Electronic Supplementary Information

Dual Response Thermosensitive Microcapsules Based on Hydrogel

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Contents

1 Experimental Details

1.1 Materials

Methyl acrylate (MA) (99%, stabilized with 4-Methoxyphenol), methyl methacrylate (MMA) (99.8%, stabilized with 6-tert-Butyl-2,4-xylenol), azobisisobutyronitrile (98.0%), and formaldehyde solution (37%, stabilized with Methanol) were purchased from TCI. Dodecanol (99%), bisphenol A (98%), acrylonitrile (AN) (99%), tween-80 (99%), ethanolabsolute (99.5%), alginic acid sodium (ALG) (AR), calcium chloride anhydeous ($CaCl_2$) (96%) and chitosan (CS) (99%, <200 mPa*s) were purchased from Innochem Co., Ltd (Beijing, China). N-Hexane (98.0%), sodium dodecyl sulfate (SDS) (99%), 1,4-butanedicl dimethacrylate (95%), triethanolamine (99%), magnesium chloride hexahydrate (99%), sodium hydroxide (99%), sodium chloride (99.5%), acetate (95%) were purchased from Aladdin Chemical Reagent Company. Crystal violet lactone (CVL) (21%) were purchased from Ark pharm. Sodium nitrite (98%) was provided by Alfa Aesar Reagent Co., Ltd. Deionized water (18.2 MΩ/cm) was purified using a Milli-Q system. (Millipore, Billerica, MA, USA).

Unless otherwise noted, the chemicals and reagents used in this study were of analytical grade.

1.2 Preparation of Thermal Expansion Microcapsules

The preparation of thermal expansion microcapsules (TEMs) was adopted by original polymerization method. Magnesium chloride solution (12 wt%) was poured into a three-necked containing sodium hydroxide solution (5 wt%) slowly. Under the action of surfactant SDS (0.01 wt%), it reacted and dispersed into a stable nano magnesium hydroxide suspension.To the above suspension, sodium nitrite (0.02 wt%), sodium chloride (1 wt%) and anhydrous ethanol (0.5 wt%) were sequentially added and stirred to be used as an aqueous phase (continuous phase).

The shell material selected AN, MMA and MA as raw materials, the ratio was 7:2:1wt, and used azobisisobutyronitrile (0.43 wt%) as initiator, 1,4-butanedimethacrylate diol (0.04 wt%) as a cross-linking agent to polymerize and cross-link the monomer on the surface of the core droplet to form a stable shell material.

The oil phase (dispersed phase) was obtained by mixing above shell material and N-hexane (foaming agent). Droped the oil phase into the water phase, stirred at 600 rpm for 1 h and fully emulsify, adjusted the temperature of the water bath to 65 °C, reacted for 8 h, filtered and washed after the reaction, and finally dried at 50 °C to obtain the thermal expansion microcapsules (TEMs).

1.3 Preparation of Thermochromic Ternary Complex

In this experiment, CVL, bisphenol A and the dodecanol were stirred at a ratio of 1:4:70wt in a water bath at 90 °C for 2 h. After cooling, thermochromic materials (TcMs) were obtained at 25 °C for colourless.

1.4 Preparation of Thermosensitive Microcapsules

First, in a water bath around 40 °C, the1.4 wt% of thermochromic materials, 5 wt% of deionized water and 0.01 wt% of SDS were mixed uniformly in beaker and sheared and

emulsified for 10 min by a high-speed shear at 6000 rpm to form a stable emulsion. Above stable emulsion, ALG and TEMs (5:1:1wt) were fully stirred and mixed, and the mixture was pumped to a pinhole with an inner diameter of 0.16 cm at a flow rate of 0.02 mL/min using a peristaltic pump, and sprayed and dropped into $CaCl_2$ solution (10 wt%) under the action of 9 kV high-voltage electric field to solidify, filtered, washed and dried at room temperature to obtain thermosensitive microcapsules.

1.5 Surface Modification of Thermosensitive Microcapsules

First, took urea, formaldehyde solution and deionized water (1:2:5wt) in a three-necked flask. After fully stirring, adjusted the pH to 8-9 with triethanolamine and reacted in a water bath at 70 °C for 30 min. After cooling urea-formaldehyde prepolymer solution was obtained. The thermosensitive microcapsules were transferred to a three-necked flask, and then added with ionized water, chitosan solution and urea-formaldehyde resin prepolymer to adjust pH to 4.5 with glacial acetic acid Then stirring (200 rpm) at 60 ℃ for 3 hours. Finally, after filtering, washing and drying at room temperature, the modified thermosensitive microcapsules (TSMs) are obtained.

