Carbohydrate Polymers 197 (2018) 614–622

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Synthesis and characterization of nano fibrillated cellulose/Cu_2O films; micro and nano particle nucleation effects

Maryam Sabbaghan[a], Dimitris S. Argyropoulos[b,*]

[a] Faculty of Sciences and Institute for Advanced Technology, Shahid Rajaee Teacher Training University, PO Box 16785-163, Tehran, Iran
[b] Departments of Chemistry and Forest Biomaterials, North Carolina State University, 2820 Faucette Drive, Raleigh, 27695-8005, NC, USA

ARTICLE INFO

Keywords:
Nano-fibrillated cellulose (NFC)
Cuprous oxide
Morphology
Semiconductor
SEM
TGA
Particle nucleation mechanism

ABSTRACT

Cubic, truncated cubic and spherical nano and micro particles of Cu_2O, can be selectively deposited onto nano fibrilated cellulose gels by the modulated alkaline reduction of Cu^{2+} ions aided by the cellulose's reducing end groups. The role of the cellulose's reducing end groups and that of externally added carbohydrate reducing agents, towards inducing various Cu_2O morphologies, is discussed with respect to the detailed nucleation effects leading to micro and nano Cu_2O particle deposition on NFC. When the reducing end groups are provided only by the cellulose's chain ends, supersaturation effects seem to be affecting the Cu_2O nucleation mechanism. However, the Cu_2O nucleation considerations were altered when mobile reducing end groups were provided by adding dextrose in the system, promoting additional particle nucleation sites. Furthermore, the effort offered the possibility to quantitatively determine the number of accessible reducing end groups (-CHO) present in NFC, expressed in mmol/g. The optical properties of the created NFC/Cu_2O films were examined by UV–vis absorption measurements, revealing band gaps ranging between 2.02–2.25 eV. The accumulated understanding expands the utility window and opens new directions for the novel utilization of nano-fibrillated cellulose, and more specifically toward semiconductor applications.

1. Introduction

Our society's increased emphasis in the search for sustainable, green and eco-friendly materials has focused its efforts (amongst others) on cellulose. In this regard, nano-fibrillated cellulose (NFC) has received significant attention due to its ease of preparation, high specific surface area, high strength and stiffness, low weight and its ability to form transparent and flexible films. The structural characteristics of NFC offer nano-fibers of diameters in the range of 20–60 nm and length of several micrometers exhibiting both amorphous and crystalline domains, in a web-like structure (Abdul Khalil et al., 2014; Kalia, Boufi, Celli, & Kango, 2014; Missoum, Belgacem, & Bras, 2013).

On the other hand, metal oxides are an indispensable component of many applications (Patil et al., 2015; Park, Baker, & Somorjai, 2015; Vedrinea and Fechete, 2016;). Amongst them, abundant metal oxide particles of copper (I) (Cu_2O) offer low toxicity, high absorptivity (in the visible spectral range) with acceptable environmental characteristics. These oxides have seen applications in diverse areas, such as gas sensors (Zhang, Liu, Peng, Wang, & Li, 2006), components in magnetic storage media (Li, Gao, Murphy, & Gou, 2004), solar energy conversion devices (Hung, Tsung, Huang, & Yang, 2010), electrodes for lithium-ion batteries (Hasan, Chowdhury, & Rohan, 2010), catalysts in the conversion of CO to CO_2 (White, Yin, & Hall, 2006), the photo-decomposition of water to O_2 and H_2 (Paracchino, Laporte, Sivula, Gratzel, & Thimsen, 2011), and as facilitators in the preparation of various compounds (Kumar et al., 2016; Xu, Han, & Chi, 2010; Xu, Wang, & Zhu, 2006). Furthermore, nontoxic Cu_2O particles with no particular documented interactions with DNA, have seen significant attention as possible components in biological and medical applications (Jong and Borm, 2008).

