Materials Letters 238 (2019) 58–61

Contents lists available at ScienceDirect

Materials Letters

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

Synthesis and characterization of novel polyethylene oxide–dinuclear Cu(II) complex electrospun nanofibers

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ARTICLE INFO

Article history:
Received 25 June 2018
Received in revised form 23 November 2018
Accepted 23 November 2018
Available online 1 December 2018

Keywords:
Dinuclear Cu(II) complexes
Electrospinning
Polymer–complex composites
EPR

ABSTRACT

Nanoscale metal composite materials with tunable properties have attracted interest in many areas, such as catalysis, electronics, and photography. Typical matrices include zeolites, metal oxides, or polymer films. This study reports for first time the incorporation of a dinuclear copper (II) complex in polyethylene oxide (PEO) fiber mat by electrospinning. EPR studies have shown that the complex remained intact and stable within the polymer fibers. The fiber morphology was characterized by SEM. The absorption of the complex allowed to monitor the composition and distribution of the metal on the material.

1. Introduction

Metal-based, nanostructured catalytic materials with high surface area are tremendously important in the catalysis of many chemical reactions of industrial relevance [1]. Here we explore a non-traditional, potential method to prepare such materials by incorporating metal clusters in electrospun fibers [2]. Polynuclear copper species are promising catalytic agents [3,4]. Copper-containing clusters function as putative catalytic sites and the polymer fibers supporting them act as a high surface area substrate.

Reports on the integration of metal complexes in a polymer matrix or zeolites for catalytic and sensor purposes demonstrate improved performance of the material compared to the neat complex, or a solution, due to the complex–polymer synergistic interactions [5–7]. Several studies report doping of polymers with luminescent complexes through electrospinning resulting in better photochemical characteristics [8,9].

This study successfully demonstrates, for the first time, the dispersion by co-electrospinning (ES) of a dinuclear copper complex within a non-woven fibrous mat of PEO. Additionally, polynuclear coordination compounds can be relatively unstable and might be easily destroyed by the large electric fields and harsh solvents involved in the electrospinning process. To assess whether such clusters can be used as electrospinning starting materials and the effects that the PEO environment has on their properties we have used a paramagnetic, dinuclear Cu(II) complex with a S = 1 ground spin state, $[Cu_2(H_2tea)_2(p\text{-methoxybenzoate})_2]$ **1** [11]. The vast majority of Cu(II) dimers are EPR-silent, they exhibit a S = 0 ground state which originates from the antiferromagnetic coupling of the two local S = 1/2 sites (a Cu^{II} ion has a d^9 electronic configuration and thus a single unpaired electron). In contrast, **1** is EPR active, its S = 1 ground state is stabilized by the strong *ferromagnetic* coupling, $J = 101\ cm^{-1}$ ($\hat{\mathbf{H}}_{exch} = J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$), of the two copper(II) spins. Moreover, the triplet ground-spins state of **1** state exhibits a modest zero-field splitting ($D = -1.14\ cm^{-1}$, $E/D = -0.04$, $g_{x,y} = 2.063$, and $g_z = 2.318$) which leads to exquisite High-Field EPR spectra, see Fig. 1. Such spectra are extremely sensitive structural distortions and have allowed us to monitor the integrity of **1** dispersed in the electrospun PEO fibers, *vide infra*. These spectra clearly demonstrate that $[Cu_2]$ clusters such as those of **1** can be dispersed intactly into polymer fibers by an electrospinning process.

