

## Well-Dispersed Copper Nanorods Grown on the Surface-Functionalized PAN Fibers and Its Antibacterial Activity

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**ABSTRACT:**  $\beta$ -Cyclodextrins/polyacrylonitrile/copper nanorods ( $\beta$ -CDs/PAN/CuNRs) composite fibers were fabricated by two steps including the preparation for the  $\beta$ -CDs/PAN composite fibers by electrospinning, and the preparation of the  $\beta$ -CDs/PAN/CuNRs composite fibers by adsorption and reduction. The  $\beta$ -CDs/PAN/CuNRs composite fibers were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, energy dispersive spectroscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy respectively. The results indicated that the CuNRs were not only successfully synthesized on the surface of composite fibers but also the CuNRs were distributed without aggregation on the composite fibers. Furthermore, microorganism *Escherichia coli* had been used to check the antibacterial efficacy of the  $\beta$ -CDs/PAN/CuNRs composite fibers. Subsequently, antibacterial tests have indicated that the composite fibers have good bactericidal effects. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41011.

**KEYWORDS:** electrospinning; fibers; nanoparticles; nanowires and nanocrystals

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### INTRODUCTION

Metallic nanoparticles have attracted extensive attention because of their unusual properties<sup>1</sup> compared to bulk metals and potential applications in optical,<sup>2</sup> electronic, chemical sensing technologies, and catalytic.<sup>3</sup> Among these metallic nanoparticles, transition metals such as copper, nickel, cobalt, and iron are particularly attractive because of their much lower cost and wide applications.<sup>4</sup> In short, the low cost and abundant raw materials have made copper nanoparticles attract increasingly attention.

In some applications, copper nanoparticles are immobilized or synthesized *in situ* on various supports, such as polymeric<sup>5</sup> and inorganic materials, including silica<sup>6</sup> and metal oxide surfaces,<sup>7</sup> microspheres,<sup>8</sup> activated carbon<sup>9</sup> and carbon nanotube,<sup>10</sup> etc. Among these materials, high-molecular polymers are important supports because of their high mechanical strength and chemical stability,<sup>11</sup> besides their large specific surface areas<sup>12</sup> and high absorption<sup>13</sup> might facilitate the interface reaction to organic compounds. Especially, high-molecular polymer fibers can be converted to carbon nanofibers. Compared with carbon films and carbon spheres, carbon nanofibers have one-dimensional structure. Because of this structure, carbon nanofibers have the features such as high specific strength, specific modulus, low density, low weight, and superb thermal stability, which make them be easily recycled. And this benefit is significantly important to industrial production.<sup>14–17</sup>

Electrospinning is a simple electrostatic method for the preparation of polymer nanofibers and composite nanofibers.<sup>18–21</sup> The electrospun fibers have been widely used because of their some specific characteristics such as large surface area-to-volume ratio and easy-preparation.<sup>22,23</sup> The diameter of the polymer fibers prepared by this method can range from tens of nanometers to several micrometers, it increases as the flow rate increases.<sup>24</sup> The variation of the applied voltage and tip-collector distance also affects the diameter and morphology of the electrospun fibers. Atmosphere control such as humidity and temperature of the spinning environment is crucial to the formation of fibers.<sup>25</sup> In addition, the molecular weight of polymer,<sup>26</sup> the surface tension of the polymer solution has a significant effect on the structure of the electrospun fibers.<sup>27</sup> What is more, the viscoelastic property of the polymer solution is also an important parameter which influences the spinnability.<sup>28</sup> Various polymers have been successfully electrospun into ultrafine fibers<sup>29–31</sup> in recent years, mostly from solutions or from melts. Electrospinning followed by calcination has also been widely applied to prepare carbon fiber materials.<sup>32,33</sup>