1.6 Characterization

1) Scanning Electron Microscope

Thermosensitive microcapsules (TSMs) and thermal expansion microcapsules (TEMs) were prepared respectively. After drying at room temperature, some of the four microcapsules were placed in an oven at 90 ℃ to expand. Scanning electron microscope (SU8020, Hitachi, Japan) was used to observe the morphology and cross section of different microspheres before and after thermal expansion, and the corresponding SEM morphology was obtained.

2) Optical Microscope

Optical microscope (DM2700M, Leica, Gremany) was used to observe the colour morphology of TSMs at different temperatures, including before and after expansion and reversible discoloration process.

3) Molecular Weight Test of Thermosensitive Microcapsules

The weight-average molecular weight, number-average molecular weight and dispersion index of microcapsules were measured by gel permeation chromatography (GPC1525, Waters, USA).

4) Fluorescence Phenomenon of Thermosensitive Microcapsules

The fluorescence phenomenon of microcapsules under the action of ultraviolet at 359-371nm was measured by fluorescence microscope (Olympus BX51, ZEISS, Gremany).

5) Chemical Composition Analysis of Thermosensitive Microcapsules

TSMs, TEMs, TcMs, CS, ALG, UF were ground with potassium bromide powder to prepare potassium bromide thin samples. Fourier transform infrared spectrometer (NICOLET IS10, Thermo Fisher Scientific Company) is used to analyse the chemical composition of microcapsules, core materials, wall materials, etc. The spectral scanning range is 4000 cm^{-1} to 400 cm^{-1}. In order to reduce the error, the spectra without samples were collected under the same conditions. The chemical elements and the composition

of chemical bonds of the microcapsules were measured by X-ray photoelectron spectroscopy (Thermo escalab 250XI, USA).

6) Particle Size Analysis

The particle size distribution before and after microcapsule expansion was analysed by Laser Particle Sizer (Mastersizer 2000, Malvern, UK).

7) Thermal Stability Analysis of Thermosensitive Microcapsules

The microcapsules were thermally analyzed using a differential scanning calorimeter (DSC214, Netzsch technology, Germany) and a thermogravimetric analyser (TG209F3, Netzsch technology, Germany).

8) Thermal Expansion Curve Test of Thermosensitive Microcapsules

Take about 0.05 g microcapsules respectively and put them into a clean alumina crucible for compaction. The height of the sample is about 0.5 mm. Put the crucible into the thermal expansion analyser and set the parameters. Raise the temperature from 25 ℃ to 200 ℃ at a constant rate of 7 ℃/min according to the program. Measure the expansion curves of several thermosensitive microcapsules. The thermal expansion ratio of microcapsules can be obtained by analysing the curves.

9) CIE1931 Colour Coordinates

X-Rite (DTP22, USA) was used to test the colour coordinates and colour wavelengths of TEMs and TcMs before and after discoloration and expansion.

