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Cellulose fiber nanocomposites displaying spin-crossover properties

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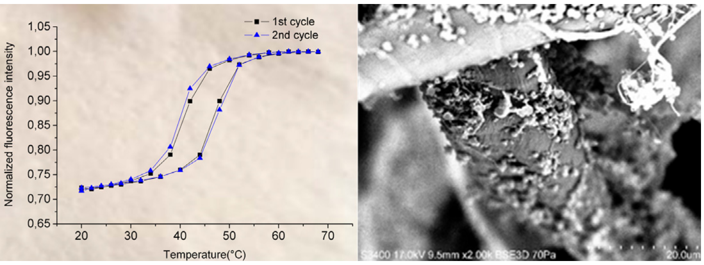
HIGHLIGHTS

- Cellulose fiber sheets were modified $[Fe(hptrz)_3](OTs)_2$ spin-crossover nanoparticles.
- Spin-crossover modified sheet was used for thermochromic, thermofluorescent effects.
- Spin functionalization can be adjusted by nanoparticle and paper fabrication.

GRAPHICAL ABSTRACT



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ABSTRACT

Linter cellulose fiber based nanocomposites were prepared by functionalizing the fibers with $[Fe(hptrz)_3](OTs)_2$ spin-crossover nanoparticles and acridine orange dye molecules. The composites were characterized by electronic (UV–vis and fluorescence) and vibrational (Raman, FTIR) spectroscopies as well as by electronic and optical microscopies. The cellulose sheets prepared from the nanocomposite show significant thermochromic and thermofluorescent effects associated with the spin transition phenomenon, providing scope for paper thermometry and anti-counterfeit applications.

1. Introduction

The biomineralization and biotemplating methods have evolved into an important research area of nanoscience and nanotechnology since they offer a possibility for the preparation of functional nanostructures and their integration into technologically useful forms. Renewable cellulose fibers and its derivatives have been proved to be good templating materials for functionalization with metal complexes and nanoparticles since they have a large number of hydroxyl groups that are accessible for chemical modification [1–9]. The spatial, structural organization of accessible and inaccessible regions on the cellulose surface influences the nano- and macroscopic adsorption properties of functionalized complex nanoparticles. For example, a controlled modification of fiber external surfaces and their lumen was achieved by alternate adsorption of polyelectrolytes and oxide nanoparticles (layer-by-layer nanoassembling) [9–11]. Lumen loaded fibers with different, functionalized nanoparticles through the pit apertures on the fiber walls offer also an efficient way for the fabrication of nanocomposites [12]. For the pulp and paper industry, such modification of individual cellulose fibers with active substances represents an appealing way to obtain new or enhanced functional properties, including either “classical properties” (durability, porosity,

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brightness, etc.) or "smart functionalities" such as sensing, anti-counterfeit or antimicrobial components.

In the present study, we exploited a tendency of $[Fe(hptrz)_3](OTs)_2$ (hptrz = 4-heptyl-1,2,4-triazole, OTs = para-toluenesulfonyl) spin crossover (SCO) nanoparticles to interact with OH groups in order to functionalize cellulose sheets with specific optical properties. The phenomenon of spin crossover between high-spin (HS) and low-spin (LS) states of $3d^4$–$3d^7$ transition-metal complexes is one of the most spectacular examples of molecular bistability [13]. This switching between the two spin states can be induced by various external stimuli (temperature, pressure, light irradiation, etc.) and is accompanied by a marked change in different physical properties, including magnetic, electric, mechanical and optical responses [14]. Recently, the synthesis of nanoparticles and other nanoscale objects of SCO complexes has received many attention for their remarkable physical properties and potential applications [15]. For example, chitosan biopolymer matrix was successfully used to control the growth of $Fe(pyrazine)[Ni(CN)_4]$ SCO particles [16], but we can also mention other examples, such as the use of mesoporous silica [17], surfactant [18,19] or organic polymer [20] matrices.

Here we describe biopolymer/SCO nanocomposites, which were elaborated by adsorbing pre-formed $[Fe(hptrz)_3](OTs)_2$ nanoparticles from a colloidal solution onto linter fibers. The $[Fe(hptrz)_3](OTs)_2$ complex forms a chain structure of $Fe^{II}(hptrz)_3$ units, whose charge neutrality is provided by the OTs^- counterions. We have chosen this compound because it is known to display an abrupt spin transition with a hysteresis loop close to room temperature [21], which is highly relevant for potential applications. In some cases acridine orange fluorescent dye molecules were also added to the composite material. As it was shown earlier [22], this type of luminescent doping allows one to transform the thermochromic properties of SCO materials into thermofluorescence in a straightforward way.

2. Materials and methods

2.1. Materials and sample preparation

Bleached linter cellulose fibers were received from Buckeye Technologies Inc. All other solvents and reagents were purchased from Sigma Aldrich and used without further purification. 4-Heptyl-1,2,4-triazole (hptrz) was obtained from N-formylhydrazine, triethyl orthoformate, and n-heptylamine by following the Bayer synthesis [23]. Iron(II) tosylate was synthesized from the reaction of metallic iron with tosylic acid [24].

