Preparation and Structures of Carbon-Copper Oxide Nanofibers from Electrospun Polyacrylonitrile Composite

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Abstract. Carbon-copper oxide nanofibers have been prepared by heat treatment of polyacrylonitrile-copper salt nanofibers. In this study, fabrication of PAN-copper salt using two different methods - firstly, synthesis of PAN-copper salt solution using electrospinning (PAN-CuAc NF), and secondly, immersion of electrospun PAN nanofiber in the copper salt solution (PAN-c-CuAc NF). Those ways had a distinct effect on the structure of carbon-copper oxide nanofibers. The morphologies and structures of carbon-copper oxide nanofibers were observed by scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDX), infrared spectroscopy (IR), X-ray diffraction (XRD), and Raman spectroscopy. The SEM image showed a randomly oriented nanofiber structure without bead formation, which average diameter of the nanofiber decreased with increasing process temperature. IR spectra and XRD patterns confirmed the formation of aromatic structures and graphite-like structures on carbon-copper oxide nanofiber. The Raman spectrum revealed that the intensity ratio (I_D/I_G) of carbonized nanofibers showed different values when the electrospun PAN composite nanofibers were synthesized using a different method, 1.59 for electrospun PAN nanofibers (CNF), 1.92 for carbonized PAN- CuAc nanofibers (C-copper oxide NF), and 0.60 for carbonized PAN-c-CuAc nanofibers (C-c-copper oxide NF). The presence of Cu element has been successfully detected in carbon-copper oxide nanofibers using EDX analysis.

Keywords: Electrospinning, Carbon nanofibers, Copper oxide, Polyacrylonitrile, Structures

1. Introduction
Carbon-metal nanomaterials have been widely fabricated using based electrospun nanofibers through stabilization and carbonization processes. Their composites design potentially used as sensor, anodes and adsorbent application due to good biocompatibility, electrical conducting properties, and high surface area [1-3]. Incorporating metal salt in a precursor system before heat treatment supports the formation of graphite-like structure and metal oxide or pure metal in one step. The metal salt is able to enhance graphitization of the utilized polymer to form a graphite shell [4].

Carbon fibers generally have low densities, high thermal and chemical stabilities in the absence of oxidizing agents, good thermal and electrical conductivities [5]. PAN is well known as a precursor in producing carbon nanofibers due to the simplicity to be converted into carbon fibers in a high yield [6].

Some researchers have been reported advantages of carbon-metal nanofibers in some applications. Fu et al. [2] successfully synthesized carbon-copper composite nanofibers for catechol detection. Carbon-copper nanofibers showed better performance than carbon nanofibers as a laccase biosensor. The presence of Cu in the composite possessed rapid response, a wide linear range, good
repeatability, reproducibility, long-term stability, and selectivity. The Carbon-SnO$_2$ nanofibers were fabricated by Bonino et al. [1] and obtained that tin oxide incorporated into carbon nanofibers was able to improve their performance when evaluated as lithium-ion battery anodes.

Most researchers synthesize carbon-metal nanofiber starting by dissolving metal salts and polymers in solvent, and after that the electrospinning process is carried out using that solution. After that the nanofiber is carbonized at a certain temperature to make carbon-metal nanofiber. [1-4, 7]. In this study, we observed the effect of methods in fabrication of electrospun PAN-copper acetate and their effect on stabilization and carbonization process to their chemical structures. Firstly, copper acetate monohydrate dissolved in NMP as solvent directly mixed with PAN before spun by electrospinning. Secondly, electrospun PAN nanofibers were immersed in a copper acetate solution and dried at room temperature. These composite nanofibers subsequently were treated by stabilization and carbonization process. The results showed those methods had a distinct effect on carbon nanofibers obtained.

2. Experimental method
Solution containing copper(II) acetate monohydrate (CuAc, Merck KGaA, Darmstadt, Germany) and polyacrylonitrile (PAN) (Mw= 150,000; Aldrich Chemistry, USA) was spun at a voltage of 12-13 kV for 4 h, the distance between the collector plate and needle was fixed at 18.5 cm and flow rate 1 mL/h. CuAc (1% w/v) solution was mixed with PAN (10% w/v) in 1-Methyl-2-pyrrolidone (NMP) (Merck Schuchardt, Hohenbrunn, Germany) at 80°C for 3 h and keep stirring at room temperature (PAN-CuAc). The second method, pristine PAN nanofibers that had been spun by electrospinning using the parameters as mentioned above was immersed in CuAc (1% w/v) solution (solvent: water) for 150 min and then dried at room temperature for overnight (PAN-c-CuAc). Furthermore, those electrospun nanofibers were heat-treated using a tube furnace (Carbolite Furnaces). Stabilization at 290°C for 2 h with a heating rate of 5°C/min under air atmosphere and proceeded to carbonization at 700°C for 1 h with 10°C/min under a pure Nitrogen atmosphere (150 mL/min).

