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Preparation of Copper Nanoparticles in Chitosan Membranes and their Application as Irreversible Humidity Indicators

Fernanda Condi de Godoi, Rodrigo Balloni Rabelo, Fernando da Cruz Vasconcellos, Marisa Masumi Beppu

School of Chemical Engineering, University of Campinas – UNICAMP
Albert Einstein Avenue 500, 13083-852, Campinas, São Paulo, Brazil
fernandacondi@gmail.com

Copper nanoparticles were prepared in chitosan (CHI) membranes via reduction of $CuSO_4.5H_2O$ with sodium borohydride (BH). The fabrication process was performed in two steps: (1) first adsorbing Cu(II) ions in the CHI membranes, followed by (2) a chemical reduction of the Cu(II) ions to zero-valent copper (using BH). This study used SEM, DSC, and XRD to examine the morphological, thermal and chemical properties of the CHI-copper membranes. The synthesized CHI-copper membranes were exposed to ambient humidity and characterized by digital-image analysis with RGB color standards. The results showed that the CHI-copper membranes produced were successfully able to detect ambient moisture shown by the color changes of the membranes (from dark brown to blue). These CHI-copper membranes hold great promise in the engineering field for the production of humidity indicators and sensors.

1. Introduction

Chitosan (CHI) is an amino-polysaccharide that is highly efficient in the recovery of metal ions from dilute solutions. The presence of amine groups in the CHI structure gives the polymer chelating properties that are very useful for metal anion uptake in solutions with pH values close to neutral (Chassary et al., 2004).

Most studies focusing on the interactions of CHI with metal ions have been carried out to only recover specific metals or remove hazardous metals from dilute solutions. However, increasing attention has recently been paid to the manufacturing of more elaborate materials based on these CHI-metal reactions (Guibal, 2005). These novel CHI-metal based materials find many applications in the fields of environmental science and technology (Wu et al., 2009; Geng et al., 2009), catalysis (Guibal, 2005; Cetinus et al., 2009), medicine (Zheng et al., 2006) and engineering for the development of biosensors (Du et al., 2007).

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In this work, CHI membranes containing metallic copper nanoparticles were synthesized. Metallic copper is formed in the redox reaction between copper ions with $NaBH_4$ (Glavee et al., 1994), as described by Equation 1:

$$2Cu^{+2}_{(aq)} + 4BH^{-}_{4(aq)} + 12H_2O \rightarrow 2Cu_{(s)} + 14H_2 + 4B(OH)_3 \quad (1)$$

The copper species produced during the CHI-copper membrane synthesis were analyzed with XRD measurements. The CHI-copper membranes also were characterized by SEM and DSC to investigate their morphological and thermal properties. The present study shows that CHI-copper membranes can be used as irreversible humidity indicators. The results showed that the CHI-copper membranes produced are able to detect ambient moisture shown by membrane color change (from dark brown to blue), characterized by digital-image analysis with RGB color standards.

2. Materials and Methods

2.1 Materials

Chitosan (CHI, high molecular weight, 85% deacetylated) was purchased from Sigma (USA), sodium borohydride (BH) was purchased from Nuclear (Brazil) and copper sulfate ($CuSO_4.5H_2O$) was obtained from Synth (Brazil). All chemicals were reagent grade and used without further purification. Ultrapure water (Milli-Q®) with a minimum resistivity of 18.2MΩ was used to produce all solutions.

2.2 Experimental procedure

Chitosan solution (1.5 wt % in glacial acetic acid solution) was cast on a Petri dish, followed by total solvent evaporation in an oven at 60°C. The CHI functional groups were neutralized by immersing the membranes in alkaline solution (1 M NaOH) during 24 hours. The CHI membranes were extensively washed to remove residual NaOH and stored in ultrapure water at 4°C. Copper ions were incorporated by immersing the membranes in a 1000 ppm copper sulfate solution, for 48 hours. Subsequently, the membranes with adsorbed copper were immersed in a solution of sodium borohydride (4 mM) during 8 minutes. The notations used for CHI membrane samples with adsorbed cooper before and after being immersed in the BH solution are CHI-[Cu.00.00] and CHI-[Cu.BH.00], respectively.

