Supplementary Information

Highly Efficient Grafting of Polyvinyl Acetate onto Cellulose Nanocrystal in Aqueous Phase

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Experimental section

Materials

Cotton pulp (DP=900) was supplied by Silver Hawk Co. Ltd. (Gaomi, China). sodium hydroxide (NaOH) and Sodium citrate dihydrate ($Na_3C_6H_5O_7.2H_2O$) with analytical grade were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Cerium ammonium nitrate (CAN), ammonium persulphate (APS), and Arsenazo III were purchased from Aladdin Chemical Reagent Corp.

Preparation of cellulose nanocrystals (CNCs)

CNCs were prepared according to our previous report[1]. Typically, 5 g of cotton pulp and 42.5 g of APS was added to induce the reaction. The reaction was performed at 80 °C for 3 h with vigorous stirring. The as-prepared sample was ultrasonically smashed using an ultrasonic cell disrupter (JY92-IIDN, Ningbo Scientz Biotechnology Co., Ltd, China) for 10 min. After the purification by centrifugation with deionized water at 8000 rpm until the supernatant turned turbid, the CNC suspension with a solid content of around 1 wt% was obtained.

Graft Polymerization of VAc on CNCs.

In the typical preparation procedure of CNCs-PVAc, the 20 mL of a 0.5 wt% CNCs suspension with certain amount of sodium citrate was first degassed by nitrogen bubbling for 20 minutes. Subsequently, 0.04 g CAN and 0.56 g VAc were added to induce the reaction. The reaction was stirred at 35 °C under an airtight surrounding for 2 h. After washed with distilled water and freeze-drying, the CNCs-PVAc powder was getted. The obtained powder is a mixture (named CNCs-PVAc) and contains both PVAc grafted CNCs (CNCs-g-PVAc) and the PVAc homopolymer. The CNCs-g-PVAc was separated by removing the ungrafted PVAc through the Soxhlet extraction with MeOH for 2 days.

Characterization

The Fourier transform infrared spectroscopy (FT-IR) spectra were collected from 4000 to 400 cm^{-1} for 32 scans at a resolution of 4 cm^{-1} using a Bruker VERTEX 70 spectrometer. Before the testing, the CNC-PVAc powder was dispersed in acetone. The obtained CNC-PVAc suspension was dropped on the surface of KBr wafer to form film. The spectra of CNC-PVAc were obtained in transmission mode.

UV-vis spectra were measured using an ultraviolet-visible light spectrophotometer (UV-2550, Shimadzu). For UV-vis measurement, Arsenazo III was prepared into the solution with a concentration of about 0.02 g/L and hydrochloric acid was added to adjust pH to 3.5. The molar ratio of cerium ion to Arsenazo III was kept at 1:1.

Scanning electron microscope (SEM) was performed with a JSM-7500F field emission SEM (JEOL, Japan) at an accelerating voltage of 3 kV. The samples were sputter-coated with gold before SEM observations.

Atomic force microscope (AFM) images were acquired using a Dimension lcon (Bruker, USA) under the intelligent mode. For AFM measurement, dilute CNC-g-PVAc suspensions (0.2 mg/mL in MeOH) suspension was spin-coated on freshly cleaved mica at 2000 rpm for 1 min.

Thermogravimetric analyzer (TGA) measurement was conducted on a NETZSCH TG209 F1 (NETZSCH Instruments, Germany). The temperature was set from 40 to 600 °C with a heating rate of 10 °C min^{-1} in nitrogen atmosphere.

The degradability of the CNC-PVAc film was examined by recording the weight changes as a function of time in soil. Before the test, the CNC-PVAc powder was hot-pressed at 170 ℃ for 5 minutes. The CNC-PVAc film with a diameter of about 4 cm and a thickness of 150 μm was obtained. The degradation test is conducted at ambient temperature.

