Research Article

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One-step preparation of metal-free phthalocyanine with controllable crystal form

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Abstract: Metal-free phthalocyanine (H_2Pc) has been widely used as photosensitive semiconductors in the organic optoelectronics field because of its unique planar molecular structure and high photocarriers' generation efficiency. Herein, this paper related to a new facile and efficient one-step method for preparing specific crystal form of H_2Pc with high crystallinity through ball-milling process, in which α-H_2Pc can be prepared directly by dry ball-milling, and β-H_2Pc and X-H_2Pc can be simply obtained through wet ball-milling in butanone solvent at different temperatures. X-ray diffraction (XRD) was used to characterize the crystal stability of α-H_2Pc, β-H_2Pc, and X-H_2Pc, which revealed that all the three crystalline H_2Pc prepared had excellent crystal stability under different mechanical conditions.

Keywords: metal-free phthalocyanine, one-step method, controllable crystal form, ball-milling, crystal stability

1 Introduction

As an important member of phthalocyanine (H_2Pc) compounds, metal-free H_2Pc has been widely used as photosensitive materials in the field of organic optoelectronics, such as organic photoconductor (OPC) [1], organic solar cells (OSCs) [2], photodynamic therapy (PDT) [3], and so on [4,5]. H_2Pc has a nearly planar molecular structure containing a highly delocalized two-dimensional 18 π electron conjugation system composed of four isoindole units. This special molecular structure makes H_2Pc have the advantages of low toxicity, high thermal-light stability, and excellent photosensitivity in the visible and near-infrared region [6]. The interaction between neighboring molecules in metal-free H_2Pc crystal is very weak, and this weak interaction makes different molecular stacking modes have similar molecular interaction energy. The change of molecular packing mode makes metal-free H_2Pc, like other semiconductor materials, also have crystal polymorphism phenomenon [7,8], for example, α-form, β-form, and X-form. Different crystal forms of H_2Pc exhibit different photophysical and photochemical properties because of the different packing mode of molecules in the unit cell. X-H_2Pc has the highest photosensitivity, followed by α-H_2Pc and β-H_2Pc [6].

Currently, the process methods for regulating the crystal form of H_2Pc mainly include thermal-induced transformation [9], vacuum sublimation [10], and crystal seed-induced transformation [11,12]. Generally, such traditional process methods always require a large amount of energy consumption, extremely high vacuum equipment, and expensive crystal seeds. In addition, the vacuum sublimation method needs post-annealing treatment to prepare specific crystal forms, and the bath preparation yield is very low. Therefore, these traditional process methods are not cost-effective and cannot be mass-production oriented.

In this paper, we report a new facile and efficient one-step method for preparing α-H_2Pc, β-H_2Pc, and X-H_2Pc through ball-milling process. The crystal form of H_2Pc can be controlled by simply adjusting the time and temperature of ball-milling process. Moreover, all the three crystalline H_2Pc prepared had excellent crystal stability under different mechanical conditions.

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2 Materials and methods

2.1 Synthesis and purification of crude H_2Pc

2.1.1 Synthesis

About 180 mL of *N*-methyl-2-pyrrolidone was placed in a 500 mL round-bottom flask equipped with a reflux condenser, mechanical stirrer, thermometer, and gas inlet tube. A steady stream of argon is passed through the solution. Then 51.2 g of phthalonitrile, 16 mL of formamide, and 3.12 g of sodium methoxide were added to the flask. The mixture was stirred at 195°C for 6 h and then cooled down to 120°C. After hot filtration, the filter cake was washed with methanol and deionized water to obtain the crude H_2Pc (42.7 g, 83%).

2.1.2 Purification

Twenty grams of crude H_2Pc was added to 120 mL of concentrated sulfuric acid at about 3°C. After stirring for 2 h, the dark solution was slowly dropped into 600 mL of well-stirred ice water. The H_2Pc particles precipitated immediately after allowing the mixture to stand for 30 min. The H_2Pc were isolated through filtration. The filter cake was washed with deionized water and dried in a vacuum freeze dryer for several hours to obtain the purified H_2Pc (18.6 g, 93%).

2.2 Preparation of α-H_2Pc, β-H_2Pc, and X-H_2Pc

2.2.1 α-H_2Pc

Twenty grams of the purified H_2Pc was placed in a sealed glass jar half-filled with 400 g of zirconia balls (ϕ = 1 mm) and rotated at 60 rpm. α-H_2Pc can be prepared when dry ball-milling time exceeds 1 h.

