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Synthesis of highly conductive polyaniline nanofibers

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ABSTRACT

Polyaniline nanofiber product synthesized by using both potassium biiodate, $KH(IO_3)_2$, and sodium hypochlorite oxidant shows high electrical conductivity of greater than 100 S cm^{-1}. The nanofiber product also shows not only a long nano-size fibril structure with average diameter of ~50 nm and length of ~4 μm but also high crystallinity. It was observed that the nanofibers synthesized using the two oxidants give both high electrical conductivity and high crystallinity compared to polyaniline synthesized using commonly known ammonium peroxydisulfate (APS) oxidant. We also found that dimensional and morphological uniformity of PANI nanofibers were greatly improved when the two oxidants were used. The long length and high crystallinity will probably be the contributing factors to have high conductivity. Order of the oxidant addition for the synthesis has no effect on quality of the product. Characterization study was made via UV/Vis absorption spectra, X-ray diffraction (XRD) and scanning electron microscopy (SEM) as well as conductivity measurement.

1. Introduction

Polyaniline has attracted considerable attention due to its low cost, simple synthesis, good optical and electrical properties with excellent environmental stability [1–6]. It also has potential applications for electronic and optical devices such as light emitting diodes, field effect transistors, sensors, electronic circuit boards, and fuel cells [1–17]. Polyaniline can exist as a salt or base in three isolable oxidation states: 1. Leucoemeraldine, the fully reduced state of polyaniline, 2. Emeraldine, the half oxidized state, and 3. Pernigraniline, the fully oxidized state. The emeraldine salt is electrically conductive while the rest are insulators [7]. Usually polyaniline can be synthesized from an aniline monomer by either chemical polymerization or electrochemical polymerization. Typically, conventional chemical synthesis of polyaniline is based on an oxidative polymerization of aniline using an oxidant in the presence of a strong acid dopant [2].

Ammonium peroxydisulfate (APS) is the most commonly known oxidant and a series of different oxidants or catalysts were also reported such as $Ce(SO4)_2$ [18], Cupric Sulfate [19], auric acid [20], $K_2Cr_2O_7$ [21], KIO_3 [22], H_2O_2 and iron(II) [23] or horseradish peroxidase (HRP) [24] where iron(II) or HRP can be a catalyst. P. Chowdhury, et al [22], have reported that they achieved as high as 10.1 S cm^{-1}electrical conductivity. Nirmalya, et al. have also reported the synthesis of high-conducting polyaniline via oxidative polymerization of aniline by MnO_2, PbO_2 and NH_4VO_3 [25]. It reported that they achieved electrical conductivity of as high as 8.0 S cm^{-1}. Recently, Li et al. have reported the synthesis of fibril polyaniline with diameters of 50–60 nm using sodium chlorite ($NaClO_2$) as an oxidant [26]. We are reporting a new synthesis method using potassium biiodate $KH(IO_3)_2$ as a new oxidant to prepare highly conductive nanofibers of polyaniline having uniform dimension. The advantages of its use compared to ammonium peroxydisulfate, the commonly used oxidant, are that this PANI has higher crystallinity, higher electrical conductivity, and longer nano-fibers. Additionally, potassium biiodate oxidant, $KH(IO_3)_2$, is more stable than ammonium peroxydisulfate so it will be another added advantage.

2. Experimental

The aniline monomer (99%, Alfa) was not distilled and was kept in refrigerator prior to use. Ammonium peroxydisulfate (APS) 98% $(NH_4)_2S_2O_8$ was purchased from Aldrich, and potassium biiodate $(KH(IO_3)_2)$ from Matheson Coleman & Bell. Other chemicals used were of analytical reagent grade. De-ionized water was used in all experiments.

2.1. Synthesis

Aniline (1 mL, 0.1 M) was dissolved in 100 mL of 1 M HCl at room temperature by magnetic stirring for 15 min. A100 mL of potassium biiodate $(KH(IO_3)_2)$ (0.012 mM) was added to the solution which was magnetically stirred for 5 min and then left without stirring overnight. In the case of co-use of potassium biiodate and sodium hypochlorite (5% NaOCl), the hypochlorite (5 ml) was added after potassium biiodate $(KH(IO_3)_2)$ (0.012 mM) was added to the solution and left for 20-min with no stirring. Each resulting green suspension product was filtered in a Buchner funnel and was then continuously washed with

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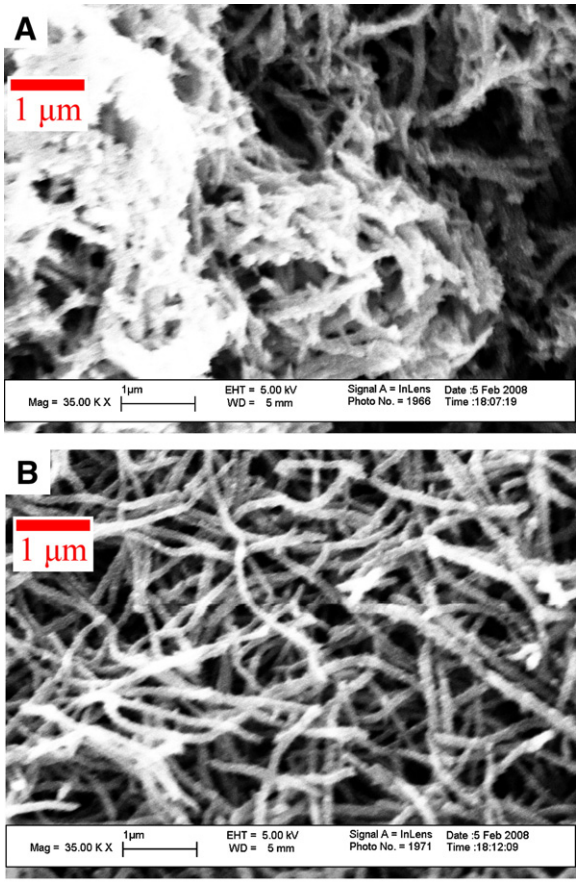