2. Structure and Composition

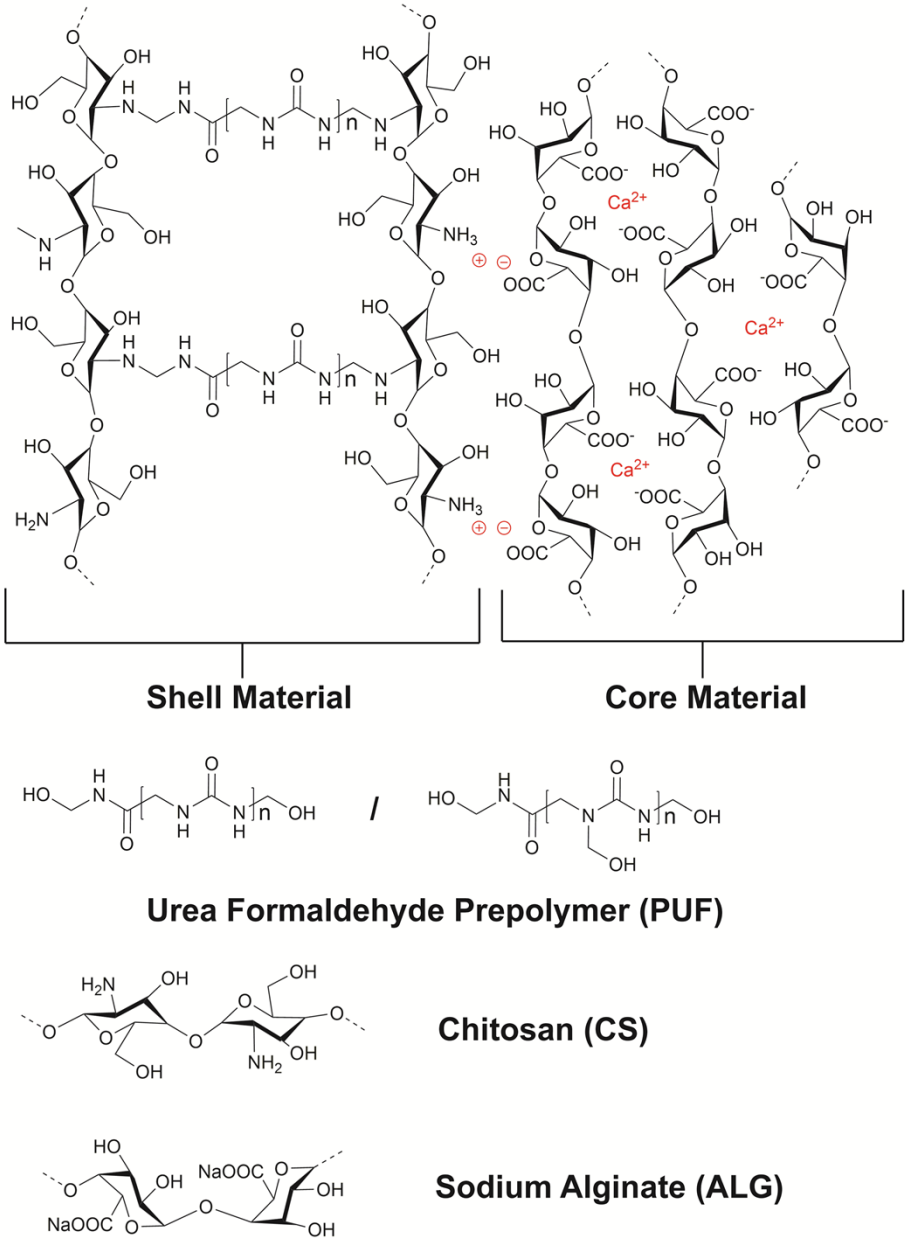

Fig. S1 The structural molecular formula of TSMs and the principle and process of the combination between core and shell material.

