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Polyrhodanine coated cellulose nanocrystals as optical pH indicators

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A simple and green approach to produce cellulose nanocrystal@polyrhodanine (CNC@PR) core-shell nanoparticles via in-situ polymerization is proposed. The core-shell nanoparticles displayed reversible colour change in response to pH, confirming their utility as an optical pH indicator. This property was retained when the nanoparticles were configured into other shapes, such as flat films or hydrogel beads.

Fabrication of core-shell nanoparticles with unique and tunable properties for various applications has been actively researched in recent years. The structure of these nanoparticles often consists of an inner core encapsulated by a shell layer composed of another material. Compared to conventional single-component nanoparticles, the core-shell structure facilitates the incorporation of diverse functionalities and processibilities starting from the shell material to the core, thereby providing synergistic effects. Among all the research topics, rendering the nanoparticles with electric or optical responsive properties are the most sought after, because the surface of nanoparticles can be easily tailored to accommodate specific electronic, optical, catalytic or fluorescence properties[1].

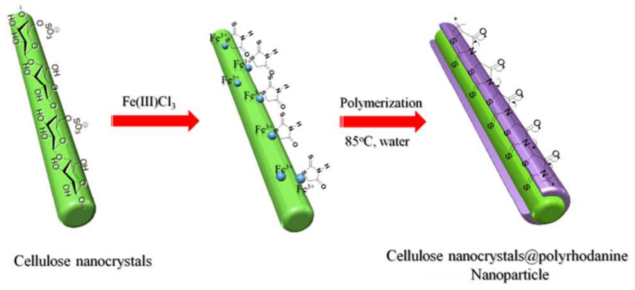
Cellulose nanocrystals (CNCs), prepared and isolated from natural cellulosic materials via acid hydrolysis, is driving new innovations in science and engineering by virtue of its good water dispersibility and eco-sustainable features[2–4]. Due to their attractive mechanical properties, CNCs and their modified forms have used as reinforcing agents in nanocomposites[5]. Besides, the chiral nematic characteristic and high surface area of rod-like particles make CNC to be an excellent template material to produce porous inorganic nanomaterials[6,7]. It is further anticipated that these nanoparticles can be used in various applications, ranging from drilling fluids, paints, industrial coatings, automotive components, building and packaging materials.

Conductive polymers (ICPs), such as polypyrrole (PPy), polyaniline (PANI) and poly(3,4-ethylene-dioxythiophene)(PEDOT) have gained increasing attention due to their low cost, unique redox behaviour, ease of synthesis, environmental and chemical stability, and relatively high conductivity[8–15]. Polyrhodanine (PR) as a conducting polymer is receiving some attention for some potential applications, such as antimicrobial agent and the removal of toxic metallic ions in water purification[16–20]. However, to the best of our knowledge, there are no reports on the reversible color response to pH.

In this communication, a simple and green approach to produce cellulose nanocrystal@polyrhodanine (CNC@PR) core-shell nanoparticles is described. The polyrhodanine shell was prepared by in-situ polymerization of rhodanine monomer using Fe(III) ions as the initiator, oxidant as well as counter-ion for doping the synthesized PR. The polymerization proceeded preferentially on the surface of cellulose nanocrystals, where Fe(III) ions were deposited on the CNC surface via electrostatic interactions. This process is simple and environmentally friendly since an aqueous solution is used. Our protocol satisfies most of the requirements for CNC modifications, such as the retention of morphology, crystalline properties and avoidance of poor dispersibility in polar solvents. CNC serves as an ideal substrate to support polymer coating and the resulting nanocomposite possesses excellent colloidal stability and does not flocculate or aggregate, thereby overcoming the poor solubility of PR in water. Due to the excellent mechanical strength and film-formation properties of CNCs, the hybrid nanoparticles can be assembled onto flat membrane substrates, or into stable hydrogel beads. This is the first reported study on the reversible color-change of polyrhodanine in response to changes in redox environment. This novel light sensitive core-shell nanomaterial responds to external stimuli, such as pH and can be configured into solution-based inks, flat films and stable hydrogel beads that display properties similar to those of dye-conjugated nanocellulose[21].