2. Methods and materials

Complex **1** was synthesized according to previously described procedure [10]. The electrospinning solutions contained 1.25%

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https://doi.org/10.1016/j.matlet.2018.11.149

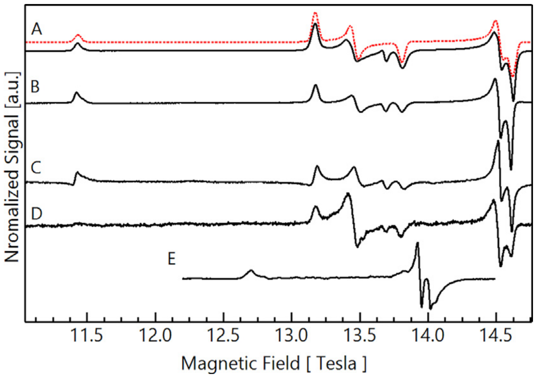
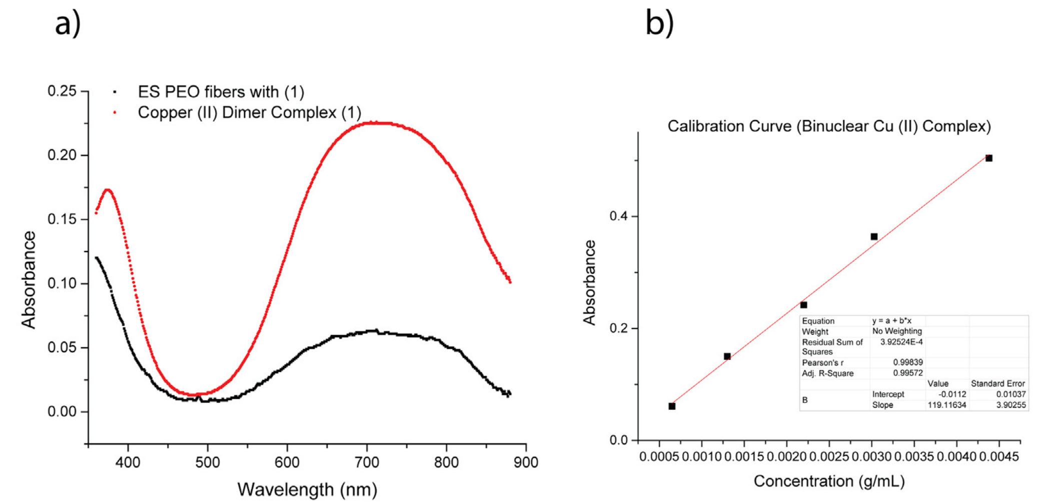


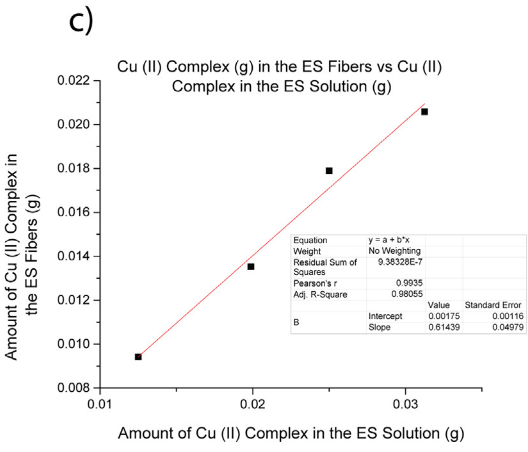
Fig. 1. High-field EPR spectra recorded at 403.2 GHz for: (A) a neat powder sample of [$Cu^{II}_2(H_2tea)_2(p\text{-methoxybenzoate})_2$], **1**; (B) PEO-**1** electrospun fibers containing 0.40 w/v % **1**; (C) PEO-**1** electrospun fibers containing 0.50 w/v % **1**; (D) PEO-**1** electrospun fibers containing 0.40 w/v % **1** and 0.200 mL saturated PANI–CSA–*m*-cresol solution. (E) Mononuclear decay product of **1**. The solid black lines are experimental spectra recorded at 30 K for A, D and 10 K for B, C, E. The dotted red trace is a simulation of the neat powder spectrum. The spectra of A–D demonstrate the presence for these samples of intact [Cu_2] dimers. The spectrum recorded for the decay product, E, is typical of mononuclear Cu(II) compounds which have a S = 1/2 ground state. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(w/v) PEO and 0.25–0.75% (w/v) of the complex **1** in chloroform. The corresponding amount of PEO was mixed with 40 mL $CHCl_3$ and stirred at room temperature until a clear solution was obtained. After that, **1** was added and stirred again. 5 mL of the resulting solution were electrospun at 25 kV, 0.8 mL/h delivery rate, using 18 gauge blunt needle at 12 cm distance from the receiving plate. The samples containing polyaniline (PANI) doped with camphorsulfonic acid (CSA) were prepared by dissolving 100 mg PANI and 50 mg CSA in 20 mL *m*-cresol. 0.200 mL of this solution were added to 5 mL of the previously described PEO-**1** solution and electrospun at 20 kV, 0.6 mL/min delivery rate, with 18 gauge blunt needle at 12 cm distance from the receiving plate. The HF EPR spectra were recorded using a custom built spectrometer described elsewhere [11]. However, in this case, microwaves of the appropriate frequency were generated using frequency multipliers and a Virginia Diodes wave generator operating at a base frequency 13 ± 1 GHz.

