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Hybrids of silver nanowires and silica nanoparticles as morphology controlled conductive filler applied in flexible conductive nanocomposites

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ABSTRACT

Flexible conductive polymer nanocomposites based on silver nanowires (AgNWs) have been widely studied to develop the next generation of flexible electronics. However, AgNWs tend to aggregate in polymer matrix that usually results in high percolation threshold. In this study, nonconductive silica nanoparticles (nano-SiO_2) were successfully co-assembled on AgNWs to form AgNWs/nano-SiO_2 hybrids and waterborne polyurethane (WPU) conductive nanocomposites filled with the hybrids were prepared. The results show that the resistivity of WPU nanocomposites filled with AgNWs/nano-SiO_2 hybrids decreased about 5000 times and the percolation threshold decreased from 10.6 vol% to 3.6 vol% due to AgNWs distribute more uniformly in WPU with the help of nano-SiO_2. The further study to mechanism of interactions between AgNWs and nano-SiO_2 suggest that the promotion of dispersion is attributed to hydrogen bonding and van der Waals force. The WPU nanocomposites embedded with AgNWs/nano-SiO_2 hybrids present excellent mechanical adhesiveness, flexibility and thermal stability.

1. Introduction

Flexible conductive polymer nanocomposites are one of the most interesting and researched areas in nanotechnology which have been extensively studied in recent years due to their potential applications in the fields of wearable electronic devices (such as electronic skins) [1,2], flexible displays [3], flexible supercapacitors [4], flexible solar cells [5], etc. In order to prepare composites with good conductivity and flexibility, various types of conductive fillers have been developed, such as graphene [6], carbon nanotubes [7], metal nanoparticles [8], noble metallic nanowires [9] or semiconducting nanowires [10,11] and their hybrid materials [12–16]. To date, silver nanowires (AgNWs, one of the most promising noble metallic nanowires) have been commonly applied in these fields as AgNWs are highly conductive and easy to synthesis. However, the dispersion of AgNWs in polymer matrix (epoxy, polyurethane, PDMS, etc.) is a big challenge that hinders the development of these materials. AgNWs tend to aggregate in these matrixes due to the intense depletion-induced interaction among AgNWs, which often results in high percolation threshold and increases the viscosity of nanocomposites so that the processing performance is poor [17]. Furthermore, the flexibility of polymer nanocomposites will decrease dramatically or even disappear when the contents of conductive fillers are high. Therefore, promoting the dispersion of AgNWs is the key to decrease the percolation threshold and improve the conductivity and flexibility of composites.

Today, hybrid materials present a high versatility to elaborate tailor-made materials. As a consequence they become competitive candidates for a variety of applications. For example, numerous hybrid fillers contains different dimensional nanostructures (carbon nanotubes [18], graphene [19], graphene oxide [20], etc.) were developed to control the morphology of conductive network due to their synergistic effect. However, these carbon materials are expensive and not eco-friendly because some hazardous chemicals such as concentrated sulphuric acid or hydrazine hydrate ($N_2H_4{\cdot}H_2O$) may be used during the production process. Silica nanoparticles (nano-SiO_2), riches in hydroxyl groups on its surface and widely used in industry, was reported to improve the conductivity of epoxy/AgNWs nanocomposites and relevant mechanism was analyzed by Monte Carlo simulations [17]. However, epoxy resin is highly undesirable to prepare flexible conductive composites in that it is a kind of relatively brittle materials [21]. And the investigation to the mechanism of interactions between AgNWs and nano-SiO_2 is insufficient. Moreover, applied the hybrid

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nanostructure of AgNWs and nano-SiO_2 to morphology control of conductive network has not been reported in previous published papers.

Herein, flexible conductive polymer nanocomposites based on AgNWs and waterborne polyurethane (WPU) was fabricated due to its extremely flexibility and good compatibility with AgNWs. AgNWs/nano-SiO_2 hybrids were prepared and embedded into WPU, indicating that hybrid nanostructure of nano-SiO_2 decorated AgNWs has a great influence on the conductivity. The resistivity of WPU nanocomposites filled with AgNWs/nano-SiO_2 hybrids decreased about 5000 times (from $2.2 \pm 0.5\ \Omega$ cm to $(4.9 \pm 0.4) \times 10^{-4}\ \Omega$ cm) and the percolation threshold decreased from 10.8 vol% to 3.6 vol%. Furthermore, the mechanism of interactions between AgNWs and nano-SiO_2 were further studied and the results suggest that the promotion of dispersion of AgNWs and improvement of conductivity is attributed to hydrogen bonding and van der Waals force between them, which provide the driving force to make nano-SiO_2 co-assembled onto AgNWs. The AgNWs/nano-SiO_2 hybrids serve as an effective conductive filler system that is low-cost, environmental friendly and can be prospectively applied to flexible conductive nanocomposites.

2. Material and methods

2.1. Materials

Silver nitrate ($AgNO_3$) was purchased from Tianjin Qilun Chemical Technology Co., Ltd. Polyvinylpyrrolidone (PVP, Mw = 1,300,000 g mol^{-1}) was bought from J&K technology Co., Ltd. (Beijing, China). Ethylene glycol and anhydrous ethanol were purchased from Tianjin Fuyu Fine Chemical Co., Ltd. (Tianjin, China). Sodium chloride (NaCl) and copper nitrate ($Cu(NO_3)_2$) were purchased from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). Fumed silica (20–60 nm in diameter) and WPU (solid content is 30 wt%) were supported by Guangzhou Xinxi Fine Chemical Factory and Guangzhou Bihong chemical technology Co., Ltd., respectively.

