| 1       | On the formation of $Bi_2S_3$ -cellulose nanocomposite films from bismuth xanthates and   |
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| 2       | trimethylsilyl-cellulose  |
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## 21 Abstract

The synthesis and characterization of bismuth sulfide-cellulose nanocomposite thin films was 22 23 explored. The films were prepared using organosoluble precursors, namely bismuth xanthates for Bi<sub>2</sub>S<sub>3</sub> and trimethylsilyl cellulose (TMSC) for cellulose. Solutions of these precursors were spin 24 coated onto solid substrates yielding homogeneous precursor films. Afterwards, a heating step 25 26 under inert atmosphere led to the formation of thin nanocomposite films of bismuth sulfide nanoparticles within the TMSC matrix. In a second step, the silvl groups were cleaved off by 27 vapors of HCl yielding bismuth sulfide/cellulose nanocomposite films. The thin films were 28 characterized by a wide range of surface sensitive techniques such as atomic force microscopy, 29 attenuated total reflection infrared spectroscopy, transmission electron microscopy and 30 31 wettability investigations. In addition, the formation of the nanoparticle directly in the TMSC matrix was investigated in situ by GI-SWAXS using a temperature controlled sample stage. 32

Keywords: cellulose nanocomposite, trimethylsilyl cellulose, ATR-IR, GI-SWAXS, bismuth
 sulfide

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#### 42 **1. Introduction**

In recent years, research on semiconducting colloidal crystals led to a wide range of solution-43 44 processable optoelectronic devices such as photocatalysts, light emitting devices, sensors, and photovoltaic cells. However, many of the used materials contain toxic metals such as cadmium or 45 lead having a negative impact on the environment during manufacturing and after disposal. A 46 sulfide forming element with a rather low reported toxicity is bismuth. Bi<sub>2</sub>S<sub>3</sub> nanoparticles and 47 nanocomposites find numerous applications in magnetic resonance imaging (Rabin, Manuel 48 Perez, Grimm, Wojtkiewicz, & Weissleder, 2006), thermoelectric devices (Y. Y. Wang, Cai, & 49 Yao, 2012), memory devices (Liu et al., 2013), photodetectors (Konstantatos, Levina, Tang, & 50 Sargent, 2008), as electrode material in lithium-ion batteries (Jung, Park, & Sohn, 2011), as well 51 52 as in electronic, optoelectronic and gas sensor devices (Ahmad, Rafiq, Rasool, Imran, & Hasan, 2013; Li, Yang, Zhang, & Zhou, 2012; Yao et al., 2008; Yao et al., 2006). In optoelectronic 53 devices, the low band gap of bismuth sulfide (1.3 to 1.7 eV (Liu et al., 2013)) is exploited for 54 55 instance. (Martinez et al., 2013; Z. Wang et al., 2010). A very convenient route to produce bismuth sulfide nanoparticles in synthetic polymer matrices is to use soluble bismuth xanthate 56 (BiXa) precursors which are decomposed after the final processing step e.g., spin coating or knife 57 blading (Kaltenhauser et al., 2013). In that case, a functioning solar cell was assembled using this 58 nanocomposite thin film as a functional layer. These works inspired us to explore whether 59 polysaccharide derivatives could be implemented in such layers. It can be expected that they are 60 capable to act as stabilizing agents to control the growth of the Bi<sub>2</sub>S<sub>3</sub> nanoparticles generated 61 from xanthate precursors to obtain nanocomposites with a better ecological footprint. The major 62 63 challenge to obtain homogeneous nanocomposites is to find a common solvent for both, the BiXa precursor and the polysaccharide derivative. Since many bismuth xanthates are readily soluble in 64 65 apolar organic solvents, trimethylsilyl cellulose (TMSC) was chosen as polysaccharide due to its

