Materials Letters 227 (2018) 33–36

Contents lists available at ScienceDirect

Materials Letters

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

Featured Letter

Preparation and thermal conductivity of copper phthalocyanine grafted boron nitride nanosheets

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ARTICLE INFO

Article history:
Received 16 March 2018
Received in revised form 30 April 2018
Accepted 7 May 2018
Available online 9 May 2018

Keywords:
Boron nitride
Copper phthalocyanine
Thermal conductivity

ABSTRACT

Copper phthalocyanine grafted boron nitride nano-sheet hybrids (CuPc-*g*-BN) were prepared for the improvement of thermal conductivity of CuPc. Hydroxyl functionalized BN (BN-OH), obtained by ball-milling of BN, was reacted with isophorone diisocyanate (IPDI) and 3-aminophenoxyphthalonitrile (3-APN) sequentially to form BN-IPDI-CN. CuPc-*g*-BN was prepared by in-situ polymerization of BN-IPDI-CN with 1,3,5-tri-(3,4-dicyanophenoxy) benzene (TPh) and CuCl. The CuPc-*g*-BN and the intermediates were characterized by TEM, AFM, XPS, FTIR and UV–vis. The results show the formation of the hybrid effectively enhances the thermal conductivity of CuPc, which is as high as 0.63 W/(m·K), with an increment of 290%, when the mass fraction of BN-IPDI-CN is 50 wt%.

1. Introduction

Metal phthalocyanines, with metallic atom entrapped in the center of the phthalocyanine ring via coordination, have attracted considerable attention owing to their fascinating properties and potential applications in electrochemical sensors [1], dielectric materials, photo-catalysts for fuel cells and organic solar cells [2,3]. Among these metal phthalocyanines, CuPc as a representative, has been studied particularly for its application in dielectric materials, and solar cells [3–5]. However, like most organic materials which are thermal insulators, the thermal conductivity of CuPc is far below the practical application value 0.6 W/(m·K) [5]. Boron nitride, a two-dimensional layered material similar to graphite [6], can be exfoliated into single layer or a few layers nanosheets with excellent properties including high thermal stability, excellent mechanical strength [7] and high thermal conductivity [8–11]. Moreover, BN, composed of strong covalent bonds between boron and nitrogen atoms ordered in an alternating manner, is an exquisite electrically insulated two-dimensional material as an excellent candidate for fabricating thermally conductive and electrically insulating polymer composites. However, the poor compatibility between BN and polymer matrix is still a challenge to obtain polymer composites with excellent properties [12].

In this study, we report the improving properties of CuPc by in situ polymerization of BN-IPDI-CN with TPh and CuCl, forming CuPc-*g*-BN hybrid. The product and the intermediates are carefully characterized and the properties of the CuPc-*g*-BN are studied.

2. Experiment section

Boron nitride micro-platelets powder was purchased from J&K chemicals. *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAc), Cuprous chloride, sodium hydroxide, hydrochloric acid were supplied by Chengdu KeLong chemicals. IPDI was purchased from Hengyi Co. Ltd. 3-APN and TPh were synthesized according to the previous literature [13].

BN powders (1.0 g) and 2 M NaOH solution (60 mL) were ball-milled for 24 h. The ball-milled product was washed with HCl until the pH was close to neutral, and then washed with deionized water to get the BN-OH. BN-OH (0.1 g) and IPDI (5 mL, 23 mmol) were added into a reactor with 100 mL DMF and reacted at 50 °C for 7 h under N_2 atmosphere. After that, 3-APN (4.0 g, 17 mmol) and stannous octoate (100 μL, 0.3 mmol) in 100 mL DMF were added into the above system and reacted at 85 °C for 5 h under N_2 atmosphere, the product was filtered and washed with DMF offering BN-IPDI-CN. CuPc-*g*-BN hybrids were prepared by the reaction between BN-IPDI-CN and TPh as well as CuCl in DMAc at 160 °C for 4 h (Fig. 1a). Four CuPc-*g*-BN hybrids namely CuPc-*g*-BN0, CuPc-*g*-BN1, CuPc-*g*-BN2 and CuPc-*g*-BN5 with 0, 10 wt%, 20 wt% and 50 wt% of BN-IPDI-CN were prepared by changing the feed ratios, respectively.

The FTIR spectra of samples were obtained by the Shimadzu 8000S spectrophotometer. UV–vis spectrum of the samples was recorded on a Shimadzu UV2501-PC spectrophotometer. AFM

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https://doi.org/10.1016/j.matlet.2018.05.035
0167-577X/