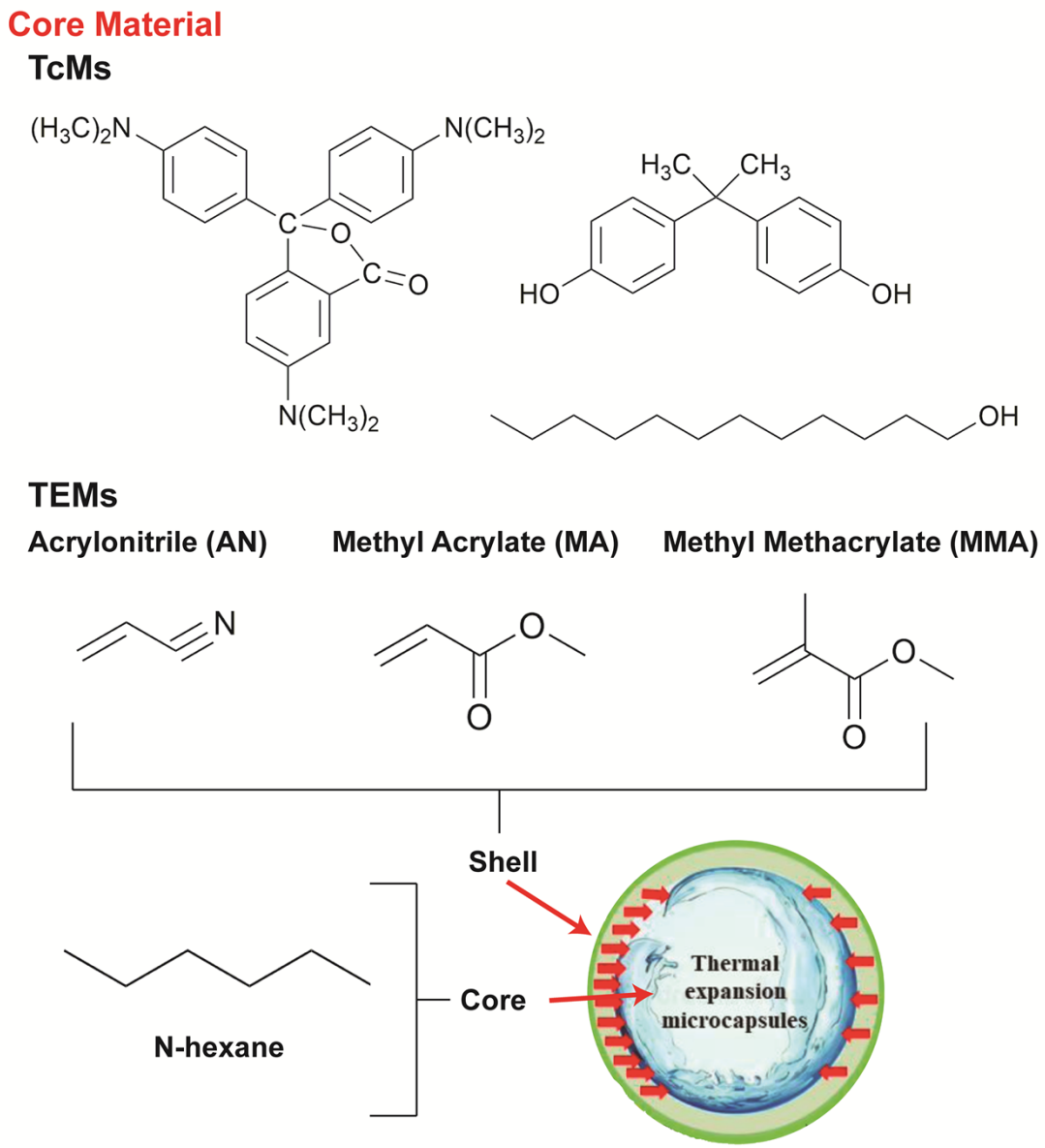

Fig. S2 Main structural components of core materials (thermochromic materials and thermal expansion microcapsules)

Synthesis mechanism of TEMs:

TEMs are microcapsules composed of core material and shell material, in which the core material is made of thermal expansion material (N-hexane) and the shell material is made of a thermoplastic copolymer. When the temperature reaches the vaporization temperature of the core material (N-hexane), the shell material softened by heat tends to expand outward due to the sharp rise of the internal pressure of the core material, so it has the function of thermal expansion. AN, MA and MMA were used as monomers to polymerize the thermal expansion shell under the action of initiator. In addition, because of a lot of anionic groups on the surface of SDS, the three monomers dissolved in water phase, under the action of anionic surfactant (SDS) and acidic environment, the solid polymer [P(AN-MA-MMA)] formed after polymerization moves to the surface of core material under the drive of acidic (H^+)

and finally forms TEMs.

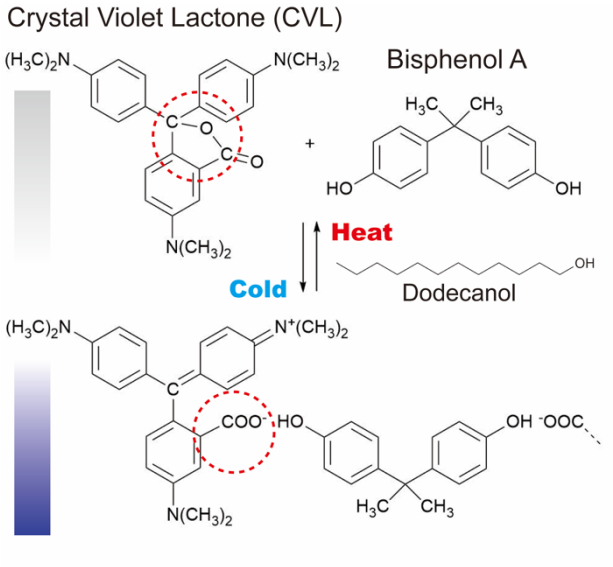

Fig. S3 Discoloration reaction mechanism of TcMs (crystal violet lactone, bisphenol A and dodecanol).

