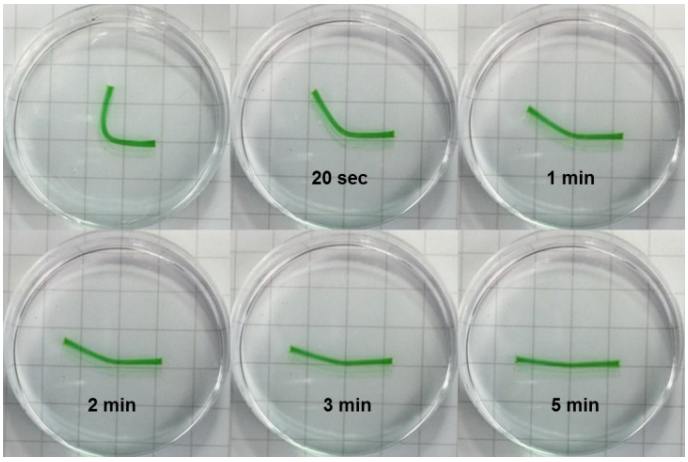

Figure S7: Time-dependent recovery procedure of the PAAm/CS-Odex-Ag^{+} hydrogel in aqueous solutions of EDTA (0.1 M).

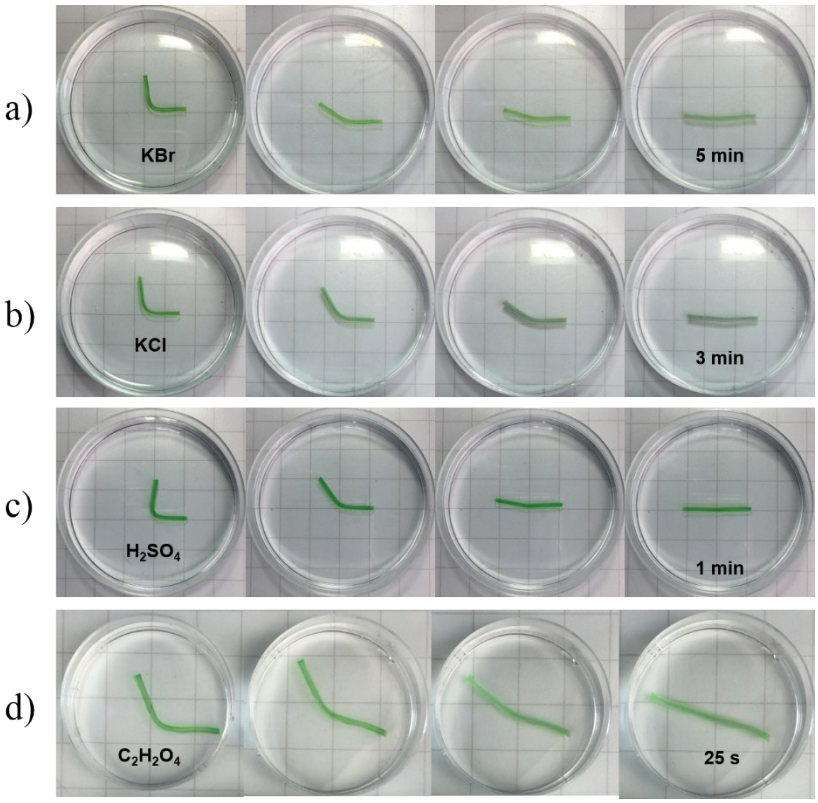

Figure S8. The shape recovery procedures of the PAAm/CS-Odex-Ag^+ hydrogel triggered by various stimuli: a) 0.1 M KBr, b) 0.1 M KCl, c) 0.1 M H_2SO_4 and d) 0.1 M $C_2H_2O_4$.

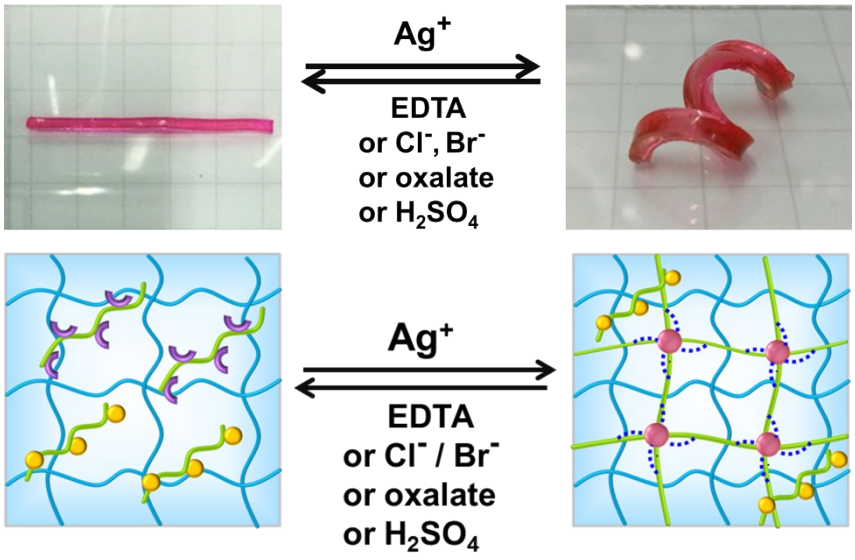

Figure S9. The shape memory behavior based on the coordination of CS with Ag^+ (up) and schematic illustration of the multi-responsive shape memory mechanism of the PAAm/CS-Odex-Ag^+ hydrogel triggered by various stimuli (bottom).

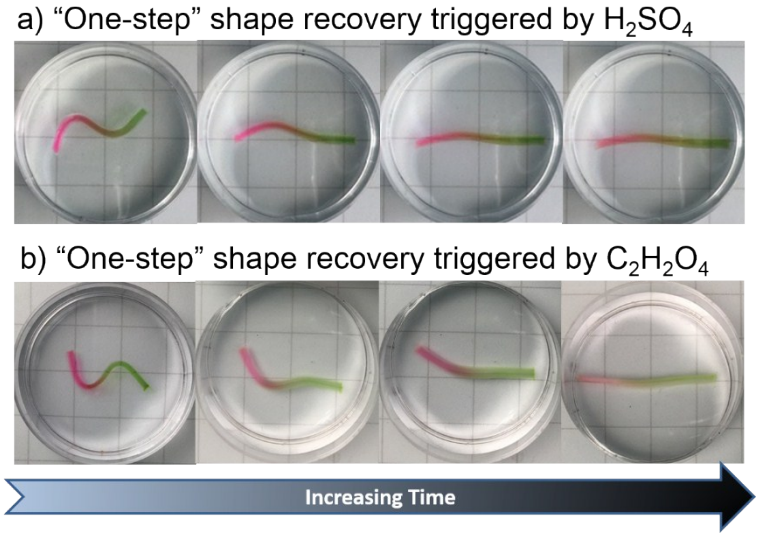

Figure S10. The “one-step” shape recovery procedures of the triple-shape memory hydrogel in H_2SO_4 (0.1 M) or $C_2H_2O_4$ (0.1 M).

Supplementary Movie S1

Movie S1 showed the tensile test of the developed hydrogel.

Movie S2 showed the compression test of the developed hydrogel.

Movie S3 showed the shape recovery produce of the hydrogel in $C_2H_2O_4$ (0.1 M).

Reference

1. J. Maia, L. Ferreira, R. Carvalho, M. A. Ramos, M. H. Gil, *Polymer,* 2005, **46**, 9604–9614.