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BRIEF COMMUNICATION

Use of BN-coated copper nanowires in nanocomposites with enhanced thermal conductivity and electrical insulation

Yongcun Zhou [1,2] · Feng Liu [1] · Chia-Yun Chen [3]

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Abstract
Copper nanowires (CuNWs), as one-dimensional nanostructures, could be highly helpful as thermal management tools because of inherent thermal conductivity, high aspect ratio, and low cost. In this study, boron nitride-coated copper nanowires (CuNWs@BN) were successfully synthesized by an amenable and rapid technique and incorporated into synthetic polyimide (PI) to increase thermal conductivity while providing electrical insulation to nanocomposites. Maximal thermal conductivity in CuNWs@BN/PI composites containing fillers loading up to 20% volume rose to 4.12 W/mK, indicating an amelioration of 23 times in comparison with that of pure PI, while volume resistivity remained greater than 4.8×10^{13} Ω cm. Such nanocomposites with high thermal conductivity and electrical insulation could constitute important tools for thermal management.

Keywords Copper nanowires (CuNWs) · Boron nitride (BN) · Thermal properties · Electrical properties · Polymer composites materials (PCMs)

1 Introduction

The rapid advent of integrated circuit chips with elevated density and high frequency demands removal of waste heat to make the device work stably [1–3]. Composites made from polymers are excellent packaging materials because they are light and cost-effective, with physical and chemical stability. Recent studies have focused on introducing various inorganic fillers into polymers to enhance the thermal conductivity of polymer-based composites. Examples include ceramic fillers, aluminum nitride [4], alumina [5], boron nitride [6], silicon nitride [7], graphene [8, 9], and carbon nanotubes [10, 11]. However, these fillers rarely generate thermal conductive chains unless high-content fillers are used. Moreover, elevated electrical conductivity hampers the use of these carbon-based products for electronic packaging and should be improved.

Here, a new approach was developed through surface modification of copper nanowires (CuNWs) to construct polyimide (PI) nanocomposite films with high thermal conductivity and good electrical insulation. This study also generated an inorganic BN nanolayer on CuNWs by heating, which prevents copper networks with electrical conductivity from forming in the PI matrix. Furthermore, the boron nitride-coated copper nanowire (CuNWs@BN) core-shell structure results in great thermal conductivity but electrical insulation associated with the special coating technology. Thermal management of insulated PI nanocomposites made of BN-coated CuNWs has been scarcely assessed.

2 Experimental

2.1 CuNWs@BN synthesis

The CuNWs@BN core-shell structure was prepared as shown in Fig. 1a. Synthesis of CuNWs was performed as described previously [12]. The CuNWs@BN core-

✉ Yongcun Zhou
yczhou@nwpu.edu.cn

✉ Chia-Yun Chen
timcychen@mail.ncku.edu.tw

[1] School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, Shaanxi, People's Republic of China

[2] State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, People's Republic of China

[3] Department of Materials Science and Engineering, National Cheng Kung University, Tainan 70101, Taiwan