3. Particle Size Analysis

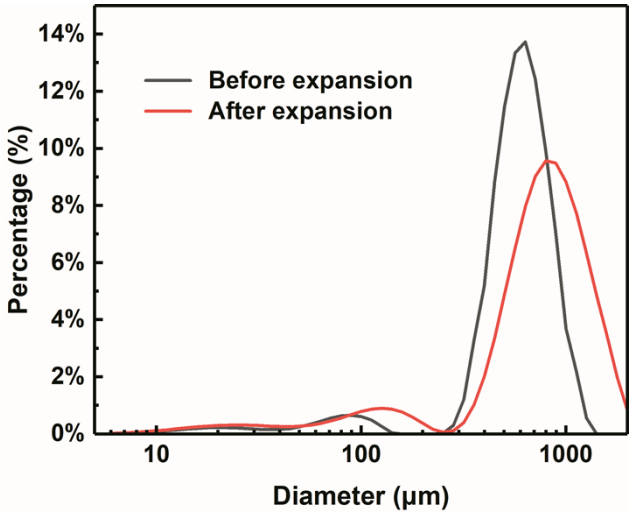

Fig. S4 Particle size analysis of TSMs before and after expansion.

4. Fluorescence microscope analysis

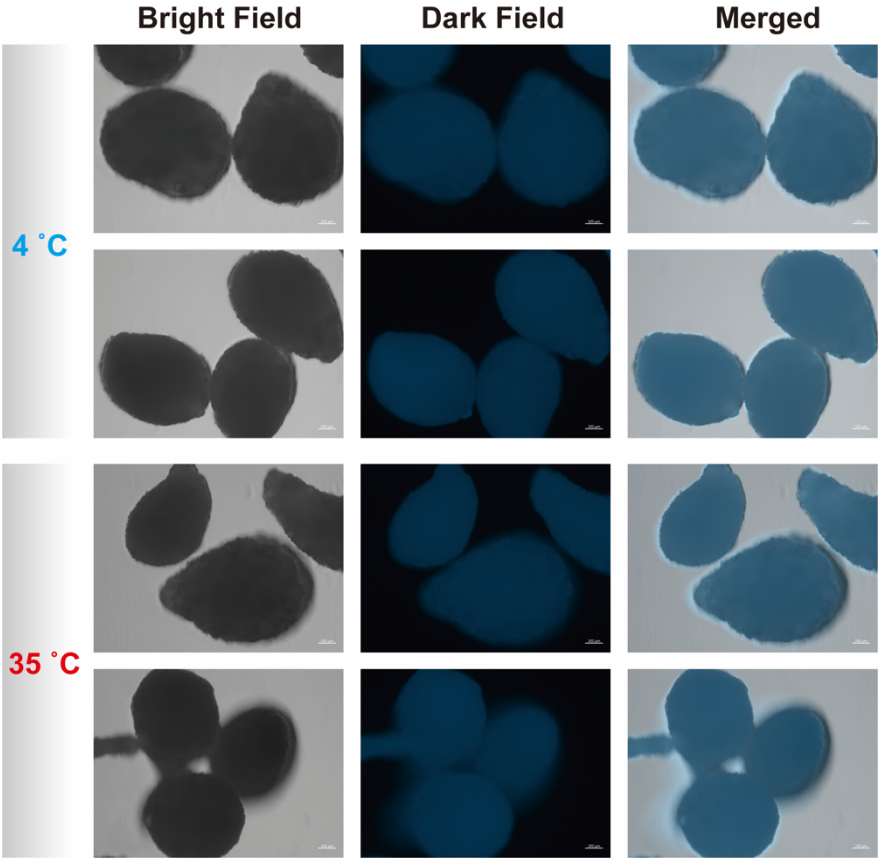

Fig. S5 Fluorescence phenomenon of TSMs at 359-371nm ultraviolet.