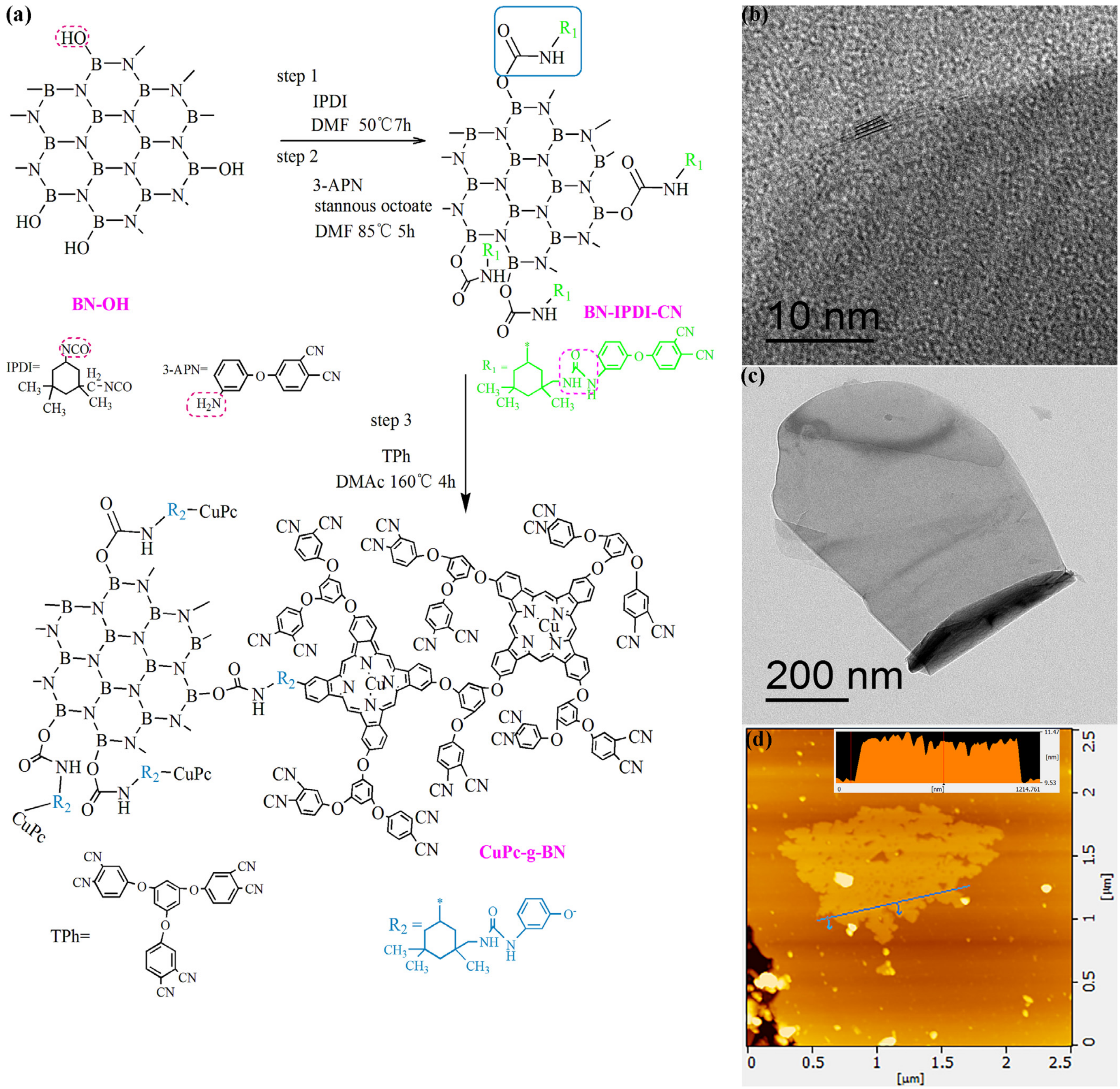

Fig. 1. (a) The synthetic route of CuPc-g-BN; (b) and (c) TEM images of BN-OH; (d) AFM image of BN-OH.

image of BN-OH was obtained by the Digital Instruments multi-mode microscope controlled by Veeco Nanoscope III. The micro-morphology of BN-OH was recorded by a ZEISS Libra 200 FE TEM. XPS results were obtained by ESCA 2000. The thermal conductivity of samples was obtained by a Netzsch LFA 457 Laser Flash Apparatus.

3. Results and discussion

BN-OH is firstly obtained by exfoliation and hydroxylation of BN micro-platelets through ball-milling with NaOH. TEM is used to analyze the exfoliation of BN. As shown in Fig. 1b, the atomic layers of BN-OH are 4 and the layer-to-layer distance of the BN-OH is approximately 0.35 Å, which is close to that of pristine BN. Fig. 1c shows the surface of BN-OH which is flat, indicating the ball-milling process has no obvious damages to the nanosheets. Fig. 1d shows the AFM image of the prepared BN-OH nanosheets. The thickness of the BN-OH nanosheets is about 1.5 nm, indicating that the BN-OH nanosheets is composed of three to four monolayers [14]. The TEM and AFM results indicate the successful exfoliation of BN micro-platelets.

XPS analysis is employed to study hydroxylation of BN. Two obvious peaks are observed at 190.5 and 398 eV in the XPS spectrum of BN-OH, corresponding to B1s and N1s, respectively. The B1 s spectrum of BN-OH can be quantitatively differentiated into two different boron species, as shown in Fig. 2a. The strong peak at 190.5 eV is coming from the B-N bond, and the weak peak at