The incorporation of metal ions or metal nanoparticles into polymer nanofibers has recently been reported by electrospinning<sup>34–36</sup> from a solution mixture of the polymer and a metal salt, followed by reduction. The application of this material as an antibacterial agent<sup>37</sup> has also been studied. A limitation of

this preparation method is that some of the metal nanoparticles are embedded within the fibers. In our work, we report that copper nanorods were synthesized on the surface of the fibers by adsorption of copper ions and subsequent reduction. The adsorption of metal ions and metal nanoparticles from aqueous solution to a substrate surface is usually controlled by the properties of the surface. Surface functional groups such as amino, carboxyl, phosphoric, imidazoline, thioamido, and amidoxime have complex ability towards metals ions and can be used to facilitate the adsorption of metal ions and metal nanoparticles.<sup>38–40</sup> Cyclodextrins (CDs) are cyclic oligosaccharides consisting of 6, 7, or 8 glucopyranose units, which are called alpha ( $\alpha$ -), beta ( $\beta$ -), or gamma ( $\gamma$ -) cyclodextrin, respectively. The structure of these molecules is toroidal, truncated cones containing an apolar cavity with primary hydroxyl groups lying on the outside and the secondary ones lying on the inside.<sup>34</sup> Cyclodextrins can form inclusion complexes with a wide variety of organic and inorganic compounds in its hydrophobic cavity.<sup>41</sup> Thus, cyclodextrins could have a wide range of applications in all kinds of fields, such as catalysis and molecular recognition.

In this article, we fabricated the  $\beta$ -CDs/PAN [poly (acrylonitrile)] composite fiber films by electrospinning technology. Copper nanorods were either synthesized on the surface by absorption of copper ions from copper nitrate solution and subsequent reduction in an  $H_2$  atmosphere. Then the product of well-dispersed copper nanorods on  $\beta$ -CDs/PAN [poly (acrylonitrile)] composite fibers were obtained. By this method, the  $\beta$ -CDs/PAN/CuNRs composite fibers were fabricated. Furthermore, antibacterial properties of the composite fibers against *E. coli* bacteria confirmed the antibacterial properties of the materials.

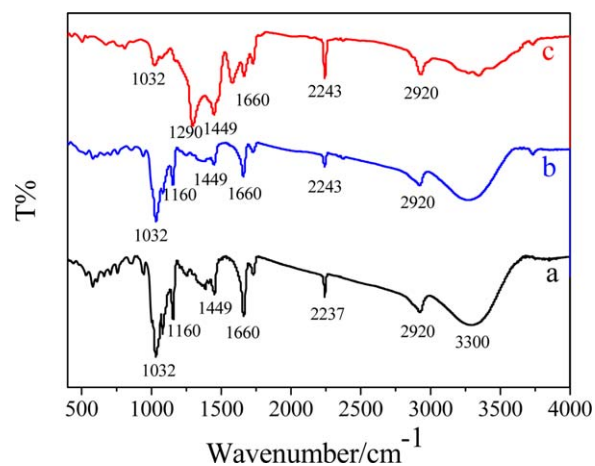
## EXPERIMENTAL

### Materials

PAN (Mw = 90,000) was purchased from Kunshan Hongyu Plastic (Kunshan China); N, N-dimethylformamide (DMF, A.R.) was supplied from Tianjin Fengchuan Chemical Reagent Science and Technology (Tianjin China);  $\beta$ -cyclodextrin ( $\beta$ -CD) and Copper nitrate hydrate [ $Cu(NO_3)_2 \cdot 3H_2O$ , A.R.] were purchased from Sinopharm Chemical Reagent (China). All the other chemicals used in the experiment were purchased in analytical purity and were used without any purification.

### Preparation of $\beta$ -CDs/PAN Composite Fibers by Electrospinning

In a typical procedure, the PAN powders were dissolved in DMF solvent to make solutions with a concentration of 10 wt %, followed by vigorous stirring to a homogeneous and clear polymer solution at room temperature. Subsequently, a controlled amount of  $\beta$ -CD was added to the resulted PAN/DMF polymer solution when its concentration was 8 wt % and stirred at 24 h to obtain  $\beta$ -CDs/PAN/DMF solutions for electrospinning. During electrospinning, the applied voltage was held constant at 15 kV, and the distance between the polymer solution and the aluminum foil collection screen was kept at 20 cm. The dry fibers were collected as a fiber mat on the aluminum foil and stored at room temperature.



