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ELECTROSPUN NANOFIBERS FROM CU_2O NANOPARTICLES AND CELLULOSE ACETATE

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Abstract

Polyol synthesis of cuprous oxide Cu_2O nanoparticles was carried out by reducing $CuCl_2.2H_2O$ with sodium hydroxide in the presence of Diethylene glycol (DEG) as a solvent and capping agent. These Cu_2O nanoparticles were reinforced in cellulose acetate (CA) matrix by electrospinning of CA/ Cu_2O in N-Ndimethyl formamid and composite nanofibrous were synthesized. The effect of nanoparticles concentration on the thermal behavior of the resultant fibrous was examined by means of differential scanning calorimetric (DSC) and infrared spectroscopy (FTIR). Also the influence of nanoparticles on the size and morphology of the nanofibers was examined by scanning electron microscopy (SEM).

Keywords : *Nanofibers, Cu_2O Nanoparticles, Cellulose acetate, Electrospinning..*

Résumé

La synthèse Polyol de nanoparticules d'oxyde cuivreux Cu_2O a été effectuée par la réduction de $CuCl_2.2H_2O$ avec l'hydroxyde de sodium en présence de diéthylène glycol (DEG) comme solvant et un agent de couverture. Ces nanoparticules ont été renforcées en acétate de cellulose matrice (CA) par électrofilage de CA / Cu_2O en N-N diméthylformamide et nanofibrous composite ont été synthétisés. L'effet de la concentration des nanoparticules sur le comportement thermique de la fibre résultante a été examiné au moyen de calorimétrique différentielle à balayage (DSC) et la spectroscopie infrarouge (FTIR). En outre l'influence des nanoparticules sur la taille et la morphologie des nanofibres a été examinée par microscopie électronique à balayage (SEM).

Mots clés: Nanofibres, *Cu2O Nanoparticules, acétate de cellulose, Électrofilage ..*

ملخص

تم في هذا العمل تحضير جريئات نانومترية لأكسيد النحاس Cu_2O باستعمال طريقة Polyol حيث تم تقليص $CuCl_2.2H_2O$ بهيدروكسيد الصوديوم في وجود Diethylene glycol (DEG) كمذيب و عامل للتغطية.
وتعززت هذه الجسيمات النانومترية في السيليلوز أسيتات cellulose acetate (CA) باستعمال طريقة الغزل الكهربائي electrospinning في وجود ثنائي ميثيل الفورماميد .تم فحص تأثير تركيز الجسيمات النانومترية على السلوك الحراري للألياف الناتجة عن طريق differential scanning calorimetric (DSC) ومطياف الأشعة تحت الحمراء (FTIR). كما تم فحص تأثير الجسيمات النانومترية على حجم وشكل الألياف النانومترية عن طريق المجهر الإلكتروني (SEM).

الكلمات المفتاحية: *ألياف النانو، **Cu2O** النانوية، خلات السليلوز، الغزل الكهربائي*

I. INTRODUCTION

Chemical preparation of mono dispersed nanoparticles involves the process of precipitation of a solid phase from solution, which includes the nucleation and growth of particles in the solution. Control of nucleation and the following growth are the key factors for the synthesis of mono dispersed nanoparticles [1]. In this work, we report high-yield synthesis of cuprous oxide nanoparticles. One dimensional (1-D) nanocomposite fibers have attracted much interest due to their enhanced electrical, electronic, optical and chemical characteristics and wide potential applications such as sensors, filtration membranes, micro electronics and photonic devices, structural reinforcement, biomedical devices, defense and security, and energy generation. Different approaches have been reported to produce nanofibers such as drawing, templates, phase separation self assembly and electrospinning [2]. Among them, electrospinning is the most bandy, low cost and high speed method to produce nanocopmpsite fibers. The electrospinning process is a technique based on the use of an electrical charge to draw fibers from a polymer-solvent solution [3]. Cellulose acetate (CA) was chosen for this study. Cellulose acetate (CA) is a well known derivative of cellulose and has been used in a broad field of applications such as adhesive, or in separation processes (e.g. filtering, reverse osmosis) [4]. Porous structures based on CA have been developed [5, 6]. However, since CA is widely used as synthetic fiber, preparation of CA fibrous structures is more popular. CA fibrous structures have been produced via the electrospinning technique and the influence of different parameters on the fiber size and morphology (such as nature of solvent and applied voltage) has been extensively studied [7, 8]. Also encapsulation of drugs and other substances into CA nanofibers has been reported [9, 10]. Electrospun CA membranes have been used in separation processes [11, 12]. CA–silver composite [13] and CA–polymer blends [14, 15] have been successfully electrospun. Other CA–polymer blends have been used as tissue engineering scaffolds [16, 17].
Therefore, the aim of this work was to develop cellulose acetate- Cu2O composite material with nanofibrous structure.