Prior to GPC testing, the CNC-PVAc was subjected to Soxhlet extraction with methanol for 2 days to separate the CNC-g-PVAc and homopolymerized PVAc. To determine the molecular weight of grafted PVAc, CNC was removed using 72% sulfuric acid in accordance with previous work[2]. During the sulfuric acid treatment, the grafted PVAc was converted to PVA. The M_n of the grafted PVAc was then analyzed using GPC (Wyatt, USA) equipped with DAWN-HELEOS-II and Optilab detector. The RID was operated at 25 °C and eluted with a 200 mM sodium chloride solution and 0.2 ‰ sodium azide at a flow rate of 0.5 mL/min. In addition, the M_n of the homopolymerized PVAc was determined by GPC (TOSOH HLC-8320, Japan) analyses using tetrahydrofuran (THF) as the mobile phase, and the PS standard was used for calibration. Samples were dissolved in THF at a concentration of 1 mg/mL, and the flow rate of the mobile phase in GPC was maintained at 0.35 mL/min.

Solid-state nuclear magnetic resonance (SSNMR) experiments were performed on a Bruker Advance III HD 400 spectrometer operating at a Larmor frequency of 100.64 MHz for ^{13}C.

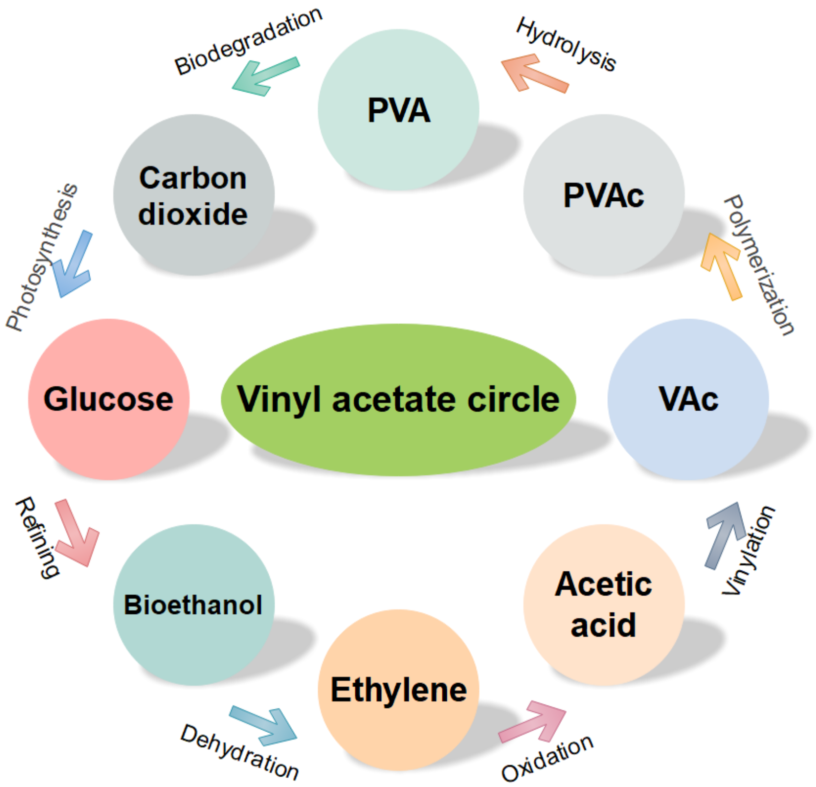

Fig. S1 Vision of the “vinyl acetate circle” wholly based on ethanol as a raw material source.

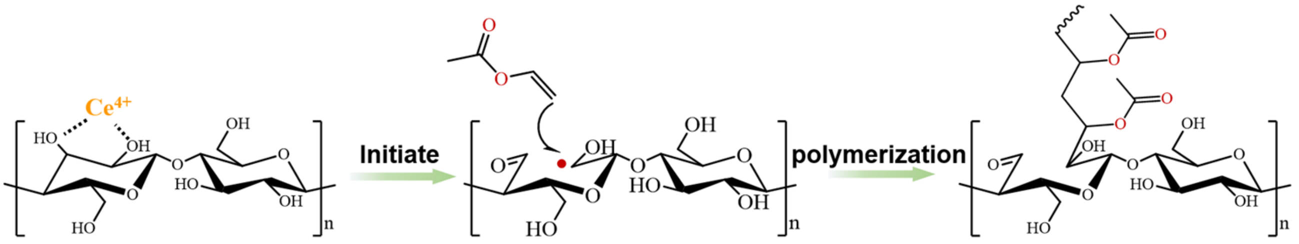

Fig. S2 Grafting mechanism of PVAc on CNC surface.

