

THESIS OF THE PH.D DISSERTATION

**Cellulose fiber functionazitation by SCO materials for smart
products**

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INTRODUCTION

Linter cellulose fiber based composites/nanocomposites were prepared by functionalising the fibers with iron(II)-triazole based spin-crossover particles and with fluorescent dye molecules doped spin crossover nanoparticles. The composites were characterized by electronic (UV-vis and fluorescence) and vibrational (Raman, FTIR) spectroscopies as well as by electronic and optical microscopies and TG, DSC analysis. The cellulose sheets prepared from the composite show significant thermochromic, thermofluorescent and photochromic effects associated with the spin transition phenomenon, providing scope for paper thermometry, anti-counterfeit and reverse printing applications.

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. 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. Here I describe biopolymer/SCO composites, which were elaborated by adsorbing pre-formed SCO particles from a colloidal solution onto linter fibers.

It is important to note that I have found difference between the absorbance of samples dried at different temperature. This property changed, when the pH of the cellulose suspension was well-controlled. In the absence of ascorbic acid the oxidation of SCO particles becomes important and the color of the handsheet changes from light violet to yellowish. The thermal variation of the reflectance of the composites was followed by optical analysis. The change was perfectly reversible, spatially homogenous and occurs rather abruptly. This abrupt change and the thermal hysteresis loop are related to the spin transition process. The thermochromic property of the material was transformed into thermofluorescence, when fluorescent dye molecules were added to the composite material.

OBJECTIVES OF THE RESEARCH

The aim of the research was the adsorption of SCO particles on cellulose fibers and investigation the as prepared composites. The cellulose sheets prepared from the SCO

composite show significant thermochromic and thermofluorescent effects associated with the spin transition phenomenon. The objectives of the research included:

- Preparation of linter cellulose fiber based composites by functionalising the fibers with spin-crossover particles of $[\text{Fe}(\text{NH}_2\text{trz})_3]\text{Br}_2$ or $[\text{Fe}(\text{Htrz})_2(\text{trz})]\text{BF}_4$ and nanoparticles of $[\text{Fe}(\text{hptrz})_3](\text{OTs})_2$ and acridine orange and pyrene-based luminophore dye molecules.
- Characterization of the composites by electronic and vibrational spectroscopies (UV-vis, fluorescence, Raman and FTIR), thermogravimetry, calorimetry, tensile tests, elemental analyses as well as by electronic and optical microscopies.

The composite cellulose sheets keep good mechanical and thermal properties and show perceptible thermochromic effects associated with a memory effect. They are rewritable by laser heating and completely erasable over several hundreds of printing cycles providing scope for inkless printing technologies and providing scope for paper thermometry and anti-counterfeit applications.

MATERIALS AND METHODS

Materials and sample preparation

Bleached linter cellulose fibers were received from Buckeye Technologies Inc. Htrz (1,2,4-triazole) was received from Alfa Aesar. FeBr_2 , $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, NH_2trz (4-amino-1,2,4-triazole) 4-Heptyl-1,2,4-triazole (hptrz) and Iron(II) tosylate were received from Sigma Aldrich. For the synthesis of SCO particles and nanoparticles three distinct solutions were prepared:

For the synthesis of the SCO complex $[\text{Fe}(\text{Htrz})_2(\text{trz})]\text{BF}_4$ two distinct solutions were prepared: 1) $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (113 mg, 0.3 mmol, 1 unit) in a solvent (1 ml, H_2O); 2) 1,2,4-triazole (69 mg, 0.9 mmol, 3 units) in a solvent (0.5 ml EtOH). The two solutions were rapidly mixed and the mixture became turbid within a few minutes followed by the establishment of a pink-purple precipitate. The precipitate was separated by centrifugation and washed twice with water. The $[\text{Fe}(\text{Htrz})_2(\text{trz})]\text{BF}_4$ particles obtained by this method showed a size distribution between ca. 1-5 μm .