II. EXPERIMENTAL DETAILS

II.1 Materials

Cellulose acetate (acetyl content Mw = 29,000), N-N dimethyl formamide, DEG (diethylene glycol) were purchased from SigmaAldrich (UK) and CuCl2.2H2O from Fluka. All Creagents were used without any further purification.

II.2 Synthesis of Fe_2O_3 nanoparticles

The α-Fe2O3 nanoparticles were synthesized by polyol method. Typically, CuCl2.2H2O was added to diethylene glycol (DEG) with magnetic stirring at ambient temperature inside a round-bottom flask equipped with a condenser. After dissolution, the mélange was heated at 70 °C during one hour. After agitation 1ml of H2O was added to the milieu. After that the solution was heated to 140 °C during 2 hours. Then, 1M of NaOH was added. Finally, and after complete dissolution, the solution was heated at 180 °C during 2 hours under vigorous agitation.

II.3 Electrospinning process

To prepare Cu2O-CA nanofibers, in a first experiment, 2 g of cellulose acetate was dissolved in 10 ml N-N dimethyl formamide (DMF) with magnetic stirring at ambient temperature during 4 hours. Thereafter, the solution of Cu2O nanoparticles was mixed with cellulose acetate solution. Afterwards, the final solution was placed in a 5 ml syringe having a needle with an internal diameter of 0.5 mm and was mounted on a home made electrospinning device (Fig. 1). Briefly, it consists of a high-voltage supplier, a collector screen and a syringe. When a constant droplet of solution was observed at the tip of the needle, an electric potential of 25 kV was applied to the needle from a high voltage power source. An aluminum foil, placed at 20 cm from the tip of the needle was used as the counter electrode to collect the material.

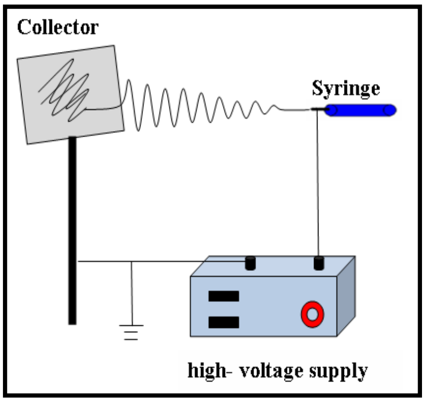

Fig. 1 Shematic of electrospinning apparatus

III. RESULTS

The X-ray diffraction spectrum of the Cu2O nanoparticles embedded in cellulose acetate nanofibers is shown in Fig 2. It was observed that all diffraction peaks indexed to cellulose acetate structure. No peaks from any other phase of Cu2O were found, due to the small quantity of nanoparticles into nanofibers. In this case we returned to use FTIR spectrometer to identify crystalline phases into nanofibers.

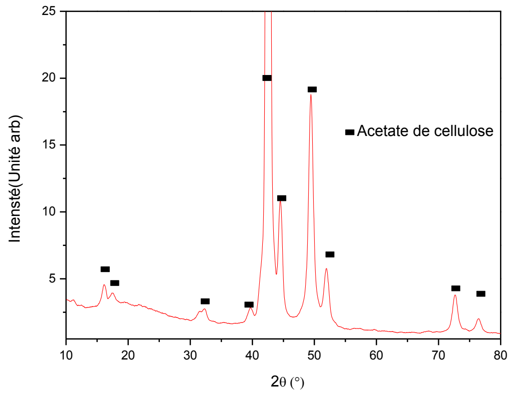

Fig. 2 XRD spectrum of Cu_2O nanoparticles embedded in cellulose acetate nanofibers.

Fig 3 Shows FTIR spectrum of nanofibers contains Cu2O nanoparticles. It is clear that the nanofibers present the same vibrations of cellulose acetate. It is possible to observe a band at 3484 cm-1 related to the hydroxyl-forming intermolecular hydrogen bonding. Also the spectrum shows absorption bands due to the CH stretching modes at 2944 and 2885 cm-1. The peaks at 1745, 1458, 1361, 1237, 1127, 1059 and 901 cm-1 are assigned to C=O stretching, CH2 deformation, CH3 deformation, C-O stretching mode of carboxylate, asymmetric stretching mode of C-O-C bridge, C-O-C stretching mode of pyranosse ring and out of plane bending mode of CH respectively [18]. It was observed for the nanofibers contain 1 and 2 ml solution of Cu2O nanoparticles two bands. The first one, around 536 cm-1, and the second one around 467 cm-1, its result from Cu (II)-Ostretching.