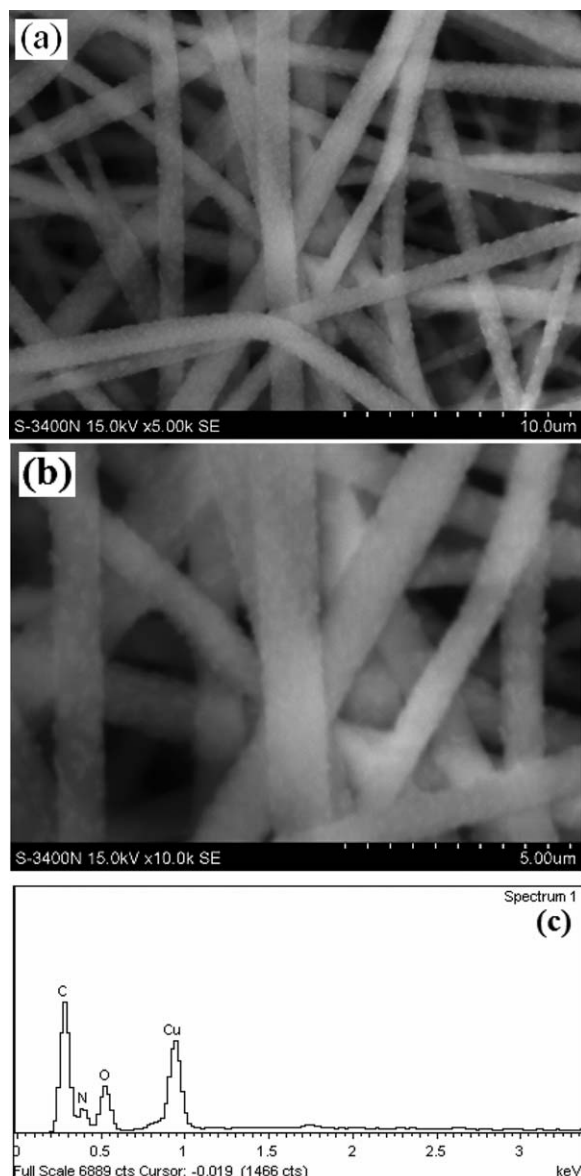
**Figure 1.** FTIR picture of (a)  $\beta$ -CDs/PAN composite fibers, (b) Cu ions loaded  $\beta$ -CDs/PAN composite fibers, and (c)  $\beta$ -CDs/PAN/CuNRs composite fibers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Preparation of $\beta$ -CDs/PAN Composite Fibers Containing Copper Nanorods

Adsorption of copper ions on the surface of the  $\beta$ -CDs/PAN composite fibers was achieved by immersing the  $\beta$ -CDs/PAN composite fibers into the copper precursor solution at room temperature. Copper nitrate hydrate, which is often used in the preparation of copper nanoparticles and copper nanorods, has been shown the advantage. The complexation of hydroxyls in the  $\beta$ -CDs with Cu ions can lead to coordination of Cu ions on the fiber surface. Cu ions were adsorbed on the electrospun  $\beta$ -CDs/PAN composite fibers peeled from the aluminum foil by dipping them in a 0.2M copper nitrate solution (100 mL). After soaking for 24 h in the blue copper nitrate solution, the white  $\beta$ -CDs/PAN composite fibers changed from white to light blue consistent with the adsorption of Cu ions on the fibers. The fibers were thoroughly rinsed with deionized water and ethanol to remove excess metal ions which were not anchored. Subsequently, the fibers were dried at room temperature. The Cu ions loaded fibers were then reduced after annealing in a 2.0 MPa  $H_2$  atmosphere at 393K for 4 h. After reduction, the fiber color changed from light blue to reddish brown, which indicating the conversion from the copper ion to copper metal.