The surface morphology was studied by scanning electron microscope (SEM) (JEOL IT-300 Japan Oxford Instrument X=MAX, UK) with energy-dispersive x-ray (EDX) analysis. Infrared spectrum analyzed by Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) Nicolet iS5 ATR iD5 Thermo Scientific (USA) for each sample using 64 scan rate in the range 500-4000 cm$^{-1}$. The phase and crystallinity structure were measured by using D8 Advance Bruker X-ray Diffractometer (XRD; Bruker, Germany) with Cu Ka ($\lambda=1.540$ Å) radiation over Bragg angle ranging from 10° to 80°. Raman spectroscopy (Bruker SENTERRA Raman Microscope) was used to characterize the structure of the carbonized electrospun nanofibers, using 532 nm laser as the excitation source and 10 mW power.

3. Results and discussion

3.1 Morphology analysis
Nanofibers that was spun using electrospinning and used as a precursor for producing carbon nanofibers had a randomly oriented structure nanofiber and without bead formation with the average diameter as shown in Table 1.

| Table 1. Average diameter of electrospun nanofibers. |
|-----------------------------------------------|
| Before heat treatment | After Stabilization | After Carbonization |
|-----------------------|---------------------|---------------------|
| PAN                   | 470.40 ±50.16 nm    | 430.69 ±50.99 nm    | 357.73 ±50.72 nm |
| PAN-CuAc              | 854.35 ±71.40 nm    | 747.25 ±72.34 nm    | 633.03 ±57.94 nm |
| PAN-c-CuAc            | 480.39 ±56.83 nm    | 393.76 ±40.99 nm    | 363.61 ±33.48 nm |

The presence of CuAc in PAN solution before fabrication in producing composite electrospun nanofibers affected enhancing the average diameter of composite nanofibers. It is probably due to the metal salt effect on electrospinning parameters used (voltage, a distance between needle and collector,
and flow rate). By the different methods, immersion technique, to obtain composite nanofibers we observed that increasing the average diameter of nanofibers took place as well. Dried copper salt coats part of the surface of the nanofibers. In that case, we hypothesize copper salt also adsorbed by pristine PAN nanofibers.

The fiber diameter is reduced along with increasing temperature process due to structural changes followed by removal of the non-carbon elements [5]. Moreover, dimension size of nanofiber sheets decreased into 50-53% for carbon nanofibers of pristine PAN (CNF) and carbon-copper oxide nanofibers that were obtained by immersion (C-copper oxide NF), respectively and about 67% for carbon-copper oxide nanofibers (C-copper oxide NF) after stabilization as well as about 40% for all nanofibers after carbonization compared with an initial size.

![Graphs](image)

**Figure 1.** Distribution of diameter electrospun of (a) PAN, (b) PAN-CuAc, and (c) PAN-c-CuAc, stabilized electrospun of (d) CNF, (e) C-copper oxide NF, and (f) C-c-copper oxide NF, and carbonized electrospun of (g) CNF, (h) C-copper oxide NF, and (i) C-c-copper oxide NF.

Nanofibers colors also changed from white of PAN, the pale green of PAN-CuAc and white slightly covered blue of PAN-c-CuAc turned into brown after stabilization and black after carbonization. When the nanofibers were bent, stabilized and carbonized electrospun C-copper oxide NF was easily brittle compared to CNF and C-copper oxide NF.
Figure 2. SEM images of (a) PAN, (b) PAN-CuAc, and (c) PAN-c-CuAc, stabilized electrospun of (d) CNF, (e) C-copper oxide NF, and (f) C-c-copper oxide NF, and carbonized electrospun of (g) CNF, (h) C-copper oxide NF, and (i) C-c-copper oxide NF.