For the synthesis of the SCO complex $[\text{Fe}(\text{NH}_2\text{trz})_3]\text{Br}_2$ [20]: 1) FeBr_2 (46 mg, 0.2 mmol, 1 unit), ascorbic acid (15 mg) in a solvent (1 ml, H_2O); 2) NH_2trz (54 mg, 0.6

mmol, 3 units) in a solvent (0.5 ml, H₂O). The [Fe(NH₂trz)₃]Br₂ particles obtained by this method showed a size distribution between ca. 400-1000 nm

For the synthesis of the SCO complex [Fe(hptrz)₃](OTs)₂: 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, H₂O); 2) hptrz (30 mg, 0.09 mmol, 1 equiv) in a solvent (2 ml, H₂O, 0.3 mL EtOH), and polymer PEG-3350 (200 mg); and 3) acridine orange (0.15 mg) in a solvent (3 ml, H₂O). The PEG-stabilized [Fe(hptrz)₃](OTs)₂ nanoparticles obtained by this method showed a size distribution between ca. 300 - 500 nm. 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 SCO complexes was prepared by ultrasonication in the presence of various ascorbic acid content. This was then added to a water or ethanol suspension of linter cellulose fibers 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.

Methods

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.

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. The CIELab coordinates were determined at room temperature using an Elrepho (AB Lorentzen and Wettre) Paper Brightness/Opacity/Color Testing Instrument. 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 600-4000 cm⁻¹ with a resolution of 4 cm⁻¹. All spectroscopic experiments were carried out in ambient air.

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.

Inductively coupled plasma-atomic emission spectrometry (ICP-AES)

An iCAP 6300 (Thermo Fisher Scientific) instrument was used to determine the amount of iron in the cellulose sheets following microwave digestion in a HNO₃ (65 %) / H₂O₂ (30 %) mixture.

Thermal analysis

Thermogravimetric (TG) data were acquired between 30 and 300 °C using a Perkin Elmer Diamond thermal analyzer under nitrogen purging gas (100 cm³min⁻¹) at a heating rate of 10 Kmin⁻¹. Differential scanning calorimetry (DSC) analysis was carried out on a Netsch DSC204 instrument under helium flow (30 cm³min⁻¹) at a heating/cooling rate of 10 Kmin⁻¹. Temperature and enthalpy were calibrated using the melting transition of standard materials (Hg, In, Sn).

SUMMARY OF THE RESEARCH

The images of cellulose fiber sheets, either unmodified (control) or functionalised by SCO particles were obtained through the scanning electron microscopy. In contrast to the SEM image of the control sample, the SCO particles modified sheet depicts a large number of bright nano-objects, which obviously contain heavier atoms than the rest of the

matrix. The micrographs basically show that the particles are randomly dispersed over the whole surface of the cellulose fibers. Because of a large number of free, accessible hydroxyl and carboxylic acid groups on the surface of cellulose fibers, those molecules complex well with metal ions and provide a stable environment for the stabilization of SCO particles. The accessible surface groups generate high surface free energy to adsorb partially positively charged nanoparticles. Hence the incorporated SCO particles can bound to cellulose macromolecules via electrostatic interaction, because the electron-rich oxygen atoms of polar hydroxyl of cellulose are expected to interact with electropositive metal cations. This assumption was evidenced during the FT-IR measurements at 3330 cm^{-1} wavenumber as the band intensity is increased after SCO particles adsorption to the cellulose surface.

Pure cellulose has no absorbance in the visible range. The UV/VIS spectra of the functionalized samples are characterised by a broad absorption band centered at *ca.* 540 nm. Based on the vast literature on iron(II)-triazole complexes we can safely assign this band to the $^1A_1 \rightarrow ^1T_1$ ligand-field transition of the LS form of the complex. The presence of this absorption band (i.e. the violet color of the dried handsheets) proves that the iron(II) ions are not oxidized during the elaboration of the handsheets. It is important to note also that we have found no significant difference between the absorbance of cellulose/[Fe(hptrz)₃](OTs)₂ samples dried at room temperature and at 95 °C. This result was obtained, however, only when ascorbic acid was added to the preparation mixture. In the absence of this additive the oxidation of SCO particles becomes important and the color of the handsheet changes from light violet to yellowish.