### X-ray Photoelectron Spectroscopy Analysis

The X-ray photoelectron spectrometer was accomplished with pass energy 200 eV for survey, 30 eV for high-resolution scans. The X-ray source was Monochromated Al K $\alpha$  150W. In order to make more in-depth investigation on whether oxide layer was present on the surface of the composite fibers, X-ray photoelectron spectroscopy (XPS) analysis was performed. The binding energy for Cu and CuO were referenced to the C 1s line (284.6 eV) of the composite fiber. It could be seen from Figure 4(a) that two peaks occurred at 932.4 and 952.2 eV were well correspond with Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> binding energies, respectively. The splitting of the 2p doublet was 19.8 eV, indicating the metallic of copper, while the Cu(2p<sub>3/2</sub>) and Cu(2p<sub>1/2</sub>) line consists of several pronounced shake-up features, characteristic of the Cu(II) oxidation state, attributed here to the formation



**Figure 2.** SEM images of the  $\beta$ -CDs/PAN/CuNRs composite fibers: (a) low-magnified, (b) further-magnified, and (c) energy dispersive spectrometer signature of the  $\beta$ -CDs/PAN/CuNRs composite fibers.

of a CuO layer (934.8 and 953.9 eV).<sup>42</sup> The software XPSpeak 4.1 was used to fit the XPS spectra peaks.

#### Characterization

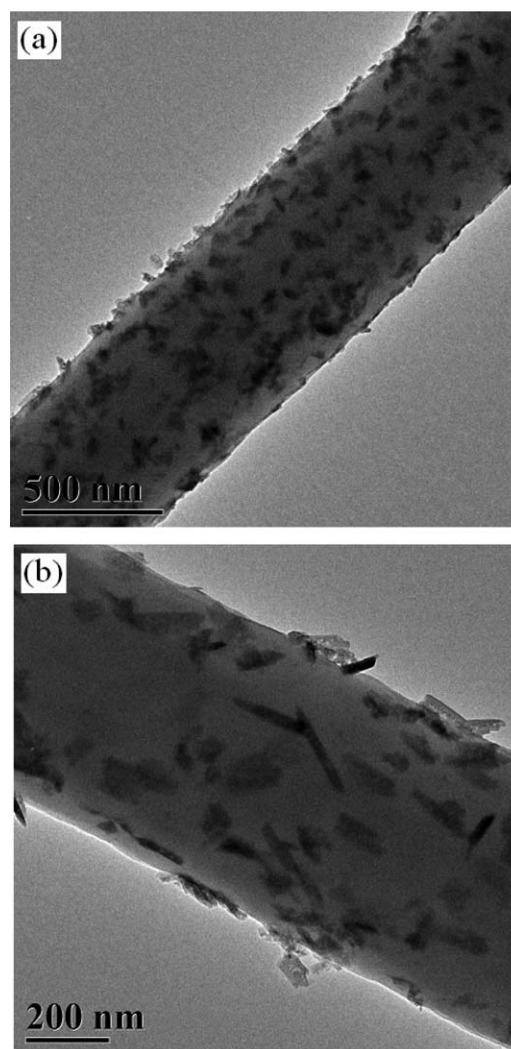
Fourier transform infrared (FTIR) spectroscopy measurements were performed by Nicolet model 6700 using KBr as background over the range of 4000–400  $\text{cm}^{-1}$ . The morphologies of the as-prepared composite fibers were observed by the scanning electron microscope (SEM, Hitachi, S-3400N, Japan) which equipped with an energy dispersive spectrometer and a transmission electron microscope (TEM, Jeol, JEM-2010, Japan). XPS was accomplished using an ESCALAB 250 multi-functional X-ray photoelectron spectrometer with pass energy of 30 eV and an Al K $\alpha$  line excitation source.