2.2.2 X-H_2Pc

Twenty grams of the purified H_2Pc and 200 mL of 2-butanone were placed in a sealed glass jar half-filled with 400 g of zirconia balls (ϕ = 1 mm). The sealed glass jar was rotated at 60 rpm at 20°C. X-H_2Pc can be prepared when wet ball-milling time exceeds 1 h.

2.2.3 β-H_2Pc

Twenty grams of the purified H_2Pc and 200 mL of 2-butanone were placed in a sealed glass jar half-filled with

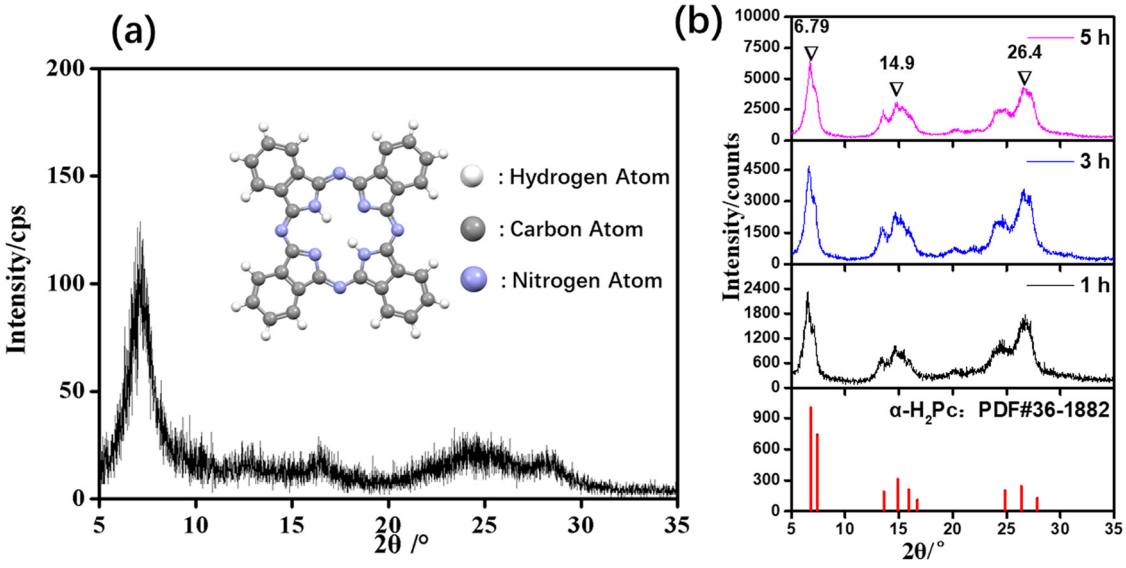

Figure 1: (a) XRD pattern of the purified H_2Pc, the inset picture is a ball–stick model of H_2Pc molecule; (b) XRD patterns of the H_2Pc obtained from different dry ball-milling time.

