



ELSEVIER

Contents lists available at ScienceDirect

Materials Letters

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

Synthesis of highly crystalline copper phthalocyanine needles by solvothermal method



Suxiang Ge^a, Yange Zhang^{a,*}, Baojun Huang^a, Shuiping Huang^b, Weiwei Tie^a, Yan Lei^a, Qin He^a, Guangliang Tu^a, Qingqing Qin^a, Sasa Niu^a, Mingtian Li^c, Dapeng Li^{a,*}, Zhi Zheng^a

^a Key Laboratory of Micro-Nano Materials for Energy Storage and Conversion of Henan Province, Institute of Surface Micro and Nano Materials, and School of Chemistry and Chemical Engineering, Xuchang University, Henan 461000, PR China

^b Quality and Technique Supervision, Inspection and Testing Center of Xuchang City, Henan 461000, PR China

^c College of Materials and Chemical Engineering, Sichuan University of Science and Engineering, Zigong 643000, PR China

ARTICLE INFO

Article history:

Received 3 July 2015

Received in revised form

6 August 2015

Accepted 4 October 2015

Available online 13 October 2015

Keywords:

Copper foil

Phthalonitrile

Crystal growth

Microstructure

Solvothermal

Ethanol

ABSTRACT

As an important organic semiconductor, copper phthalocyanine has been widely used in various photo/electronic devices. Until now, the one-step synthesis of copper phthalocyanine micro/nano-crystals is mainly limited to the high cost physical vapor deposition technology. Herein, for the first time, we proposed a green and low-cost solvothermal method for direct synthesis of highly crystalline copper phthalocyanine needles in nontoxic anhydrous ethanol medium at 190 °C. The purification of the as prepared copper phthalocyanine needles just required washing unreacted reactants with ethanol. The structures and morphologies of the copper phthalocyanine needles were characterized by Raman spectroscopy, X-ray powder diffractometer, and scanning electronic microscopy, respectively. Moreover, the thermal and photoelectronic performances were investigated preliminarily.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Copper phthalocyanine (CuPc), as an excellent blue pigment widely used in industrial paints, has made a tremendous contribution to human society since the first half of the 20th century. In recent years, the applications of CuPc have been extended to organic field-effect transistors [1], organic solar cells [2], gas dielectric transistor [3], electrocatalyst [4], catalyst [5], photovoltaic device [6], and so on. It is noted that the high-quality CuPc single crystals as the important component of above devices exhibit excellent properties, therefore, controllable synthesis of CuPc single crystals is desirable to pursue the satisfied performance.

In most literatures published recently, physical vapor transport is a practical method used for one step fabrication of micro/nanometer-sized CuPc crystals array [1,6–9]. Besides, the organic vapor phase deposition (OVPD) technology was suitable for highly controllable fabrication of CuPc nanocrystals thin film [2,10–13]. However, all the above methods required high evaporation temperature (> 400 °C), or high vacuum degree (about 10⁻⁶ Torr), or

inert gas (He, Ar), leading to high energy consumption. In 2008, Xia and Du reported one-step solvothermal synthesis of needle-like CuPc single crystals in quinoline at 270 °C by using copper acetate tetrahydrate and 1,3-diiminoisoindoline as reactants [14,15]. Unfortunately, this method depends on the relative high temperature and toxic quinoline solvent. Therefore, the green and low-cost method for synthesis of CuPc single crystals is still in research.

In our previous work, we found that needle-shaped manganese phthalocyanine (MnPc) crystals could be successfully prepared by a green solvothermal route with ethanol as reaction medium [16]. According to the above enlightenment, herein, we firstly proposed an environment-friendly and low-cost solvothermal method for synthesis of highly crystalline CuPc needles in ethanol at 190 °C for 3 h by using cheap copper foil and phthalodinitrile as reactants. Notably, the as-prepared CuPc needles could be purified easily just by washing the unreacted reactants on CuPc surface with ethanol. The morphology and structure of CuPc needles were confirmed by SEM, XRD, and Raman, respectively. Besides, the thermal performance and transient photovoltage (TPV) spectroscopy of CuPc needles were investigated preliminarily.

* Corresponding authors.

E-mail addresses: zhangygzhang@163.com (Y. Zhang), lidapengabc@126.com (D. Li).

2. Experimental method

2.1. Materials

o-phthalonitrile (> 99%) was purchased from Shanghai D&B Chemicals Technology Co., Ltd. Copper foil (99.9%) was purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Measurements

FT-IR spectrum was performed on a Thermo Nicolet Nexus FT-IR spectrometer with the standard KBr pellet method. Elemental analysis was carried out by using an Elementar Vario ELIII Elemental Analyzer. The optical photograph of CuPc samples was recorded by using Olympus SZX7 instrument and the optical microscope of Raman spectrometer (Renishaw inVia). A Zeiss EVO LS-15 Scanning electron microscopy (SEM) was used to observe morphologies of CuPc crystals. X-ray diffraction (XRD) pattern was recorded by using a Bruker D8 ADVANCE X-ray powder diffractometer with Cu K α radiation. Thermogravimetry and differential scanning calorimetry (TG-DSC) analysis was performed by using a Netzsch STA 409PC thermal analyzer in nitrogen over a range of 50–850 °C at a heating rate of 10 °C/min. Transient photovoltage (TPV) curve measurement was performed as the following operation. A sample chamber like a parallel-plate sandwich-like capacitor consisted of a film of ITO, Mica spacer, and layer of CuPc needles on the Cu foil substrate from top to bottom in sequence. An ultrafast laser pulse ($\lambda=355$ nm and a pulse width of 4 ns) through a third-harmonic Nd:YAG laser (Quantel Brilliant Eazy: BRILEZ/IR-10) was employed as the light source. The transient surface photovoltage data was recorded by a 500 MHz digital oscilloscope (TDS 3054C, Tektronix).