Several methods have been developed for the preparation of cuprous oxide, including thermal, sono-chemical and chemical reduction methods as well as metal vapor synthetic approaches (Dhas and Raj, 1998; Vitulli and Bernini, 2002; Wang, Nikitin, & McComb, 2008).

Cellulose composites offer possibilities of improved optical, mechanical, thermal, electrical and biological properties (Hubbe, Rojas, Lucia, & Sain, 2008; Osong et al., 2016). When metal oxides are deposited on cellulose their tendency for self-induced aggregation can be modulated and/or prevented, allowing for the creation of specific structures of pre-determined morphologies and size (Hu, Chen, Yang, Li, & Wang, 2013).

Sedighi et al., (Sedighi, Montazer, & Samadi, 2014) have prepared

* Corresponding author.
E-mail addresses: dsargyro@ncsu.edu, dimitris.argyropoulos@ncsu.edu (D.S. Argyropoulos).

https://doi.org/10.1016/j.carbpol.2018.06.011
Received 31 March 2018; Received in revised form 13 May 2018; Accepted 2 June 2018
Available online 04 June 2018
0144-8617/

cotton/Cu_2O nano-composites by precipitating Cu_2O particles on cotton fabrics of good tensile using copper sulfate and a reducing agent (glucose) at elevated pH's. These fabrics showed considerable antibacterial behavior against *staphylococcus aureus* and *Escherichia coli* (Sedighi et al., 2014). Furthermore, the same team examined the photocatalytic activity of the cotton fabrics toward the daylight induced photo-degradation of methylene blue (Montazer, Dastjerdi, Azdaloo, & Mahmoudi Rad, 2015). Errokh et al., (Errokh et al., 2016) have investigated the controlled surface oxidation of cellulose fibers aimed to generate carboxylic acid groups on it so as to act as a binding site for the adsorption of Cu^{2+} via electrostatic coordination. Subsequently, the adsorbed Cu^{2+} ions were converted to Cu_2O by dipping the treated cotton fibers into an aqueous solution of hydrazine monohydrate or hydroxylamine (Errokh et al., 2016). In other efforts, the presence of Cu_2O nanoparticles-on functionalized cellulose-based aerogels was reported *via* the in situ deposition of Cu_2O nanoparticles (Xiuping et al., 2017). Octahedral Cu_2O nanoparticles were thus reported to be formed and anchored onto the surface and inner walls of the cellulose matrix. The cellulose-based aerogel with its 3D porous structure possessing various functional groups (e.g. $-COO^-$, $-NH_2$, $-OH$) was promoted as a micro reactor for the synthesis of octahedral Cu_2O nanoparticles (Xiuping et al., 2017).

In this effort, we examine the details of the modulated alkaline reduction of copper sulfate aimed at depositing Cu_2O onto nano-fibrillated cellulose gels. Our work is focused at revealing the role of the cellulose's reducing end groups towards inducing various Cu_2O morphologies. Finally, this is compared with the use of dextrose as an external reducing agent revealing intricate details of nucleation effects leading to micro and nano Cu_2O particle deposition on NFC.

2. Materials and methods

2.1. Materials

A sample of Nano Fibrillated Cellulose was provided by Stora Enso Corporation in the form of a gelatinous material containing approximately 5% by weight of solid polysaccharide. Dextrose, copper sulphate pentahydrate and sodium hydroxide were procured from fisher scientific. All chemicals were of the highest purity and were used thus without further purification.

2.2. Preparation of NFC/Cu_2O

Copper (II) sulfate pentahydrate was used as the copper source. Solution A containing specified concentrations of $CuSO_4{\cdot}5H_2O$ and solution B containing specified concentrations of dextrose were initially prepared (Table 1). The following solutions were used for the preparation of NFC/Cu_2O in the absence of external reducing agent (S1-7). 25 mL of copper (II) sulfate aqueous solution A (Table 1) were mixed with a suspension of 4 g of NFC (1 mmol) in 21 mL distilled water (25 mL total volume of suspension).