2.3 Water sensitivity test

CHI-[Cu.BH.00] membranes (a total of 10 samples, 2.5x2.5 cm) were exposed to an ambient temperature of ~25°C and relative humidity of ~ 60% during 24 hours (the resulting sample was denominated CHI-[Cu.BH.01]).

2.4 Membrane characterization

The membrane surface microstructure was observed by scanning electron microscopy (SEM - LEO 440 Electron Microscopy Ltd., England). Samples were prepared by cryofracture in liquid nitrogen.

DSC thermograms of the membranes were obtained with a differential scanning calorimeter (DSC-50, Shimadzu, Japan), under a nitrogen atmosphere with a flow of 50 mL/min, and at a heating rate of 10°C/min in the range of 25°C to 500°C.

XRD was performed with an X-ray diffractometer (D/Max-2200, Rigaku, Japan) with Cu K radiation. The X-ray source was operated at 40 kV and 40 mA. Diffraction intensity was measured in the reflection mode at a scanning rate of 2°/min for 2θ = 10-90°.

2.5 Analysis of digital images

Images of CHI-[Cu.BH.00] and CHI-[Cu.BH.01] were taken with a DSC-W170 Sony digital camera. The images were taken using an indirect constant artificial lighting produced by a white cool fluorescent lamp of 18 W. Camera-sample distance was set to 20 cm, and the camera focus was adjusted automatically. RGB color values were measured for each image pixel, with Matlab® 7.3's image processing tool box. The RGB color histogram indicates how much of each of the red, green, and blue colors are present in the image. The color is expressed as an RGB triplet (R,G,B), each component of which can vary from zero to a defined maximum value (in this case 255). If all three components are at zero, the result is black; if all are at their maximum value, the result is white.

3. Results and Discussion

3.1 SEM Analysis

SEM images of CHI-[Cu.00.00], CHI-[Cu.BH.00] and CHI-[Cu.BH.01] membranes revealed the formation of dendritic copper grown on the surface of these membranes (Figure 1). Each dendrite has various branches with sizes in the range of few micrometers (approximately 1 - 15 μm).

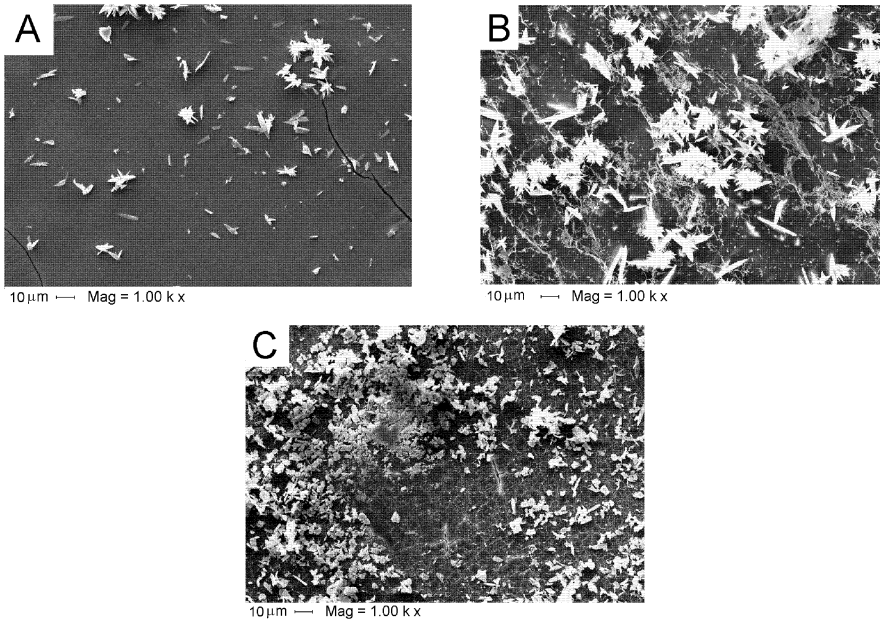

Figure 1: SEM images of: (a) CHI-[Cu.00.00], (b)CHI- [Cu.BH.00] and (c)CHI-[Cu.BH.01].(scale bar = 10μm)

3.2 DSC Analysis

DSC was used to examine possible interactions between copper ions and the CHI polymeric matrix. Figure 2 shows an endothermic peak between 100 – 150°C, corresponding to the water removal from the membranes, observed for all samples.

