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Enhanced electrical conductivity of Ag-mercaptosuccinic acid-redoped polyaniline nanoparticles during thermal cycling above 200 °C

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ABSTRACT

Ag-doped polyaniline (PANI) nanoparticles are prepared via doping–dedoping–redoping with the thiol group in mercaptosuccinic acid (MSA) providing the linkage between PANI molecules and Ag atoms. Ag-MSA-doped PANI maintains the electrical conductivity well above the room-temperature value of 3.0 S/cm up to 220 °C, reaching its maximum (9.0 S/cm) at 180 °C. In addition, Ag-MSA-doped PANI nanoparticles show remarkable stability against repeated thermal aging at 120 °C. The room-temperature conductivity, in fact, increases by a factor of ∼3 after 3 cycles of thermal aging. The enhanced stability against repeated thermal aging is attributed to the formation of uniformly distributed Ag nanoparticles within the PANI particles upon heating.

1. Introduction

Among various conducting polymers, polyaniline (PANI) has attracted a great deal of interest due to its exceptional environmental stability and unique doping characteristics, which generated a wide range of potential applications in electronic devices, chemical sensors and batteries [1]. As with all conducting polymers, thermal stability is a key issue to be resolved before taking full advantage of the unique properties of the material. The emeraldine base form of PANI is thermally stable up to 400 °C [2]. PANI in protonated form which exhibits higher electrical conductivity than the base form, however, suffers from rapid deterioration of the electrical conductivity upon thermal aging even at 75 °C [3]. The thermal degradation of the protonated PANI is typically attributed to a complex combination of factors including chain rearrangement, deprotonation, decomposition of PANI, oxidation, and crosslinking [4]. Over the years, much effort has been directed toward improving the thermal stability of the protonated PANI. Proposed methods include various dopants, copolymerization with aliphatic monomers, blending with other polymers, composites with metal and preparation of PANI in colloidal form [5–10]. Success, so far, has been a marginal improvement, still limiting the thermal stability of the protonated PANI below 100 °C.

Noble metals such as Au and Ag have been used to synthesize metal particle-decorated nanostructures such as nanofibers [11–13] and nanoballs [14] Ag/PANI core-shell structures have been also reported [15]. Although noble metal-decorated PANI nanomaterials exhibits enhanced electrical conductivity [11] and even memory effect, none of these synthesized have been reported to improve the thermal stability of the protonated PANI. In this work, we explore the possibility of improving the thermal stability of the protonated PANI by doping with silver atoms. We demonstrate that doping the PANI nanoparticles with Ag can greatly increase the thermal stability of the acid-doped PANI even after repeated thermal cycling. To introduce silver atoms into the PANI nanoparticles via Ag–S bonding, mercaptosuccinic acid (MSA) is doped onto the PANI nanoparticles. Because the thiol group in MSA behaves as an inhibitor in the PANI nanoparticle synthesis, resulting in low molecular weight, doping–dedoping–redoping method using a dodecylbenzene sulfonic acid (DBSA) micellar solution as an intermediate dopant [16] was employed.

2. Experimental procedure

2.1. Materials and sample preparation

Ag-MSA-redoped PANI was prepared via doping–dedoping–redoping process which is schematically described in Fig. 1. In the initial doping step, DBSA-doped PANI nanoparticles were synthesized from the DBSA micellar solution as previously reported [16].

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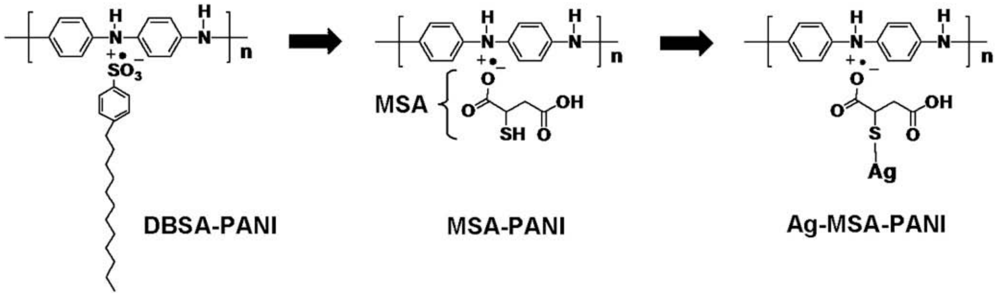

Fig. 1. Schematic diagram for Ag-doping of PANI using MSA.

DBSA-doped PANI nanoparticles were dedoped using a NaOH solution (1 M) to obtain the emeraldine base form, which was then redoped using a MSA solution (0.1 M). Ag atoms were attached to MSA via S–Ag bonding by adding an aqueous $AgNO_3$ solution into the MSA-redoped PANI (MSA-PANI) solution. Ag-MSA-PANIs with two different Ag-doping levels, 0.05 M- and 0.1 M-Ag-MSA-PANI were produced by using 0.05 M and 0.1 M $AgNO_3$ solutions. Excess Ag was removed by washing the prepared Ag-MSA-PANI particles in 0.1 M HNO_3.