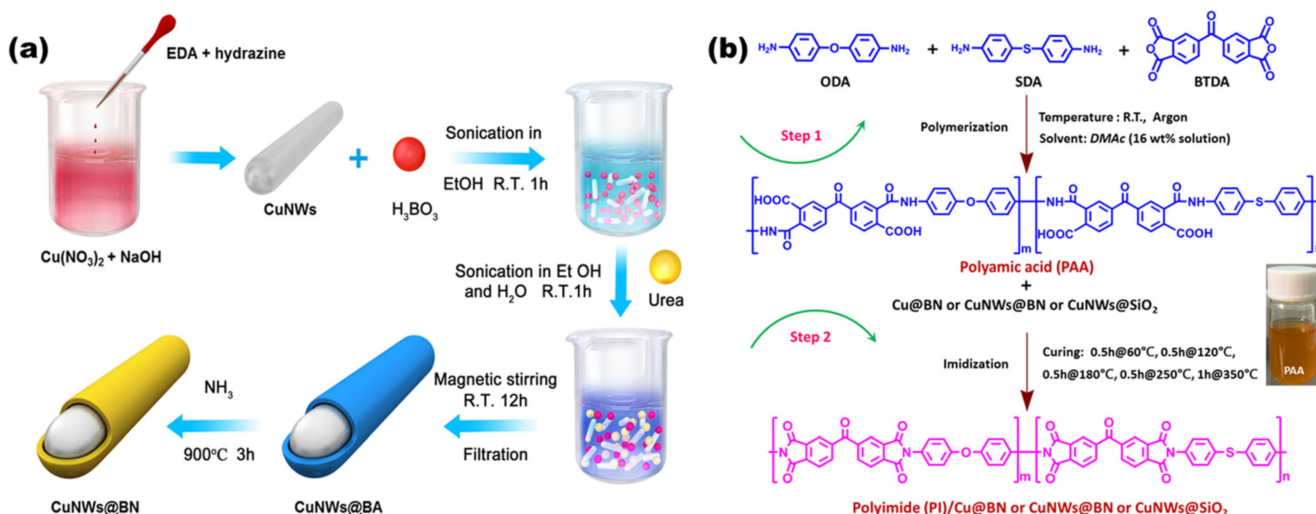


Fig. 1 Schematic representation of the **a** fabrication of the CuNWs@BN core-shell structure and **b** formation of Cu@BN/PI, CuNWs@BN/PI, and CuNWs@SiO_2/PI nanocomposites via in situ polymerization

shell structure was prepared via direct impregnation. First, H_3BO_3 (16 g) particles and 200 proof dehydrated ethanol (150 mL) were mixed in a 500-mL round-bottom flask and submitted to sonication (1 h in ambient conditions). After gradual dissolution of H_3BO_3, urea (100 g) was added and ultra-sonicated for 1 h. The resulting taupe powder was vacuum-dried at 60 °C for ≥ 12 h. The temperature was raised at a rate of 5 °C/min to achieve optimal working temperature, with ammonia gas flowing at 200 mL/min. After heating at 900 °C for 3 h and cooling under ammonia, core-shell CuNWs@BN nanopowders were obtained.

2.2 Synthesis of the PI precursor and preparation of CuNWs@BN/PI film

Synthesis of PI precursor polyamide acid (PAA) and preparation of CuNWs@BN/PI, Cu@BN/PI, and CuNWs@SiO_2/PI nanocomposites were carried out simultaneously via a two-step process (Fig. 1b). Step 1 in Fig. 1b shows that ODA, SDA, and BTDA were pretreated with 16 wt% DMAc solution by ultrasonication and mechanical agitation at room temperature in an argon atmosphere. Polymerization was continued for 12 h until a tawny viscous uniform PAA solution was obtained (inset photo of Fig. 1b). In step 2, three kinds of nanopowders, including Cu@BN, CuNWs@BN, and CuNWs@SiO_2, were added into the viscous composite PAA solutions, which were poured onto clean dry glasses, before thermal imidization at different treatment temperatures. Finally, pure PI and four different volume fractions of films with Cu@BN, CuNWs@BN, and CuNWs@SiO_2 fillers, respectively, were obtained.

3 Results and discussion

The CuNWs and CuNWs@BN were assessed for morphological features and size by transmission electron microscopy (TEM) and scanning electron microscope (SEM), and typical results are shown in Fig. 2. Figure 2a shows that the CuNWs obtained in large amounts measured approximately 15 μm and 45 nm in length and diameter, respectively (inset of Fig. 2a). PVP enabled adsorption on CuNWs via Cu–O coordination bonds [11, 13]. As shown in Fig. 2b, BN-coated CuNWs showed increased diameters in comparison with those of CuNWs, meanwhile the 10 nm-thick BN shell nanolayer covered the whole surface of Cu nanowires in a uniform manner (inset of Fig. 2b). Figure 2c shows the micrographs of 20 vol% CuNWs@BN/PI nanocomposite films and a pure PI film (inset of Fig. 2c). As shown in the inset of Fig. 2c, pure PI films were yellowish, and Northwestern Polytechnical University logo was clear. CuNWs@BN/PI films were greenish-black, and had high flexibility. Films based on pure PI and 20% CuNWs@BN filler content were transparent to absolutely opaque. An SEM image of fracture surfaces of a CuNWs@BN/PI composite film (partially enlarged in Fig. 2c) is shown in Fig. 2d. Figure 2d shows that CuNWs@BN fillers underwent tight embedding in the PI matrix of CuNWs@BN/PI films reaching 20%, suggesting that these composite films were highly compatible and homogeneous. These findings suggested that thermally conductive fillers are spread in the PI precursor solution; this is very crucial for improving thermal conductivity in composite films. Figure 3 depicts thermal conductivity levels and enhancement for Cu@BN/PI, CuNWs@BN/PI, and CuNWs@SiO_2/PI composites with various nanofillers. As shown in Fig. 3, thermal conductivity increased with filler loading. In addition, CuNWs@BN/PI had elevated thermal conductivity in