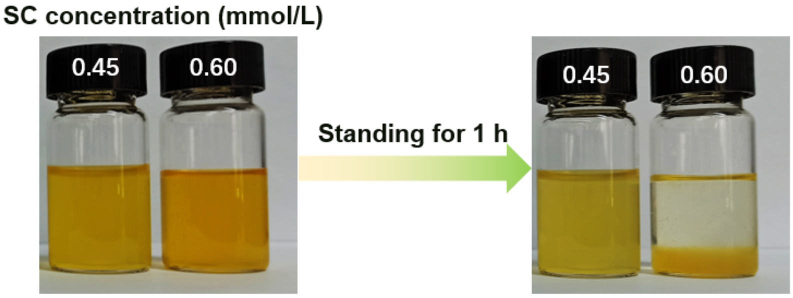

Fig. S3 State of CAN solution standing for 1h at SC concentration of 0.45 and 0.60 mmol/L.

Table S1 Effect of CAN concentration on grafting yield, grafting efficiency and conversion rate.

Entry	CAN (mmol/L)	Grafting yields (%)	Conversion rate (%)	Grafting efficiency (%)
CNC-PVAc$_{3.6\text{-}45}$	3.6	241.95±0.92	82.93±2.74	49.52±2.01
CNC-PVAc$_{3.2\text{-}45}$	3.2	253.50±6.50	84.87±2.74	49.52±2.01
CNC-PVAc$_{2.7\text{-}45}$	2.7	259.35±1.20	82.47±0.02	56.35±0.28
CNC-PVAc$_{2.3\text{-}45}$	2.3	189.45±12.23	57.44±3.07	59.09±0.66
CNC-PVAc$_{1.8\text{-}45}$	1.8	97.60±19.09	51.24±3.40	33.98±4.42