The following procedure was followed for the preparation of NFC/Cu_2O in the presence of external reducing agent (SD1-3). 21 mL of dextrose solution B was mixed with 4 g of NFC (1 mmol) in distilled water (25 mL total volume of suspension).

The mixture was kept under magnetic stirring so as to homogenize the suspension (30 min) and then heated to 50 °C using an oil bath. A specified amount of solid sodium hydroxide (Table 1) was added to the mixture and the suspension was heated at 80 °C for 30 min. The pH was measured at the end of the reaction (Fig. 1 in supplementary data).

The reddish suspension was then thoroughly washed to remove unreacted copper ions and base. The solid was then re-suspended (x2) in 40 mL of water each time and once in 40 mL of ethanol (96%). Finally, it was washed with 40 mL of water (x2) followed by shaking and centrifugation as specified above (Jouan centrifuge, CR 422, 3000 rpm, 5 min).

The NFC/Cu_2O composite films were prepared using a doctor blade with thickness settings of 1 mm. The resulting films were allowed to dry at room temperature. The thickness after drying was determined to be about 0.03 mm.

For the preparation of control samples S4 and SD3, 25 mL of distillated water were mixed with a suspension of 4 g of NFC (1 mmol) in 21 mL distilled water (25 mL total volume). The suspension was then heated with continuous agitation at 50 °C using an oil bath. A specified amount of solid sodium hydroxide (Table 1) was added to the mixture and the suspension and the temperature was increased to 80 °C and kept for 30 min. The product was finally washed as previously specified.

2.3. X-ray diffraction (XRD)

Wide-angle XRD patterns were collected using a Rigaku Smart Lab X-ray diffractometer using Cu target to generate the X-rays using Kα radiation (CuKα radiation, $\lambda = 0.15418$ nm) in the range of 15–65° 2θ. The diffraction data was acquired using a step size and count time of 0.05° 2θ and 3 s/step, respectively.

2.4. Thermogravimetry (TGA)

A TA Instruments thermo-gravimetric analyzer (model Q500) was used. The temperature gradient was 10 °C/min and the flow of nitrogen was set at 50 mL/min. The weight loss (%) was determined by measuring the residual weight remaining at 600 °C.

2.5. Ion coupled plasma spectrometry (ICP)

Accurately weighed (0.3 g) film samples were dissolved using 10 mL of "Omni pure" Nitric Acid (concentrated) and heated the sample to 95 °C for approximately 30 min until the material was completely dissolved. The solution was then subjected to ICP analysis. The copper content of the solutions was determined using a Perkin-Elmer Corporation's Optima 8000 ICP Optical Emission Spectrometer.

2.6. Field-emission scanning electron microscopy (FE-SEM)

An FEI Verios 460L SEM was used to probe the microstructure of the deposited Cu_2O particles on the NFC films. The electron beam had an energy of 1 keV with a current of 50 pA and a stage bias of 500 V. The Verios allows for high resolution (0.7 nm is achievable at 1 kV) at low voltage, which allows insulating samples to be observed without the need for a conductive coating. EDS (energy dispersive X-ray spectroscopy) was also used to confirm that the visualized particles and cubes were indeed composed of Cu. As anticipated, oxygen and carbon were also detected. The size of Cu_2O particles on the SEM images were measured using image-J software.

2.7. UV–vis

Diffuse reflectance UV–vis (DR-UV–vis) spectra were acquired on a Shimadzu UV-VIS-NIR Spectrophotometer UV-3600 in the wavelength range of 300–800 nm in the solid state.

3. Results and discussion

3.1. Rational for reaction conditions and mechanism

The sought NFC/Cu_2O composite materials were synthesized by the alkaline reduction of copper sulfate using the NFC's and/or an external sugar's (dextrose) aldehyde groups as the reducing agents. The concentrations and experimental conditions specified in Table 1 describe two series of reactions labelled S (S1-7) where no external reducing agent was used, and a series SD (SD1 to SD3) where dextrose was used as the external reducing agent (Fig. 1).