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Polyacrylonitrile gold nanoparticle composite electrospun fibers prepared by *in situ* photoreduction

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ABSTRACT

Gold nanoparticles (AuNP) were formed *in situ*, while electrospinning a polyacrylonitrile (PAN) solution of $HAuCl_4$ under UV light without using heat or chemical reducing agents. The resulting fibers were purple in color due to the formation of AuNP inside and on the surface of the nanofibers. TEM images showed spherical and uniformly dispersed particles inside the polymer fibers. The concentration of Au^{+3} in the PAN solution is directly proportional to the size of the generated particles, with average diameter of 21.4 nm and 5.8 nm for the 0.044 M and 0.022 M solutions, respectively.

1. Introduction

There has been growing interest in composite nanofibers due to the unusual chemical, optical and electronic properties they exhibit owing to their high surface area-to-volume ratio and quantum size effects, also known as nano-effects [1]. The nano-effects can contribute unusual strength, high surface energy and reactivity as well as high thermal and electrical conductivity to electrospun nanofibers [2]. The incorporation of metal nanoparticles into nanofibers offers the dual functionality of both nanostructures, resulting in composite nanomaterials that have promising applications in many fields including catalysis, drug delivery and sensing [3,4]. Also, the polymers in composite nanofibers may stabilize the nanoparticles and prevent aggregation that can decrease catalytic activity [5]. Electrospinning is a simple technique used to produce fibers in the nanometer range [6]. Such nanofibers can be generated using different electrospinning techniques such as solution and bubble electrospinning; with the latter one resulting in finer fibers [7,8]. In solution electrospinning, a conical shaped polymer drop is formed as high voltage is applied. In bubble electrospinning, conical bubbles are formed on the polymer solution surface as voltage is applied to an electrode inserted inside a gas tube located in a polymer solution [9]. In both methods, when the electrostatic force overcomes the surface tension, polymer jets are ejected towards a grounded collector. On the way to the collector, the solvent evaporates and nanofibers are formed as a non-woven mat.

Gold nanoparticles (AuNP) continue to generate interest because of their promising use in sensors, drug delivery, memory devices, bioimaging and cancer therapy [10]. AuNPs can be prepared by different chemical, physical, or even biosynthetic methods. The size, shape, and composition of the NPs can be tailored for different applications [11]. Many research groups have synthesized polymer/AuNP composites using different approaches. For example, pre-synthesized AuNPs have been dispersed in polymer solutions then electrospun. Kim et al. reported the incorporation of pre-synthesized AuNP into polymer nanofibers via electrospinning [12]. Gomathi et al. synthesized a cholesterol sensor by electrodepositing AuNP and immobilizing the cholesterol oxidase enzyme on chitosan nanofibers [13]. Baker et al. prepared AuNPs less than 1 nm on espun polyaniline nanofibers for bistable memory devices [14]. Deniz et al. used laser ablation to generate AuNPs in a PVP solution which was then electrospun [15]. Alternatively, polymer/$HAuCl_4$ solutions have been electrospun followed by, post-treatment with reducing agents to obtain polymer/AuNP composite nanofibers [16].

In this study, we present a novel method for synthesizing uniformly dispersed AuNPs *in situ* while electrospinning. The AuNPs were formed by electrospinning under UV light. This is a one step, easy and fast way to synthesize a polymer/AuNP composite. The combination of electrospinning and photolysis may have potential applications in other areas such as for *in situ* photopolymerization and photocrosslinking. To the best of our knowledge, this technique has not previously been reported.

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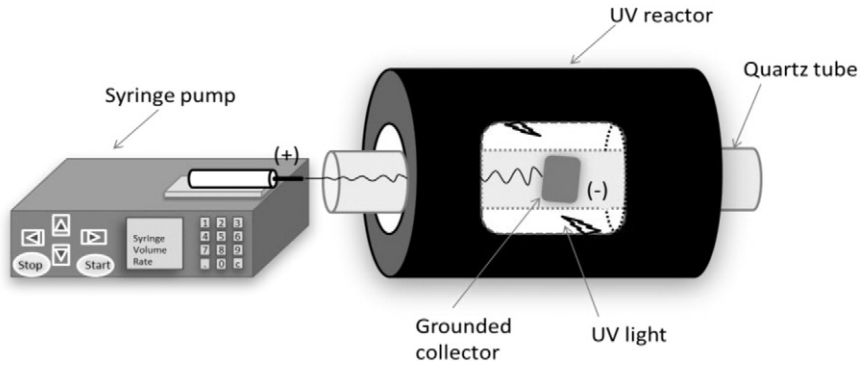

Fig. 1. Schematic illustration of the electrospinning/photolysis set up.