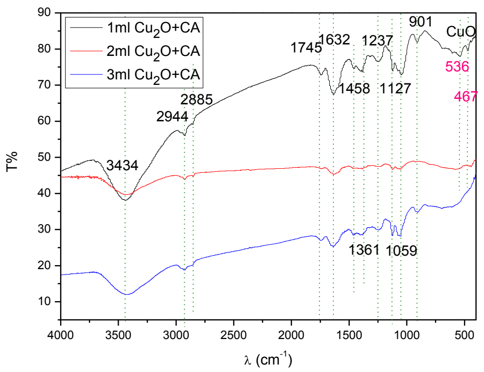

Fig. 3 FTIR spectrum of Cu_2O nanofibers.

DSC thermograms of the nanofibers are shown in Fig 4. All spectrums show the same aspect, it’s containing three regions. The first one contain endothermic events at 50 °C and 64 °C for nanofibers contain 2 and 3 ml nanoparticles solution respectively. Its can attributed to water evaporation. The second one show endothermic peaks at 137, 166, and 172 °C for the three concentrations respectively. It’s due to cellulose acetate decomposition and diethylene glycol evaporation. The nanofibers contain 3 ml show an endothermic peak at 276 °C attributed to DEG evaporation.

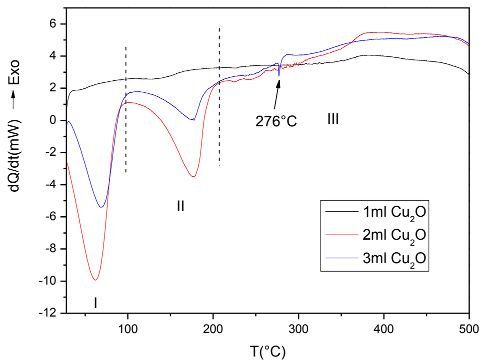

Fig. 4 DSC thermograms of Cu_2O nanofibers.

Fig 5 Shows SEM images of the nanofibers that were synthesized by electrospinning. It was observed that there is any individual nanoparticles can be observed in the nanofibers due to their small size to nanofibers. Also, the morphology of the electrospun fibers greatly depends on the nanoparticles solution concentration. Electrospinning of 1 ml nanoparticles solution in cellulose acetate nanofibers resulted in beaded fibers. However, as the concentration of nanoparticles solution increased, it was observed that the fibers having very few beads, which is due to the higher polymer chain entanglements in the solution and this is very essential to maintain the continuity of the jet during the electrospinning process for uniform fiber formation. In the present work it was observed that the diameter of the synthesized nanofibers was significantly affected by the solution concentration. It could be observed that with the increase in concentration of nanoparticles solution the fibers diameter also increases. This trend in variation in diameter with concentration was not affected by the presence of cellulose acetate solution, because its concentration is the same in all nanofibers. The variation in fiber diameter with concentration could be associated to the differences in DEG concentration, which has high viscoscity.

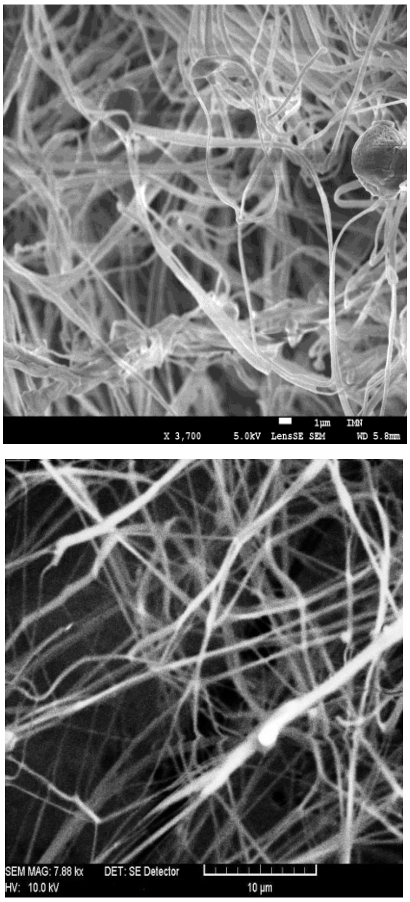

Fig. 5 SEM images of Cu_2O nanofibers (a: with 1 ml, b: with 2 ml)