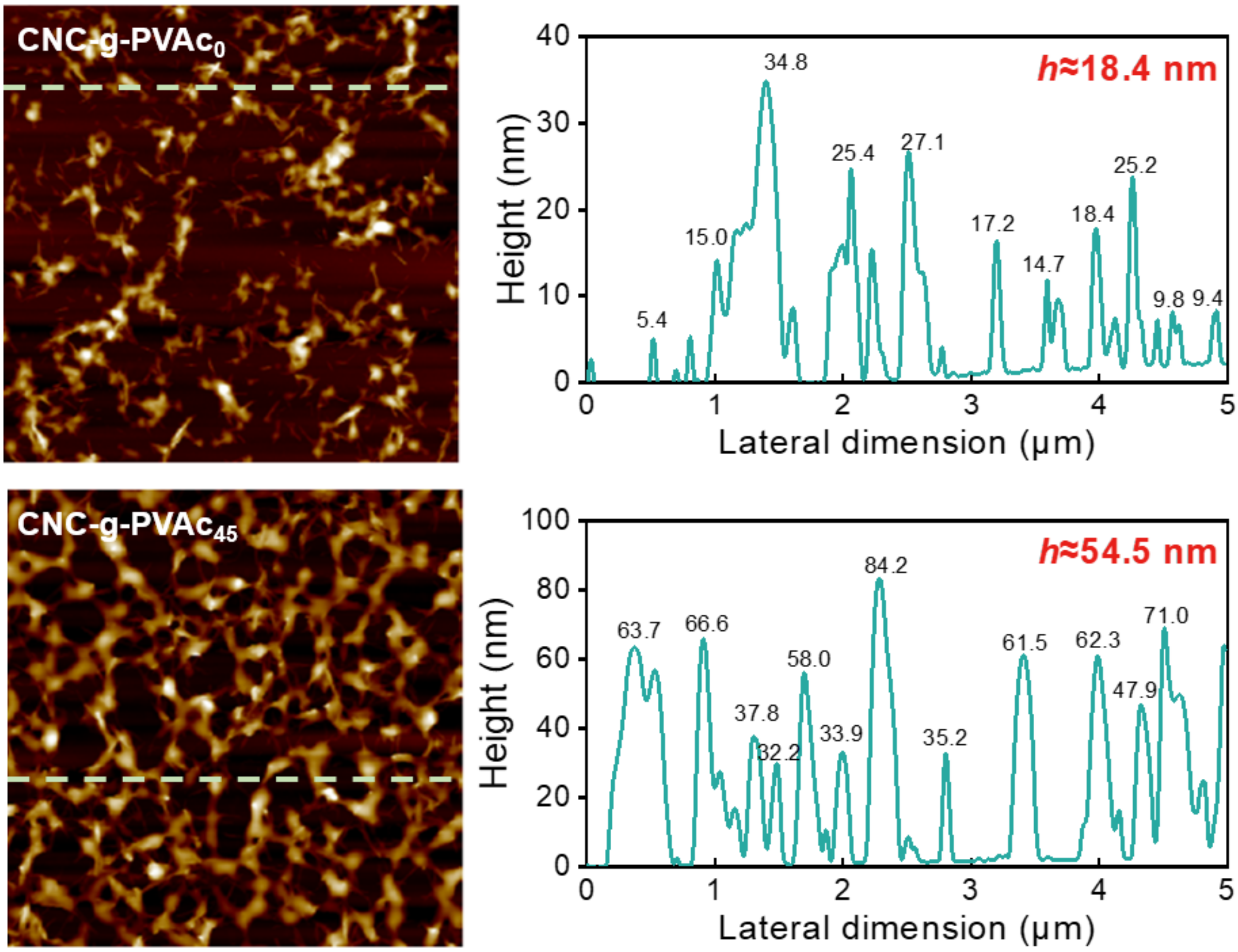

Fig. S4 AFM height comparison of CNC-g-PVAc$_0$ and CNC-g-PVAc$_{45}$.

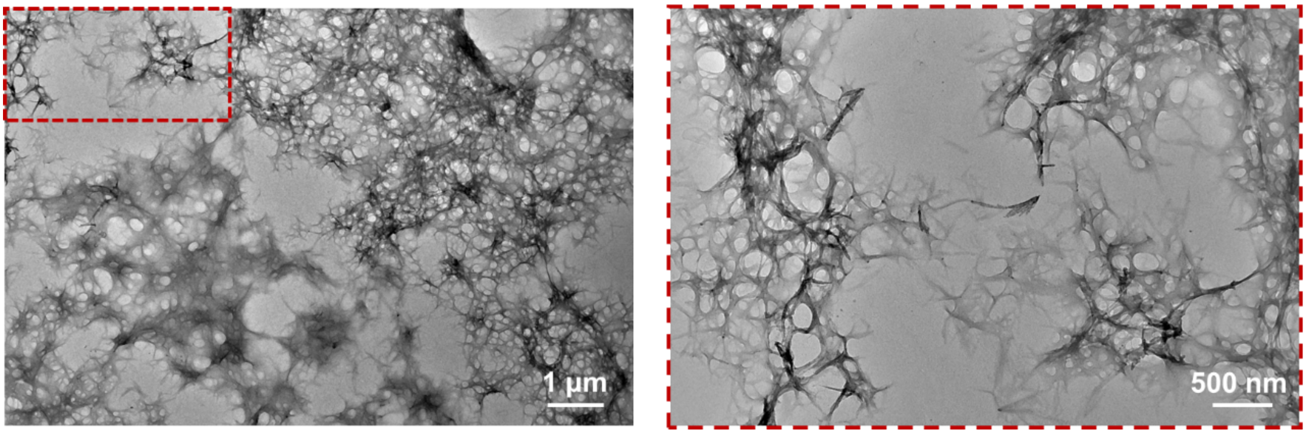

Fig. S5 TEM images of CNC-g-PVAc$_{45}$.

