Composites Science and Technology 146 (2017) 169–176

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Highly electrically conductive and stretchable copper nanowires-based composite for flexible and printable electronics

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ARTICLE INFO

Article history:
Received 17 March 2017
Received in revised form
18 April 2017
Accepted 22 April 2017
Available online 25 April 2017

Keywords:
Copper nanowires
Chemical treatment
Dispersion
Stretchable conductors
Printable electronics

ABSTRACT

Copper nanowires (CuNWs) have been considered for the promising application as conductive element of stretchable conductors due to ultrahigh aspect ratio, outstanding conductivity, great flexibility and low-cost. However, controllable synthesis, surface oxidation, poor dispersity have always been main limitations to their application in stretchable conductors. Herein, highly conductive, stretchable and fully printable CuNWs-based composites (PNCNs) by infiltrating CuNWs into poly(styrene-blockbutadiene-block-styrene) (SBS) with a facile, cost-effective and scalable method were reported. CuNWs of high quality, chemical treatment by vacuum filtration way and special dispersion method facilitate fabrication of PNCNs of high performance. As-prepared PNCNs have superior electrical conductivity of 1858 S cm^{-1}, high break elongation of 920%. Moreover, PNCNs are stable after 1000 cycles for a bend radius of 4.0 mm and electric performance was not affected by twisting. Importantly, PNCNs can be printed on paper to fabricate flexible circuits which exhibit excellent electric performance at different tension conditions.

1. Introduction

Wearable electronics and stretchable conductors have gained increasing attention for a variety of new applications such as flexible displays [1,2], smart sensors [3–7], artificial skins [8–10], elastomeric circuits [11,12], implantable devices [13], and so on [14,15]. Generally, stretchable conductors consist of elastic matrix materials and conductive primitives. Elastic matrix materials contribute of excellent elasticity and conductive primitives provide high electrical conductivity. To realize excellent performance of stretchable conductors, many efforts have been made to research all kinds of new materials for the electrical conductive components such as carbon nanotubes (CNTs) [16–18], graphene [19,20], conducting polymers [21,22], metal nanomaterials [23–25]. However, carbon-based nanomaterials, such as CNTs and graphene, were limited by high material cost prepared with physical methods and relatively low electrical conductivity prepared with chemical methods for their applications. Owing to their instability and the poor conductivity, conducting polymers are inviable for stretchable conductors as well. Metal nanomaterials, such as silver nanowires have high aspect ratio, excellent conductivity and good flexibility have been reported widely for the application in stretchable conductors, however, the high cost and the scarcity of silver become the main limitation for their large-scale applications.

Recently, copper nanowires (CuNWs) have attracted extensive concerns for their potential application in stretchable conductors due to ultrahigh aspect ratio, outstanding electrical conductivity, great flexibility and low cost [26]. The recent dramatic progresses of CuNWs have opened a new vision in the field of wearable electronics, such as stretchable conductors [27,28] and printed electronics [29]. However, due to their intricate issues, such as controllable synthesis, surface oxidation, poor dispersity, assembling CuNWs with polymers to fabricate stretchable conductors possessing both high conductivity and outstanding stretch ability by facile, cost-effective, and scalable process still remains a challenging task until now [26]. Cheng's group [28] reported manufacturable conducting rubber ambers and stretchable conductors

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http://dx.doi.org/10.1016/j.compscitech.2017.04.030
0266-3538/

by infiltrating PDMS into CuNW-PVA aerogels. The resulted stretchable conductors exhibited good mechanical property but the electrical conductivity was low which was only 8.1 S cm^{-1}. Yang's group [30] reported CuNWs percolation network stretchable electronics and minimized Cu oxidation problem by ultrafast plasmonic nanoscale welding using a circularly polarized laser, but the welding process was restricted by the special machine.

Herein, we reported a highly electrically conductive and stretchable printable CuNWs-based composites (PCNCs), composed of CuNWs and poly(styrene-blockbutadiene-block-styrene) (SBS) which can be directly printed on paper to obtain flexible electric circuits. The PCNCs were fabricated by mixing CuNWs with polymer solution with facile dispersion method, followed by direct evaporating of CuNWs/SBS suspension at room temperature. The obtained PCNCs exhibited an excellent electrical conductivity of 844 S cm^{-1} and a high break elongation of 472% for using only 40 wt fraction percent (wt%) CuNWs in PCNCs (1858 S cm^{-1} at 50 wt%). Moreover, the electric performance of PNCNs was stable after 1000 cycles for a bend radius of 4.0 mm. Importantly, PNCNs can be printed on paper to fabricate flexible electrical circuits which exhibit excellent electric performance at different tension conditions. The results indicated that this kind of new conductive composites by simple, cost-effective and scalable process could pave the way for CuNWs-based printable flexible electronics and wearable electronics.