3. Results and discussion

Fig. 1 shows a series of HF EPR spectra recorded for **1**, for **1** co-electrospun with PEO matrix as well as on a composite matrix consisting of PEO and a doped conducting polymer (PANI–CSA).





d)

%1 in the ES solution (w/v)	%1 in the fibers (w/w)	%Cu(II) in the fibers (w/w)	PEO/Cu(II) ratio in the fibers
0.25	15.9	2.8	30.2
0.40	17.7	3.1	26.5
0.50	32.7	5.7	11.8
0.63	30.9	5.4	12.8
0.75	40.7	7.1	8.3

Fig. 2. (a) Absorption spectra of **1** and PEO-**1** fibers; (b) calibration curve for **1**; (c) relationship between electrospinning solution–fiber composition; (d) comparison of the composition of the ES solution and the composition of the fibers.

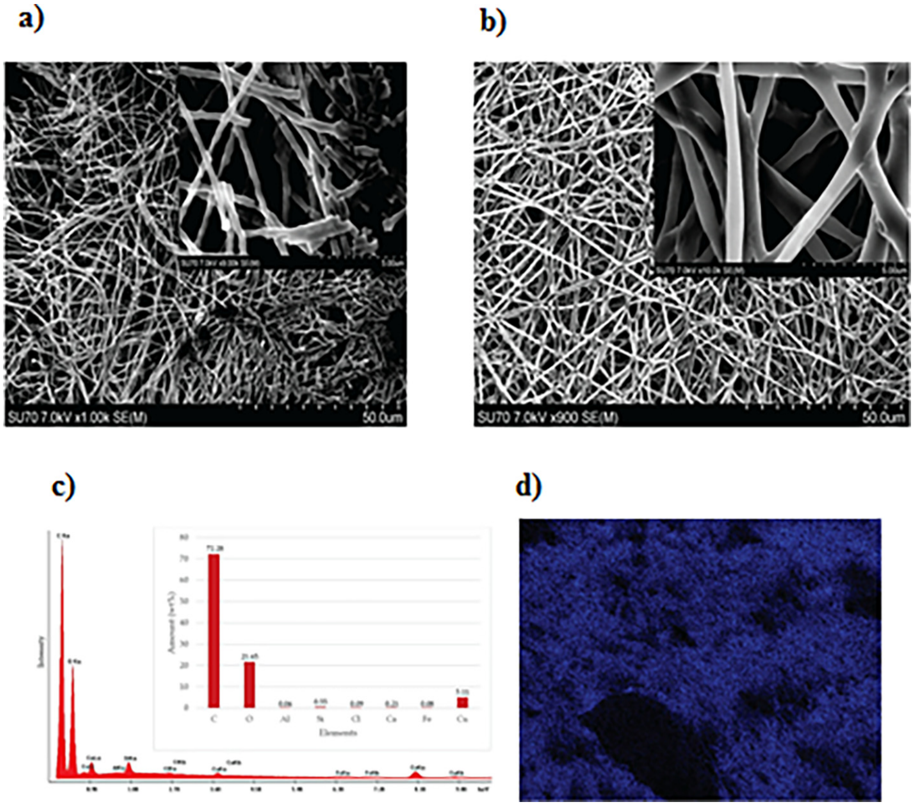


Fig. 3. Scanning electron microscopy analysis on PEO–Cu dimer complex fiber composition. (a) SEM of electrospun PEO fiber mat without copper at ×1k and ×9k. (b) Electrospun PEO–Cu complex fiber mat at ×900 and 10k. Elemental analysis of PEO–Cu dimer complex fiber composition. (c) SEM–EDS spectrum of the fiber composition on PEO–Cu complex electrospun fiber mat. (d) Distribution of Cu(II) on the fiber matrix from elemental analysis image on electrospun PEO–Cu dimer complex fibers.

Comparison of the simulated spectrum of **1** with the experimental spectra of **1** (B–E) in different polymer matrices, and the spectrum of the mononuclear Cu(II) complex E show that the complex remains intact and stable during the electrospinning process. *m*-Cresol was utilized as a solvent for the mixture of PEO–PANI–CSA instead of chloroform due to the lower solubility of the conducting polymer in most available solvents. The produced fibers were similar in morphology to those obtained from chloroform. The experimental spectra A–D on Fig. 1 are identical with the spectrum of complex **1** and are not affected by the composition of the fiber matrix.

The absorption spectra of complex **1** in methanol showed a broad absorption band at 714 nm and ε_{max} 119 L mol^{-1} cm^{-1} due to a d–d transition. The strong absorption at 280 and 300 nm has previously been attributed to the ligand-to-metal charge transfer (LMCT) transitions. A small shoulder at 370 nm has also been observed which is attributed to the internal transition of the methoxybenzoate ligand. The polymer matrix in general did not affect the shape and the molar absorptivity of the complexes. Only a slight bathochromic shift of the 280–300 nm band and the 370 nm shoulder in the complex–PEO spectrum were observed (Fig. 2a and b).