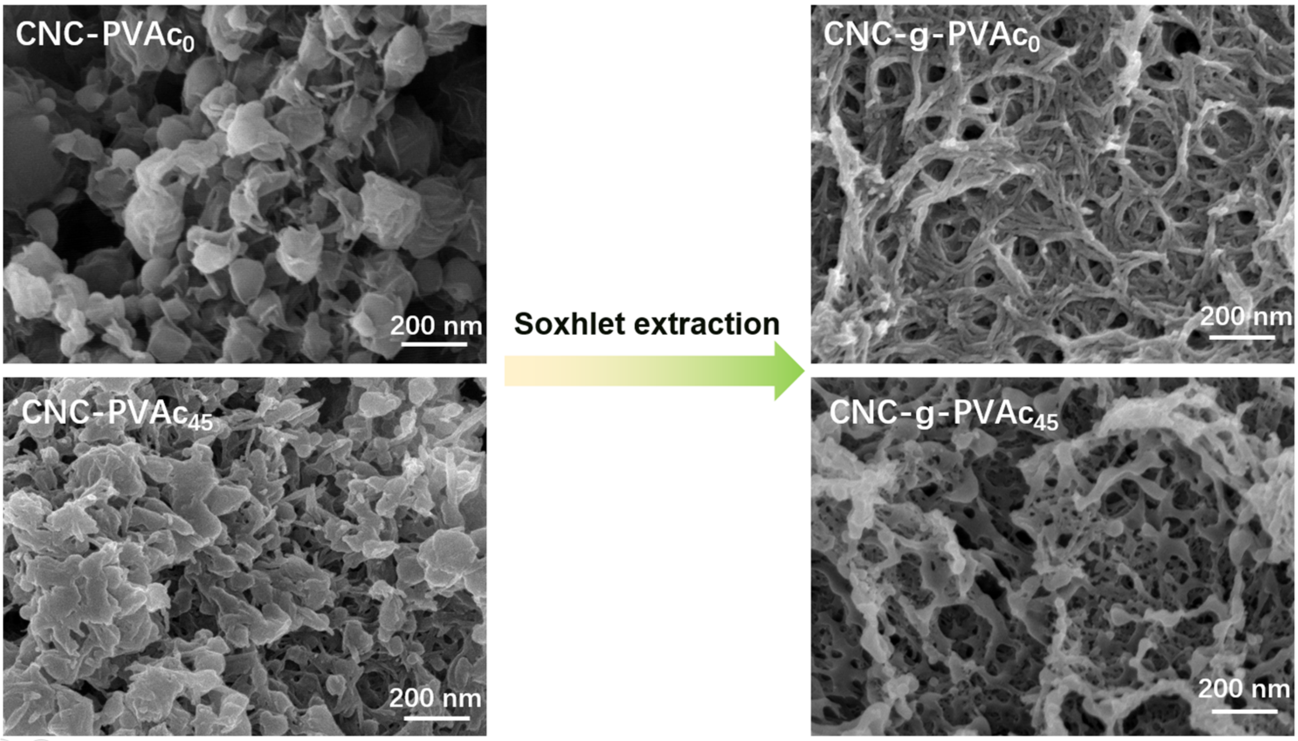

Fig. S6 SEM images of CNC-PVAc and CNC-g-PVAc powder.

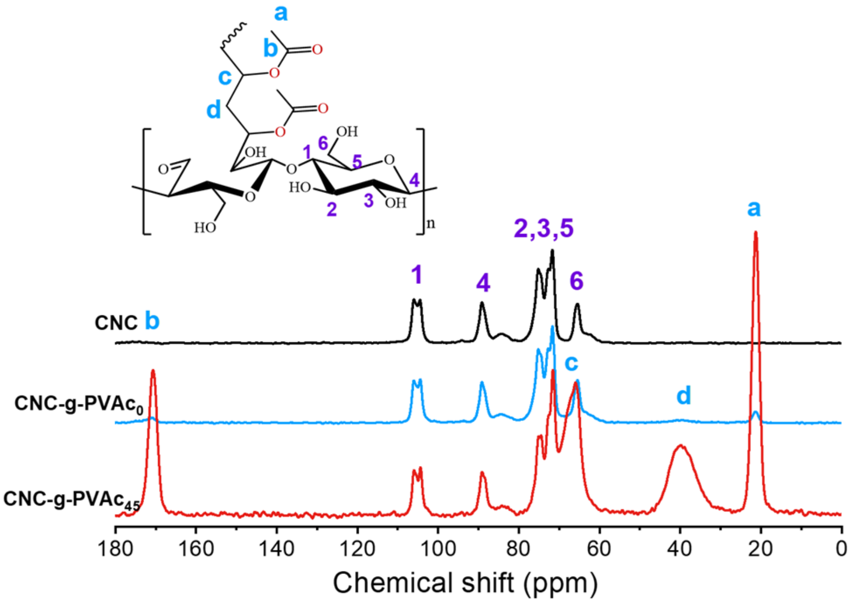

Fig. S7 Solid-state ^{13}C NMR spectra of CNC, CNC-g-PVAc$_0$ and CNC-g-PVAc$_{45}$.