2.2. Preparation of ultra-long AgNWs

Ultra-long AgNWs (length > 40 μm) were synthesized according to the polyol process with hydrothermal treatment with assistance of Cl^- and Cu^{2+} [22,23]. Typically, 1.375 mg $Cu(NO_3)_2$ and 2.750 mg NaCl was successively dissolved in 110 mL ethylene glycol in 250 mL three-necked flask at ambient temperature and then 0.30 g PVP (Mw = 1,300,000 g mol^{-1}) was added to the solution. Then the mixed solution was heated at 180 °C under mechanical stirring at 170 rpm for 1.0 h to dissolve PVP and remove needless trace water molecules. After the system cooled to room temperature at dry environment, 0.33 g $AgNO_3$ powders was added to the solution under mechanical stirring at 270 rpm for 10 min until $AgNO_3$ powders dissolved completely. The obtained solution was then transferred into PTFE tank and sealed in a stainless cylinder and then kept at 145 °C for 12 h in an oven. The obtained silver-gray products were washed several times by centrifugation process using anhydrous ethanol. The resulting pure AgNWs were re-dispersed in anhydrous ethanol with concentration of 5 mg mL^{-1}.

2.3. Preparation of nano-SiO_2 dispersions and AgNWs/nano-SiO_2 hybrids

Nano-SiO_2 dispersions were prepared as follows: 5.0 g fumed silica (20–60 nm in diameter) was dispersed in 100 mL anhydrous ethanol and homogenized in an ultrasonic bath for 2.0 h. The obtained milky dispersions were then centrifuged at 4000 rpm for 10 min to remove the larger size aggregates and the upper suspensions were obtained and diluted to 2.5 mg mL^{-1}. AgNWs/nano-SiO_2 hybrid materials were prepared via dropping certain volume of 2.5 mg mL^{-1} nano-SiO_2/ethanol dispersion into 20 mL 5.0 mg mL^{-1} AgNWs/ethanol dispersion in a 100 mL beaker and fully homogenized in an ultrasonic bath for 5 min. The obtained precipitates was collected and dried in an oven at 60 °C for 24 h.

2.4. Preparation of WPU nanocomposites filled with AgNWs and AgNWs/nano-SiO_2 hybrids

To discuss the percolation threshold of conductive nanocomposites in absence of nano-SiO_2, a serious of WPU/AgNWs nanocomposites with different mass ratio of AgNWs were prepared through mixing 20 mL 5.0 mg mL^{-1} AgNWs/ethanol dispersion with a certain quality of WPU by homogenized in an ultrasonic bath for 5 min and then the homogeneous mixture was poured to PTFE mold (2.5 cm in width and 3.0 cm in length) and dried in an oven at 60 °C for 24 h. The WPU nanocomposites embedded with AgNWs/nano-SiO_2 hybrids were prepared by adding the obtained undried hybrid materials into WPU matrix and homogenized by glass rod. Next, the mixture was coated on target substrates by scalpel and dried in an oven at 60 °C for 24 h.

2.5. Characterization

The UV–vis absorption spectroscopy was taken at ambient temperature on HP 8453E spectrometer (HP Co. Ltd., America) using a quartz cell with a 1 cm optical path. X-ray diffraction (XRD) patterns were collected using Bruker D8 ADVANCE diffractometer (Bruker Co. Ltd., Billerica, America) with Ni-filtered Cu Kα radiation (λ = 0.15418 nm) in the range of 5–90° with a scanning speed of 2°/min at 40 kV and 40 mA. The weight loss curve of dried AgNWs was measured in nitrogen atmosphere by TA instrument (TA Co. Ltd., Pennsylvania, America), the heating rate is 10 °C/min. The DSC results were collected in nitrogen or oxygen atmosphere using TA instrument (TA Co. Ltd., Pennsylvania, America), and the heating rate is 10 °C/min. The morphology of AgNWs and nanocomposites were observed by Nano SEM 430 instrument (FEI Co. Ltd., Hillsboro, America). To observe the cross section of nanocomposites, the nanocomposites films were immersed in liquid nitrogen for 3 min and freeze fractured. To avoid the charging effect, all the samples were sprayed with a thin platinum layer before SEM observation. Transmission electron microscopy (TEM) images were taken by JEOL JEM-2100HR instrument (EDAX Inc., Mahwah, America), accelerating voltage was operated at 200 kV. For TEM characterization, a drop of AgNWs/ethanol dispersion was deposited on copper grids with continuous carbon films and dried at room temperature. X-ray photoelectron spectroscopy (XPS) analysis was carried out using Kratos Axis Ultra DLD electron spectrometer (Kratos Co. Ltd., Manchester, England). Fourier Transform Infrared Spectroscopy (FTIR) spectrum was collected by a Bruker VERTEX70 FTIR spectrometer (Bruker Co. Ltd., Billerica, America) at room temperature using KBr disc technique. The resistance (ρ, Ω) of the nanocomposites films was recorded on a KEITHLEY 2182A NANOVOLTMETER and the resistivity (R, Ω cm) of nanocomposites films was calculated by equation: $R = \rho S/L$, where L (cm) and S (cm^2) is the length and cross sectional area of the sample, respectively. Mechanical adhesiveness of nanocomposites was measured by 3M peeling test method [24,25]. Typically, a 12 mm-wide piece of 3M scotch tape (3 M Company, Minnesota, America) was attached on the sample and peered off the sample after 2 min. The process was repeated several times using a new piece of tape for every test and the mechanical adhesiveness was evaluated by measuring the resistivity after each tape tests. The bending flexibility was investigated