5. Component Structure Analysis

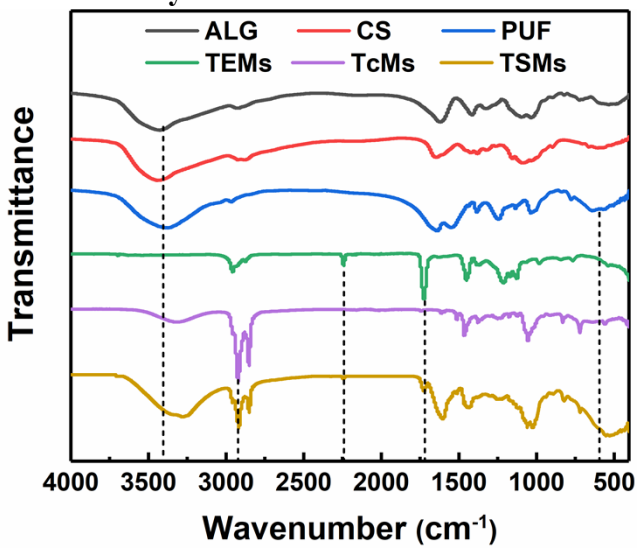

Fig. S6 FTIR of composition and structure of ALG, CS, PUF, TEMs, TcMs and TSMs.

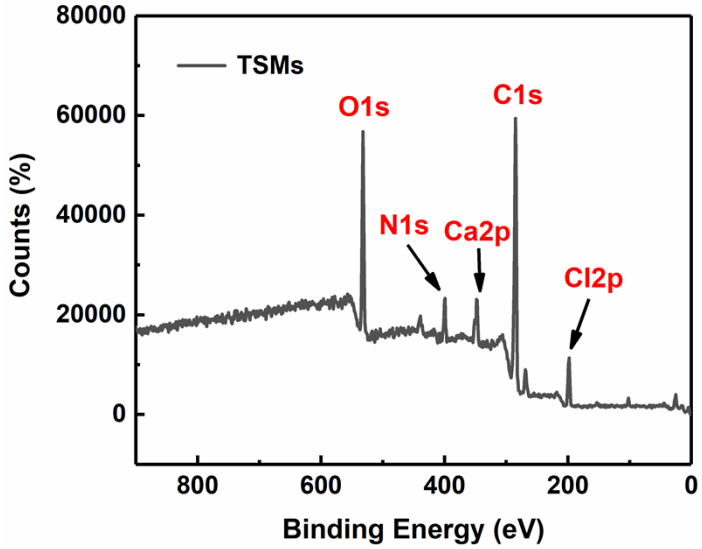

Fig. S7 XPS full spectrum scanning of TSMs.

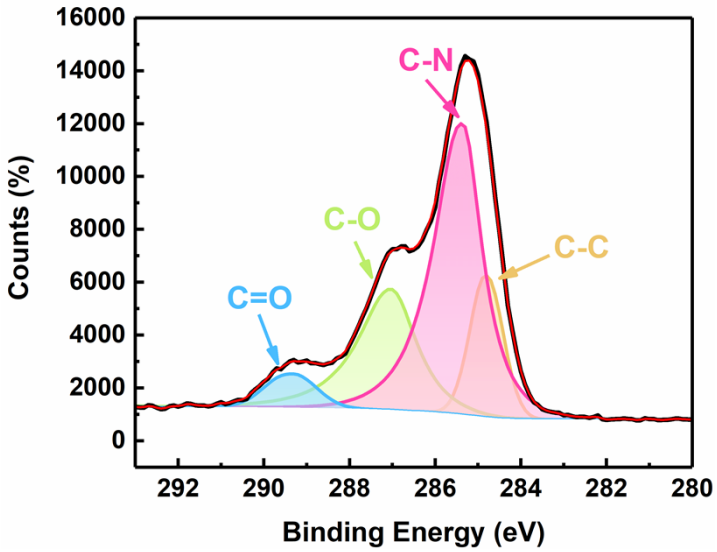

Fig. S8 C 1s XPS spectra of TSMs.

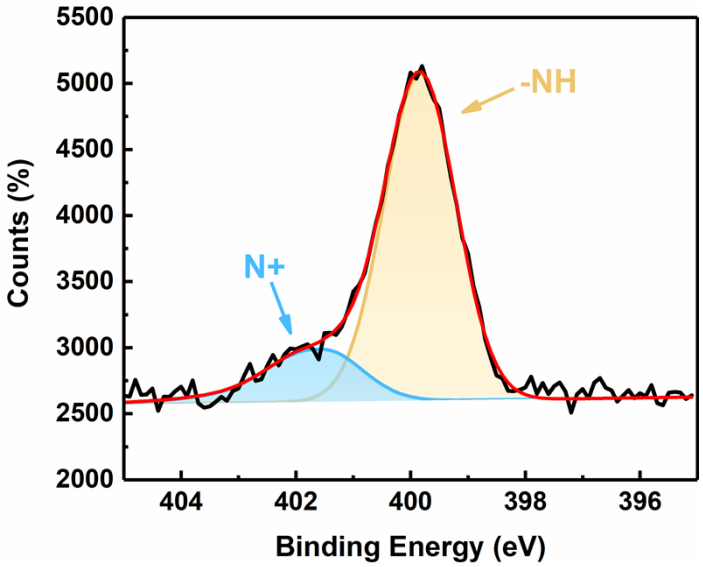

Fig. S9 N 1s XPS spectra of TSMs.