For the synthesis of SCO nanoparticles three distinct solutions were prepared: (1) Iron(II) tosylate hexahydrate (15 mg, 0.03 mmol, 1 equiv), ascorbic acid (3 mg), and polyethylene glycol (PEG-3350, 200 mg) in a solvent (2 ml, H_2O); (2) hptrz (30 mg, 0.09 mmol, 1 equiv) in a solvent (2 ml, H_2O, 0.3 ml EtOH), and polymer PEG-3350 (200 mg); and (3) acridine orange (0.15 mg) in a solvent (3 ml, H_2O). For the synthesis of undoped particles the first two solutions were rapidly mixed and the mixture became turbid within a few seconds followed by the establishment of a pink precipitate. The precipitate was separated by centrifugation and washed twice with the same solvent that was initially utilized. The PEG-stabilized $[Fe(hptrz)_3](OTs)_2$ nanoparticles obtained by this method showed a size distribution between ca. 300 and 500 nm (Fig. 1). For the synthesis of the doped particles the luminescent dye was first added to the ligand solution before the reaction with the iron salt.

For the preparation of the cellulose nanocomposites, first a colloidal solution of $[Fe(hptrz)_3](OTs)_2$ (30 mg in 5 ml of water) was prepared by ultrasonication in the presence of various ascorbic acid content (0, 20, 60 and 100 wt%). This was then added to a water suspension of linter cellulose fibers (0.135 g of fibers in 150 ml of water) and further sonicated. After filtration and drying, the samples (modified and unmodified cellulose fiber sheets) were conditioned at 50% relative humidity and a temperature of 23 °C.

In a similar experiment, before the adsorption of the $[Fe(hptrz)_3](OTs)_2$ particles, the cellulose fibers were pre-functionalized with a polyelectrolyte bilayer of positively charged polyelectrolyte PDDA (poly(diallyldimethylammonium chloride)) and negatively charged PSS (poly(sodium styrene sulfonate)). The water suspension of linter cellulose fibers was first mixed with an aqueous solution of PDDA (20 wt% vs. dry fibers) and washed twice by water following centrifugation. The same procedure was then repeated by PSS (13 wt% vs. dry fibers).

2.2. Methods

2.2.1. Electron microscopy

A HITACHI S-3400N instrument was used for scanning electron microscopy (SEM) imaging of both modified and unmodified fibers. The images were obtained at an operating voltage of 17 kV. The nanoparticles were imaged by transmission electron microscopy (TEM) by means of a JEOL JEM-1010 (100 kV) microscope. TEM samples were prepared by deposition of the nanoparticle suspension on a carbon-coated microscopy copper grid.

2.2.2. Electronic and vibrational spectroscopies

A Fluoromax-4 (Horiba) spectrofluorimeter was used to acquire fluorescence excitation and emission spectra, which were corrected for the instrument response (as implemented in the software). UV/VIS diffuse reflection spectra were recorded on a Lambda-35 spectrophotometer (PerkinElmer Instruments) equipped with an integrating sphere. Raman spectra were collected in the 150–2300 cm^{-1} frequency range using a LabRAM-HR (Horiba) Raman microspectrometer. The 632.8 nm line of a He/Ne laser (ca. 1 mW) was used as the excitation source and a spectral resolution of ca. 3 cm^{-1} was obtained. IR spectra were recorded on a Spectrum-100 (Perkin Elmer) FTIR instrument in ATR mode between 600 and 4000 cm^{-1} with a resolution of 4 cm^{-1}. All spectroscopic experiments were carried out in ambient air.

2.2.3. Optical microscopy

Variable temperature fluorescence microscopy images have been recorded using an Olympus BX51 microscope equipped with a CCD camera (DU934N-BV, Andor Technology) and a ×50 magnification objective (LMPLFLN-50x, Olympus). The excitation and the collected light beams were filtered by band-pass filters centered at 452 nm and 543 nm, respectively. Variable temperature optical reflectance microscopy images were acquired using a MOTIC SMZ-168 stereomicroscope equipped with MOTICAM 1000 color camera operated in the green spectral range (around 540 nm). In both microscopy experiments the sample temperature was controlled by means of a Linkam THMS600 liquid-nitrogen cryostat. Prior to measurements the samples were desolvated at 70 °C for 30 min under a nitrogen flow. Then, they were cycled between 70 and 20 °C at rate of 4 °C/min.

3. Results and discussion

3.1. SEM

The scanning electron microscope images of cellulose fiber sheets, either unmodified (control) or functionalized by $[Fe(hptrz)_3](OTs)_2$ nanoparticles, are presented in Fig. 2. The modified sample surfaces were investigated both in backscattered electron (BSE) and secondary electron (SE) modes. In BSE mode the image contrast strongly depends on the atomic number of