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Short communication

A novel and green route for solvothermal synthesis of manganese phthalocyanine crystals

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ABSTRACT

A novel, facile, and green route was proposed for solvothermal synthesis of manganese phthalocyanine (MnPc) crystals. The quadrangular prism-like MnPc crystals could be obtained at 190 °C during 3 h with manganese acetate and phthalodinitrile as reactants. The common ethanol was used as solvent and no other chemical additives were required in this reaction system. It is noted that purification of as prepared MnPc crystals was very simple and just required the removal of unreacted reagents washing by hot ethanol and water. Compared to the reported method, this simple synthesis route shows many advantages, such as low cost, facile preparation and purification, especially the nontoxic ethanol used as reaction medium.

1. Introduction

Metal phthalocyanine (MPc) is a kind of promising complex which has centrosymmetric planar macrocycle with various metal ions on its central cavity [1,2]. For the characteristics of highly conjugation of MPc molecules and their π–π interaction between parallel Pc rings, some MPcs could grow into well-defined crystals for the applications of high grade pigment, optoelectronics and photovoltaic devices [3–5]. It is well known that the crystallographic quality of crystals strongly affects their properties, performance, and applications [6–8]. Thus, the adoption of appropriate method for preparation of MPc crystals is important not only for their physical properties but also production costs. Over the past years, more than 70 kinds of MPc compounds had been synthesized via organic reactions by means of simple glass apparatus, and most of them could be purified by the method of recrystallization or column chromatography [9]. Though the yield and purity of these MPc were considerable, the preparation process is time-consuming and labor intensive. Besides, some noxious solvent are often involved.

Solvothermal synthesis is a convenient method for controlling the structures and morphologies of materials. Up to now, the investigation upon one step synthesis of MPc crystals via solvothermal reaction was less reported. To our knowledge, Du and Xia proposed a direct synthesis method of copper phthalocyanine (CuPc) big crystals by solvothermal reaction [10,11]. Shao's group reported the solvothermal synthesis of hierarchical zinc phthalocyanine (ZnPc) nanostructures [12], hierarchical flower-like iron tetranitrophthalocyanine (TNFePc) nanostructures, and hollow spheres of copper tetranitrophthalocyanine (TNCuPc) [13,14]. Nevertheless, solvothermal synthesis is only developed for these limited MPc, Therefore, exploring solvothermal route for other MPc crystals is significant and worthwhile.

In MPc family, manganese phthalocyanine (MnPc) is less studied. Up to now, only two literatures on MnPc preparation had been published in 1960 [15] and 1985 [16], respectively. It is noted that

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ammonium molybdate ($(NH_4)_6Mo_7O_{24}$) catalyst and 1,2-propanediol solvent with high boiling point and viscosity were necessary in their preparation process. Moreover, the as prepared MnPc was just not well-defined crystals and needed to be further purified. Therefore, it is necessary to develop a facile, green, and low-cost method for MnPc preparation.

In this study, we proposed a green method for solvothermal synthesis of MnPc crystals. The well-defined quadrangular MnPc crystals could be fabricated in the solvothermal reaction system of phthalodinitrile, manganese acetate, and ethanol medium within 3 h following with a facile purification process. It is noted that none of noxious solvent and additive was used both in the fabrication and purification process. The as-obtained MnPc crystals were investigated by scanning electronic microscopy (SEM), X-ray powder diffractometor (XRD) and X-ray single crystal diffractometor. The thermal performance was evaluated by the thermogravimetry-differential scanning calorimetry (TG-DSC).

Fig. 1. Optical micrograph of as prepared MnPc crystals synthesized at 190 °C for 3 h.

2. Experimental method

2.1. Materials

O-phthalonitrile (>99%) was purchased from Shanghai D&B Chemicals Technology Co., Ltd. Manganese (II) acetate tetrahydrate, ethanol were AR grade and 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. Mass spectrometry (MS) analysis was recorded using Thermo Finnigan LCQ Advantage instrument. Elemental analysis was obtained by using an Elementar Vario ELIII Elemental Analyzer. Thermogravimetry and differential scanning calorimetry (TG-DSC) were carried out by using a Netzsch STA 409 PC thermal analyzer in nitrogen at a heating rate of 10 °C/min. A Zeiss EVO LS-15 Scanning electron microscopy (SEM) was used to observe morphologies of MnPc crystals. X-ray diffraction (XRD) patterns were investigated using a Bruker D8 Advance X-ray powder diffractometer with CuKα radiation. The molecule structure and crystal-packing diagram was investigated by an X-ray single crystal diffractometor of Bruker SMART APEX CCD.