The LS to HS spin transition of the iron(II)-triazole complex upon heating results in the reversible bleaching of the the $^1A_1 \rightarrow ^1T_1$ ligand field absorption in the visible range. The extremely weak $^5T_2 \rightarrow ^5E$ absorption of the HS state in the near-infrared range (centred around 850 nm) could not be detected. The thermal variation of the reflectance of the composites were followed around 540 nm by cycling the cellulose/[Fe(hptrz)₃](OTs)₂ sample between 20 and 70 °C, between 20 and 45 °C (composite cellulose/[Fe(NH₂trz)₃]Br₂) or between 20 and 120 °C (composite cellulose/[Fe(Htrz)₂(trz)]BF₄). This change is perfectly reversible, spatially homogenous and occurs rather abruptly around 54 °C in the heating mode and 51 °C in the cooling mode (cellulose/[Fe(hptrz)₃](OTs)₂), around 116 °C and 85 °C for composite of cellulose/[Fe(Htrz)₂(trz)]BF₄ and 32 °C and 25 °C for composite of cellulose/[Fe(NH₂trz)₃]Br₂. This abrupt change and the thermal hysteresis loop are

unambiguously related to the spin transition process in the SCO complexes. On the evidence of the room temperature CIELab color space coordinates of the composites, the L^* value of control cellulose (*ca.* 94) is close to diffuse white (100), while this value decreases in the colored (i.e. LS) state of the composites to *ca.* 82 indicating increasing optical density. This difference defines the contrast of LS and HS state of the composites, which is easily perceptible by eye. The color contrasts (a^* , b^*) indicate, as can be expected, a change from light yellow to magenta. Positive changes in the a^* direction indicate a shift to red color, negative changes from cellulose in b^* values represent blue color shift.

The use of a focused laser beam is raster scanned on the sample to achieve photothermal heating. We have used the laser beam of our Raman microspectrometer to print patterns into our samples. Raman spectra of the cellulose/[Fe(NH₂trz)₃]Br₂ composite recorded within the heating branch of the thermal hysteresis region using different excitation powers. In these conditions the composite is in the LS state in the absence of laser irradiation. Indeed, for low power excitation we obtained spectra displaying Raman frequencies (253, 197, 130 cm⁻¹), which have been unambiguously assigned to the LS state of these complex. When increasing the laser power above a threshold value a significant change occurs, in particular in the low frequency region of the spectra with the vanishing of the LS marker peaks and the concomitant rise of new peaks around 140 cm⁻¹ characteristic of the HS state. After switching off the laser power the spin state of the complex remains HS since the temperature of the experiment falls within the hysteresis region.

If the separation between a pair of energy levels associated with the luminophore matches closely an energy level spacing of the SCO centre (in a given spin state) the excited state energy can be transferred to the latter. This way the thermochromic property of the material can be transformed into thermofluorescence. The [Fe(hptrz)₃](OTs)₂ nanoparticles were doped by acridine orange molecules and [Fe(Htrz)₂(trz)]BF₄ nanoparticles containing a pyrene-based luminophore. The luminescence excitation and emission properties of these latter remain virtually unchanged in the cellulose nanocomposite: the excitation and emission maxima are observed at 500 nm and 525 nm, respectively. The thermal variation of the fluorescence intensity of the nanocompoiste at 543 nm reveals the thermal hysteresis characteristic of the the spin transition of iron(II)-triazole based complexes. The change in the luminescence intensity upon the spin transition can be well explained by the relevant absorbance changes brought about by the

spin crossover phenomenon at 543 nm: the fluorescence becomes more intense in the HS state where the absorbance is bleached. It is interesting to note that contrary to the more commonly observed thermal quenching of the luminescence (due to thermal population of non-emitting states), the emission intensity in our nanocomposites increases with increasing temperature. Indeed, in a control experiment when we immobilised simply acridine orange molecules on the linter fibers (without adding any SCO material) we observed only a monotonous decrease (i.e. thermal quenching) of the luminescence intensity with increasing temperature. In addition it is interesting to notice that this latter sample exhibited some photobleaching as well, which (in the same experimental conditions) is not apparent in the sample containing SCO nanoparticles.