2. Experimental

2.1. Materials

$CuCl_2$ (AR), glucose (AR), oleylamine (OM) and lactic acid were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Oleic acid (OA) was supplied by Alfa Aesar Reagent Co., Ltd. SBS (Mn = 140000 g mol^{-1}, weight fraction of styrene = 30%), Isopropanol (IPA) and Chloroform ($CHCl_3$) were obtained from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of copper nanowires

CuNWs were synthesized using a modified method that reported previously [31]. In a typical process, 8 mL of OM, 0.08 mL of OA and 15 mL of ethanol were added to 800 mL beaker under magnetic stirring. Then, $CuCl_2$ (4 mmol) and glucose (4 mmol) were loaded to a 250 mL beaker containing 80 mL of H_2O under magnetic stirring. After $CuCl_2$ and glucose dissolved, transferred them to aforementioned 800 mL beaker and diluted to 400 mL with water. Followed by magnetic stirring for 12 h at room temperature condition, then stirring for 10 h at 50 °C. Subsequently, the mixture was transferred to a Teflon-lined autoclave of 500 mL capacity and heated at 120 °C for 12 h. Finally, the reddish brown CuNWs were obtained by centrifuging.

2.3. Chemical treatment of copper nanowires

As-prepared CuNWs were firstly transferred to $CHCl_3$ with the concentration of 1 mg/mL. Next, lactic acid was added to CuNWs/$CHCl_3$ suspension with a ratio of 1 mg CuNWs: 0.02 mL lactic acid. After shaking for 10 s, mixture was vacuum filtrated through an organic membrane (0.45 μm pore size) followed by the washing with IPA for two times. Once no free IPA was left on the filter paper, both CuNWs and the filter membrane were transferred to vacuum oven, evaporating the solvent kept for 30 min at 50 °C in vacuum condition. Finally, CuNWs were obtained without any copper oxides and residual organics.

2.4. Fabrication of the copper nanowire-based composites

CuNWs after chemical treatment were transferred to SBS/$CHCl_3$ solution (5 wt%) at different weight fraction of CuNWs in CuNWs/SBS mixture as 20 wt%, 30 wt%, 40 wt%, 50 wt% respectively. CuNWs and SBS/$CHCl_3$ solution were homogeneous mixed by two steps: firstly, the mixture was mixed in an automatic planetary gravity mixer (SINO Co., Ltd., VM300SL) at 1800 rpm/min for 10 min. Secondly, the mixture was dispersed using ultra-turrax (IKA, T25) at 9000 r/min for 1 min. Then, the as-obtained CuNWs/SBS/$CHCl_3$ solution was poured in PTFE mold, evaporating $CHCl_3$ at room temperature resulting in copper nanowire-based stretchable conductor.

A mask with serpentine pattern was placed on paper, then, as-prepared CuNWs/SBS/$CHCl_3$ solution was poured in the mask, obtaining CuNWs-based flexible electric circuits after $CHCl_3$ was evaporated at room temperature.

2.5. Characterization

The morphology and microstructure were analyzed by a field emission scanning electron microscopy (FE-SEM, FEI Nova Nano SEM 450). The X-ray diffraction (XRD) pattern was obtained on an X-ray diffractometer (Rigaku D/Max 2500) with monochromated Cu Ka radiation (l = 1.54 Å). The tensile tests were carried out on a stretching machine (AG-X Plus 100N) with a speed of 20 mm min^{-1}. The electrical resistance was recorded by a two-probe method using a digital multimeter (Tektronix DMM4050). LED characteristics were characterized on a Keithley 4200SCS semiconductor characterization system. Fourier transform infrared (FTIR) spectra were recorded with a ruker Vertex 70 spectrometer (Bruker Optik GmbH, Ettlingen, Germany) in the range of 4000–400 cm^{-1}. The ultraviolet–visible (UV–Vis) absorption spectrum was recorded with an UV–Vis–NIR spectrometer (Shimadzu UV-3600).

3. Results and discussion

The CuNWs were synthesized by modified hydrothermal method, the ratio of copper salt, reducing agent and capping agent is the key to synthesize CuNWs of high quality [32]. Fig. 1a–b and Fig. S1 show SEM images of the CuNWs, as-prepared CuNWs exhibited diameters of around 45 nm and the lengths of more than 100 μm, possessing ultrahigh aspect ratio of more than 2.2×10^3. As analyzed by an XRD pattern in Fig. 1c, the three diffraction peaks at $2\theta = 43.3°$, 50.9° and 73.6° correspond to the diffraction from (111), (200) and (220) planes of face-centered cubic copper (JCPDS # 03-1018) [30], which confirmed that CuNWs were synthesized successfully by analyzing of SEM and XRD. And CuNWs with some organic residual on the surface can be dispersed in chloroform ($CHCl_3$) uniformly (Fig. 1d). The high-quality CuNWs are the foundation of the preparation of high conductive conductors.

Fig. 2 schematically illustrates the fabrication of highly conductive and stretchable printable CuNWs-based composites. As-prepared CuNWs were treated with lactic acid by the vacuum filtration way to remove residual organics and copper oxides simultaneously, resulting in improved electric conductivity. Moreover, the morphology of CuNWs was not affected by lactic acid treatment process due to the transitorily contact between lactic acid and CuNWs during shaking and the phases separation was present after shaking (Fig. 2b) which prevents CuNWs further etched. Then, the acid-treated CuNWs were mixed with SBS by special dispersion method to avoid the aggregation and entanglement of CuNWs. For the dispersion process, the automatic planetary gravity mixer firstly was used to disperse block dry CuNWs into SBS, and entangled copper nanowires were dispersed at high shear