#### Antibacterial Test

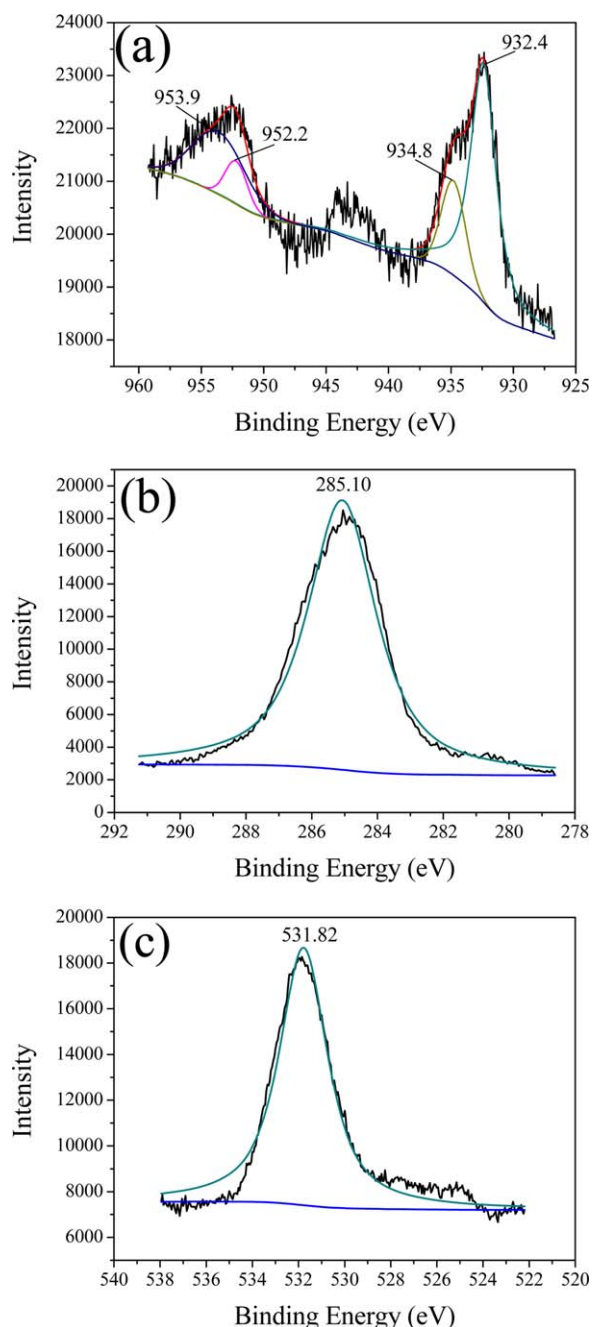
The antibacterial activities of the composite fibers were tested qualitatively by an inhibition zone method. It was carried out by making samples from copper-free  $\beta$ -CDs/PAN composite fibers and copper containing  $\beta$ -CDs/PAN/CuNRs composite fibers. The samples were cut into squares with side length 10 mm. The test has been carried out as follows, a cell suspension of  $4.8 \times 10^5$  cells/mL (100  $\mu\text{L}$ ) was inoculated over a plate containing solidified nutrient agar medium onto disposable sterilized petri plates by spread plate method. Then, the prepared composite fiber samples were gently placed over the solidified agar gel under aseptic conditions. Plates were incubated for 24 h at 310 K, and then observation of the zones of inhibition was investigated.

#### RESULTS AND DISCUSSION

Figure 1 showed the FTIR spectra of (a)  $\beta$ -CDs/PAN composite fibers, (b) Cu ions loaded  $\beta$ -CDs/PAN composite fibers, and (c)  $\beta$ -CDs/PAN/CuNRs composite fibers. The peaks for the  $\beta$ -CDs/PAN composite fibers in Figure 1(a) can be assigned as follows: 2920  $\text{cm}^{-1}$  (CH stretching in CH and CH<sub>2</sub> groups), 2237  $\text{cm}^{-1}$