excellent solubility in aprotic solvents at high degrees of substitution with TMS groups. TMSC 66 67 has several further advantages in this context: its solubility can be fine-tuned by the degree of substitution, it is rather light- and thermostable under exclusion of air/moisture (Wolfberger et al., 68 2015) and it is a good film forming polymer (T. Mohan et al., 2013; Orelma, Filpponen, 69 70 Johansson, Laine, & Rojas, 2011). Further, the conversion into cellulose proceeds via a gas phase reaction employing vaporous HCl (Ehmann et al., 2015; Eero Kontturi & Lankinen, 2010). In 71 contrast to other regeneration procedures, the nanocomposite films do not come in contact with 72 any liquids during the regeneration, preventing undesired alterations in terms of morphology and 73 structure. The regeneration procedure using acidic vapors was just recently exploited to generate 74 metallic Bi-NP/cellulose nanocomposites in a very efficient way by photoreduction of a bismuth 75 precursor in toluene solution (Breitwieser et al., 2015). An advantage by using biobased materials 76 in such nanocomposites is to circumvent or at least reduce the use of synthetic polymers in 77 advanced materials to lower the impact on the environment. Particularly cellulosic materials are 78 well suited for this purpose since they are renewable and, if the degree of substitution with 79 functional groups is low, they are also biodegradable. In the case of TMSC, it was already 80 demonstrated some decades ago that this particular cellulose derivative has a rather good life 81 cycle performance.(Cooper, Sandberg, & Hinck, 1981) 82

Here, we combine the TMSC precursor route for cellulosic thin films with the BiXa strategy to generate  $Bi_2S_3$  nanoparticles. The goal is to realize  $Bi_2S_3$  cellulose nanocomposite thin films. The particular role of the TMSC is to provide a matrix which allows for controlling the growth and shape of the nanoparticles.

87 The paper is constructed as follows: after a detailed characterization of the film forming
88 properties of various BiXa/TMSC films, these films were thoroughly analyzed and subjected to a

heat treatment. The formation of the particles was monitored by *in-situ* grazing incidence X-ray
scattering using a temperature controlled heating stage. All samples have been analyzed in detail
after the heating step and after conversion to cellulose using HCl vapors was accomplished.

# 92 **2. Experimental**

93 2.1 Materials

Trimethylsilyl-cellulose (TMSC; Avicel pulp DS: 2.7-2.9), purchased from TITK Rudolstadt, and 94 bismuth xanthate (bismuth(III)-O-3,3-dimethylbutan-2-yl dithiocarbonate, denoted as BiXa in the 95 96 following), synthesized according to a literature procedure, (Kaltenhauser et al., 2013) were used as starting materials for the thin film preparation. Hydrochloric acid (37 wt.%), chloroform (99 97 98 wt.%) and sulfuric acid (95 wt.%) were purchased from VWR chemicals. Hydrogen peroxide (30 wt.%) was obtained from Sigma-Aldrich. All chemicals were used without further purification. 99 100 Silicon wafers (Siegert Wafer), glass slides (Roth), Au-coated glass slides (SPR102-AU), Filter 101 Chromafil® Xtra PVDF-45/25 0.45 µm, petri dishes (20 ml; 5 cm diameter) were used as 102 obtained.

103 2.2. Methods

#### 104 2.2.1 ATR-IR spectroscopy

105 The experiments were performed with an ALPHA FT-IR spectrometer (Bruker; Billerica, MA, 106 USA). For the measurements, an attenuated total reflection (ATR) unit was used with 48 scans at 107 a resolution of 4 cm<sup>-1</sup> and a scan range between 4000 and 400 cm<sup>-1</sup>. The data was analyzed with 108 OPUS 4.0 software.

109 2.2.2. AFM

Atomic force microscopy (AFM) images were recorded in the tapping mode (non-contact mode) on a Veeco Multimode Quadrax MM AFM (Bruker; Billerica, MA, USA). For the scanning, silicon cantilevers (NCH-VS1-W from NanoWorld AG, Neuchatel, Switzerland) were used with an average spring constant of 42 N/m (Force Constant) and with a resonance frequency of 270 -320 kHz. All measurements were performed at room temperature and under ambient atmosphere. The calculation of the root mean square roughness (calculated from a 6 x 6 µm image) and the image processing was done with the Nanoscope software (V7.30r1sr3; Veeco).