3.2 IR spectra analysis
The IR spectra are shown in Figure 3-4. The characteristic peaks of electrospun PAN nanofibers were observed at around 2938 cm\(^{-1}\) attributed to CH\(_2\) stretching, 2242 cm\(^{-1}\) of C≡N stretching and 1452 cm\(^{-1}\) of C-H bending in CH\(_2\). In pristine PAN spectra, a strong band at 1693.19 cm\(^{-1}\) resulted from C=O group and medium intensities at 1282.42, 1110.80, and 1002.80 cm\(^{-1}\) attributed to C-N stretching from NMP as residual solvent after spinning. Besides, residual NMP also appeared at 1671.98 and 983.52 cm\(^{-1}\), respectively for C=O stretching and C-N stretching in PAN-CuAc spectrum. The existence of CuAc in composite nanofibers was indicated by a medium intensity at 1070.30 cm\(^{-1}\) for C-O stretching of acetyl function groups. Differences between PAN-c-CuAc spectrum and others were a weak intensity at 1689.34 cm\(^{-1}\) and a medium intensity at 1558.20 cm\(^{-1}\) which also attributed to C=O and C-N of NMP. It probably was affected by the coating method that decreased the NMP content in electrospun PAN nanofibers structure.
Figure 3. The IR spectra of electrospun of (a) PAN, (b) PAN-CuAc and (c) PAN-c-CuAc.

Figure 4. The IR spectra of stabilized electrospun of (a) CNF, (b) C-copper oxide NF, and (c) C-c-copper oxide NF, and carbonized electrospun of (d) CNF, (e) C-copper oxide NF, and (f) C-c-copper oxide NF.

On the stabilization of electrospun nanofibers at 290°C, the intensity of C≡N stretching of PAN at 2242.81 cm⁻¹ decreased and shifted to 2229 cm⁻¹. In this process, a little nitrile groups change into amide groups [8] and initiated dehydrogenation of backbone and cyclization of nitrile groups which was proven by a strong peak at 1581 cm⁻¹ for N-H bending in amide band II, C=N stretching and C=C stretching. As the result, a peak at 1452 cm⁻¹ for C-H bending in CH₂ of PAN spectrum widened and shifted to 1361 cm⁻¹ for C-H bending with a shoulder at 1253 cm⁻¹ for mixed C-N stretching and C-C stretching. A strong and broad band at around 1300 cm⁻¹ assigned to C-H in aromatic compound structure. A medium intensity band also appeared at 806 cm⁻¹ attributed to C=C-H [8]. Carbonized CNF which was
heated at 700°C had not shown characteristic peaks of PAN but appeared a peak at 1552 cm\(^{-1}\) attributed to C-C stretching and 1211 cm\(^{-1}\) attributed to C-H stretching of aromatic structure. The presence of copper oxide in PAN composition nanofibers was not detected in their IR spectra.

### 3.3 X-ray diffraction analysis

**Figure 5.** XRD pattern of electrospun (a) PAN, (b) PAN-CuAc and (c) PAN-c-CuAc nanofibers before and after heat treatment.

XRD patterns confirmed the structural properties of electrospun nanofibers before and after heat-treatment. As shown in Figure 5, electrospun PAN nanofibers have some typical peaks, a strong peak at 2θ=16.96° as well as two low-intensity peaks at 2θ= 27.71° and 49.90°. The existence of Cu in composite nanofibers was appeared at 2θ=43.38° and 43.58° corresponding to the (111) for FCC lattice of metallic Cu [2, 4, 9] beside of typical peak of PAN at 2θ=16.95°, weak intensity at 26.92° and 50.68° and also 2θ= 16.96°, 27.56° and 50.25°, respectively for PAN-CuAc and PAN-c-CuAc.

In the stabilization process, the linear structure of PAN is converted to a cyclic structure [3, 5] thus induced 2θ= ~16.9° was lost and ~25° attributed to graphite-like structure broadened followed by increasing the intensity. Subsequently, dehydrogenation and denitrogenation have been started during carbonization process. In 700°C and inert atmosphere (N\(_2\)) condition, CNF spectrum showed a broad and high intensity at 2θ=24.31° indicated graphite-like structure. However, C-copper oxide NF and C-c-copper oxide NF patterns showed distinct typical intensities. Three peaks at 2θ=13.05°, 31.64° and 42.05° of C-copper oxide NF strongly attributed to graphene-like structure [10] and partial structure of graphene and graphite observed in C-c-copper oxide NF. A weak intensity at 2θ=13.11° assigned to graphene-like structure and an intensity at 2θ=25.65° for graphite-like structure. A typical peak of PAN at 2θ= ~50° shifted to ~48° occurred to stabilized and carbonized nanofibers. Here, no peak identified of copper was probably due to the low concentration of metal salt mixed in composition [2, 3].
3.4 Raman spectroscopy analysis