**Figure 3.** TEM images of the  $\beta$ -CDs/PAN/CuNRs composite fibers.



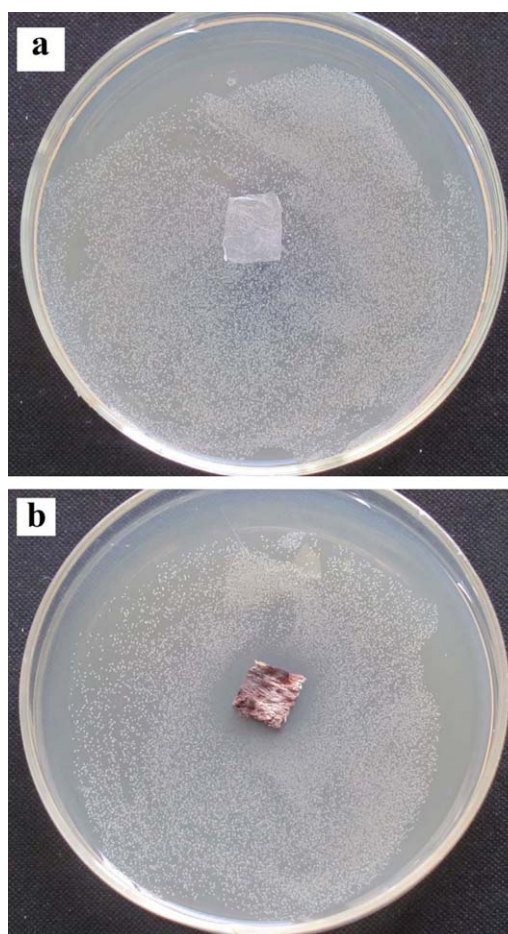
**Figure 4.** X-ray photoelectron spectra of the  $\beta$ -CDs/PAN/CuNRs composite fibers: Cu 2p and CuO 2p of the (a) composite fibers, (b) C 1s, and (c) O 1s. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

( $\text{C}\equiv\text{N}$  stretching),  $1660\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  stretching),  $1449\text{ cm}^{-1}$  (CH blending),  $1160\text{ cm}^{-1}$  (CH skeletal vibration),  $1032\text{ cm}^{-1}$  ( $-\text{CH}_2\text{O}-$  stretches). The strong broad band ranging from  $3100$  to  $3700\text{ cm}^{-1}$  usually corresponds to the combination of stretching vibration bands of both OH and NH groups, suggesting these peaks are typical  $-\text{OH}$  on  $\beta$ -CD. The absorption peaks from  $580\text{ cm}^{-1}$  to  $950\text{ cm}^{-1}$  were assigned to the skeletal vibration of  $\beta$ -CD. Compared with Figure 1(b) and (a), there's no obvious change. From Figure 1(c), the peak at  $1290\text{ cm}^{-1}$

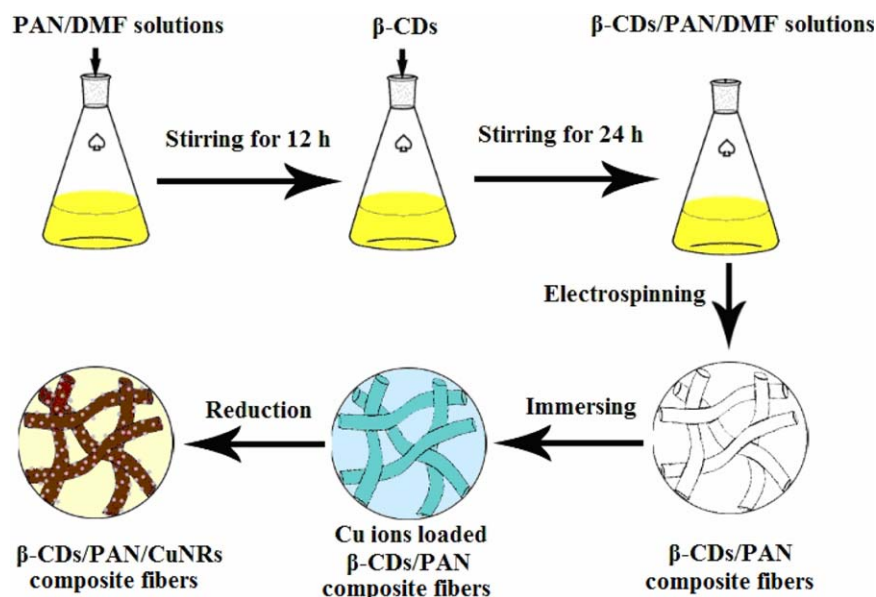
can be assigned to CH stretching. The band of the  $\text{C}\equiv\text{N}$  at  $2237\text{ cm}^{-1}$  was shifted to  $2243\text{ cm}^{-1}$  after the introduction of CuNRs, which because of the coordination bond between the lone pair electrons of cyano group's outer layer rail and copper's empty orbital. The change indicated the interaction between CuNRs and the  $\text{C}\equiv\text{N}$  of PAN.