Fig. 1. SEM of polyaniline prepared using $KH(IO_3)_2$ oxidant: A) with stirring, and B) with no stirring.

hydrochloric acid (1 M HCl) and acetone until the filtrate became colorless, and dried in a 60 °C oven overnight. Approximately 10 mg of the above precipitate of emeraldine salt (ES) was added to 100 mL ammonium hydroxide (1 M NH_4OH) and magnetically stirred overnight in which the hydroxide de-protonated the chloride doped polymer. The mixture became blue-purple in color. The resulting blue suspension product was filtered in a Buchner funnel and was continuously washed with DI water until the filtrate was colorless and dried in a 60 °C oven overnight.

2.2. Characterization

2.2.1. Scanning Electron Microscopy

All samples were imaged on a Zeiss-LEO Model 1530 Variable Pressure Field Emission Scanning Electron Microscope operating at an accelerating voltage of 5 kV, and each dried sample for SEM imaging was prepared by coating each sample on carbon conductive tape. Each sample was then attached to aluminum sample holder using the carbon tape.

2.2.2. UV–Vis absorbance spectroscopy

Absorbance spectra from 800 to 200 nm were obtained on a Shimadzu UV–Vis 1601PC spectrometer using a quartz cell of 1 cm path-length. Emeraldine base sample were dissolved in *N*-methyl-2-pyrrolidone (NMP) to prepare a dark blue solution for the measurement.

2.2.3. Electrical conductivity measurement

The standard four probe technique using a Keithley 797A instrument was employed to measure the electrical conductivity of a pellet made with each polyaniline sample.

2.2.4. XRD analysis

Measurements were taken on a Rigaku Ultima III X-ray diffractometer using Cu Kα radiation.

3. Results and discussion

Potassium biiodate, $KH(IO_3)_2$, is a primary standard substance that can be used as an oxidant. In addition to its versatility, it has an advantage of a high equivalent weight, especially, when used to standardize bases. Potassium biiodate decomposes according to the following reaction:

$$KH(IO_3)_2 \rightarrow K^+ + H^+ + 2\,IO_3^-$$

$$2\,IO_3^- + 12\,H^+ + 10e \rightarrow I_2 + 6H_2O$$

According to the literature [27], iodate ion (IO^-_3) gives kinetically the fastest reaction among bromate (BrO^-_3) and chlorate (ClO^-_3) due to its highest activity. Fig. 1A shows scanning electron microscope (SEM) image of polyaniline nanofibers synthesized with potassium biiodate oxidant solution. The oxidant solution was added into

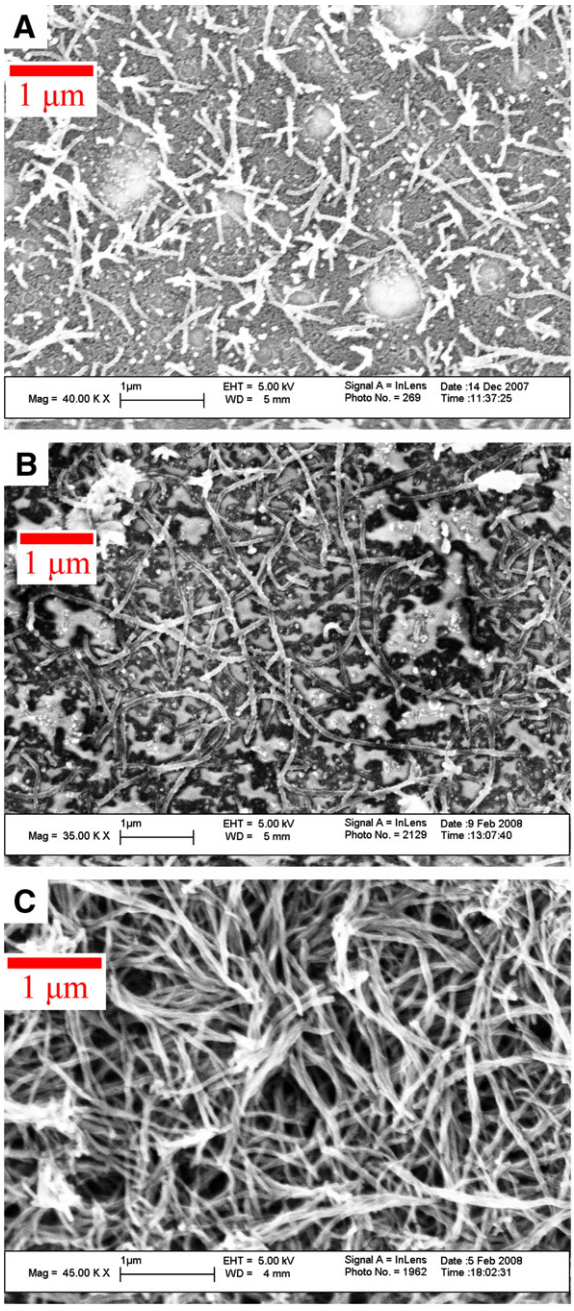

Fig. 2. SEM of polyaniline coated on PET substrate via in situ polymerization A) With APS oxidant, B) With $KH(IO_3)_2$ oxidant, and C) With co-use of $KH(IO_3)_2$ oxidant and NaOCl oxidant.