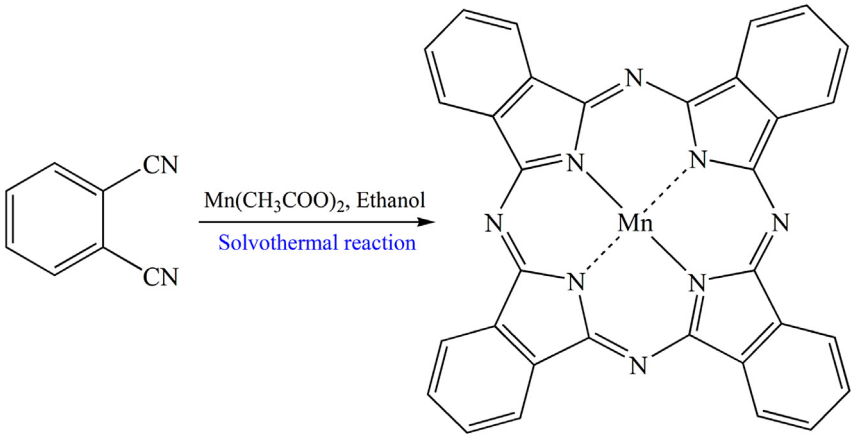
2.3. Typical procedure of MnPc synthesis

The schematic map for MnPc synthesis is shown in Scheme 1. Specifically, a 6 mmol of *o*-phthalodinitrile, 1.5 mmol of manganese acetate tetrahydrate, and suitable amount of absolute ethanol were placed in a 50 mL Teflon-lined autoclave, and then the autoclave was maintained at 190 °C for 3 h. After natural cooling to room temperature, the black green needle-shaped crystals were taken out from the bottom of autoclave and washed with hot ethanol and water to remove the residual reagents. Finally, the MnPc crystals were dried at 100 °C in vacuum overnight for characterization. Yield: 45%. Elemental analysis: Anal. Calcd. for $C_{32}H_{16}MnN_8$: C, 67.73; H, 2.84; N, 19.75. Found: C, 67.52; H, 2.66; N, 19.65. MS: calcd. for [M], m/z = 567.09, found m/z = 567.6 $[M+H]^+$. FT-IR, (KBr pellets) 728(s), 904(w), 1080(s), 1120(s), 1164(w), 1289(w), 1334(s), 1475(w), 1504(w), 1608(w), 1641(w), 3436(s) cm^{-1}.

3. Results and discussion

3.1. The morphology of MnPc crystals

The optical image of as synthesized MnPc crystals is shown in Fig. 1. It is obvious that these MnPc crystals have different size, and the length of big crystals could exceed 10 mm under the typical



Scheme 1. Synthesis route of MnPc crystals.

synthesis conditions. Moreover, under natural sunlight illumination, these crystals, especially the long needle-like crystals reflected bright black green brightness, which illustrated the good crystallography of MnPc crystals. For the obvious observation of crystal surface, some small crystals were selected to perform the SEM morphology analysis. From Fig. 2a and b, we found that these crystals had well-defined quadrangular shape. Besides, the detailed SEM images magnifying to 1000 times shows that these quadrangular crystals have different morphologies on the top/bottom planes, such as closed surface (Fig. 2c), hollow surface (Fig. 2d), and irregular surface (Fig. 2e). Also, the distinct optical image of Fig. 2f indicated that MnPc crystals was black green and showed the quadrangular shape.

3.2. The crystal structure of MnPc

X-ray diffraction technology is a practical tool to analyze the configuration of molecules and their crystallographic structures. First, the detailed structure information of MnPc crystal was determined by X-ray single crystal diffraction method. Fig. 3a and Fig. 3b show the molecular conformation of MnPc complex and the crystal-stacking diagram of MnPc, respectively. In detail, the molecular formula sum is $C_{32}H_{16}MnN_8$, belonging to monoclinic system, and the space group is P121/n1 (14). The cell parameters are $a = 14.599(2)$ Å, $b = 4.7742(7)$ Å, $c = 17.302(3)$ Å and $\beta = 105.71(0)^\circ$, and the cell volume is 1160.86(72) Å^3. (More detailed structural parameters of MnPc crystals were recorded in supplementary information of Table. S1–4.) Furthermore, we performed the XRD analysis for the as obtained MnPc samples. From curve a of Fig. 4, it is clear that the MnPc show excellent crystallographic quality, and the predominate diffraction peaks could be determined from the $(\bar{1}01)$ and (101) crystal planes according to the simulated XRD pattern from the single crystal model (curve b of Fig. 4). Also, the results documented that the simulated powder X-ray diffraction pattern matched well with the measured one. To the best of our knowledge, this is the first report upon the determination of index of crystallographic planes (corresponding 2θ in the range of 5–10°) of MnPc crystals.