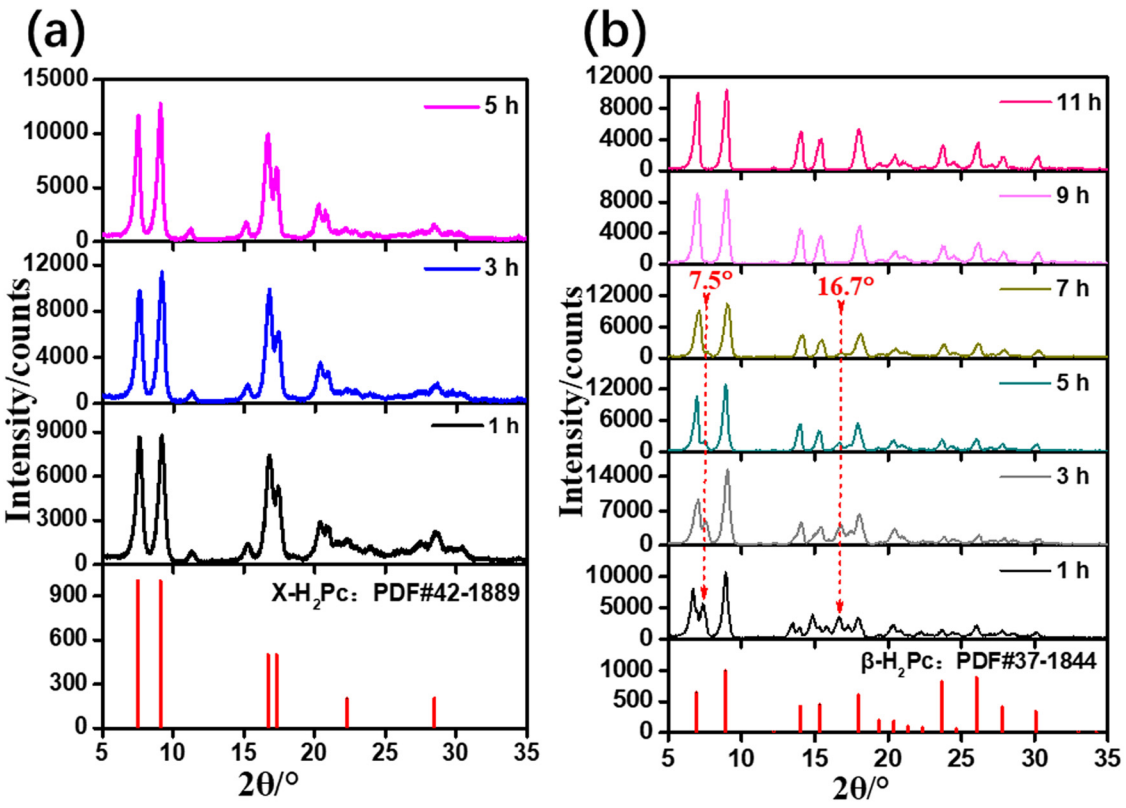

Figure 2: XRD patterns of the H_2Pc obtained from different wet ball-milling time at 20°C (a) and 30°C (b).

400 g of zirconia balls (ϕ = 1 mm). The sealed glass jar was rotated at 60 rpm at 30°C. β-H_2Pc can be prepared when wet ball-milling time exceeds 9 h.

2.3 Crystal form stability

The crystal form stability of the prepared H_2Pc was respectively studied by wet ball-milling and ultrasonic in 2-butanone under different time.

2.4 Solvent recovery

2-Butanone was used as a crystal form transformation regulating solvent in the transformation of X- and β-H_2Pc. To save cost and reduce environmental pollution, the solvent recovery of 2-butanone was carried out, and the specific operation steps were as follows: the mixture after ball-milling was first filtered through a 100 mesh sieve to obtain the zirconia balls and butanone dispersion of H_2Pc, and then the butanone dispersion of H_2Pc was centrifuged at 5,000 rpm to obtain H_2Pc solid and butanone mixture. Finally the 2-butanone mixture was distilled at 80°C to obtain a pure 2-butanone solution. The average recovery of 2-butanone was about 91.2% after repeated recovery calculation.

3 Results and discussion

Figure 1a shows the X-ray diffraction (XRD) pattern of the H_2Pc after purification. As observed, the intensity of all diffraction peaks in this diffraction pattern is particularly

Table 1: Relationship between $C_{X-H_2Pc}/C_{\beta-H_2Pc}$ and wet ball-milling time.

Time (h)	$I_{7.5°}$ (counts)	$I_{9.0°}$ (counts)	$I_{7.5°}/I_{9.0°}$ (%)	$C_{X-H_2Pc}/C_{\beta-H_2Pc}$ (%)
1	5,486	10,726	51.1	51.1
3	5,060	15,413	32.8	32.8
5	2,233	12,893	17.3	17.3
7	1,253	10,386	12.1	12.1
9	326	9,506	3.4	3.4
11	260	10,373	2.5	2.5

weak, for instance, the intensity of the strongest diffraction peak at 7.2° is only 129 cps. This phenomenon indicates that the crystal form of the purified H_2Pc is amorphous, which as the raw material is very beneficial to transform amorphous H_2Pc into other target crystal forms. Figure 1b presents the XRD patterns of the purified H_2Pc after dry ball-milling treatment at different time. It can be found that the longer the ball-milling time, the stronger the intensity of XRD diffraction peak. This suggests that the crystallinity of the purified H_2Pc increases with the prolongation of dry ball-milling time. Meanwhile, the characteristic diffraction peaks of the XRD patterns obtained in this experiment are in good agreement with the standard JCPDS card No. 36-1882 of α-H_2Pc. Furthermore, according to CCDC No. 118412, the detailed unit cell parameters of α-H_2Pc are as follows: space group: C_2/n (15), cell: a = 26.121(4) Å, b = 3.7970(7) Å, c = 23.875(3) Å, α = 90°, β = 94.16(2)°, γ = 90° [13]. The very typical peaks at 6.8°, 14.9°, and 26.4° of the XRD patterns could be indexed to (200), (004), and (113) crystal planes of α-H_2Pc, respectively. Therefore, α-H_2Pc can be simply prepared by direct dry ball-milling of the purified H_2Pc.

