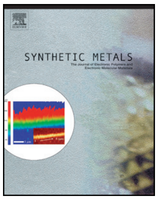
Synthetic Metals 217 (2016) 79–86

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Fabrication of highly conductive graphene flexible circuits by 3D printing

Di Zhang[a], Baihong Chi[c], Bowen Li[a], Zewen Gao[a], Yao Du[a], Jinbao Guo[a], Jie Wei[b,a,*]

[a] *College of Materials Science and Engineering, Beijing University of Chemical Technology, No.15, Bei San Huan East Road, Chao Yang District, Beijing, China*
[b] *Beijing Engineering Research Center for the Synthesis and Applications of Waterborne Polymers, Beijing 100029, China*
[c] *College of Mechanical and Electrical Engineering, Beijing University of Chemical Technology, No.15, Bei San Huan East Road, Chao Yang District, Beijing, China*

ARTICLE INFO

Article history:
Received 25 December 2015
Received in revised form 5 March 2016
Accepted 11 March 2016
Available online 25 March 2016

Keywords:
3D print
Graphene
Flexible circuits

ABSTRACT

Fused depositing modeling (FDM) is a fast, efficient process among 3D printing techniques. In this paper, we report the fabrication of the 3D printed flexible circuits based on graphene. Modified two-step in-situ reduced method is used to synthesize reduced graphene oxide (r-GO), whose conductivity can reach to 600 S/cm. Polylactic acid (PLA) and r-GO are mixed by melt blending. The SEM images show that the r-GO can be homogenous dispersed in the PLA. The 3D print-used composites filaments with the diameter of 1.75 mm are fabricated through melt extrusion. The conductivity of the composite filaments from 3D printer can reach to 4.76 S/cm (6 wt% r-GO). The orientation of r-GO occurs during the extrusion process, which contributing to increase the conductivity of the filaments. The composite also exhibit superior mechanical property. The printed 2D and 3D flexible circuits have strong interface bonding force between the layers. The filaments from 3D printer can replace the copper wire because of the high conductivity. This arbitrary 3D graphene-based structure printing technic may open a new prospect in electronic and energy storage fields.

1. Introduction

Organic electronic devices, such as fuel cell, solar cell, supercapacitor, sensor, etc, have been greatly updating in the laboratory-scale research during the past few decades. Even so, finding a fast and cost-effective method for fabricating high conductive flexible circuit is the main barrier before closing the gap between laboratory-scale research and industrial application. It is quite challenging to establish a system which combining cost-effective and high-performance materials with fast and scalable micro-fabrication technology. We and others have done a lot of work to fabricate micro or nano flexible circuit. Innovative technique including nanoimprinting [1], screen printing [2], dip-pen lithography [3], micro contact printing [4], inkjet printing [5], etc., have been used. However, all these method can barely be applied to practical scalable production because of the small amount, expensive materials or the slow, unstable fabricating process. The state-of-the-art micro-fabrication technology is lightscribe [6], in which the laser from a DVD drive was used to precisely reduce the graphene oxide (GO) film on the disc, then the circuits of reduced graphene oxide (r-GO) were formed. The principal weakness of this latest technique lies in the poor physical properties of r-GO reduced by the high temperature laser, which can be proved by the fact that this kind of circuit can be applied to strain sensor [7]. The discovery of graphene in 2004 terminated the longstanding debate on purely two-dimension materials. Because of its unique structure and remarkable properties [8], graphene has been applying to any fields we can imagine. In terms of organic electronic field, many researchers have successfully implemented graphene or polymer-graphene composites into lithium ion batteries [9], supercapacitors [10], solar cell [11] and sensors [12] so forth. However, recently some authoritative researchers have raised doubts on this 'graphene fever'. They thought that all the previous data of graphene-based electrochemical energy-storage devices (EESD) are not real breakthrough. Due to various reasons, graphene still cannot replace the currently wide-used carbonous materials. They appeal that more work should be done aiming at practical application so that we can clarify whether graphene can meet the market's performance requirements [13]. The doubts from these authoritative researchers may possible bring a pause on graphene-based EESD research, retrieving our thought back to the pristine but wide practical properties of graphene such as high electrical and thermal conductivity.

---

[*] Corresponding author.
E-mail addresses: weij@mail.buct.edu.cn, weijie-2008@hotmail.com (J. Wei).

http://dx.doi.org/10.1016/j.synthmet.2016.03.014
0379-6779/© 2016 Elsevier B.V. All rights reserved.