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#### 118 2.2.3. Stylus profilometry/Determination Film Thickness

Layer thickness was measured on a Bruker DekTak XT surface profiler. The scan length was set to 1000  $\mu$ m over the time duration of 3 seconds. The diamond stylus had a radius of 12.5  $\mu$ m and the force was 3 mg with a resolution of 0.333  $\mu$ m/sample and a measurement range of 6.5  $\mu$ m. The profile was set to *hills and valleys*. For the determination of the film thickness a silicon wafer sample was scratched five times (up to the silicon surface). This measured profile was then used to calculate the thickness of the different coatings.

125 2.2.4 Contact angle and surface free energy determinations

To determine the static contact angle and the surface free energy (SFE), a drop shape analysis system DSA100 (Krüss GmbH, Hamburg, Germany) with a T1E CCD video camera (25 fps) and the DSA1 v 1.90 software was used. For the measurements, 3  $\mu$ l droplets of Milli-Q water ( $\geq$ 18 M $\Omega$  cm<sup>-1</sup>) and diiodomethane as test liquids in the sessile drop mode were deposited on the substrates at 25 °C. Each sample was measured at least three times. The contact angle calculations were performed using the Young-Laplace equation and for the determination of thesurface free energy the Owens-Wendt-Rabel & Kaelble method was employed.

133 2.2.5. UV-Vis spectroscopy

The UV-Vis absorption spectra of the samples (on glass substrate) were measured on a Shimadzu
UV-1800 UV spectrophotometer. The absorbance was determined in a range from 200 - 1100 nm
at 25 °C under ambient atmosphere.

137 2.2.6. GI-SWAXS

The 2D in situ GISAXS and GIWAXS experiments were performed at the high-flux SAXS 138 139 beamline 5.2L of the electron storage ring ELETTRA (Trieste, Italy). The X-ray energy was 8 keV. The beamline has been adjusted to a q-resolution  $(q=4\pi/\lambda*\sin(2\theta/2), 2\theta)$  being the 140 scattering angle) between 0.1 and 3.5 nm<sup>-1</sup> (GISAXS). During the temperature scan, data were 141 142 recorded with framing rate of 6 s using a Pilatus 1M detector (Dectris). For detection of the GIWAXS signal, a Pilatus 100K detector from Dectris was used. As calibration standard silver 143 behenate with a lamellar spacing of 58.38 Å and p-bromo benzoic acid were used. The sample-to-144 detector distance was 1516.55 mm and the incidence angle was set to 0.83°. 145

The *in situ* heating was performed using the Anton Paar DHS1100 heating stage (temperature range 5-1100 °C, sealed with Kapton windows) which was continuously rinsed with gaseous nitrogen under steady flow conditions. The heating rate was set to 10 °C/min.

149 2.2.7. Scanning Transmission Electron Microscopy (STEM)

150 STEM investigations were done on a Titan<sup>3</sup> G2 60-300 from FEI at 300 keV accelerating voltage.

151 The microscope is equipped with a CS-corrector to correct the spherical aberration in the STEM

mode to obtain atomic high resolution with a lateral resolution below 1 Ångström. Bright field (BF) and high angle annular dark field (HAADF) STEM images were recorded with detectors from Gatan. Energy dispersive X-ray spectroscopy (EDXS) was performed with four highsensitivity SDD X-ray spectrometers (Super-X) from Bruker. The STEM image was further used for the determination of the nanoparticle size distribution.

### 157 2.2.8. Film Preparation

The different substrates (silicon wafers (1.4 x 1.4 cm), glass slides (1.4 x 1.4 cm) and gold coated 158 glass slides (2.0 x 1.0 cm)) were cleaned with "piranha" acid ( $H_2SO_4:H_2O_2 = 7:3$  (v/v)) for 30 159 160 min (10 min for gold slides) and neutralized afterwards with distilled water. For the film preparation, TMSC (1 wt.%) was dissolved in CHCl<sub>3</sub>, filtered and combined (1:1 (v/v)) with the 161 bismuth xanthate solution (1 wt.%, 5 wt.%, 10 wt.% in CHCl<sub>3</sub>). The solution (180 µl) was 162 163 deposited onto the different substrates and spin coated at 4000 rpm for 60 s (acceleration 2500 rpm/s). The *in-situ* synthesis of the Bi<sub>2</sub>S<sub>3</sub> nanoparticles was performed by thermal conversion 164 (185 °C over a period of 30 min, heating rate = 10 °C/min) of bismuth xanthate on a heating 165 plate. After the thermal conversion, the films were exposed to HCl vapors for 12 minutes (created 166 by 2 ml 12 wt% HCl in a petri dish) to obtain fully regenerated cellulose/Bi<sub>2</sub>S<sub>3</sub>-nanoparticle thin 167 films. 168

