Silver-nanoparticle-embedded ultrafine polyimide fibers prepared via in situ techniques

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Introduction

Polyimide-silver (PI-Ag) hybrid nanofibers, due to the combination of the excellent mechanical, thermal and chemical resistance properties of the polyimide matrix and the superior optical, electrical, catalytic and antimicrobial properties of the incorporated silver species, are believed to be promising candidate materials in the fields of catalysis, anti-bacteria, sensors, drug and wound dressings, optical information storage, surface enhanced Raman scattering, and etc. Here, we report our efforts on the synthesis of the silver-nanoparticle-embedded ultrafine PI fibers.

Results and Discussion

Two different approaches were employed in our work, i.e., the in situ single stage self-metallization technique, which develops the PI-Ag nanofibers by thermally treating the precursor nanofibers prepared directly from a mixture solution of poly(amic acid) (PAA) and (trifluoroacetylacetonoto) silver(I) (AgTFA) via electrospinning, and the direct ion-exchange self-metallization technique, which works by using the electrospun PAA ultrafine fibers, as the starting matrix, and then loading silver(I) into the polymer matrix through the ion exchange reactions of the carboxylic acid groups in PAA macromolecules with the silver ammonia complex cations ($[Ag(NH_3)_2]^+$), followed by thermal treatment under nitrogen environment. These two methods are rather different but have a common feature of generating silver nanoparticles via an in situ and spontaneous way from a polyimide precursor/silver precursor blend.

In our present work with pyromellitic dianhydride (PMDA)/4,4'-oxydianiline (4,4'-ODA) polyimide as the matrix, ultrafine polyimide nanofibers embedded with silver nanoparticles with diameters less than 20 nm [Figure 2] were successfully fabricated. The hybrid nanofibers were characterized by Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA). Thermal treatment environment plays a key role in the ultrafine fiber preparation process. Serious polyimide decomposition occurred when treating silver(I)-doped precursor fibers under air conditions, and the silver nanoparticle-incorporated ultrafine PI nanofibers were obtained only under inert atmospheres in the present experiment. Isothermal thermo-gravimetric analysis [Figure 3] on the $[Ag(NH_3)_2]^+$ ion-exchanged PAA precursor fibers indicates that silver has considerably strong catalytic effect on the decomposition of the polyimide nanofibers at high temperatures (over 250 °C) and oxygen plays an essential role in the degradation process, accounting for the observed thermal degradation behavior. Antibacterial Quinn tests conducted against gram-negative bacterium E. coli [Figure 4] suggest that our PI-Ag nanofibers posses excellent antibacterial properties with an antibacterial activity of 99.99%.

Conclusions

Ultra-fine polyimide (PI) fibers incorporated with silver nanoparticles were successfully fabricated using the pyromellitic dianhydride (PMDA)/4,4'-oxydianiline (4,4'-ODA) polyimide as the matrix via the single stage self-metallization method and the direct ion exchange self-metallization technique. The silver nanoparticles embedded in the ultrafine PI fibers were controlled with diameters in less than 20 nm and uniformly distributed on the fibers. Due to the catalytic oxidative degradation effect of the incorporated silver nanoparticles, the thermal decomposition temperature of the hybrid fibers at 10% weight loss were decreased about 130 °C in air as compared to the pristine PI. However, the finally obtained PI-Ag ultrafine fibers still possess a high thermal stability (378 °C), which is adequate for many high-temperature applications. Besides, the PI-Ag nanofiber exhibits excellent antibacterial properties in the antibacterial Quinn test, demonstrating its potential applications as biomaterials.

Reference

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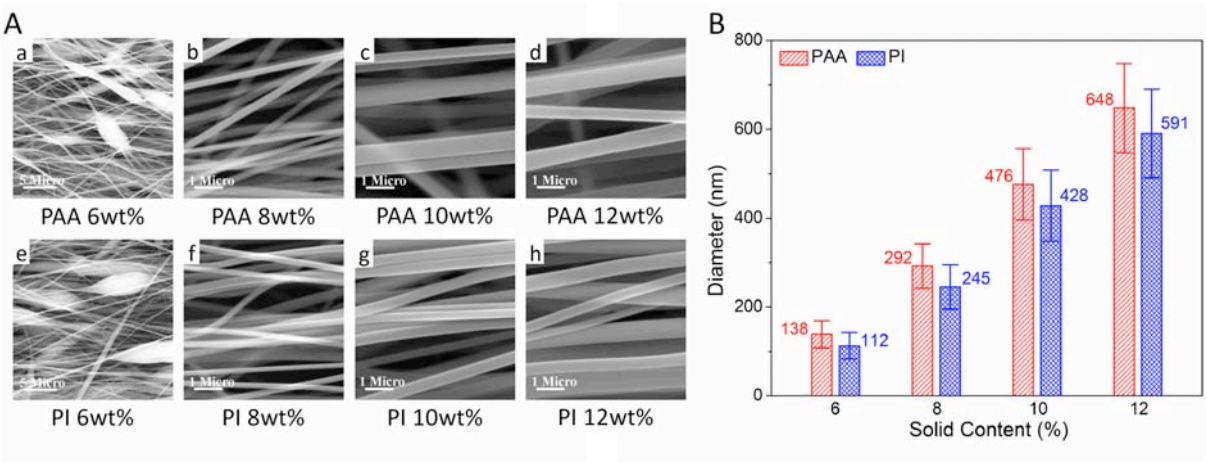