3D printing has brought a revolution to materials manufacturing industry because its additive manufacture technology broke the traditional manufacturing mode [14]. 3D printing has been widely applied in electronics [15] chemistry [16], physics [17], tissue engineering [18] and other fields [19] since arbitrary 3D structures can be fabricated. But few reports combine chemistry with 3D printing. Fused deposition modeling (FDM) is the most common used technique among 3D printing technologies, in which the 3D structure is established by extruding materials layer-by-layer through the capillary nozzles, thus allowing various kinds of materials used in FDM. In this report, we used the modified two step in-situ reduced method [20] to synthesize the high-conductive graphene, whose conductivity can reach to 600 S/cm, as the filler of PLA. PLA and graphene are homogeneously mixed by melt blending, after which graphene can be well dispersed in the PLA substrate. Then the composites were processed to fabricate the composite filament with the diameter of 1.75 mm, which is the material of 3D printer. We printed the 2D flexible circuits on different substrates. The composite circuits have a strong interface bonding force with the substrate, and the filaments from the 3D printer exhibit conductivity up to 4.76S/cm (6 wt%). We have proved that the graphene had a process of orientation during the deposition, that is, the extrusion process. The orientation of graphene will help to improve the conductivity of the composite. The 3D flexible circuits exhibit good bonding force between layers, indicating that the 3D structure can maintain the same good mechanical property in both axial direction and transverse direction.

The materials used, both PLA and graphene, can be massive produced in a cheap way, demonstrating that the whole experimentation can be well transferred in practical application. Fig. 1 shows the process of graphene-based 3D printing in this report. As far as we know, this is the first time to use the PLA-graphene composite to print flexible circuits. The whole graphene-based 3D manufacturing process in this report will have a wide potential application [25] and may bring a new prospect in electronic and energy storage field.

2. Experimental

2.1. Materials

The natural graphite flakes were purchased from Shenzhen Nanotechnologies Co., Ltd. All the chemical reagents in the modified Hummers method were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. The 4-iodoaniline was purchased from Tokyo Chemical Industry. PLA was purchased from MakerBot, America. All chemical reagents are analytically pure and used without further purification.

2.2. Modified two step in-situ reduce method of synthesizing high conductive graphene

GO was synthesized by the modified Hummers method [21]. Then the GO was first chemical reduced by 4-iodoaniline: 0.05 g GO was dissolved in 100 ml concentrated sulfuric acid (98% H_2SO_4) and ultrasonicated for 30 min. Move the solution to a flask, slowly add 1.8 g 4-iodoaniline and 0.69 g $NaNO_2$ to the flask and keep stirring for 1 h at 60 °C. After cooling, wash the product by DMF and ethyl alcohol until colourless, then vacuum-dried for 24 h at 60 °C. The second reduction of GO is thermal reduction: put the first chemical reduced GO (c-r-GO) in a corundum boat and put it in the tube furnace at 1050 °C for 1 h under the argon atmosphere. If needed, all the quantities above can be multiplied.

2.3. Fabrication of the 3D-print used composite filament

The threadlike PLA were smashed by a pulverizer, then the smashed PLA and second thermal reduced graphene (t-r-GO) were put together into the HAAKE twin-screw melt mixer, the operation temperature and time is 160 °C and 15 min, respectively, and the screw revolving speed is 80 r/min. The produced composite was cut into pieces before cooling, then smashed them into powder by a pulverizer. A mini single screw extruder was used to transfer the composite powder to the filaments with the diameter of 1.75 mm.

2.4. Fabrication of the 2D and 3D flexible circuits

The 2D or 3D flexible circuit were designed by MakerBot or other three dimensional design software. Different substrate-paper, polyimide (PI) film-were put in the platform (X–Y plane) and fasten tightly, then circuits were printed on them. The 3D flexible circuits were printed directly in the platform. The heating temperature of the 3D printer is 210 °C. The PI film were soaked in the H_2O_2-H_2SO_4 solution (volume ratio 1:3) for 12 h beforehand.

2.5. Mechanical test and electronic test

The stretching test bars with different graphene ratio (t-r-GO) were printed. Five test bars of every graphene ratio were stretched. The average size of the stretch cross section is 5.4 mm × 2.05 mm, the stretching speed is 50 mm/min. The Young's modulus was determined by using a 0.2% strain offset linear slope method. The fore-probe method was used to measure the conductivity of the wafer samples. Two-point method was used to measure the conductivity of the filaments through the equation: $R = L/\sigma S$, where R is the resistance of the sample, L and S are the length and the cross sectional area of the filament, respectively, and σ is the conductivity of the sample.

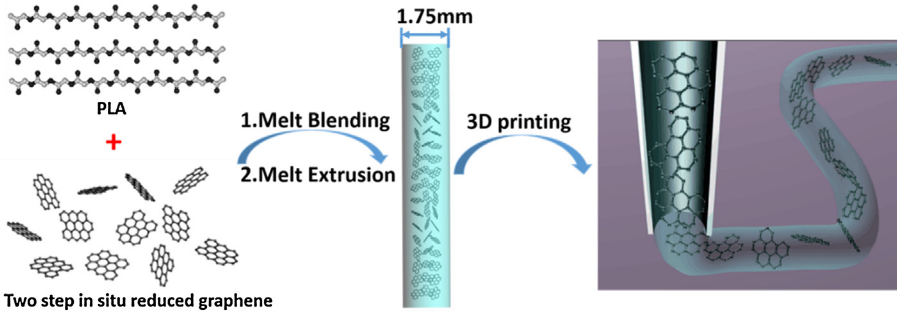


Fig. 1. Simplified schematics depicting the process of graphene-based 3D printing using the technique of FDM.