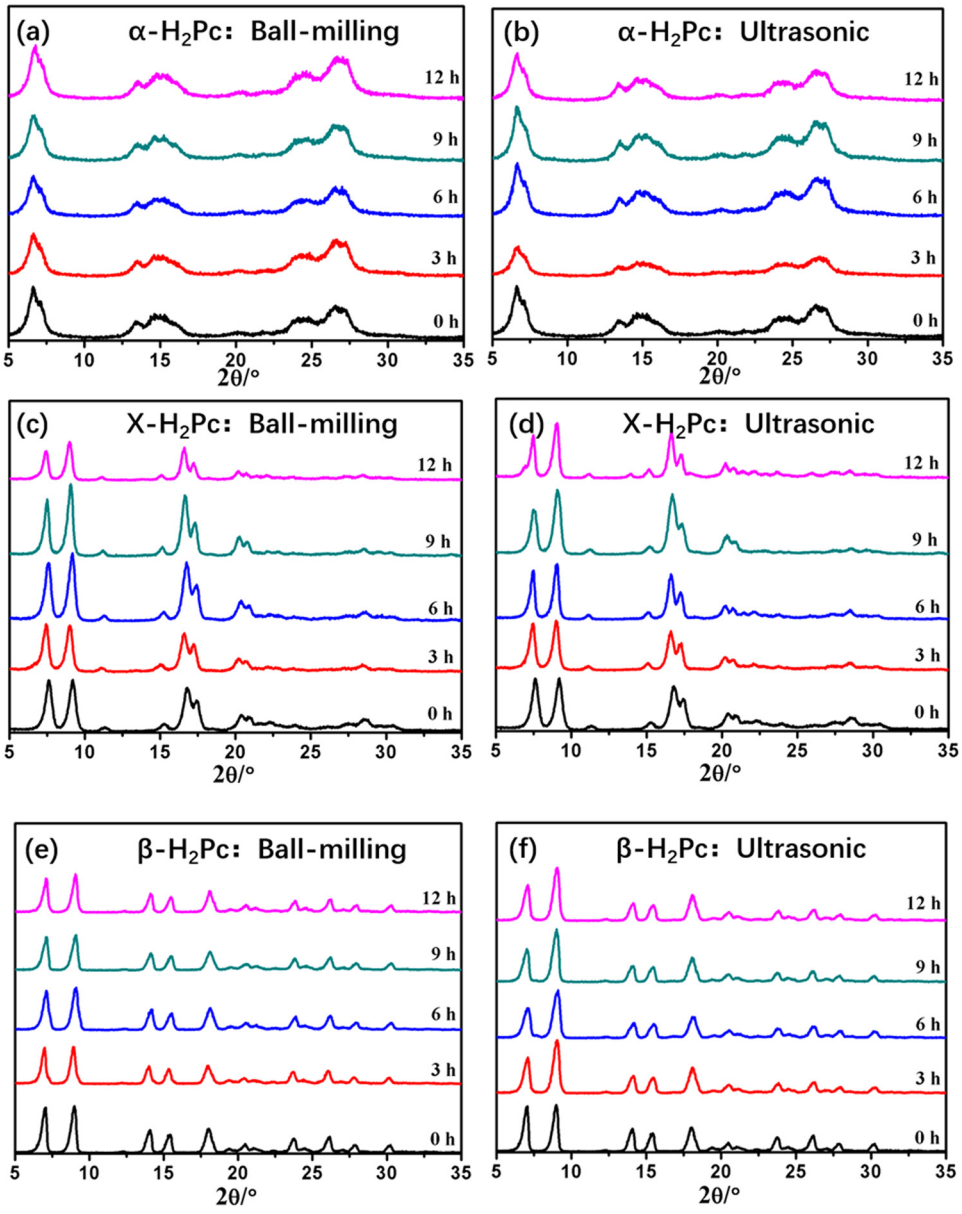

Figure 3: XRD patterns of α-, X-, and β-H_2Pc before and after ball-milling treatment (a, c, and e) and ultrasonic (b, d, and f) for 0–12 h, respectively.