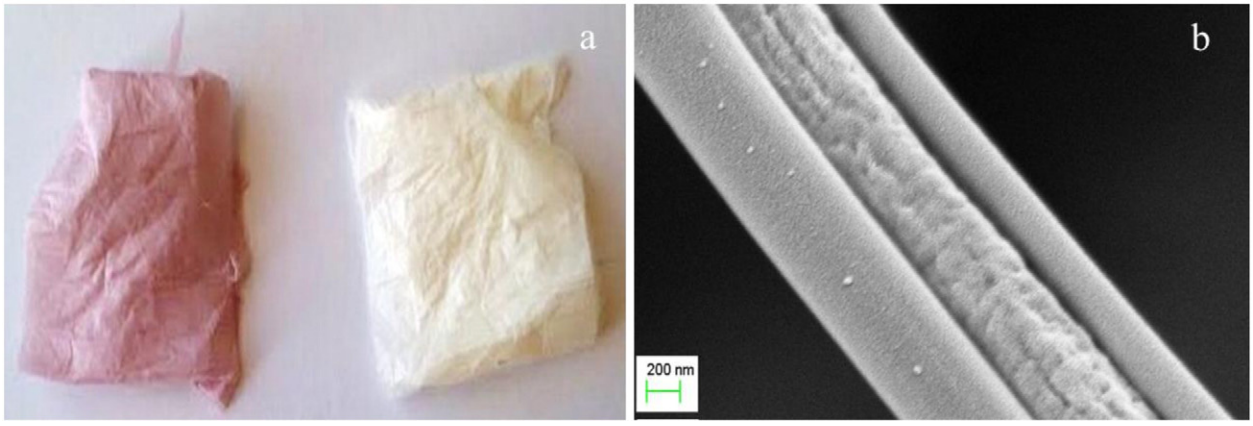

Fig. 2. (a) (left) Purple fibers produced by in situ electrospinning of PAN/Au^{3+} under UV light. (right) Off white control fibers that were exposed to UV light after electrospinning. (b) SEM image of PAN/AuNP composite espun fibers.

2. Experimental

2.1. Materials

Polyacrylonitrile (150,000 MW) was purchased from Pfaltz and Bauer. Dimethylformamide (DMF) and gold(III) chloride hydrate ($HAuCl_4 \cdot H_2O$) were purchased from Aldrich. The UV reactor was a Rayonet reactor containing eight 254 nm UV lamps (RMR-2537).

2.2. Preparation of PAN/AuNP composite nanofibers

The electrospinning solution was prepared by combining 9 mL of DMF with 1 g of PAN followed with stirring at 80 °C for 2 h. After the PAN solution cooled to room temperature, 4 mL of the PAN solution was added to 0.06 g and 0.03 g of $HAuCl_4$ to make 0.044 M and 0.022 M solutions, respectively. These solutions were stirred in the dark overnight. The electrospinning setup is shown in Fig. 1, where

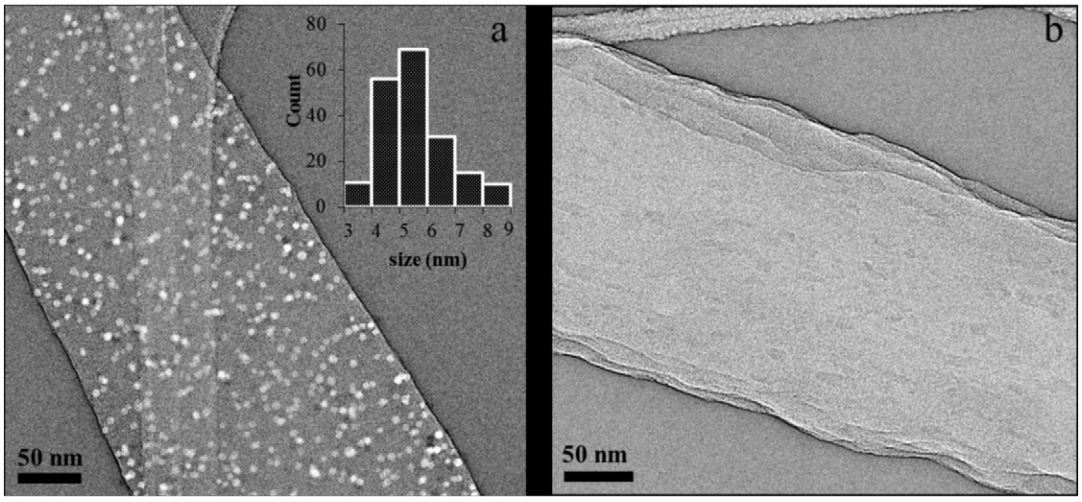

Fig. 3. TEM images of PAN/AuNP nanofibers produced from 0.022 M solution of $HAuCl_4$. (a) *In situ* electrospun under UV light for 1 min; inset shows the size distribution of the corresponding AuNP. (b) Exposed to UV light for 1 min after being electrospun.