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Electro-responsive silver nanowire-shape memory polymer composites

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ABSTRACT

Silver nanowire (Ag NW)–shape memory polymer composites in bilayer structure were fabricated which exhibited flexibility and superior electrical conductivity. The morphologies of the Ag NWs and the composites were investigated by multiple tools. The composites were able to maintain most of the conductivity as elongation of 12% by measuring the sheet resistance under different stretchable status. Furthermore, the electro-triggered shape recovery behaviors of the composites were disclosed by experimental measurements and modeling simulation.

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1. Introduction

Shape memory polymers (SMPs) are one set of intelligent polymers which are capable of response and actuation under external stimuli [1]. The SMPs research in early stage commonly emphasized on thermal responsive SMPs which utilized thermal transitions of the polymer molecules as the switching mechanism. Besides, exploration of the SMPs being responsive to various types of external stimuli has been catching increasing interests in recent years, including light- [2] and multiple [3] stimuli responsive SMP as well as path-dependent multi-shape effect based on nanocellulose [4,5] and magnetic and electrical stimuli-responsiveness based on Fe_3O_4 nanoparticles [6] and carbon nanotubes [7]. Silver nanowires (Ag NWs) have been widely explored towards stretchable and transparent conducting electrodes [8]. They also have been used as electrode in the semiconductor area for superluminescent light emitting diodes (SLEDs) [9,10]. The Ag NW–polymer composites were extended in applications of capacities sensor [11] and healable transparent conductors [12]. However, there has been little literature reporting Ag NW-containing SMP composites by far. In this study one set of flexible and conductive Ag NW–SMPU composites were firstly fabricated. The electro-triggered shape recovery was disclosed. The findings may greatly benefit the development of multi-functional SMPs in the fields of wearable electronics and so on.

2. Experimental

The Ag NWs and SMPU were synthesized according to the previous literature [4,12]. The Ag NWs suspension in methanol was able to be stable for three days at the aid of ultrasonic treatment. Three composite samples were fabricated, which were labeled as C1, C2 and C3 according to the compositions. The morphologies of the Ag NWs and the composites were investigated by TEM (JEM-100CXII microscope), SEM (Hitachi, S-4800) and AFM (Multimode 8 SPM AFM system, Bruker, USA). The sheet resistance was measured by using a Fluke 73III multimeter. The electro-triggered shape recovery was measured by a bending test method [13] with a DC power supply (Micronta 0–30 V variable power supply).

3. Results and discussion

Fabrication of Ag NW–SMPU nanocomposites: Fig. 1a shows the TEM image of the synthesized Ag NWs. The average length was determined to be in the range 15–20 μm and the diameter was in the range of 80–120 nm. Spin-coating produced Ag NWs percolating network on a pre-cleaned glass substrate the AFM image of which is shown in Fig. 1b. It was obviously observed that the Ag NWs contacted with each other, constructing a percolating network. Afterwards, the Ag NW–SMPU composites were fabricated by a transfer method [12]. The process is schematically illustrated in Fig. 1c: Ag NWs suspension in 5 mg/ml of methanol was deposited on a release substrate; then, SMPU solution in N, N-Dimethylacetamide (DMAc) was added onto the silver film before drying in an oven at 70 °C for 24 h; finally, the composites,

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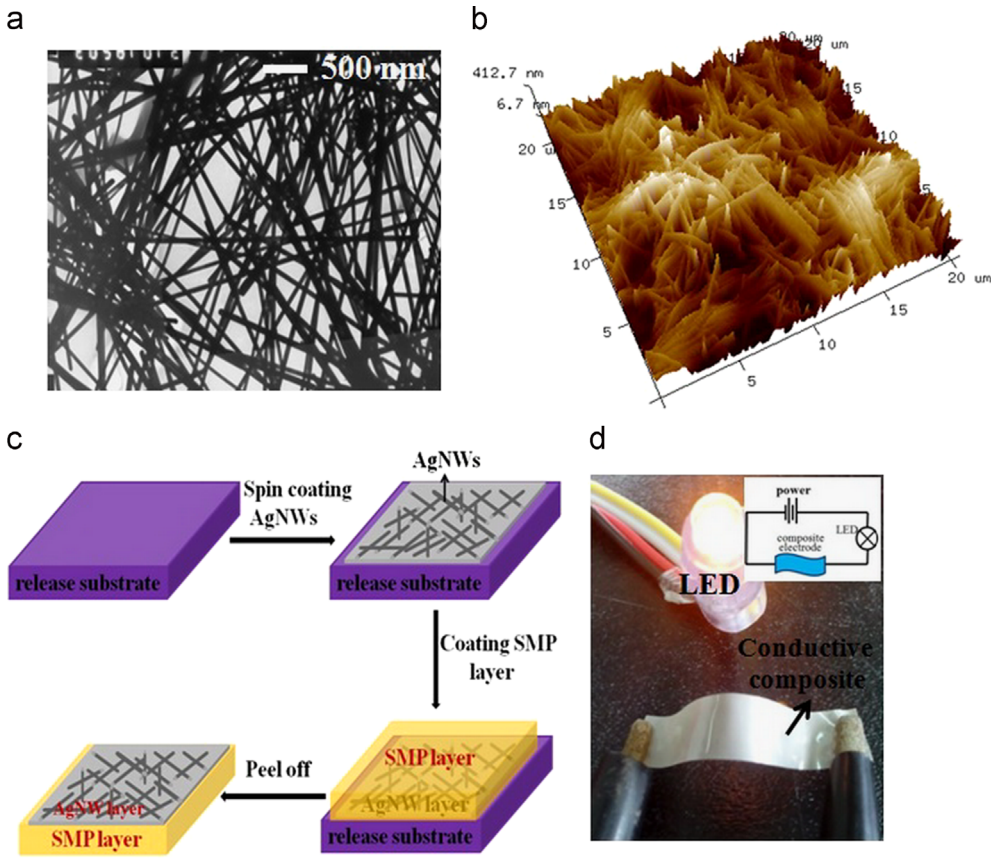

