

One-Pot Synthesis and Self-Assembly of Copper Phthalocyanine Nanobelts through a Water-Chemical Route

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A water-chemical route to synthesize copper phthalocyanine (CuPC) is reported in this paper. The molecules were self-assembled into regular β -CuPC single-crystal nanobelts simultaneously. The molecular structure of CuPC in the nanobelts was characterized by UV–vis absorption spectroscopy, MALDI-TOF-MS, and elemental analysis. The morphology and crystal phase of the nanobelts were investigated by electron microscopy and X-ray diffraction, respectively. Crucial factors for the formation of CuPC nanobelts were also investigated. The cooperative effect of the surfactant and copper powder was important for the formation of CuPC. The CuPC nanobelts were obtained through a self-assembly process. In addition, a phase transition process, which resulted in the formation of β -CuPC single-crystal nanobelts, took place with prolonged time.

Phthalocyanines (PCs) have attracted much interest in applications for decades because of their unique physical and chemical properties.¹ With the development of nanoscience and nanotechnology, considerable attention has been focused on nanosized copper phthalocyanine (CuPC) owing to its excellent optoelectronic and electronic properties.² For instance, the CuPC nanostructure prepared by an organic vapor-phase deposition³ has been employed as high-performance photovoltaic cells and organic field-effect transistors. This vapor technique, however, suffered from disadvantages of high temperature, special template, and limited amounts of single crystals. Other conventional methods such as reprecipitation are not suitable for the PCs because of their limited solubility in normal organic solvents. On the other hand, as a direct, mild, and simple method, the hydrothermal technique was widely used in the

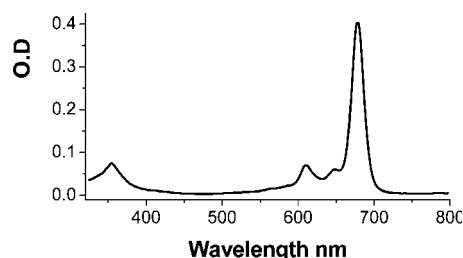


Figure 1. UV–vis absorption spectrum of the synthesized CuPC in α -chloronaphthalene.

preparation of inorganic frameworks⁴ and the synthesis of inorganic–organic hybrid materials.⁵ Inspired by the hydrothermal technique, we have developed a water-chemical route to obtain CuPC nanomaterials. The marked feature of this approach is that the use of water as a reaction solvent obviously avoids environmental problems usually caused by organic solvents. In this Communication, we synthesized CuPC and the molecules were simultaneously assembled into regular β -CuPC one-dimensional nanobelts. This approach not only enriches PC cyclization chemistry but also provides a new strategy to synthesize single-crystal nanostructures of PCs, which could be important and applicable in the synthesis of other organic nanostructures with an environmentally friendly reaction.

In a typical preparation, CuPC was synthesized in an aqueous solution with sodium dodecyl sulfate (SDS) at 150–180 °C (Supporting Information). Figure 1 shows the UV–vis absorption spectrum of the synthesized CuPC in α -chloronaphthalene. It shows two typical distinguishable absorption bands centered at 680 (Q-band) and 350 (B-band) nm.⁶ MALDI-TOF-MS: 575.3(M). Anal. Calcd for CuPC: C, 66.72; N, 19.45; H, 2.80. Found: C, 65.90; N, 19.05; H,

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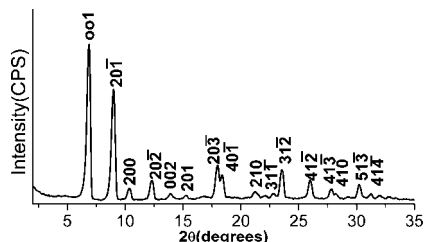


Figure 2. XRD patterns of the sample synthesized at 150 °C for 5 days.