## 169 **3. Results and Discussion**

170 3.1. Film preparation

The first step in the preparation of the nanocomposite thin films was to evaluate under which conditions homogenous films of TMSC and BiXa were formed by spin coating (Figure 1). We

- 173 chose as starting point 1 wt.% solutions of TMSC in CHCl<sub>3</sub> and added different amounts of BiXa
- 174  $(1, 5, and 10 wt.\% in CHCl_3, respectively).$



Figure 1. Schematic representation of the manufacturing steps of BiXa/TMSC nanocompositefilms.

In all cases, macroscopically clear solutions were obtained which were stable over a period of 179 more than 30 minutes. These solutions were placed on silicon substrates and subjected to spin 180 181 coating (4000 rpm, 2500 rpm s, t = 60 s). After spin coating, all the films showed a smooth and homogeneous appearance by naked eye, which already gave a first hint that TMSC and BiXa 182 were compatible in both, solution and solid state. The next step was to evaluate the thermal 183 conversion of the BiXa to the Bi<sub>2</sub>S<sub>3</sub> particles inside the films. It is known from literature 184 (Kaltenhauser et al., 2013) that BiXa starts to decompose at ca 150 °C to form Bi<sub>2</sub>S<sub>3</sub> concomitant 185 with the formation of other volatile compounds. COS and 3,3-dimethylbut-1-ene are the typical 186 species of the decomposition of xanthates via the Chugaev rearrangement (Pradhan, Katz, & 187

Efrima, 2003). Although H<sub>2</sub>S is not directly formed via the Chugaev mechanism, traces may evolve during the decomposition of BiXa via other pathways. This could potentially lead to (partial) regeneration of TMSC via acid induced desilylation to cellulose along with the release of TMSCl as reported for related cases where HCl vapors have been employed. (Eero Kontturi, Thüne, & Niemantsverdriet, 2003)

193 3.2. ATR-IR spectroscopy

A very suitable method to monitor chemical reactions such as hydrolysis in thin films is ATR-IR
spectroscopy. It can be clearly seen in Figure 2 (A) that neither the addition of the xanthate to the
TMSC, nor the heating step caused regeneration of TMSC to cellulose.



Figure 2. A) Comparison of the ATR IR reference spectra (BiXa, TMSC and cellulose) with nanocomposite thin films having a BiXa concentration of 5 wt.%. B) Comparison of ATR IR spectra of TMSC/BiXa nanocomposites at different BiXa contents. More data is available in the Supplementary Materials (Fig. S1 and S2)

For the non-treated BiXa/TMSC film, typical bands for xanthates as well as for TMSC were detected. The bands at 1238 cm<sup>-1</sup> and 1207 cm<sup>-1</sup> can be attributed to the asymmetric C–O–C stretching vibrations, and those at 1047 and 1017 cm<sup>-1</sup> to the C–S stretching vibrations of the xanthate.