The thermal properties of the cellulose composites were further analyzed using DSC. The control cellulose shows only the well-known broad endothermic peak of native cellulose around *ca.* 80 °C during the first heating, which corresponds to an irreversible structural reorganization. This phenomenon was also observed in the composites. In addition the composites show heat capacity anomalies, which correspond to the latent heat of the spin transition. The corresponding peaks are observed around 111 °C (LS to HS transition upon heating) and 73 °C (HS to LS transition upon cooling) in composite cellulose/[Fe(Htrz)₂(trz)]BF₄ and 35 °C (first heating) 39 °C (second heating) and 33 °C (cooling) in composite cellulose/[Fe(NH₂trz)₃]Br₂.

The thermal stability (in inert nitrogen atmosphere) of the control and composite cellulose sheets can be depicted from the thermogravimetry data. It can be clearly seen that heating the samples up to 100 °C drives off absorbed moisture. Between *ca.* 100 – 270 °C the control sample exhibits virtually no weight loss. The [Fe(Htrz)₂(trz)]BF₄ modified cellulose composite shows nearly similar thermal stability though a slight weight loss (~5 %) occurs already between *ca.* 170 - 250 °C. The [Fe(NH₂trz)₃]Br₂ composite remains stable up to ~220 °C, but above this temperature the thermal degradation escalates. We have not carried out a detailed investigation of the thermal degradation process, but clearly the weight loss in this latter case indicates that the cellulose fibers are decomposed below 300 °C. We believe that [Fe(NH₂trz)₃]Br₂ particles act as catalytic impurities and initiate rapid depolymerization of the cellulose. Oxygen traces in the carrier gas may also contribute to this process. On the other hand, in composite of cellulose/[Fe(Htrz)₂(trz)]BF₄ boron atoms might intervene chemically as inhibitors in the oxidation reaction.

The stability of the composites is remarkable. After the elaboration of the handsheets we have carried out a few tenths of heating-cooling cycles. Then we stored the samples during 9 months in ambient conditions (air, daylight, office temperature) and we have not observed any significant degradation of the thermochromism. We have carried out more than 1000 thermochromic cycles in ambient air and we were still able to continue to print patterns into the paper without any substantial loss of contrast. Concerning the thermofluorescent properties their reproducibility was confirmed for several readout cycles indicating that spin transition properties of the composites are very robust.

THESIS

1. It has been stated that cellulose fibers after SCO adsorption control the particle agglomeration on its surface. Cellulose not only bonds the $[\text{Fe}(\text{Htrz})_2(\text{trz})]\text{BF}_4$ and $[\text{Fe}(\text{NH}_2\text{trz})_3]\text{Br}_2$ micro particles on the surface, but control the particle growths as well. The micrographs about the modified fibers shows homogeneously dispersed particles on the whole surface. The particle agglomeration and size control observations make the cellulose composite's colour similar like the particle itself in case of $[\text{Fe}(\text{Htrz})_2(\text{trz})]\text{BF}_4$.
2. It has been stated that the cellulose/ $[\text{Fe}(\text{NH}_2\text{trz})_3]\text{Br}_2$ composite is stable until 220°C , but above this temperature the thermal degradation escalates as the particles acts as catalytic impurities and initiate depolymerisation of cellulose. The $[\text{Fe}(\text{Htrz})_2(\text{trz})]\text{BF}_4$ modified cellulose composite shows nearly similar thermal stability like control though a slight weight loss ($\sim 5\%$) occurs already between ca. $170 - 250^\circ\text{C}$.
3. It has been stated that the presence of cellulose in the acridin doped cellulose sample virtually do not change the luminescence excitation and emission properties under thermal interaction. Hence the intensity changes in the cellulose/SCO/luminofor composites is caused by the SCO spin transition solely.
4. It has been stated that the reversible optical reflectance changes due to the thermal heating and cooling exhibited as hysteresis loop are unambiguously related to the spin transition process and the cellulose do not alter it. That

hysteresis loop can be observed in the examination of the particle itself and composite as well with no more than 2°C degree shift.

5. It has been verified that cellulose/[Fe(NH₂trz)₃]Br₂ composite possesses photochrome properties. However to achieve high-spin state higher excitation laser power is needed compare to the pure SCO particles.

PUBLICATIONS FROM THE TOPIC OF THE DISSERTATION

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