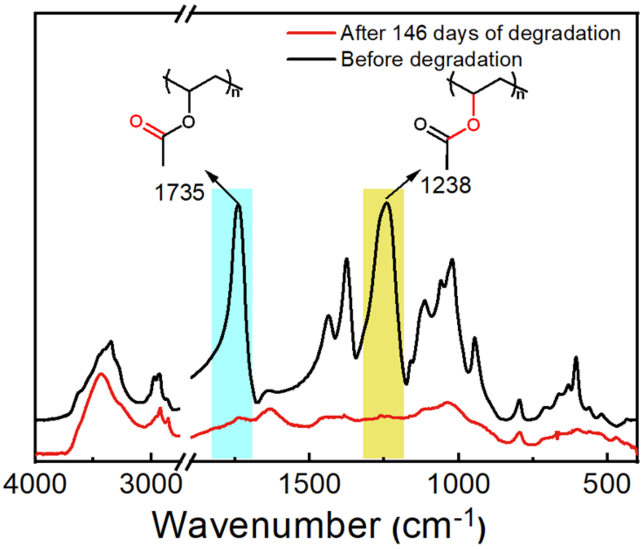

Fig. S8 Comparison of FT-IR spectra of CNC-PVAc film before degradation and 146 days after soil burial.

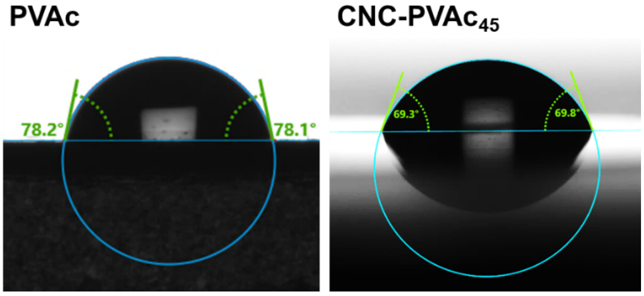

Fig. S9 Water contact angle of PVAc and CNC-PVAc$_{45}$.

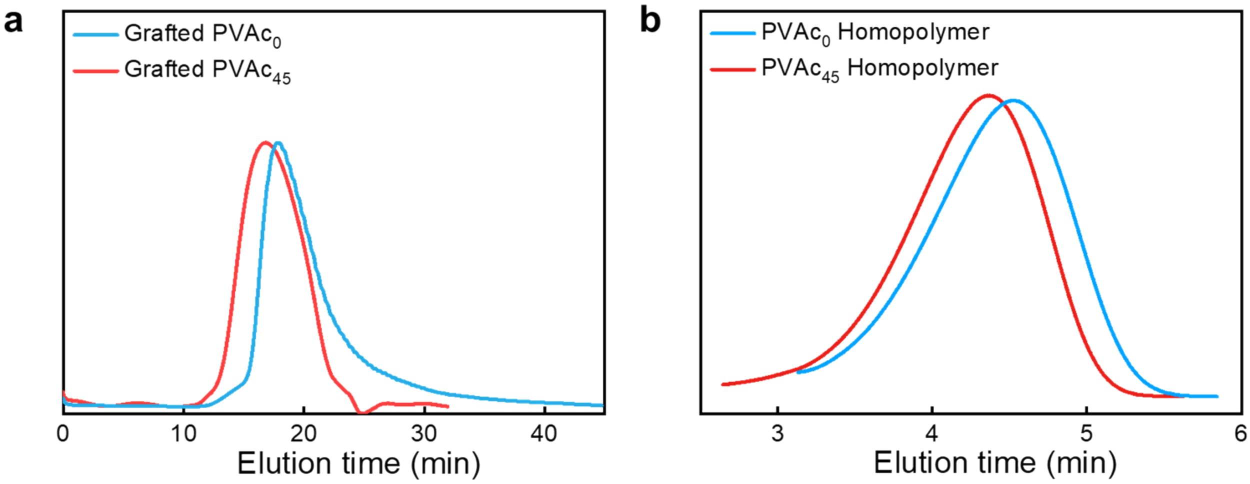

Fig. S10 GPC curves of (a) grafted PVAc and (b) PVAc homopolymers.