Development of simple and versatile strategies for surface coating (polydopamine, polypyrrole etc.) is challenging, particularly when a homogenous coverage of the surface is desired[22]. The surface coating process depends on the coating material and other parameters, such as solvent types, pH, and temperature. Due to the limited solubility of rhodanine monomer in water, a relatively high temperature of 85 °C was used for the polymerization to ensure a homogeneous reaction mixture. Scheme 1 illustrates the typically process to prepare core-shell CNC@PR nanoparticles. $FeCl_3$ (22.5mM) was added to 20 mL of well-dispersed CNCs (supplied by

Celluforce Inc.) (0.2 wt. %), and the mixture was vigorously magnetic stirred for 6h. The resulting CNC-Fe(III) complexes were introduced dropwise into the prepared rhodanine monomer solution (22.5 mM). Upon addition, the coordination bond between the ferric ions and oxygen, sulphur, and nitrogen atoms on the rhodanine monomers was formed. The oxidative polymerization of rhodanine proceeded for 24 hrs and the final products were recovered.



Scheme 1 Schematic illustration on the fabrication of CNC@PR nanoparticles.

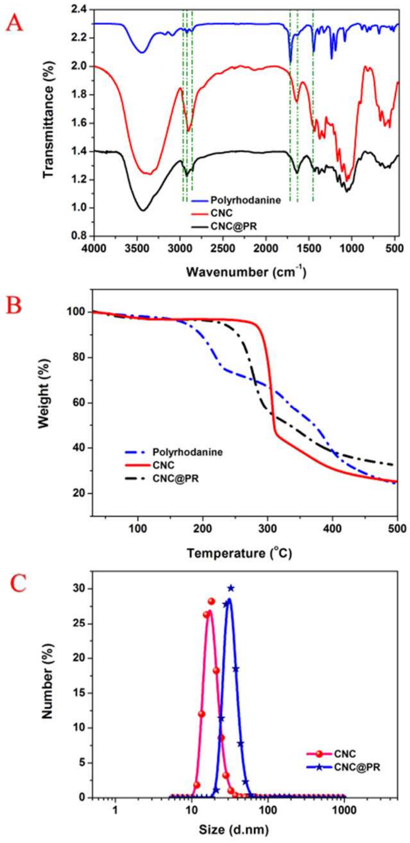


Figure 1 (A) FTIR spectra of polyrodanine, pristine CNC and CNC@PR nanoparticles (B) Thermogravimetric analysis (TGA) of polyrodanine, pristine CNC and CNC@PR nanoparticles (C) Particle size distribution curves of CNC and CNC@PR in a colloidal solution, determined by DLS at 90°

The polymerization of rhodanine was evaluated by Fourier transform infrared spectroscopy (FTIR). Figure 1A presents the results for polyrhodanine, pristine CNC and CNC@PR samples; specific peaks for polyrhodanine were observed for CNC@PR. The split peaks, between 3000 and 2850 cm^{-1}, were assigned to C-H stretching vibration of methylene group and O=C-H structure in the heterocyclic ring. The peak around 1710 cm^{-1} is associated with the stretching vibration of C=O and the peaks around 1637 and 1390 cm^{-1} correspond to C=C group stretching and C=N^{+} bond stretching. To further confirm the coating of CNC with polyrhodanine, the ζ-potential (Table 1) of the nanoparticles in MiliQ water was measured at pH 7. The pristine CNC nanoparticles possessed a negative value of -54.1 mV due to the abundance of sulphate ester groups on the surface. For CNC@PR nanoparticles, the absolute value of ζ-potential decreased to -30.3 mV (still negative), indicating that some of the negatively charged sites on the surface were shielded by polyrhodanine coating.

Table 1 Summary of the results from elemental analysis and ζ-potential measurement

	N%	C%	H%	S%	ζ-Potential (mV)
CNC	0.023	41.106	5.619	0.844	-54.1±2.34
CNC@PR	0.812	38.564	5.306	5.873	-30.3±3.56

Table 1 also summarizes the elemental analysis of polyrhodanine coated nanoparticles and pristine CNC. Compared to pristine CNC, CNC@PR displayed a large increase in the sulphur and nitrogen and a small reduction in carbon and hydrogen contents. The observed increase in the sulphur content on the core-shell nanoparticle confirmed the successful coating of PR on CNC. The thermal analyses of core-shell CNC@PR were characterized and compared to the behaviour of pure polymer and pristine CNC (Figure 1B). Pure polyrhodanine displayed a three-stage degradation process, in agreement with literature[16,19]. Core-shell nanoparticles possessed a lower degradation onset temperature (210 °C) than pristine CNC, indicating the presence of polyrhodanine coating on the surface of CNC. The particle-size distribution of the nanoparticles was determined by dynamic light-scattering measurements (Figure 1C). The CNC nanoparticles exhibited a hydrodynamic diameter of 18.2 nm (18.2±2.7 nm). After coated with polyrhodanine, the mean diameter of the particle increased to 29.6 nm (29.6±3.8 nm). The morphology of the nanoparticles was characterized by TEM. The images in Figure 2 show that the core–shell nanoparticles were well-dispersed on the copper grid. Compared to pristine CNCs, the CNC@PR particles displayed a rougher morphology and a larger size, confirming the coating of polyrhodanine on the surface of the CNCs.