IV. CONCLUSION

The present study shows the synthesis of Cu2O nanoparticles by polyol method. After that, CA- Cu2O composite nanofibrous materials were prepared via the electrospinning technique. The crystallographic analyze showed that all diffraction peaks indexed to CA structure. The infrared spectroscopy showed the crystallization of cuprique oxide. The DSC revealed that the structural properties are strongly modified with temperature in correlation with infrared spectroscopy. The SEM showed the increasing of fibers diameters with increasing nanoparticles concentration.

REFERENCES

[1] Hongtao Cui, Yongmei Feng, Wanzhong Ren, Tao Zeng, Hongying Lv and Yanfei Pan . Recent Patents on Nanotechnology. 3, 32-41(2009).

[2] Di Zhang, Suying Wei and Zhanhu Guo., Mater. Res. Soc.Vol. 1240- (2010)

[3] D. Zhang, W. Suying, G. Zhanhu. Materials Research Society, 1240, 06-10 (2010).

[4] Rodrigues F.G, Monteiro D.S, SilvaMeireles C, Assuncao R.M.N, Cerqueira D.A, Barud H.S, Ribeiro S. J. L, Messadeq Y. (2008). Synthesis and characterization of cellulose acetate produced fromrecycled newspaper. Carbohydrate Polymers 73:74–82.

[5] Fischer F, Rigacci A, Pirard R, Berthon-Fabry S, Achard P. (2006). Cellulose based aerogels. Polymer47: 7636–7645.

[6] Reverchon E, Cardea S. (2007). Production of controlled polymeric foams by supercritical CO2. The Journal of Supercritical Fluids 40: 144–152.

[7] Han S.O, Youk J.H, Min K.D, Kang Y.O, Park W.H. (2008). Electrospinning of cellulose acetate nanofibers using a mixed solvent of acetic acid/water: Effects of solvent composition on the fiber diameter. Materials Letters 62: 759–762.

[8] Tungprapa S, Puangpam T, Weerasombut M, Jangchud I, Fakum P, Semongkhol S, Meechaisue C, Supaphol P. (2007). Electrospun cellulose acetate fibers: Effect of solvent system on morphology and fiber diameter. Cellulose 14: 563–575.

[9] Chen L, Bromberg L, Hatton T.A, Rutledge G.C. (2008). Electrospun cellulose acetate fibers containing chlohexidine as a bactericide. Polymer 49: 1266–1275.

[10] Tungprapa S, Jangchud I, Supaphol P. (2007). Release characteristics of four model drugs fromdrug-loaded electrospun cellulose acetate fibermats. Polymer 48: 5030–5041.

[11] Ma Z, Kotaki M, Ramakrishna S. (2005). Electrospun cellulose nanofibers as affinity membrane. Journal of Membrane Science 265: 115–123.

[12] Zhang L, Menkhaus T.J, Fong H. (2008). Fabrication and bioseparation studies of adsorptive membranes/felts made from electrospun cellulose acetate nanofibers. Journal of Membrane Science 319: 176–184.

[13] Son W.K, Youk J.H, Park W.H. (2006). Antimicrobial cellulose acetate nanofibers containing silver nanoparticles. Carbohydrate Polymers 65: 430–434.

[14] Chen C, Wang L, Huang Y. (2007). Electrospinning of thermo-regulating ultrafine fibers based on polyethylene glycol/cellulose acetate composite. Polymer 48: 5202–5207.

[15] Zhang L, Hsieh Y.L. (2008). Ultra-fine cellulose acetate/ poly (ethylene oxide) biocomponent fibers. Carbohydrate Polymers 71: 196–207.

[16] Entcheva E, Bien H, Yin L, Chung C.Y, Farrell M, Kostov Y. (2004). Functional cardiac cell constructs on cellulose-based scaffolding. Biomaterials 25: 5753–5762.

[17] Salgado A.J, Gomes M.E, Chou A, Coutinho O.P, Reis R.L, Hutmacher D.W. (2002). Preliminary study on the adhesion and proliferation of human osteoblasts on starch-based scaffolds. Materials Science and Engineering C 20: 27–33.

[18]. Haci Ali Gulec, Arzu Topacli, Cafer Topacli, Nedim Albayrak, Mehmet Mutluc. Journal of Membrane Science, 350, 310–321(2010).