3.3. The thermal analysis of MnPc crystals

The thermal stability of MPcs is important for their application in semiconductor devices. To evaluate the thermal performance of the as prepared MnPc crystals, DSC and TG were performed over a range of 50–1000 °C at a heating rate of 10 °C/min (Fig. 5). It is clear that only the weak weight loss of 1.36% was observed in TG curve (below 600 °C), which means the good thermal stability and wide suitability in high temperature environments. The obvious decrease of mass in TG curve, 27.52% centered at ~648 °C and 8.97% centered at ~889 °C illuminated the thermal decomposition of organic framework of MnPc. Besides, the endothermic and exothermic peak in DSC curve also testified the two stages of weight decrease.

4. Conclusion

A novel, facile and green solvothermal synthesis of needle-like MnPc crystals was developed. The manganese acetate and

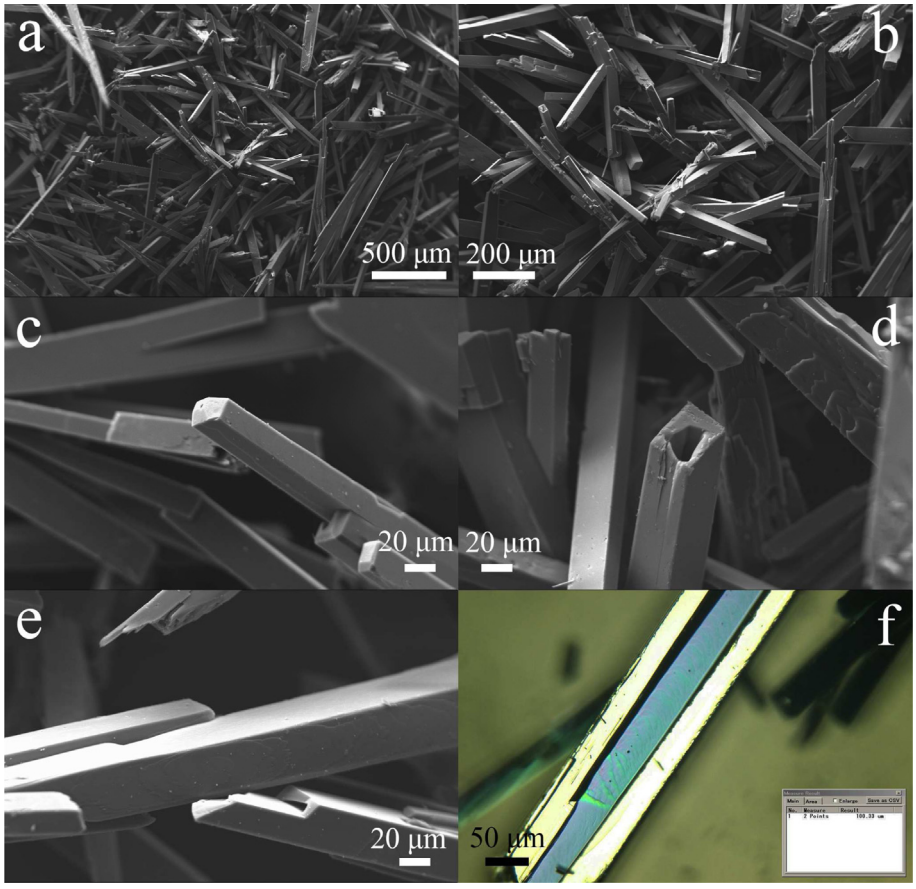


Fig. 2. SEM and optical morphology images of MnPc crystals synthesized at 190 °C for 3 h (a) and (b) Low magnified SEM morphologies of MnPc quadrangular crystals. (c), (d) and (e) High magnified SEM morphologies of MnPc quadrangular crystals with different end surface. (f) Optical morphology of a single MnPc crystal magnified to 200 times.