Figure 1. (A) SEM images for the ultrafine PAA fibers and the corresponding PI nanofibers prepared from (a, e) 6 wt% PMDA/ODA PAA solution, (b, f) 8 wt% PMDA/ODA PAA solution, (c, g) 10 wt% PMDA/ODA PAA solution, and (d, h) 12 wt% PMDA/ODA PAA solution, and (B) the diameter variations of the ultrafine fibers with the concentration of the PAA solutions. The as-spun ultrafine PAA fibers were cyclodehydrated to the corresponding ultrafine PI fibers by being thermally treated to 300 °C over 2 h and then kept at 300 °C for 2 h.

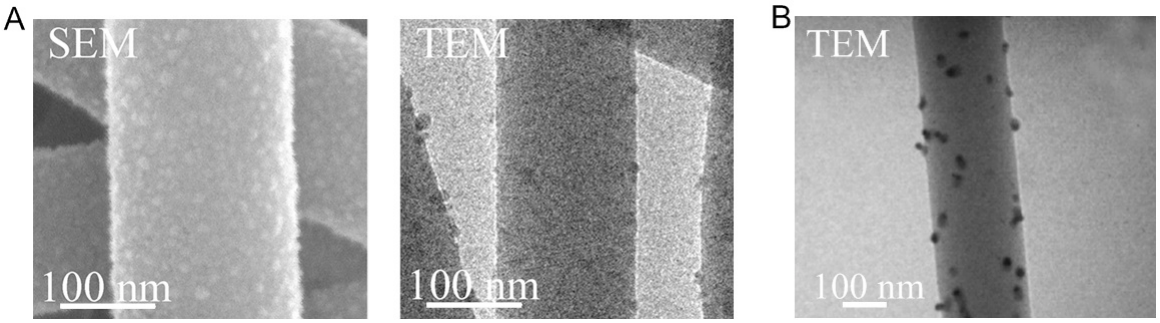

Figure 2. (A) SEM and TEM images for the ultrafine PI-Ag fibers prepared via the direct ion exchange process. The PAA fibers were ion-exchanged in a 0.01 M aqueous $[Ag(NH_3)_2]^+$ solution for 20 s followed by thermal treatment to 300 °C for 2h in N2. (B) TEM images for the PI-Ag nanohybrid fibers (2 wt% Ag) prepared via the in-situ single stage self-metallization process using AgTFA as the silver precursor.

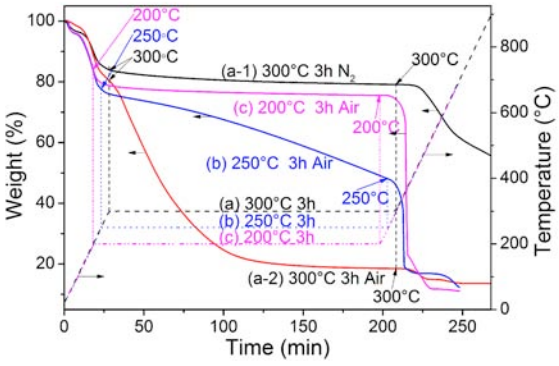

Figure 3. The isothermal TGA curves measured at different temperatures in nitrogen and air atmospheres for the PAA ultra fine fibers ion exchanged in a 0.01 M aqueous $[Ag(NH_3)_2]^+$ solution for 20 s.

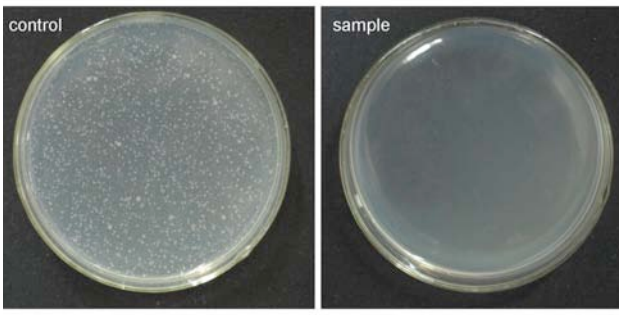

Figure 4. Photographs of colonies of E. coli incubated on agar plates obtained from cultivated suspensions with (control) and without (sample) silver-doped polyimide fibers.