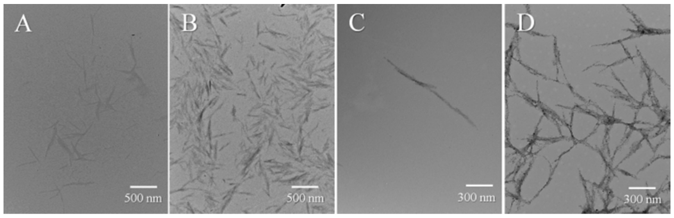


Figure 2 TEM images of pristine CNCs (A, C) and CNC@PR (B, D) nanoparticles. In order to highlight the contrast, C and D samples were stained with Ferric ions.

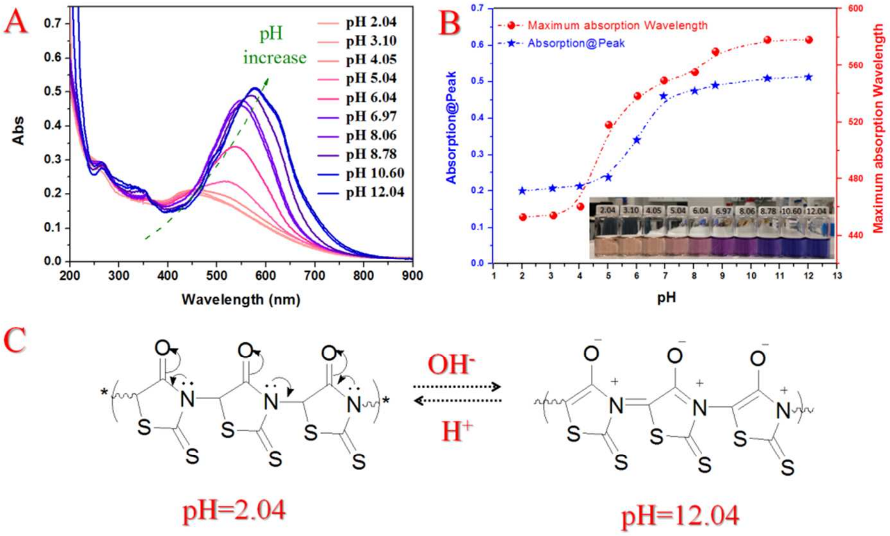


Figure 3 (A) Summary of the UV-Vis spectra of a 0.01wt% CNC@PR dispersion over a pH range from 2.04 to 12.04 (B) Sigmoidal plots of maximum absorption wavelength and absorbance@peak versus pH. Inserted picture shows the macroscopic color of CNC@PR dispersions at different pH values (C) Structure change of polyrhodanine during protonation and deprotonation.

The pH is commonly used to monitor the solution conditions in various fields, such as food, clinical diagnostics, bio-processing, and wastewater treatment. Optical sensing based on changes of spectroscopic properties in response to pH provides a useful way to simplify the analysis. UV-Vis absorption analysis was used to characterize the dispersion of CNC@PR nanoparticles. Figure 3A shows the UV-Vis absorption spectra of core-shell nanoparticle as pH was increased. The intensity or wavelength at maximum absorption was identified at various pH values (Figure 3B). The intensity at the maximum absorption wavelength displayed a typical "S" shape, increasing continuously from 0.207 to 0.512 with increasing pH values from 2.04 to 12.04. The maximum absorption wavelength was red-shifted from 453 to 578 nm showing the same trend as the intensity. At pH 12.04, the PR on the surface existed in a doped state as reflected by the presence of a polaron band transition at about 492 and 578 nm, which is attributed to the π-π* transition of the conjugated polymer backbone. As the pH of the solution decreased to 2.04, the polaron bands gradually blue-shifted to 453 nm, indicating a decrease in the conductivity. By using the Tauc Plot, the band gap of the core-shell nanoparticle in the doped state (pH=12.04) was calculated to be around 5.8 eV (see ESI-Figure S1). The inserted picture in Figure 3B shows the color change of the composite nanoparticle as the pH of the solution changes. The color varied from pale red to blue violet when the pH was increased from 2.04 to 12.04, and the results were consistent with the UV-Vis spectra shift shown in Figure 3A. The response of the coating was reversible; the color changed from blue violet to pale red with decreasing pH. The reversible color change of 0.01wt% CNC@PR dispersion when 1M NaOH or 1M HCl was added can be viewed from the video included in the ESI. This pH-induced redox reversibility showed that the CNC surface was coated with PR and that the core-shell nanoparticles could potentially be used in pH sensing devices. The anti-interference (some common metal ions [50mM] and organic compounds) of this pH indicator were also demonstrated (see ESI-Figure S2). The reversibility and pH indication remained the same for colorless metal ion systems (ionic strength may have an influence on the stability of the colloidal suspension, leading to flocculation), but may be influenced by colorful metal ions (skyblue Cu^{2+} and brown Fe^{3+}). For systems containing acetone and methanol (ratio of 1:1), the color and reversibility were almost identical to the control sample except for the brightness which was induced by the different refractive index of the organic compounds. Ammonium hydroxide was also utilized to adjust the pH values, and the optical behavior and reversibility were retained. The detailed process was recorded in a video, which is available in the supporting information (see ESI).