Figure 2(a,b) showed the SEM images of the  $\beta$ -CDs/PAN/CuNRs composite fibers. It indicated smooth and super-long fibers had been prepared successfully by electrospinning. The diameter of the nonwoven fibers ranges from 600 to 1000 nm. Moreover, the nanorods were uniformly distributed across the surface of each fiber without aggregation, offering high level exposure of the nanorods surface. Figure 2(c) showed the energy dispersive spectrum of the  $\beta$ -CDs/PAN/CuNRs composite fibers, it was in good agreement with the XPS results.

In order to study the microstructure of the composite fibers in more details, the TEM was carried out. From Figure 3, it could be clearly seen that the composite fibers were of relatively smooth surface without secondary nanostructures. The diameter of the fibers ranged from 600 to 1000 nm. The TEM images indicated that there was essentially no change to the nonwoven



**Figure 5.** Photographs of the antibacterial test results of composite fibers samples against *E. coli*: (a)  $\beta$ -CDs/PAN and (b)  $\beta$ -CDs/PAN/CuNRs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Scheme 1.** Scheme of the procedure used to prepare the  $\beta$ -CDs/PAN/CuNRs composite fibers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

fibers' morphology during the growth of the CuNRs. And, the CuNRs were attached on the surface of the composite fibers.

Figure 4 showed the XPS spectra of the composite fibers. The presence of CuO was because of the composite fibers exposed in air. The peak fitting of the composite fibers also proved the existence of CuO. The XPS spectra for the C 1s region around 285.1 eV was shown in Figure 4(b). The binding energy with peak at 285.1 eV was assigned to C—C groups. Figure 4(c) presented the spectra of O 1s for the  $\beta$ -CDs/PAN/CuNRs composite fibers. The peak at 531.8 eV was related to surface hydroxyl groups (O—H). All of these results gave the insight that the heterostructures were composed of CuNRs and PAN. Through the comparison of the peak area ratio (by XPSpeak4.1), the Cu/CuO intensity ratio = 4.09.<sup>43,44</sup>

Figure 5 showed the results of antibacterial test. The white cloudy area indicated bacterial growth in Figure 5(a), whereas transparent area surrounding the  $\beta$ -CDs/PAN/CuNRs composite fibers in Figure 5(b) showed the zone of inhibition. It can be seen that there is a continuous growth in bacterial cells in the presence of  $\beta$ -CDs/PAN composite fibers while a killing kinetic action can be seen on the  $\beta$ -CDs/PAN/CuNRs composite fibers. Some of the recent reports describe antimicrobial activity of the materials that contain copper particles or copper ions. Sheikh et al. reported that the PU containing copper nanoparticles can be used as antimicrobial membrane materials.<sup>45</sup> Du et al. have reported that the chitosan nanoparticles loaded copper ions interact with bacterial cell membranes of *E. coli* (K88), causing structural change and cell death.<sup>46</sup> Mary et al. suggested that the copper ions and copper nanoparticles-loaded chemically modified cotton cellulose fibers showed fair biocidal action against *E. coli*.<sup>47</sup> In this study, we suggest that the fibers after reduction which loaded copper nanoparticles possess fair antibacterial property.

## CONCLUSION

In summary,  $\beta$ -CDs/PAN/CuNRs composite fibers were successfully synthesized by electrospun, adsorption, and reduction method, respectively. The CuNRs were evenly and well dispersed on the composite fibers. We have conducted the same antibacterial experiment for many times, and get the same results. Also, the antibacterial test has been conducted to ensure that the obtained composite fibers can be used as antimicrobial membrane materials and antibacterial dressing, further applications for future water purification systems and the filtration membrane.

## ACKNOWLEDGMENTS

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