For the TMSC fraction, the Si-C vibration at 852 cm<sup>-1</sup> and 752 cm<sup>-1</sup> are characteristic. By 206 207 increasing the amount of BiXa in the films, the relative intensity of bands associated with TMSC was significantly reduced (Fig 2B) since the spectra have been normalized on TMSC band at 208 1462 cm<sup>-1</sup>. Therefore any incorporation of compounds into the film, will decerase the relative 209 intensity of bands solely corresponding to TMSC. For instance, the band at 1121 cm<sup>-1</sup> can be 210 211 assigned to symmetric C-O-C stretching vibrations of both, TMSC and BiXa; therefore the 212 relative band intensities remained rather constant by increasing the BiXa content. Bands associated with the BiXa (1238 cm<sup>-1</sup>, 1207 cm<sup>-1</sup>) vanished after exposure to elevated 213 temperatures indicating a decomposition of the xanthate, while leaving the TMSC untouched. 214 215 This was proven by a distinctive spectrum for TMSC exhibiting all characteristic bands for Si-C and Si-O-C vibrations. It can be concluded that neither the heating step at 195 °C nor the formed 216 volatile side products in the conversion of BiXa to Bi<sub>2</sub>S<sub>3</sub> caused the TMSC films to regenerate. 217 218 However, a separate HCl treatment indeed induced regeneration from TMSC to cellulose as proven by the appearance of typical bands associated with cellulose at 1024 cm<sup>-1</sup> (C-O 219 stretching; aromatic C–H in plane deformation), 1064 cm<sup>-1</sup> (C–O stretching) and 3000–3600 cm<sup>-1</sup> 220 (OH stretching) (T. Mohan et al., 2012). 221

# 222 3.3. Particle formation - GI-SWAXS and STEM

In order to get more insights in the heat-induced conversion of the BiXa into the corresponding
bismuth sulfides, combined GI-SAXS and GIWAXS studies using monochromatic X-rays have

been performed. The setup of the experiment comprised a temperature-controlled sample stage 225 226 which was flushed with dry nitrogen to prevent oxidation by air during the illumination with the synchrotron beam. After positioning the samples, the temperature was steadily increased and the 227 228 scattering patterns were recorded. It can be clearly seen that the scattering contrast started to 229 increase at ca 120 °C and reaches a maximum at ca. 195 °C. This can be attributed to the formation of Bi<sub>2</sub>S<sub>3</sub> nanoparticles, which provide a higher scattering contrast compared to the 230 small precursor molecules (Fig. 3) The formation of the nanoparticles was further evidenced in 231 two movies demonstrating the heat induced conversion of BiXa to Bi<sub>2</sub>S<sub>3</sub> (Supplementary 232 materials section). Further proof for the presence of the bismuth sulfides was provided by 233 analysis of the reflection planes of the GI-WAXS patterns (Fig. 4). The main diffraction peaks at 234 2.8 Å, 3.1 Å, 3.5 Å, 3.7 Å, 3.9 Å, 5.4 and 7.0 Å were nearly identical as those reported for 235 orthorhombic Bi<sub>2</sub>S<sub>3</sub> in literature (Joint Committee on Powder Diffraction Standards JCPDS Card 236 237 No. 17-320).



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Figure 3. Heat induced growth of Bi<sub>2</sub>S<sub>3</sub> nanoparticles in a TMSC film upon increase of
temperature from 25 to 195 °C monitored by *in situ* GI-SAXS. Left: TMSC:BiXa ratio of 1:1,
Right: TMSC: BiXa ratio of 1:10. Please note the different intensity scales for both scattering
curves.



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Figure 4. Scattering patterns of a TMSC/BiXa film before and after the heating procedure
monitored by *in situ* GI-WAXS. The BiXa concentration was 10 wt.% in those films.

A crucial question is the shape and the size of the nanoparticles grown in the film. Besides 247 248 SWAXS, bright field and high angle annular dark field TEM are very suitable methods to determine particle dimensions in thin films. However, sample preparation was a bit tricky, since 249 we had to ensure the same conditions for the TEM sample as for the other films using Si-wafers 250 as support. Since the films could not be peeled off the substrate nor deposited onto carbon grids 251 (the polymer coating melts at 150 °C) we decided to deposit the TMSC/BiXa mixture on a NaCl 252 grid, followed by the heating step and subsequent careful dissolution of the grid in water. Figure 253 5 illustrates the results of the 5 wt.% BiXa sample with different magnifications after the heating 254

step. The images indicated that the formed nanoparticles were rod shaped with a diameter of 254 25 $\pm$ 4 nm and a length of 80 $\pm$ 7 nm. An EDX spectrum of the Bi<sub>2</sub>S<sub>3</sub> nanoparticles is depicted in the supporting materials (Fig. S4). Most of the particles were homogenously distributed in the matrix. However, some spots feature a higher particle density. The origins of this behavior remain unclear and could be either related to sample preparation or to the particle growth (Figure 5).