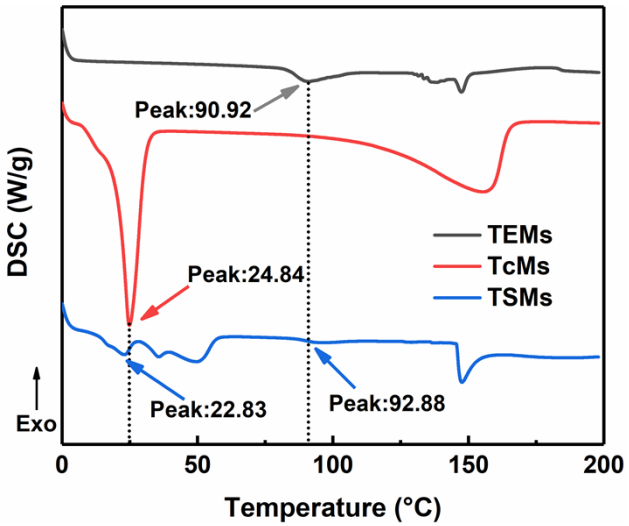

Fig. S10 DSC of TEMs, TcMs and TSMs.

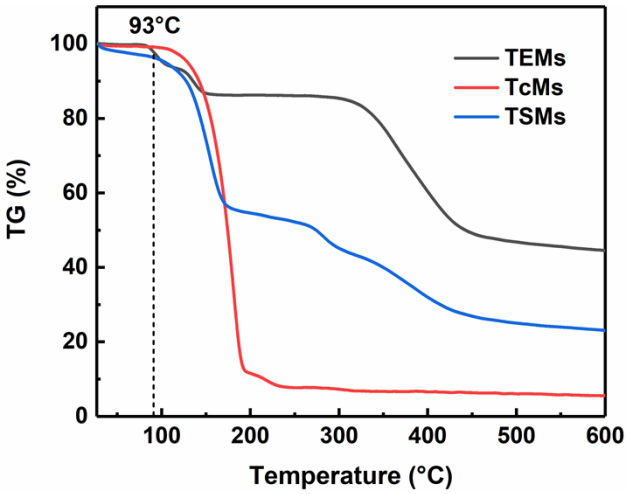

Fig. S11 TGA of TEMs, TcMs and TSMs.

6. Performance Analysis

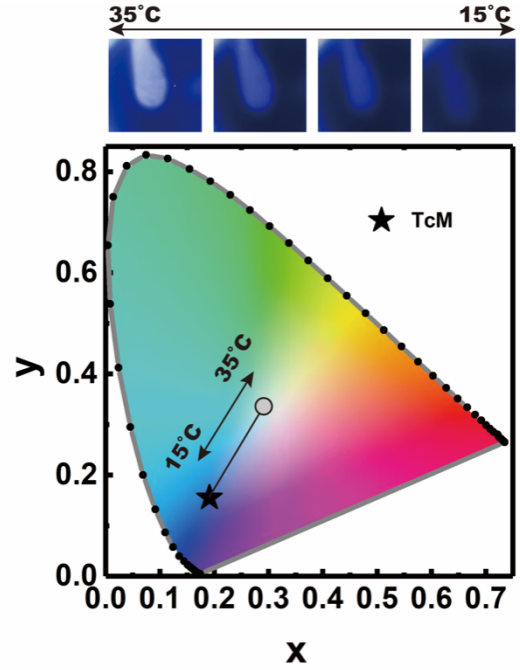

Fig. S12 CIE1931 colour coordinate diagram of TcMs discoloration.