Figure 6 showed a typical Raman spectrum (800-2000 cm\(^{-1}\)) of carbonized electrospun nanofibers. The two prominent vibrational peaks at 1355 and 1578 cm\(^{-1}\) for CNF, 1346 and 1573 cm\(^{-1}\) for C-copper oxide NF, and 1392 and 1588 cm\(^{-1}\) for C-copper oxide NF attributed to D- and G-band vibrations, indicative of disordered and ordered graphitic structures, respectively [1, 7, 11-12]. Carbonized electrospun CNF and C-copper oxide NF had a more intense D band than the G band, which is related to the increase in the amount of the disordered phase. In contrast to carbonized electrospun C-copper oxide NF which had a lower D peak than the G band confirms that the material contains fewer defects [13]. That was also supported by the \(I_D/I_G\) value. The ratio of the intensity of the D to G bands \((I_D/I_G)\), \(R\), indicates the degree of the order in the graphitic material of the carbonized electrospun nanofibers [11, 12]. Those bands were fitted using a Gauss. The \(I_D/I_G\) values for the carbonized electrospun of CNF, C-copper oxide NF and C-copper oxide NF were calculated 1.59, 1.92 and 0.60, respectively. The higher \(I_D/I_G\) value of carbonized electrospun revealed more defects and lower \(I_D/I_G\) value for fewer defects [13].

![Figure 6](image1.png)

**Figure 6.** Raman spectrum of carbonized electrospun of (a) CNF, (b) C-copper oxide NF and (c) C-copper oxide NF.

The intensity ratio showed that the microstructure of carbonized electrospun nanofibers had a different effect when composite electrospun metal-nanofibers were synthesized using distinct methods.

3.5 Elemental analysis

Elemental content analyzed by EDX was showed in Table 2. Pristine PAN nanofibers have three main elements which were detected namely C, N, and O. The existence of Oxygen content in the sample strongly caused by NMP as residual solvent after spinning. The detected Oxygen content of stabilized nanofibers was the highest that was led by the initiation of dehydrogenation and cyclization during the stabilization process [5]. In contrast to carbonized nanofibers, C content was higher than O due to aromatic structure had been formed with a little amount of N and O sourced from PAN structure and
metal oxide. Cu content has been successfully detected in stabilized and carbonized C-copper oxide NF and C-c-copper oxide NF.

**Table 2.** Elemental content by EDX analysis.

| Sample(s)                  | C     | N     | O     | Cu  |
|----------------------------|-------|-------|-------|-----|
| PAN                        | 74.25 | 20.75 | 5.00  | -   |
| PAN-CuAc                   | 71.43 | 20.37 | 5.10  | 3.10|
| PAN-Cu-Ac                  | 70.77 | 20.77 | 3.93  | 4.53|
| Stabilized CNF             | 65.70 | 20.07 | 14.23 | -   |
| Stabilized C-copper oxide NF | 64.79 | 19.35 | 11.88 | 3.98|
| Stabilized C-c-copper oxide NF | 63.01 | 20.96 | 12.12 | 3.90|
| Carbonized CNF             | 84.25 | 10.69 | 5.06  | -   |
| Carbonized C-copper oxide NF | 77.08 | 12.59 | 3.72  | 6.62|
| Carbonized C-c-copper oxide NF | 73.04 | 13.85 | 3.76  | 9.35|