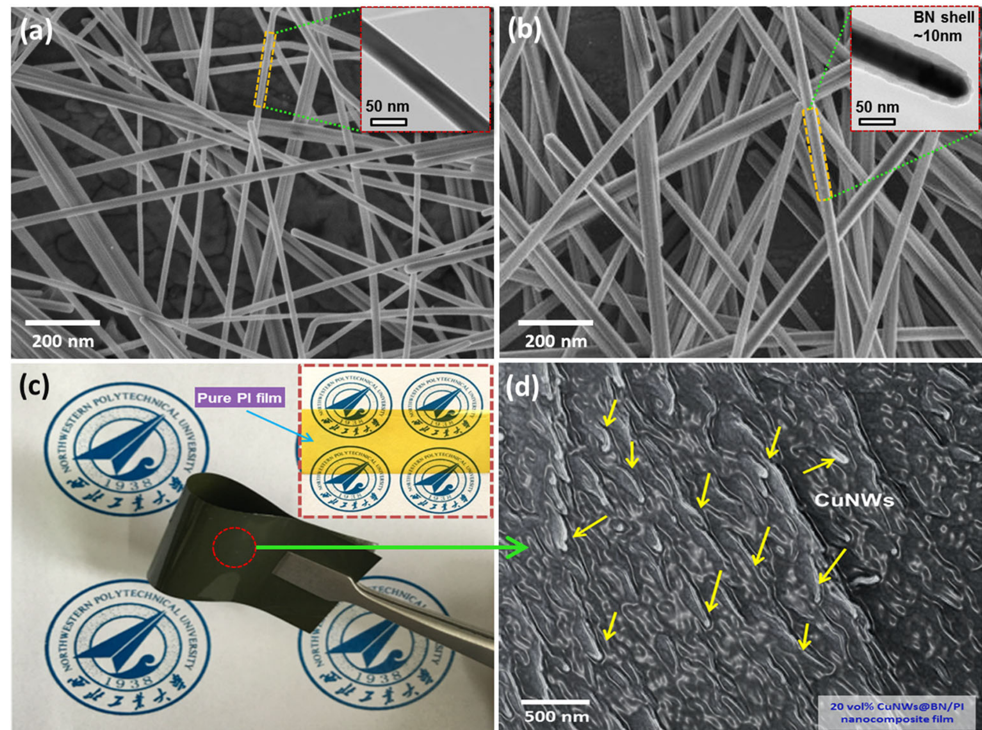


Fig. 2 SEM micrographs of **a** copper nanowires and **b** core-shell CuNWs@BN, with partly magnified TEM images in insets of **a** and **b**, respectively. Micrographs of **c** gray-black and flexible CuNWs@BN/PI films, with synthetic pure PI film (inset). **d** SEM image of partially enlarged structures of **c**

comparison with the remaining two materials, with a maximum of 4.12 W/mK at 20% filler loading. Filler efficiency is defined by thermal conductivity enhancement (TCE):

$$\mathrm{TCE} = \frac{K_c - K_m}{K_m} \quad (1)$$

where K_c and K_m are thermal conductivities of the composite and the matrix material, respectively. As depicted in Fig. 3b, the increased matrix thermal conductivity surpassed those of Cu@BN/PI, CuNWs@SiO_2/PI, and CuNWs@BN/PI composites at four different filler loadings. The following two reasons may explain the thermal conductivity trend. (1) For Cu@BN/PI and CuNWs@BN/PI films, CuNWs possess high aspect ratio, enabling optimal thermal conductivity in comparison with copper-based nanoparticles. Therefore, the current findings suggest metal nanowires enhance thermal conductivity in polymeric composite materials in comparison with metal nanoparticles. (2) When comparable filler loadings were used for CuNWs@BN/PI and CuNWs@SiO_2/PI films, BN had a theoretical thermal conductivity approximating 33 W/mK, compared to 7.6 W/mK for silica. This clearly explains why CuNWs@BN/PI films have enhanced thermal conductivity compared with CuNWs@SiO_2/PI counterparts. Furthermore, upon surface modification, OH groups on the BN nanolayer highly ameliorated the spread of CuNWs in the solvent or polymer matrix, reducing porosity and forming efficient thermal conductivity networks in PI composite films.