2.3. Typical synthesis procedure of CuPc

The sketch map for CuPc synthesis is shown in Scheme 1a. Specifically, 100 mg *o*-phthalodinitrile, a piece of Cu foil ($3.0 \times 0.5 \times 0.1$ mm³), and 21 mL ethanol were placed into a 28 mL Teflon-lined autoclave, then the autoclave was sealed and maintained at 190 °C for 3 h. After natural cooling to room temperature, the tiny pure blue needle-shaped crystals could be taken out from the bottom of autoclave and washed with hot ethanol to remove the residual reagents on CuPc surface. Finally, the resulting CuPc crystals were dried at 100 °C in vacuum overnight for characterization. Yield: 21%.

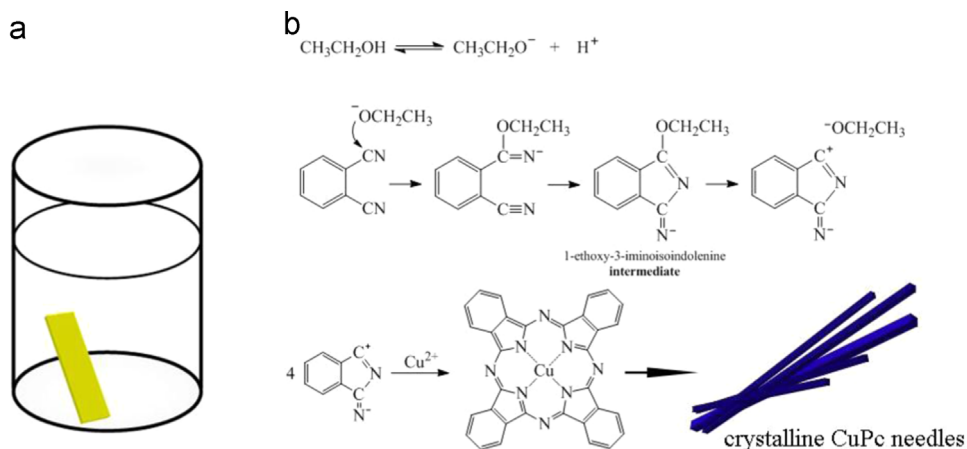
3. Results and discussion

For the synthesis of metal phthalocyanine using phthalodinitrile as raw material, *n*-pentanol solvent and strong organic base (DBU or DBN) were usually necessary. However, none of these reagents was used in our preparation. We believe that the formation of CuPc crystals should undergo the following process [17]. (I) The nucleophilic attack of ethoxy anion to cyano group in phthalodinitrile and the formation of 1-ethoxy-3-iminoisindole-nine intermediate. (II) The ionization of Cu atom on Cu foil surface. (III) The participation of Cu ion in cyclization of intermediate. (IV) The formation of CuPc molecule and the growth of crystals via the π - π interactions between the parallel CuPc molecules (Scheme 1b). The FT-IR absorption peaks at 730, 900, 1287, 1334, 1465, 1507, 1610 cm⁻¹ testified the phthalocyanine skeletal vibration. The absorption peaks at 1090, 1120, 1166 cm⁻¹ could be assigned to the in-plane C–H bending vibrations (Fig. S1 of Supplementary material). In addition, the elemental analysis results of C 66.54, H 2.71, N 19.32 approved the pure product of CuPc (Anal. Calcd. for C₃₂H₁₆CuN₈: C, 66.72; H, 2.80; N, 19.45).

The shape of as prepared crystalline CuPc needles was recorded by the optical microscope. Fig. 1 shows that the CuPc needles have different size and length, and the maximal length of some needles could exceed 2 mm (Fig. 1a and b). Under the low magnification ($\times 20$), it is observed that these needles reflected bright purple (Fig. 1c–e), which illustrated the good crystallinity of CuPc crystals formed in solvothermal process. The detailed surface morphology of these CuPc needles was observed by SEM. Fig. 1f and g display the surface morphologies of straight CuPc needles with magnification times of 300 and 1000, respectively. From detailed observation in Fig. 1h, we found the CuPc needles with about several hundreds nm to 10 μ m in diameters, and some big crystals show obvious regular quadrangular shape (Fig. 1i).

The XRD pattern of the resulting CuPc needles was recorded in Fig. 2. All the diffraction peaks can be well indexed to β -CuPc with lattice parameters of $a=14.646$ Å, $b=4.696$ Å, $c=17.316$ Å, and $\beta=105.49^\circ$ (JCPDS card file, 39–1881, monoclinic, P21/n). In addition, the SAED pattern (inset of Fig. 2) indicated that the CuPc needles are single crystals. Besides, the molecular structure of CuPc was characterized by using Raman spectroscopy technology (Fig. S2 of Supplementary material).

The thermal stability of CuPc crystals is a practical evaluation for their application in organic semiconductor device. From Fig. 3a, it can be observed that almost no weight loss was observed below 550 °C, which means the good thermal stability of as prepared CuPc needles. The obvious weight loss in TG profile can be found in the range of 550–680 °C (37.12%) and 680–805 °C (5.56%).



Scheme 1. (a) Sketch map of the autoclave containing a piece of Cu foil; (b) sketch map of the formation mechanism of CuPc molecule and crystals.

Download English Version:

<https://daneshyari.com/en/article/1641738>

Download Persian Version:

<https://daneshyari.com/article/1641738>

[Daneshyari.com](https://daneshyari.com)