4. Conclusion
Carbon-copper oxide nanofibers have been successfully synthesized by carbonizing of electrospun polyacrylonitrile-copper salt nanofibers. Polyacrylonitrile-copper salt nanofibers were prepared by two methods. Firstly, the electrospinning process used copper acetate/PAN solution. Secondly, immersing of PAN nanofibers in copper acetate solution. The heat treatment process has affected the reduction in the dimensions of the electrospun nanofibers sheet size and the average diameter of the nanofibers. Electrospun carbon-copper oxide nanofibers that were obtained by immersing method (C-c-copper oxide NF) was more brittle than CNF and C-copper oxide NF. IR spectrum showed the aromatic structure of carbon nanofibers formation and XRD pattern analyzed the graphite-like structure of all stabilized carbon nanofibers and partially structure of graphene-like for C-c-copper oxide NF. No peak identified of copper was probably due to the low concentration of metal salt in composition. Nevertheless, EDX analysis supported the presence of C, N, O and Cu elementals for carbon-copper oxide nanofibers. The intensity ratio (I_D/I_G) of the Raman spectra showed differences in the process of making polyacrylonitrile-copper salt nanofibers precursors affect the micro structure of carbon-metal nanofiber.

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References
[1] C. A. Bonino, L. Ji, Z. Lin, O. Toprakci, X. Zhang, and S. A. Khan, “Electrospun carbon-tin oxide composite nanofibers for use as lithium ion battery anodes,” *Applied Materials & Interfaces*, vol. 3, pp. 2534-2542, May. 2011
[2] J. Fu, H. Qiao, D. Li, L. Luo, K. Chen, and Q. Wei, “Laccase biosensor based on electrospun copper/carbon composite nanofibers for catechol detection,” *Sensors*, vol. 14, pp. 3543-3556, Feb. 2014
[3] S. Kim, B. Bajaj, C. K. Byun, S. Kwon, H. Joh, K. B. Yi, and S. Lee, “Preparation of flexible zinc oxide/carbon nanofiber webs for mid-temperature desulfurization,” *Applied Surface Science*, vol. 230, pp. 218-224, Sep. 2014
[4] N. A. M. Barakat, B. Kim, S. J. Park, Y. Jo, M. Jung, and H. Y. Kim, “Cobalt nanofibers encapsulated in a graphite shell by an electrospinning process,” *Journal of Materials Chemistry*, vol. 19, pp. 7371-7378, Aug. 2009
[5] X. Huang, “Fabrication and properties of carbon fibers,” *Materials*, vol. 2, pp. 2369-2403, Dec. 2009
[6] S. Kim, Y. Kuk, F. Jin, and S. Park, “Synthesis of polyacrylonitrile as precursor for high-performance ultrafine fibrils,” *Bulletin Korean Chemical Society*, vol. 35, pp. 407-414, Nov. 13

[7] Y. Zhou, J. He, H. Wang, K. Qi, B. Ding, S. Cui, “Carbon nanofibers yarns fabricated from co-electrospun nanofibers,” *Materials and Design*, vol. 95, pp. 591-598, Jan. 2016

[8] H. Kakida, and K. Tashiro, “Mechanism and kinetics of stabilization reaction of polyacrylonitrile and related copolymers II. Relationships between isothermal DSC thermograms and FT-IR spectral changes of polyacrylonitrile in comparison with the case of acrylonitrile/methacrylic acid copolymer,” *Polymer Journal*, vol. 29, pp. 353-347, Oct. 1996

[9] A. Khan, A. Rashid, R. Younas, and R. Chong, “A chemical reduction approach to the synthesis of copper nanoparticles,” International Nano Letters, vol. 6, pp. 21-26, Mar. 2016

[10] H. N. Lim, N. M. Huang, S. S. Lim, I. Harrison, and C. H. Chia, “Fabrication and characterization of graphene hydrogel via hydrothermal approach as a scaffold for preliminary study of cell growth,” International Journal of Nanomedicine, vol. 6, pp. 1817-1823, Aug. 2011

[11] E. Zussman, X. Chen, W. Ding, L. Calabri, D. A. Dikin, J. P. Quintana, R. S. Ruoff, “Mechanical and structural characterization of electrospun PAN-derived carbon nanofibers,” *Carbon*, vol. 43, pp. 2175-2185, May. 2005

[12] S. Lee, J. Kim, B. C. Ku, J. Kim, H. I. Joh, “Structural evolution of polyacrylonitrile fibers in stabilization and carbonization,” *Advances in Chemical Engineering and Science*, vol. 2, pp. 275-282, Apr. 2012

[13] R. Muzyka, S. Drewniak, T. Pustelny, M. Chrubasik, G. Gryglewicz, “Characterization of graphite oxide and reduced graphene oxide obtained from different graphite precursors and oxidized by different methods using raman spectroscopy,” *Materials*, vol. 11, pp. 1050, Jun. 2018