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Flexible transparent heaters based on silver nanotrough meshes

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ABSTRACT

Flexible transparent heaters based on silver nanotrough mesh were prepared by thermal evaporation of silver on sacrificial nanofiber templates fabricated by electrospinning. Due to the specific preparation process, the heaters have many advantages like large area uniformity, low resistance, high transparency, mechanical flexibility and strong adhesion to substrates. A rapid and effective heating (rising from 25 °C to 100 °C in 50 s) is obtained at a DC input of 7 V with a visible light transmittance as high as 87%, which results in a relatively high figure of merit for transparent heaters. Therefore, silver nanotrough mesh can be a promising candidate for transparent heating applications.

1. Introduction

Transparent heaters, special resistors that can generate joule heat and pass the visible light through simultaneously are extensively used as defogging windows and mirrors with growing market demands [1–3]. Optical transmittance (T_R) and sheet resistance (R_S) are the two most important parameters that determine the performance of transparent heaters. High T_R makes transparent heaters suitable for various applications where clear visibility is required, such as periscopes and windshield of vehicles. Low R_S is required not only for rapid heating but also for maintaining high saturated temperature under low input power. However, in practice T_R and R_S usually have to compromise with each other.

So far, tin-doped indium oxide (ITO) has dominated the transparent heating market for many years due to its outstanding optoelectronic properties. However, the increasing price of indium source, slow thermal response and lack of flexibility limit ITO's further industrial applications [4,5]. Currently, emerging candidates to replace ITO as transparent conductors or heaters include carbon nanotubes (CNTs), graphene, metal nanowires (NWs), metal wire meshes, and various hybrid films [6–27]. Among them, carbon-based transparent heaters suffer from high R_S due to the high contact resistance between adjacent nanotubes and sheets [6–11]. Metal NWs and meshes have much better electrical conductivities due to their high electron concentration. However, chemically synthesized metal NWs tend to aggregate into clusters during the solution-based dispersion processes, which results in a nonuniform thermal distribution [12]. As an alternative, well-defined or random metal meshes have been fabricated by lithography [16–18] or using micro-cracks [19–21] and nanofibers [22–25] (NFs) as templates, respectively.

In particular, electrospinning is a convenient method to produce polymer NF networks which can be used as templates for metal meshes [28,29]. Recently, Y. Cui's group have prepared high-performance metal nanotrough (NTR) mesh-based transparent conductor using electrospun NF networks as templates [24]. However, to our knowledge, the heating performance of such kind of metal NTR meshes has not been investigated. In this work, we will demonstrate that Ag NTR meshes prepared by electrospinning NF networks and subsequent thermal evaporation of silver can be used as a new type of transparent heater, which can reconcile the discordance between high T_R and low R_S.

2. Experimental and characterization

The fabrication process of Ag NTRs mainly involves three key steps. Firstly, polyvinyl alcohol (PVA) powder (Mn = 80 000, Shanxi Chemical Co. Ltd.) was added into deionized water with a concentration of 8 wt% and stirred at 90 °C for 4 h to prepare the precursor. Then, PVA solution was loaded into a syringe with a metallic spinneret onto which a 15 kV voltage was applied. Free-

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standing NFs were collected by a square copper frame. The diameter of PVA NFs was in the range of 200–400 nm. Secondly, PVA NF networks were covered by 135 nm-thick silver by thermal evaporation. Due to the shadowing effect in vacuum evaporation, only the side facing the tungsten boat of PVA NFs was covered by silver. Finally, the silver coated PVA NF networks were transferred onto flat or curved substrates (Supplementary Fig. S1), then the PVA NF templates were dissolved by water vapor from an ultrasonic humidifier. By depositing two counter electrodes on the opposite edges, Ag NTR mesh transparent heaters were obtained. Surface morphologies of Ag NTR meshes were characterized by a scanning electron microscope (Hitachi S-4800 SEM). The specular transmission spectra were measured by a Hitachi UV4150 spectrometer. Sheet resistances were measured by the four-probe method. FT-IR spectra were measured by a Nicolet IS 10 apparatus. Heat distribution of transparent heater was measured by an infrared thermometer (Cason CA380) and a thermal imager (RNO IR-160P).