The amount of Cu(II) in the complex has been calculated from the absorption at 714 nm with pure complex **1** used as a standard (Fig. 2b). Electrospinning of solutions containing 0.25–0.75% (w/v) 1 resulted in 16–41% 1 on the fibers, correspondingly (Fig. 2c). The amount of Cu(II) on the fibers was 2.8–7.1% (w/w) (Fig. 2d).

Comparison of morphology of the electrospun nanofibers from different PEO/dimer ratio revealed smoother and longer fibers resulted from increasing the concentration of the dimer (dimer–polymer weight ratio) in the electrospinning solution. Fig. 3a from the SEM shows the topological characterization of the sample. This correlation was confirmed by indicated fragmented fiber formation from lower concentration of solution (Fig. 3a), due to the applied electric field and surface tension [11,12]. Therefore, we conclude that critical value for fiber formation is 0.5% (w/v) of dimer within the dimer/polymer solution. Solutions below the critical point will experience fiber formation with beads, short fragmented fibers, and other complexions.

Energy dispersive X-ray spectroscopy (EDS) spectrum shown in Fig. 3c collected on 0.5% (w/v) dimer and PEO fiber distinctly identifies Cu as an elemental component in the fiber matrix. Other important peak contribution can be seen from carbon from the polymer. Using SEM–EDS Hitachi showed even distributions on elemental mapping in Fig. 3c and d with 72% C, 22% O, and 5% Cu.

4. Conclusion

This study has demonstrated for first time that a dimer copper (II) complex can be preserved and incorporated in a polymer matrix by electrospinning. Copper is distributed uniformly throughout the non-woven fiber mat. These results are of importance for future investigations on the catalytic properties of the copper dimer complexes as well as on the possibility for molecular and ionic imprinting.

Acknowledgements

We acknowledge the support from NSF FGLSAMP, NSF FGLSAMP Bridge to Doctorate HRD #1400837, and Alfred P. Sloan Foundation Minority PhD Program #2012-3-07. This work was performed in part at NHMFL which is supported by the NSF

Cooperative Agreement No. DMR-1157490 and the State of Florida. S.A.S. acknowledges partial support from U. of I.

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