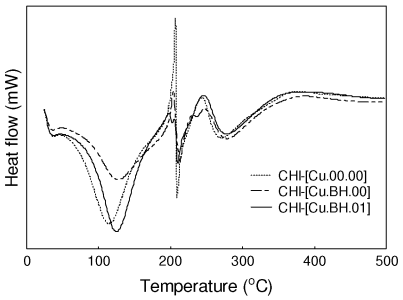

Figure 2: DSC thermograms of CHI-[Cu.00.00], CHI-[Cu.BH.00] and CHI-[Cu.BH.01].

The exothermic peak attributed to the thermal decomposition of chitosan is reported at approximately 309°C (Sreenivasan, 1996). The position of this peak was observed to have shifted to lower temperatures (230–260°C) for all samples, indicating a reduction in thermal stability, which may be due to a decrease in CHI membrane crystallinity with the incorporation of the copper ions in the polymeric matrix.

3.3 XRD Analysis

X-ray diffraction was used to identify the copper nanoparticles in the CHI-[Cu.BH.00] membrane. Figure 3 presents the XRD spectrum showing the diffraction peaks that correspond to metallic copper, observed at $2\theta = 43.3^{o}$, and cuprous oxide, at $2\theta = 23.9^{o}$ (Guan et al., 1984 and Salavati-Niasari et al., 2008).

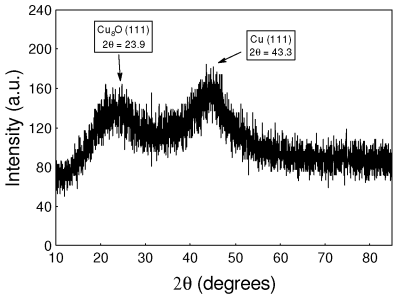

Figure 3: XRD pattern for the CHI-[Cu.BH.00]membrane.

3.4 RGB analysis

RGB color histograms were obtained to measure the color change that occurred when the CHI-[Cu.BH.00] membranes were exposed to humidity, producing CHI-[Cu.BH.01] membranes. Figures 4 and 5 show the RGB histograms (each curve represents the average of 10 samples of each type of membrane). As expected the histograms for the dark CHI-[Cu.BH.00] membranes (Figure 4) presented all RGB

colors in the range of approximately 0 – 50, whereas the blue CHI-[Cu.BH.01] membranes (Figure 5) showed RGB colors in the range of 25 – 100 for red, 40-160 for blue, and 80-160 for green .

The color difference of the CHI-[Cu.BH.00] membranes before and after exposure to moisture is probably occasioned by the oxidation reaction between copper metal, oxygen and water, as described by Equations 2 and 3.

$$2Cu^{0}_{(s)} + O_{2(g)} + 2H_2O \rightarrow 2Cu^{+2}_{(aq)} + 4OH^{-}_{(aq)} \quad (2)$$

$$Cu^{0}_{(s)} + 2H_2O \rightarrow Cu^{+2}_{(aq)} + H_{2(g)} + 2OH^{-}_{(aq)} \quad (3)$$

Future studies will be performed to determine in which relative humidity conditions the membranes begin to show color change. The color change kinetics will be reported by relative changes of the RGB histograms.

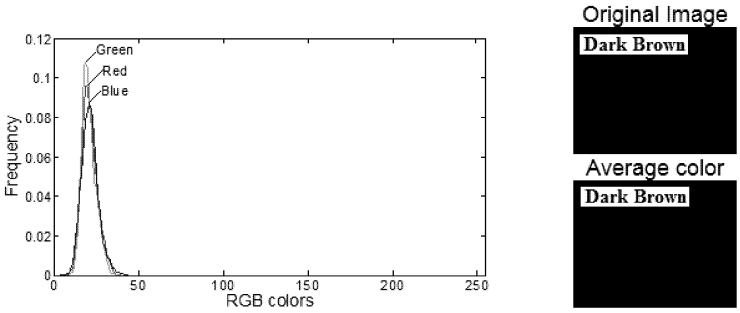

Figure 4: RGB histogram for the CHI-[Cu.BH.00] membranes.