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Figure 5. Bright field (left) and high angle annular dark field (right) TEM images of 5 wt.%
Bi<sub>2</sub>S<sub>3</sub>-NP in a TMSC matrix at different magnifications.

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265 3.4. Morphology - AFM

While the above mentioned methods clearly provided proofs for the successful conversion of the BiXa to the sulfides, a very interesting question was to which extent the morphology was affected by the heating process. It can be clearly seen that the heating process itself did not induce changes in neat TMSC. However, the addition of BiXa into the TMSC matrix led to slightly rougher surfaces. Interestingly, the effect of the concentration on morphology on non-treated films was rather small (Table S2; Supplementary materials). However, situation changed after the
heat treatment. All the images showed homogenously distributed features and a significant
increase in the roughness of the films, relating to the amount of BiXa in the films.

The morphology of the nanocomposite films was analyzed by atomic force microscopy before and after the modification steps. In Figure 6, the AFM images of the non-treated films (A, D, G, J) at three different xanthate concentrations and there modifications (B, C, E, F, H, I, K, L) are depicted. The images clearly showed that particles were formed.





**Figure 6.** TMSC matrix (A, B, C) with 1 wt.% BiXa (D, E, F), 5 wt.% BiXa (G, H, I), 10 wt.%

280 BiXa (J, K, L); Z-scale (A, D, G, J) = 40 nm, Z-scale (B, C, E, F, H, I, K, L) = 130 nm

The surface morphology as well as the roughness of the native films was altered by increasing theBiXa concentration (see Table S2). However, after the heating step, 80-100 nm small structures

are present in the films which can be attributed to the generated Bi<sub>2</sub>S<sub>3</sub> nanoparticles. For the films 283 284 containing 5 and 10 wt.% BiXa, this effect was very pronounced (Figure 6, H and K) while the surface morphology of the film containing 1 wt.% BiXa was not affected (for a smaller Z-scale 285 see Fig. S5, Supplementary aterials). Besides changes in morphology, the film thickness 286 287 decreased since a large fraction (67 wt.%) of BiXa consists of organic material, which was converted to volatile compounds during the heating step, finally leaving the TMSC film. 288 Consequently, the decrease in layer thickness correlated with the amount of BiXa in the films. 289 The 1 wt.% samples featured a decrease of 103 to 62 nm, the 5 wt.% from 248 to 92 nm and the 290 largest decrease was observed for the 10 wt.% sample (482 to 118 nm). As films shrank, the 291 roughness of the surface increased, especially for the samples containing 5 wt.% (2.83 nm to 11.4 292 nm) and 10 wt.% (2.78 nm to 20.9 nm) BiXa. 293

After the heat treatment step, the TMSC fraction of the nanocomposite was converted to cellulose by exposing the films to vaporous HCl over a period of 12 minutes. Although the thickness of the films decreased again after the regeneration of the material due to the loss of silyl groups, the morphology as well as the roughness remained unaffected by the treatment. During the entire modification process (heating and regeneration) the film thickness was reduced by 75 - 80% of their initial values.

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305 3.5. Surface wettability and surface free energy

A further aspect when it comes to applications is the wettability of the nanocomposites and their interaction with other materials. Particularly the surface free energy (SFE) is an important parameter in the design of multi-layer applications. Therefore, the contact angles of different liquids (water and diiodomethane, Fig. S6, Supplementary materials) of the nanocomposites were determined using the sessile drop approach.



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Figure 7. Static water contact angles and surface free energies of the native, heat treated andregenerated sample.