Figure 2a shows XRD patterns of the H_2Pc obtained from different wet ball-milling time at 20°C. The characteristic diffraction peaks of the XRD patterns are consistent with the standard JCPDS card No. 42-1889 of X-H_2Pc. The intensity of obvious peaks indicates the prepared X-H_2Pc with a high degree of crystallinity. Furthermore, according to CCDC No. 1232684, the detailed unit cell parameters of X-H_2Pc are as follows: $P2_1/a$ (14), cell: a = 10.63 Å, b = 23.15 Å, c = 4.89 Å, α = 90°, β = 95.98°, γ = 90° [14]. The characteristic peaks at 7.5°, 9.1°, 16.7°, 17.3°, 22.3°, and 28.5° could be indexed to (020), (110), (200), (140), (121), and (231) crystal planes of X-H_2Pc, respectively. Therefore, X-H_2Pc can be readily obtained by wet ball-milling at 20°C for only 1 h.

Figure 2b presents the XRD patterns of the H_2Pc obtained from wet ball-milling at 30°C. Clearly, the characteristic peaks of X-H_2Pc at 7.5° and 16.7° decrease with the increase in wet ball-milling time, which proves that X-H_2Pc gradually transforms into β-H_2Pc. According to the standard JCPDS cards of X-H_2Pc (PDF#42-1889) and β-H_2Pc (PDF#37-1884), it is known that the strongest diffraction peak position is at 7.5° for X-H_2Pc and 9.0° for β-H_2Pc. Therefore, the relative abundances of X-H_2Pc and β-H_2Pc ($C_{X-H_2Pc}/C_{\beta-H_2Pc}$) can be quantitatively analyzed according to the peak intensity ratio of the two strongest diffraction peaks. Table 1 shows the relationship between $C_{X-H_2Pc}/C_{\beta-H_2Pc}$ and wet ball-milling time. After wet ball-milling for 9 h, the $C_{X-H_2Pc}/C_{\beta-H_2Pc}$ is only 3.4%, which proves that the crystal form of the prepared H_2Pc is almost completely transformed to β-H_2Pc (JCPDS card No. 37-1844). According to CCDC No. 130922, the detailed unit cell parameters of β-H_2Pc are as follows: space group: $P2_1/a$ (14), cell: a = 19.870(7) Å, b = 4.731(7) Å, c = 14.813(7) Å, α = 90°, β = 121.98(4)°, γ = 90° [15]. The characteristic peaks at 7.0°, 9.0°, 17.9°, and 26.0° could be indexed to (001), (20-1), (40-2), and (41-2) crystal planes of β-H_2Pc, respectively. Consequently, β-H_2Pc can be easily prepared by wet ball-milling in 2-butanone solvent at 30°C for 9 h.

As we all know, H_2Pc compounds have the crystal polymorphism phenomenon and are prone to crystal transformation under mechanical forces. Therefore, the common mechanical forces, such as ball-milling and ultrasonic, are used to investigate the crystal stability of the prepared α-, X- and β-H_2Pc. As shown in Figure 3, none of the three crystal forms of H_2Pc presents obvious change in the XRD patterns after ultrasonic or ball-milling treatment for 1–12 h. The characterization results indicate that the α-, X-, and β-H_2Pc prepared by dry/wet ball-milling present excellent crystal stability.

4 Conclusions

In summary, we developed a new facile and efficient method for preparing α-, X-, and β-H_2Pc through ball-milling process. α-H_2Pc can be prepared directly by solvent-free dry ball-milling process. X-H_2Pc and β-H_2Pc can be simply obtained through wet ball-milling in butanone solvent at 20°C and 30°C, respectively. Both ball-milling and ultrasonic experiments proved that all the prepared α-, X-, and β-H_2Pc had excellent crystal stability. We believe that this work will significantly promote the development of the crystalline transformation process of H_2Pc with reduced preparation time and cost.

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Conflict of interest: The authors state no conflict of interest.

Data availability statement: All data generated or analyzed during this study are included in this published article.

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