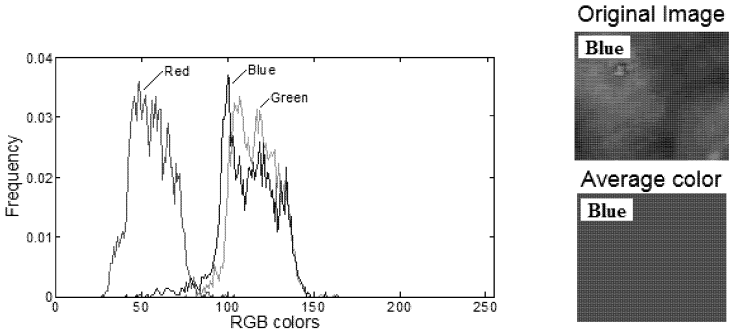

Figure 5: RGB histogram for the CHI-[Cu.BH.01] membranes.

From the present results, the CHI-[Cu.BH.00] membranes are promising as irreversible humidity indicators to be used in smart devices.

5. Conclusions

Chitosan membranes containing copper nanoparticules were successfully fabricated. XRD analysis confirmed the formation of metal copper and copper oxide

species. The RGB histograms were able to quantify the membrane color change as a result of ambient humidity. Furthermore, the CHI-copper membranes may be used to explore CHI-metal reactions in new materials that find wide applicability in the engineering and medical fields, and in particular as irreversible humidity indicators and biosensors.

Acknowledgments

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References

Cetinus S.A., Sahin E. and Saraydin D. 2009, Preparation of Cu(II) adsorbed chitosan beads for catalase immobilization, Food Chemistry, 114, 962-969.

Chassary P., Thierry V. and Guibal E. 2004, Metal anion sorption on chitosan and derivative materials: a strategy for polymer modification and optimum use, Reactive and Functional Polymers, 60, 137-149.

Du Y., Luo X., Xu J., and Chen H. 2007, A simple method to fabricate a chitosan-gold nanoparticles film and its application in glucose biosensor, Bioelectrochemistry, 70, 342-347.

Geng B., Jin Z., Li T. and Qi X. 2009, Preparation of chitosan-stabilized Fe^0 nanoparticles for removal of hexavalente chromium in water, Journal Science of the Total Environment, 407, 4994-5000.

Glavee G.N., Klabunde K.J., Sorensen C.M. and Hadjipanayis G.C. 1994, Borohydride Reduction of Nickel and Copper Ions in Aqueous and Nonaqueous Media. Controllable Chemistry Leading to Nanoscale Metal and Metal Boride Particles, Langmuir, 10, 4726-4730.

Guan R., Hashimoto H. and Kuo K.H. 1984, Electron-Microscopic Study of the Structure of Metastable Oxides Formed in the Initial Stage of Copper Oxidation. II. Cu_80, Acta Crystallographica Section B, 40, 560-566.

Guibal E. 2005, Heterogeneous catalysis on chitosan-based materials: a review, Progress in Polymer Science, 30, 71-109.

Salavati-Niasari M., Davar F. and Mir N. 2008, Synthesis and characterization of metallic copper nanoparticles via thermal decomposition, Polyhedron, 27, 3514–3518.

Sreenivasan K. 1996, Thermal stability studies of some chitosan – metal ion complexes using differential scanning calorimetry, Polymer Degradation and Stability, 52, 85-87.

Wu S., Liou T. and Mi F. 2009, Synthesis of zero-valent copper-chitosan nanocomposites and their application for treatment of hexavalent chromium, Carbohydrate Polymers, 100, 4348-4353.

Zheng Y., Yi Y., Qi Y., Wang Y., Zang W. and Du M. 2006, Preparation of chitosan–copper complexes and their antitumor activity, Bioorganic and Medicinal Chemistry Letters, 16, 4127-4129.