As shown in Figure 7, the non-treated TMSC/BiXa films exhibited static water contact angles of ca  $100^{\circ}$ , regardless of the BiXa concentration used for film preparation. Interestingly, even after the heat treatment step, i.e. the conversion of BiXa to Bi<sub>2</sub>S<sub>3</sub>, the films retained their hydrophobic character with just minor differences compared to the non-treated ones. These minor differences may be related to alterations in surface roughness, although we do not have hard evidence for this. Moreover, this data was a further proof (besides IR spectroscopy) that the TMS groups were not cleaved off by the formed volatile side products during BiXa decomposition. This was reflected in the SFE of those films featuring a rather large dispersive and a low polar contribution. After a final HCl treatment step, the water contact angles decreased to values which were in a typical range for cellulose films ( $25^{\circ}$ ). Further SFE (ca 72 mJ/m<sup>2</sup>) increased having a rather large polar contribution of ca 30 mJ/m<sup>2</sup>. The reason for this effect was the elimination of the nonpolar alkyl chains and TMS groups.

326 3.6. UV-Vis spectroscopy

Since Bi<sub>2</sub>S<sub>3</sub> is known as material with a low band gap, UV-VIS was employed to check the 327 328 suitability of this material as light absorber in TMSC and cellulose films. For this purpose, the 329 films have been deposited on glass slides instead of silicon wafers. Fig. 8 compares the TMSC/BiXa films before and after thermal treatment. It can be clearly seen that after the heat 330 treatment the initial absorption band of the BiXa at ca. 380 nm vanished while the characteristic 331 332 spectrum of  $Bi_2S_3$  nanoparticles with an onset between 800 – 900 nm appeared. The TMSC and regenerated cellulose matrix material (for TMSC and TMSC heated see Fig. S7) did not absorb in 333 the Vis region and therefore did not affect the absorption of the Bi<sub>2</sub>S<sub>3</sub> nanoparticles. 334



Figure 8. UV-VIS absorption spectra of the 10 wt.% native, heat treated, regenerated andcellulose reference sample.

The determination of the band gap of the nanocomposite films yielded 1.76 eV which is within the range of reported values for bismuth sulfides. Additional data can be found in the Supplementary Materials (Figure S8).

### 341 **4. Conclusions**

In summary, we successfully demonstrated the generation of bismuth sulfide cellulose nanocomposites based on BiXa and TMSC. Spin coating of chloroform solutions containing BiXa and TMSC onto solid substrates yielded for a variety of BiXa:TMSC ratios homogeneous films, whereas the BiXa was successfully converted in all cases to rod-like  $Bi_2S_3$  nanoparticles in a subsequent heating step under exclusion of oxygen and moisture. The conversion of the BiXa to the  $Bi_2S_3$  nanoparticles was further monitored *in-situ* using GI-SWAXS experiments at a synchrotron facility and yielded together with TEM particle with a diameter of  $25\pm4$  nm and a

length of 80±7 nm. The morphology of the films depends on the ratio of the initial amount of 349 350 BiXa in the films and ranged from smooth (1 wt.%) to rough (10 wt.%). After the particles had formed, the silvl groups were cleaved off using HCl vapors under TMSCl elimination to obtain 351 352 cellulose-Bi<sub>2</sub> $S_3$  nanocomposite films. This procedure affected the roughness as well as the 353 thickness of the films since this conversion was associated with a shrinkage of the film due to the formation of hydrogen bonds (E. Kontturi et al., 2011). Depending on whether the silvl groups 354 were cleaved or not, the wettability of the nanocomposite films was either hydrophobic or 355 hydrophilic. This enables a maximum in flexibility given the case if these films should be 356 embedded into devices. In principle, it is further possible to obtain partially regenerated films 357 358 (Tamilselvan Mohan et al., 2011) whereas in this case the resulting surface free energies are somewhere in between fully regenerated cellulose and non-regenerated TMSC, opening further 359 the processing window for making devices. Finally, the conversion of the BiXa to the bismuth 360 361 sulfide particles resulted in a change of color due to the low band gap (1.76 eV) of the nanoparticles which was quantified by UV-Vis spectroscopy. It clearly turned out that the 362 observed absorptions correspond well to already published spectra of Bi<sub>2</sub>S<sub>3</sub> nanoparticles. In 363 364 future studies, we will focus how to use this approach in the generation of cellulose based photovoltaic devices. 365

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