2.2. Measurement

The electrical conductivity of the samples was measured using a four-point-probe apparatus. For conductivity and thermal stability measurements in air, the nanoparticle powders were pelletized under high pressure. In-situ electrical measurement was performed with a Keithley 2000 multimeter equipped with a hot stage (Mettler Toledo FP82HT). Fourier transform infrared spectrometer (FT-IR, Nicolet 740) was used to probe the chemical composition of the samples. UV–vis spectroscopy was performed with a UNICAM 8700 spectrometer to determine the doping characteristics. For structural study, transmission electron microscopy (TEM, JEOL 2010) was employed.

3. Results and discussion

Fig. 2 shows FT-IR spectra of MSA-PANI and 0.1 M-Ag-MSA-PANI nanoparticles. Both spectra contain the characteristic peaks near 1570 and 1490 cm^{-1} corresponding to the C=C stretching of benzenoid and quinoid rings, with other peaks in good agreement with the previous spectroscopic results of acid-protonated PANI [12]. Note that bands related to SO_3^- are not observed from both spectra indicating that DBSA was successfully dedoped. Instead, the absorption band related to the C–S stretching in MSA is visible at 698 cm^{-1} which shifts to 668 cm^{-1} (marked in Fig. 2) when doped with Ag. Presence of Ag in Ag-MSA-PANI was further confirmed by energy-dispersive X-ray spectroscopy (EDS). In fact, EDS analysis showed that Ag and S exist approximately in 1:1 ratio. The FT-IR result together with EDS verifies that PANI was successfully doped with Ag using MSA as a linking molecule.

Fig. 3 displays UV–vis spectra of the dedoped-PANI, DBSA-PANI, MSA-PANI and 0.1 M-Ag-MSA-PANI. In the case of the dedoped-PANI with relatively high resistivity, two absorption bands at 320 and 670 nm are observed. These two bands are due to the presence of benzene and quinone segments in the polymer chain. In the case of both DBSA-PANI and MSA-PANI, two peaks appear at 350 and 420 nm, which can be assigned to π–π^* and polaron–π^* transitions, respectively. The band centered at 850 nm is due to the π–polaron transition. These three distinct absorption bands are indicative of a doped polyaniline [5,10]. These results show that MSA was successfully doped onto PANI by the doping–dedoping–redoping process in agreement with the FT-IR result. For Ag-MSA-PANI, however, the peak of 850 nm is broadened and a small free carrier tail band appears beyond 860 nm which may be due to the delocalized polaron band structure [17]. These results possibly indicate that the addition of large silver atoms to MSA-PANI via sulfur–silver bonding may have changed the structure of MSA-PANI.

Room-temperature conductivities, σ_0 for MSA-PANI, 0.05 M- and 0.1 M-Ag-MSA-PANI were 5.5×10^{-3}, 3.0 and 2.0 S/cm,

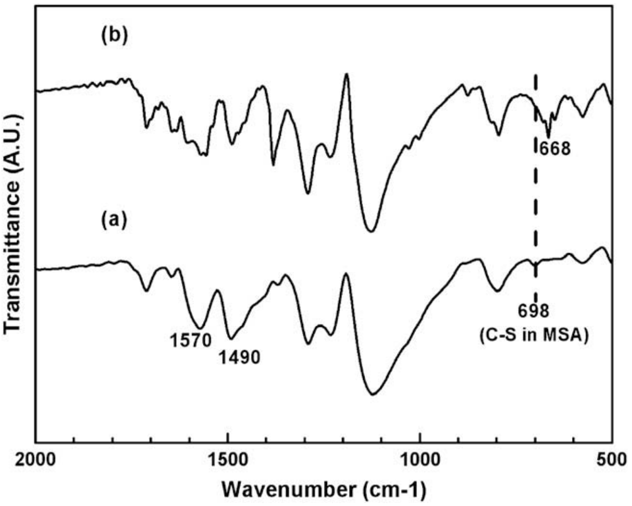

Fig. 2. FT-IR spectra of (a) MSA-PANI, (b) Ag-MSA-PANI.

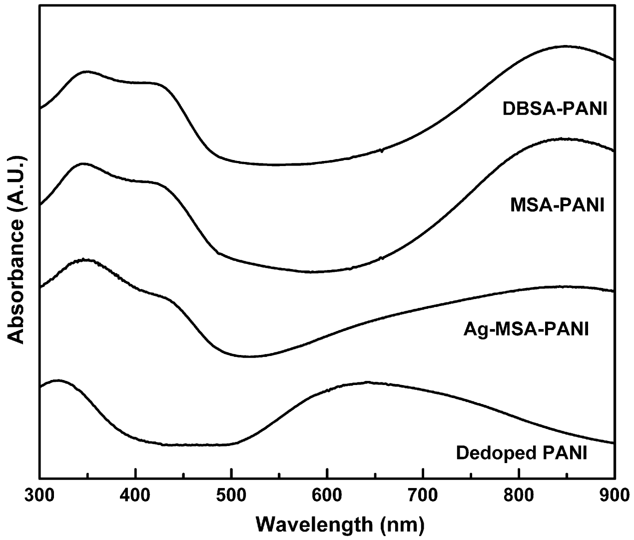

Fig. 3. UV–vis spectroscopy of DBSA-PANI, dedoped-PANI, MSA-PANI, and Ag-MSA-PANI in methanol solution.