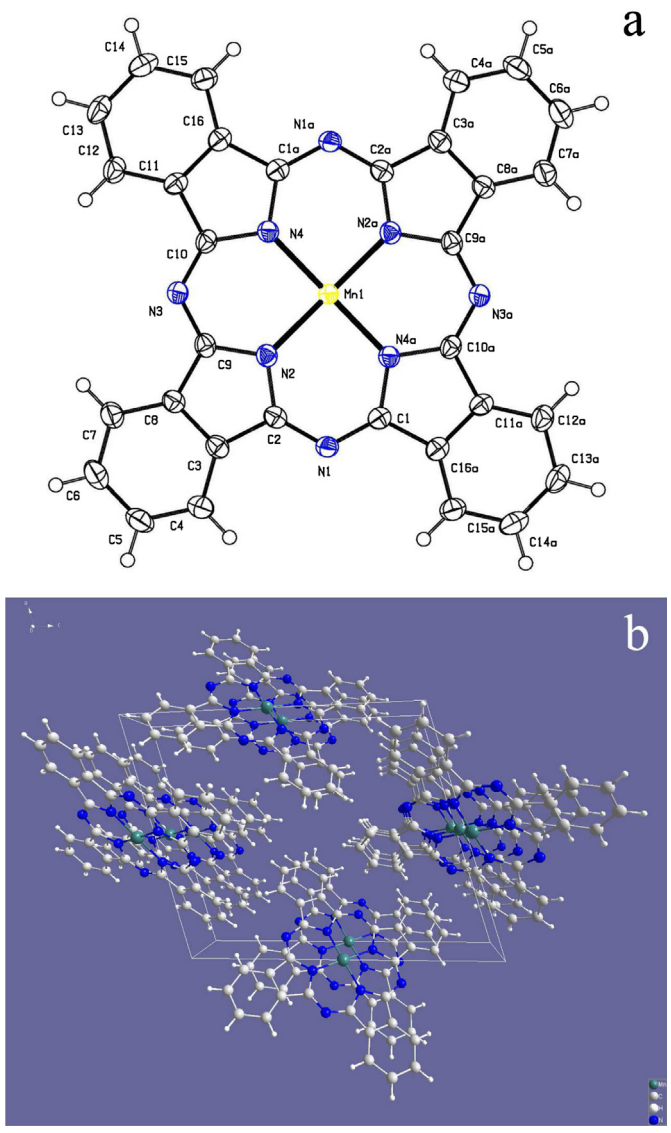


Fig. 3. (a) The crystallographically determined structure of MnPc complex. (b) The eclipsed stacking representation of MnPc crystal based on the single crystal X-ray diffraction.

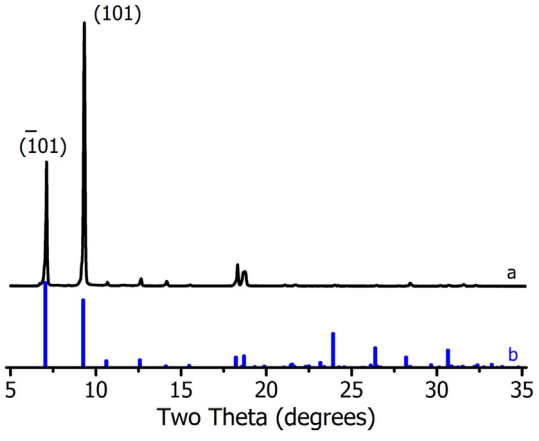


Fig. 4. (a) XRD pattern of as prepared MnPc crystals synthesized at 190 °C for 3 h. (b) The simulated XRD pattern from the single crystal diffraction models shown in blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

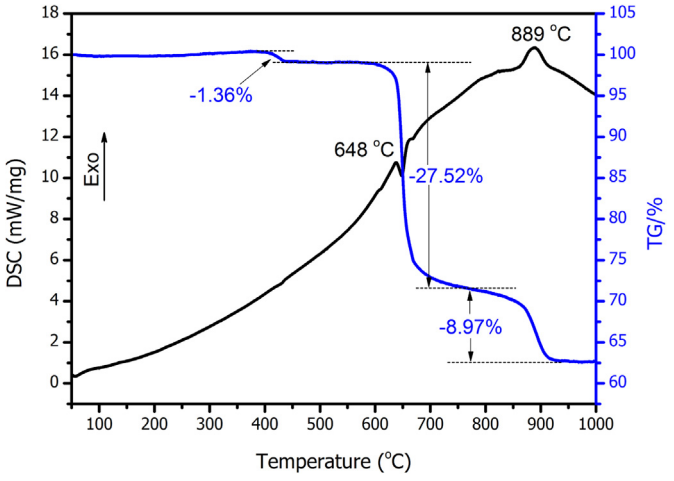


Fig. 5. TG-DSC curves for MnPc crystals.

phthalodinitrile were used as raw and common ethanol as reaction medium. It is noted that none of any other chemical additives was required in preparation process. The as-prepared MnPc crystals show well-defined quadrangular shape and good crystalline. Besides, the good thermal stability of MnPc crystals was verified on the basis of TG-DSC measurement. To the best of our knowledge, this is the first report on solvothermal synthesis of well-defined MnPc crystals.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2014.08.012.

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