Fig. 1. TEM (a) and AFM (b) images of Ag NWs; (c) schematic illustration of composites fabrication process; (d) the LED turned on as the composite was applied with voltages (the inset shows the circuit connecting with the composites).

comprising a layer of Ag NWs percolation network inlaid in the surface layer of the SMPU, was peeled off. They were flexible and highly conductive. When the composites were connected into a typical circuit, applying as low as 1.5 V of voltage was sufficient to allow the LED to turn on (Fig. 1d), no matter the composites were in the states of straight or stretchable.

Morphologies of the Ag NW–SMPU composites: The surface and bulk morphologies of the composites were investigated by SEM, which are shown in Fig. 2. The Ag NWs, randomly distributing on the surface layer of the composites, were found to be well dispersed, constructing a conductive percolating network one part of which was left on the surface while the other part was embedded into the polymer matrix (Fig. 2a). As a result, the composite surfaces obtained electrical conductivity which was robust to some extent due to the immobilization effect of the polymer matrix. The observation was in agreement with the previous reported morphologies of the Ag NWs percolating network [14]. The SEM images of the cross section of the composites are shown in Fig. 2b–d. The composites were in clear bilayer structure where the upper and bottom layers were continuous Ag NW-containing conductive layer and the dielectric SMPU layer. Obvious interface existed between the two layers. The overall thickness of the samples was around 30 μm comprising the conductive layers of 17.2 μm, 13.16 μm and 9 μm for C1, C2 and C3, respectively. Given that the SMPU utilized in this study was non-crystalline, it was reasonable that no obvious polymer crystals were observed neither on surface nor in the composite bulk.

Electrical conductivity and electro-responsive shape recovery of the composites: In order to further evaluate the relationship between stretchability and conductivity, the sheet resistance (R_s) of the composites was measured under different elongation percentages, which is shown in Fig. 3a. The three samples exhibited superior conductivity at their original status where the resistance was less than 5 Ω/sq. R_s moderately increased as elongated and kept below 200 Ω/sq even as the composites were stretched by 12%. However, further elongation caused a dramatic increase in the resistance value, followed by cessation of the conductivity. The results might be due to the increase in the length of the conductive path, causing difficulties for the electrons to pass through. Eventually, the conductive path broke and resulted in the cessation of conductivity [15]. Moreover, the composites exhibited electro-responsive shape recovery. The datasets of the recovery ratio versus time were recorded and fit using a standard sigmoidal function: $R(t)=R_\infty/(1+e^{-(t-\tau)})$ [13], where R_∞ and τ are the fitting parameters standing for the final recovery ratio and the characteristic time (shown in Fig. 3b). The datasets were found to be (82%, 1.1 s), (68%, 2.0 s) and (51%, 3.4 s) for the composites C1, C2 and C3, respectively. The results indicated that the composites having higher Ag content were able to not only obtain more completed recovery, but also reach the maximum recovery speed in a shortened time. Assuming all the heat from electrical (Joule) heating was taken by the sample, i.e. no convective heat loss: $dT/dt \propto U^2/R$. Here U, R, t and T are applied DC voltage, sample resistance, time and temperature, respectively. The composites having higher Ag NWs contents had lower R. Thus, the heating effectiveness was promoted. Much more Joule heat was produced to trigger the thermal transition of the SMPU, leading to better shape recovery of composites in the same period. Fig. 3c shows the photographical demonstration of shape recovery of C1. The bent angle obviously changed within 3 s as the composite was applied as low as 5 V of voltages. It has been known that hybrid conductive nanofillers could reduce the entanglement in conductive network structure, thus increasing the conductivity and resistivity-strain sensitivity [16]. In our study more than one type of fillers, rather

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