This novel hybrid nanomaterial can be shaped into a variety of configurations, such as film since CNC nanoparticles possess good film forming property. An aqueous suspension of 1wt% CNC@PR was deposited onto a glass slide and allowed to dry at room temperature for 2 days to produce a film. The UV-Vis absorption spectra of the film when exposed to small amounts (100μL) of 1M NaOH or 1M HCl were measured. The results showed that the maximum absorption peaks at acidic and alkaline conditions of the film were similar to the nanoparticle in aqueous solutions (Figure 4). The maximum absorption wavelengths for the films upon adding 1M HCl, water at neutral pH and 1M NaOH were 524, 549, and 649 nm, respectively. The change in the color and possibly the opacity could present opportunity for its use as a smart window material. Incorporating the core-shell nanoparticle into chitosan hydrogel beads to produce colorful beads that respond to pH of the surroundings was also demonstrated (see ESI-Figure S3). These examples illustrate that the core-shell nanoparticle can be integrated into different structures and used as chemical sensors for direct visualization.

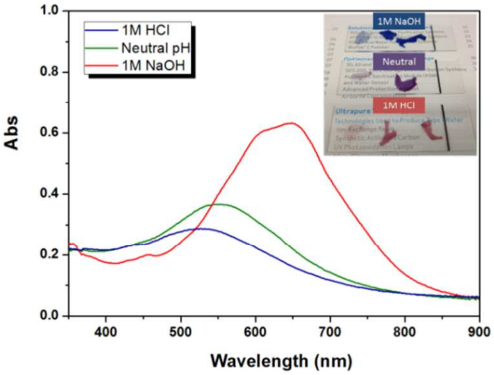


Figure 4 The UV-Vis spectra of CNC@PR films upon adding 1M HCl, water at neutral pH and 1M NaOH. The insert shows the colours of films pealed from the glass slides.

Conclusions

In summary, we have demonstrated a simple and green approach to fabricate cellulose nanocrystal@polyrhodanine (CNC@PR) core-shell nanoparticles by in-situ polymerization in aqueous solution. These CNC@PR core–shell nanoparticles reversibly responded to changes in pH. The color gradually changed from pale red to blue violet when the pH was increased from 2.04 to 12.04. The reversible response of the hybrid nanomaterial to pH was retained when shaped into different forms, such as 1D printable inks, 2D flat film, membranes, and 3D hydrogel beads. These pH-responsive core-shell nanostructures possess colloid stability, high surface area and good mechanical strength. Such system holds promise for the development of cheap and environmentally friendly pH sensing devices.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, reaction and synthesis procedures, instruments, figures and demonstration video. See DOI: 10.1039/c000000x/

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Graphic Abstract for TOC

Polyrhodanine coated cellulose nanocrystals as optical pH indicators

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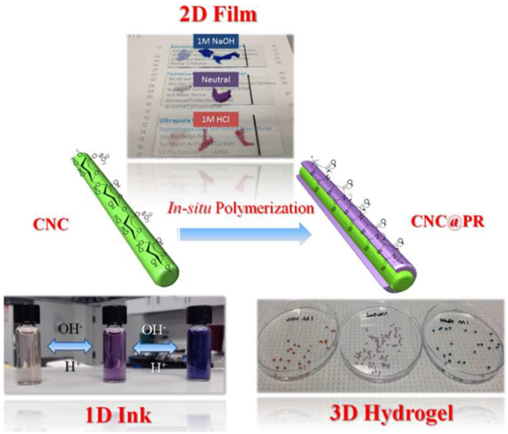

Abstract:

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