Polyrhodanine coated cellulose nanocrystals as optical pH indicators

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1. Materials and reagents

Cellulose nanocrystals (CNCs) were produced and provided by CelluForce Inc. with an average charge density of 0.26 mmol/g. Other reagents or chemicals were purchased from Sigma-Aldrich and used without further purification. Hydrochloric acid (HCl 1M) solution and sodium hydroxide (NaOH 1M) solution were diluted from standard solutions.

2. Instruments and characterizations

☐ **FTIR spectra** were acquired at room temperature using a Bruker Tensor 27 FT-IR spectrometer with a resolution of 4 cm⁻¹ and a scanning number of 32 from 400 to 4000 cm⁻¹.

☐ **UV-Vis spectra** were acquired a Cary 100 Scan Varian.

☐ **Dynamic light scattering** and **ζ-potential** experiments were conducted on a Malvern Instrument Zetasizer Nanoseries.

☐ **Thermal analyses** were performed on a TGA Q600 TA Instrument (Lukens Drive, Delaware, U.S.A.) (Temperature program: 10°C/min until 100°C, maintained at 100°C for 5 mins then 10°C/min until 500°C, maintained at 500°C for 2 mins).

☐ A Philips CM10 TEM microscope was used to capture the **Transmission electron microscopy** (TEM) images using a 60 keV acceleration voltage. Each sample for TEM characterizations was prepared by spraying a 0.5wt% aqueous dispersion onto copper grids (200 mesh coated with copper) and allowed to dry.to characterize the morphology of the samples.

☐ **Elemental analysis** was carried out using a Vario Micro cube, Elementar Americas, Inc. Carbon, hydrogen, nitrogen, and sulphur content of the samples were determined by repeated measurement and the average values reported.

3. Preparation of CNC@PR nanoparticles

$FeCl_3$ (22.5mM) was added into a well-dispersed 20mL CNC solution (0.2 wt %), and the mixture vigorously magnetic stirred for 6h. The resulting CNC-Fe(III) complexes were quite viscous and had a lemon yellow colour. Rhodanine monomers (22.5mM) were dissolved in 20mL deionized water (DI water) and heated up to 85°C with vigorous stirring to ensure that the monomers dissolved completely. The CNC-Fe(III) complexes were introduced dropwise into the dissolved rhodanine monomer solution. Vigorous magnetic stirring was applied and the temperature was maintained at 85°C during the whole polymerization process. After 24h, cellulose nanocrystal@polyrhodanine (CNC@PR) core-shell nanoparticles were obtained after ultrafiltration with 100nm pore size filter-paper membranes and rinsed several times using millipore-Q water until the filtered solution became colourless and transparent. For further characterizations, CNC@PR powders were produced by freeze drying.

4. Preparation of CNC@PR reinforced chitosan beads

A mixed solution was prepared by dissolving 300mg chitosan powder and 30mg CNC@PR in 40 mL of a 1% (v/v) acetic acid solution. The solution was dropped into a precipitation bath containing 250 ml of 0.50 M NaOH, which neutralized the acetic acid within the chitosan gel and caused the coagulation of spherical uniform chitosan gel beads. The aqueous NaOH solution was stirred using a magnetic stirrer. The wet chitosan gel beads were extensively rinsed with distilled water to remove any NaOH, filtered and collected in a vial.
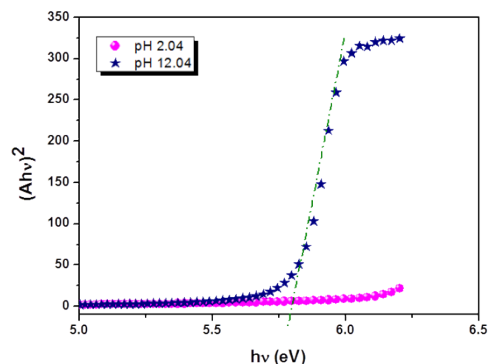

Figure S1 Tauc Plot obtained from the UV-Vis data and used to calculate the band gap of the CNC@PR nanomaterials
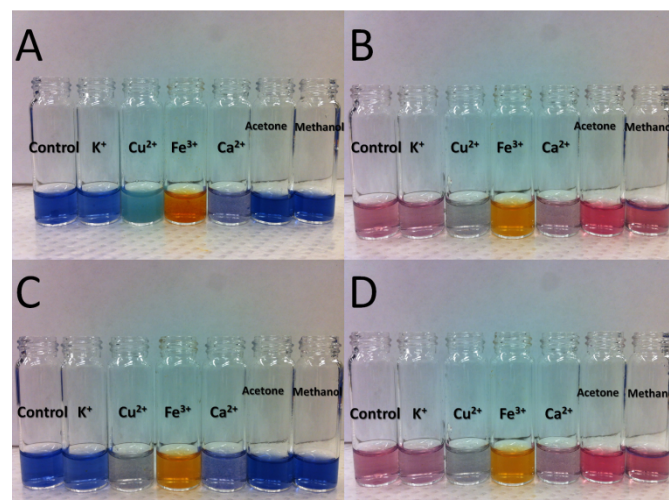

Figure S2 Color presented in different systems when tuning the pH for 2 times (CNC@PR samples with concentration of 0.01 wt% were used. A: adding 1M NaOH; B: adding 1M HCl after A; C: adding 1M NaOH after C; D: adding 1M HCl after C)
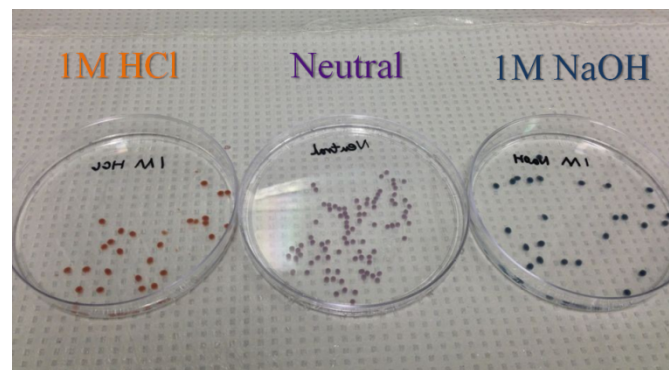

Figure S3 Visible color change of CNC@PR reinforced chitosan beads in solutions with different pH values