Next, volume and surface resistivity levels of Cu@BN/PI, CuNWs@BN/PI, and CuNWs@SiO_2/PI composites with various filler loadings were assessed in ambient con-

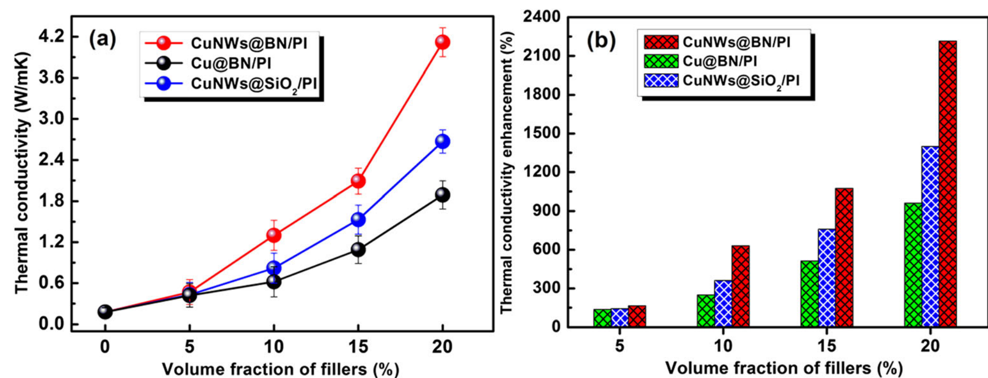
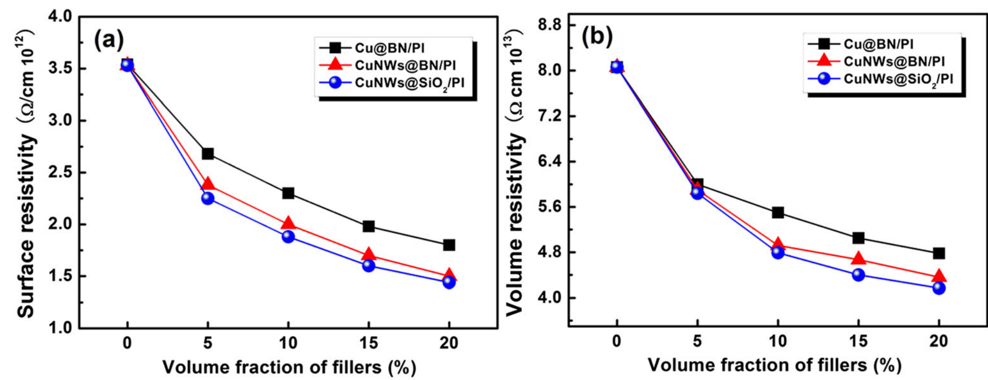


Fig. 3 Thermal conductivity levels (**a**) and enhancement (**b**) for Cu@BN/PI, CuNWs@BN/PI, and CuNWs@SiO_2/PI nanocomposites with various filler volume fractions



c. 4 Effects of filler loading on electrical resistivity of Cu@BN/PI, CuNWs@BN/PI, and CuNWs@SiO_2/PI nanocomposites. **a** Surface resistance. **b** Volume resistance

ditions. As depicted in Fig. 4, volume and surface resistivity levels of all three materials were progressively reduced with increasing filler loading. Compared with Cu@BN/PI films, CuNWs@BN/PI materials showed reduced volume and surface resistivity levels since CuNWs had an elevated aspect ratio compared with Cu nanoparticles at comparable filler loadings, indicating that the BN shell nanolayer insulates better in comparison with silica. Despite the gradual decrease of volume and surface resistivity levels observed for the above three films, their resistance remained within an acceptable range for electronic packaging and/or electrical insulation of materials [2, 14–23]. This likely resulted from surface modification of CuNWs via introduction of an inorganic insulating nanolayer efficiently preventing electrically conductive networks of CuNWs from being formed within the PI matrix.

4 Conclusions

PI-based nanocomposite films with high thermal conductivity retaining electrical insulation were generated through incorporation of BN-coated CuNWs. The maximum thermal conductivity of 20 vol% filler loading CuNWs@BN/PI film could reach 4.12 W/mK, representing approximately 23-fold-increase relative to that of pure PI. The thin BN nanolayer (about 10-nm thickness) coated on CuNWs strongly enhanced the spread of CuNWs in the PI matrix as well as interactions at the interface between CuNWs and the matrix. Furthermore, CuNWs@BN/PI films showed high electrical insulation because of BN shell insulation, and volume resistivity remained higher than 4.8×10^{13} Ω cm. Therefore, CuNWs@BN/PI films, as thermal management materials possessing great thermal conductivity and electrical insulation, could be used for high-temperature microfabrication of heat dissipative devices in microelectronics.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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