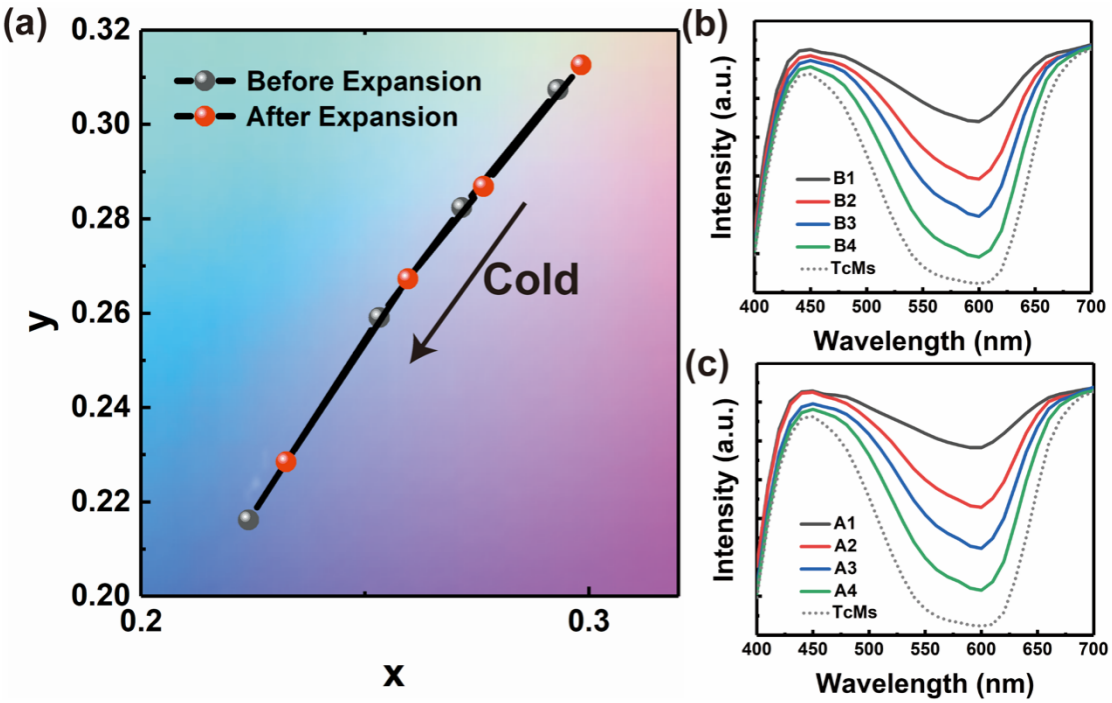

Fig. S13 (a) CIE1931 colour coordinate diagram of discoloration of TSMs before and after expansion. (b) Colour wavelength curve of discoloration process of TSMs before expansion. (B1~B4 denotes the wavelength variation of TSMs during the cooling process before expansion, and the dotted line is the wavelength of TcMs) (c) Colour

wavelength curve of discoloration process of TSMs after expansion. (A1~A4 denotes the wavelength variation of TSMs during the cooling process after expansion, and the dotted line is the wavelength of TcMs)

7. Application

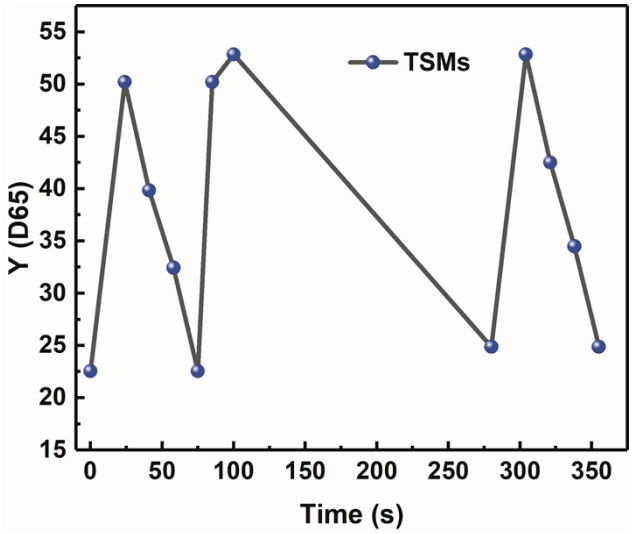

Fig. S14 Colour depth change under dual response of TSMs.

Video S1: TSMs expansion process (independent microcapsules) (MP4)

Video S2: Dual response demonstration of thermosensitive microcapsules (MP4)