3. Results and discussion

Fig. 1(a) shows a typical SEM image of two cross-linked PVA NFs. In contrast to the conventional interweaved electrospun NFs, our PVA NFs can be welded into each other at the joint point if optimized precursor concentration and electrospun setup are used. Because of the shadowing effect in vacuum evaporation, only the upper side of PVA NFs is covered with close-packed silver nanoparticles, as shown in Fig. 1(b). Compared with chemically synthesized Ag NW networks, our Ag NTR meshes possess three advantages. Firstly, thanks to the smooth joints of welded PVA NFs, Ag NTRs with conform morphology of PVA NFs are tightly interconnected together, as shown in Fig. 1(c), which significantly reduces the junction resistance between Ag NTRs. Secondly, the electrospun PVA NFs have the length to diameter ratio up to 10^6, which is about three orders of magnitude higher than chemically synthesized metal NWs [15]. Therefore, Ag NTR meshes have fewer broken points and lower R_S (see Fig. 1(d)). Thirdly, the randomness of the electrospun NFs in micro-scale will statistically result in a uniform R_S distribution of Ag NTR meshes in macro-scale. As shown in Supplementary Fig. S2, a survey of R_S throughout a $100 \times 100\ \text{mm}^2$ Ag NTR mesh gives a relative standard deviation of 8.5%, indicating that the Ag NTR mesh is one of the promising candidates for large-scale transparent heating or conducting applications. Fig. 2(a) shows thermal images of Ag NTR mesh heaters on flat and curved glass. The uniform thermal distribution in the entire heating area consists with the small relative standard deviation of R_S obtained in the R_S survey. Additional heat dissipation at the edge of the heater results in relatively low temperature in comparison with the central region. Moreover, Fig. 2(b) shows the cyclic thermal stability of the Ag NTR mesh transparent heaters on glass substrate. The heating tests were done by applying 5 V pulse voltage for 24 cycles and both the pulse width and interval were 30 s. The long term thermal stability of Ag NTR-based transparent heaters was tested by applying 5 V constant voltage for 24 min. As shown in Fig. 2(b), the maximum heating temperatures remain steady for both pulse and constant voltages, indicating the good heating stability of the Ag NTR mesh heaters. To further investigate the Joule heating behavior of Ag NTR mesh heater, the in-put-voltage applied to the heater was increased from 5 to 9 V by 1 V step and was kept at each voltage for 5 min. The surface temperatures of the Ag NTR mesh heater were measured once the thermal equilibrium was reached. The maximum obtainable average surface temperature of Ag NTR mesh was 255 °C (see Fig. S3(a)). Ampacity of Ag NTR mesh is 1.45 A and the corresponding current carrying density is calculated to be $2.2 \times 10^5\ \text{A cm}^{-2}$. If we further increased the in-put-voltage to 10 V, the surface temperature increased to 307 °C temporarily and then started to decline quickly due to the fusion and disconnections of Ag NTRs, as shown by the SEM image in Fig. S3(b). Intriguingly, the R_S of Ag NTR mesh decreased gradually from 7.5 to 6.2 Ω/sq with the temperature increasing from room temperature to 255 °C (see Fig. S4 in the supplementary). Our result is consistent with Kulkarni's report in which R_S of Au wire based heaters decreased with elevating heater temperature due to the coalition of metal nanoparticles [30].

To estimate the performance of Ag NTR meshes as transparent conductors or heaters, a range of Ag NTR meshes with different T_R and R_S were prepared by altering the electrospinning time. Fig. 2(c) plots the T_R at 550 nm wavelength *versus* R_S of various transparent heaters made of Ag NTR, ITO [31], Ag NW [12,14,25], CNT [6,9], and graphene [11]. It can be seen that the R_S of the Ag NTR meshes are 14 Ω/sq, 23 Ω/sq, 49 Ω/sq with T_R at 550 nm of 80%, 87%, 95%. The optoelectronic properties of Ag NTR are better than those of CNT, graphene and some of Ag NWs. In particular, Ag NTR meshes possess lower R_S than commercial ITO on PET substrate whose R_S is 70 Ω/sq ($T_R = 88\%$) [31]. The relation between T_R and R_S for bulk-like transparent conducting films can be expressed as:

$$T_R^{-1/2} - 1 = \frac{\sigma_{\text{Op}}}{2\sigma_{\text{dc,B}}} \frac{1}{(R_S/Z_0)} \tag{1}$$

where Z_0 is the impedance of free space (377 Ω), $\sigma_{\text{dc,B}}/\sigma_{\text{Op}}$ is the ratio of DC dark conductivity to optical conductivity, which is often used to rate the performance of transparent conductors [32,33]. Fig. 2(c) shows a log–log plot of the ($T_R^{-1/2}$–1) *versus* R_S/Z_0 for Ag NTR meshes. A slope of −1 acquired by fitting the data to Eq. (1) indicates that the conductivity of Ag NTR meshes is bulk-like. Then the value of $\sigma_{\text{dc,B}}/\sigma_{\text{Op}}$ for Ag NTR meshes is extracted to be 114 from the intercept on y-axis in Fig. 2(d). The high $\sigma_{\text{dc,B}}/\sigma_{\text{Op}}$ in our Ag NTR meshes can be collectively accounted for by their bulk-like conductivity and low junction resistance.

Fig. 3(a) shows the temperature-time profiles of a Ag NTR mesh heater on 0.15 mm-thick glass with $T_R = 87\%$ and $R_S = 23$ Ω/sq. By applying different bias voltages (1–7 V), the temperature of the heater increased gradually from ambient temperature to certain saturated values once the thermal equilibrium was achieved. For example, the heater reached 100 °C within 50 s by applying a 7 V input voltage. Generally, the thermal response behaviors of electrical heaters mainly depend on the input power, the heat losses by convection and radiation, as well as the specific heat capacities of both conductors and substrates. In order to quantitatively analyze the thermal response of the Ag NTR mesh transparent heaters, we adopted the approach proposed by Ji et al. [13], in which the temperature–time relationship at different input powers can be described as:

$$T \approx T_0 + \frac{1}{\alpha}\frac{U^2}{AR}\left[1 - \exp\left(-\frac{\alpha}{C_2 m_2/A}t\right)\right] \tag{2}$$

In the above equation, A, m_2 and C_2 are the area, mass and specific heat capacity of the substrate, respectively; U is the bias voltage; R is the resistance of the heating film; T and T_0 are the instantaneous and initial temperatures of the heater; α is defined as heat transfer constant and can be expressed as: $\alpha = (h_1 + h_2) + 4(\varepsilon_1 + \varepsilon_2)$, where h_1, ε_1 and h_2, ε_2 are the convective heat-transfer coefficients and the surface emissivities of the heating film and the substrate, respectively. s is the Stefan–Boltzmann constant. A series of α (26–39 $\text{W m}^{-2}\ \text{K}^{-1}$) for different bias voltages are extracted by fitting data in Fig. 3(a) to Eq. (2). It is known that h_2 of glass is 10 $\text{W m}^{-2}\ \text{K}^{-1}$ for each side, the thermal emissivity of glass ε_2 is known to be 0.9 [10]. The thermal emissivity of the Ag NTRs, ε_1, is assumed to be the same as the bulk value of 0.02. Then, the total