Table S2 The molecular weight of surface-grafted PVAc and PVAc homopolymer

Entry	surface-grafted PVAc			PVAc homopolymer	
	M_n (kg/mol)	*D*	σ_{grafts} *10^2 (chains/nm^2)	M_n (kg/mol)	*D*
CNC-PVAc$_0$	75.31	1.96	0.55	27.18	9.29
CNC-PVAc$_{45}$	269.9	2.50	1.28	40.01	11.42

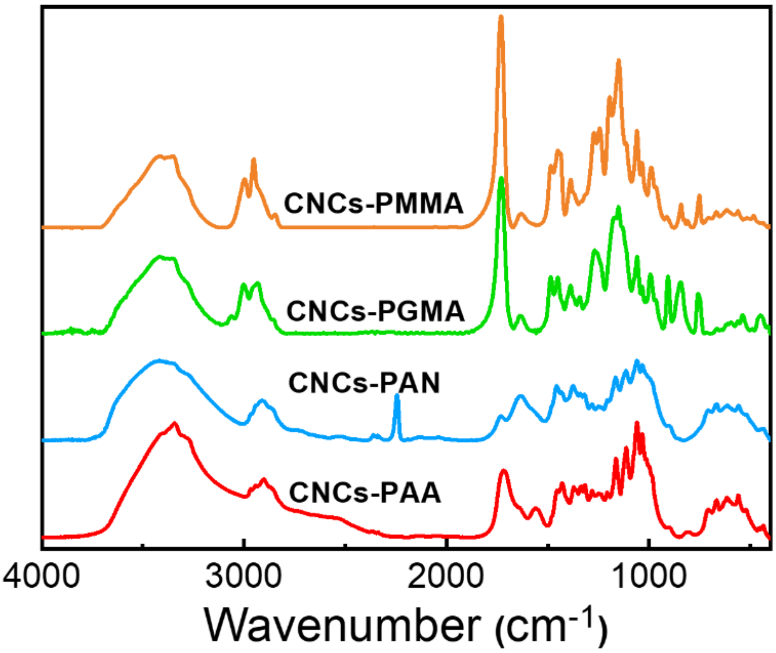

Fig. S11 FTIR spectra of the CNC-PMMA, CNC-PGMA, CNC-PAN and CNC-PAA.

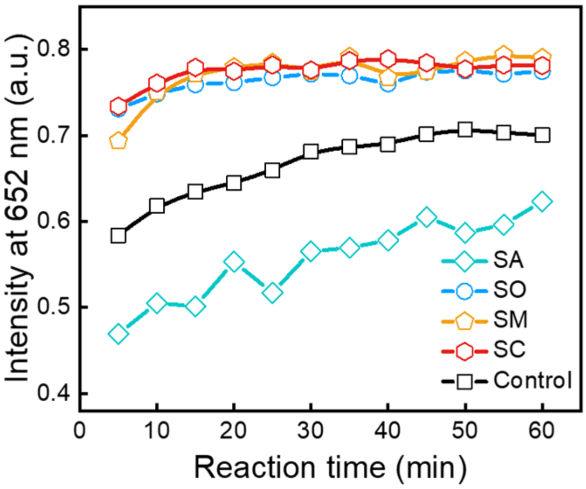

Fig. S12 Effect of Carboxylates type Absorbance intensity at 652 nm of CNC/CAN/Arsenazo III mixtures with the initiation time of 5-60 minutes.

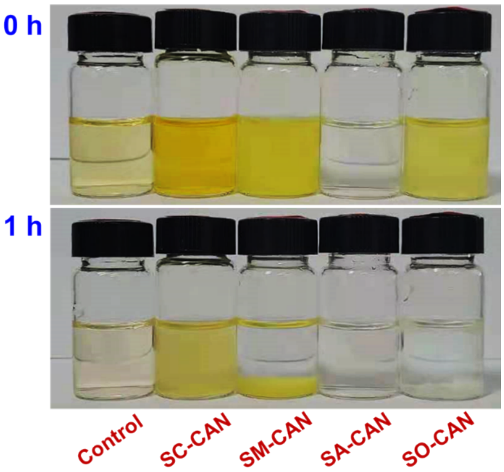

Fig. S13 Status of CAN in different carboxylate solutions when stored for 0 and 1h.

1. Y. Liu, L. Liu, K. Wang, H. Zhang, Y. Yuan, H. Wei, X. Wang, Y. Duan, L. Zhou and J. Zhang, *Carbohydr. Polym.*, 2020, 229, 115572.

2. K. Littunen, U. Hippi, L.-S. Johansson, M. Österberg, T. Tammelin, J. Laine and J. Seppälä, *Carbohydr. Polym.*, 2011, 84, 1039-1047.