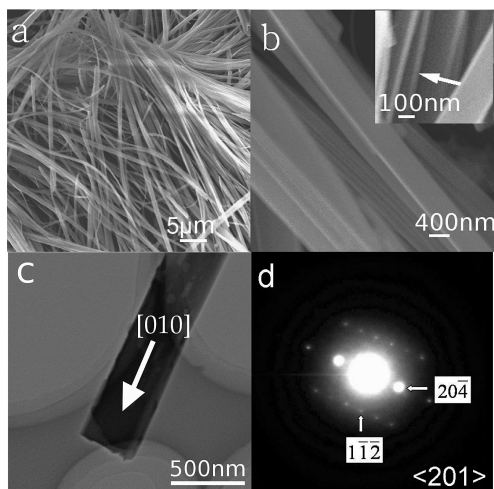


Figure 3. (a) Low-magnification SEM image of the CuPC nanobelts. (b) High-magnification SEM image of the CuPC nanobelts (inset: an individual belt with a thickness of ca. 60–70 nm). (c) TEM image of an individual CuPC nanobelt. (d) Its corresponding electron-diffraction pattern.

2.91. All of the results above confirmed the formation of the target product of CuPC.

The X-ray diffraction (XRD) patterns for the final product (Figure 2) fit the β -CuPC peaks very well,⁷ which indicates that β -CuPC is formed in the reaction. Figure 3 shows the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the products. Figure 3a gives the overall view of the CuPC samples, in which lots of uniform beltlike structures of tens of micrometers in length are observed. A higher resolution image (Figure 3b) reveals that most of the CuPC belts are 400–500 nm wide and several tens of nanometers thick. A typical TEM image of a CuPC belt is shown in Figure 3c, and the electron diffraction (SAED) pattern for the corresponding area is shown in Figure 3d. The XRD pattern did not change when the electron beam scanned across individual belts, indicating that these nanobelts are single crystals. The SAED pattern was indexed with lattice constants obtained from the powder diffraction data: $a = 19.40(7)$ Å, $b = 4.79(0)$ Å, $c = 14.62(8)$ Å, and $\beta = 120.93(3)^\circ$. The results from parts c and d of Figure 3 indicate that the β -CuPC belts grow along the [010] direction, which coincides with the stacking of planar CuPC molecules in the β -phase along this direction through π - π interaction.

For a complete view of the formation mechanism of the β -CuPC single-crystal nanobelts, a series of comparison experi-

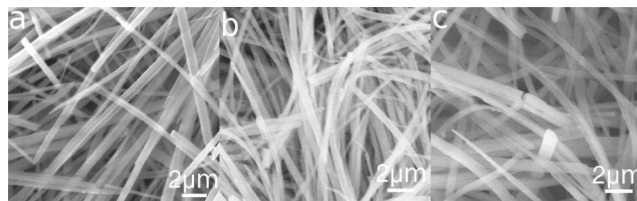


Figure 4. SEM images of CuPC nanobelts produced: (a) in water without SDS; (b) in water with SDS; (c) in a $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution with SDS.

ments were carried out. First, we investigated the role of SDS in the formation of these nanobelts. In general, SDS could act as a soft template to form size-controlled structures⁸ or as an emulsion agent in an emulsion reaction.⁹ As for the soft template, the surfactant SDS should influence the morphology of the final nanostructures.¹⁰ We compared the synthesized product with those prepared without surfactants, as shown in Figure 4a,b, where the only difference of the synthesis conditions was the presence or absence of SDS. We found that (1) there was no difference between the morphology of the nanobelts and (2) the yield of CuPC decreased from 10% to 1% when SDS was absent. These results suggested that SDS just affected the yield of CuPC other than the morphology of the products. The possibility of SDS as a soft template was reasonably ruled out. Therefore, SDS acted as an emulsion agent to provide a hydrophobic microenvironment, which could be favorable to preventing the phthalonitrile precursor from being hydrolyzed in water. For this reason, the CuPC nanobelts were formed through a self-assembly process driven by π - π and van der Waals interactions.¹¹

In order to study how the copper powders affected the reaction, the copper powder was replaced with CuCl_2 , $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, respectively. It was found that there was no obvious difference in the observed morphology of the final product (Figure 4c). However, the yield decreased to less than 1%. The possible reason is that copper powders could optimize the cyclization process and would not be hydrolyzed as those copper salts were, which thereby provided more Cu nucleuses. The activated surface of copper metal¹² served as an impulse to reach the energetic barrier, and finely divided copper powder could act as “matrixes” for the PC-core formation.¹³ Therefore, copper powders are more suitable for the preparation of CuPC in this reaction than those copper salts.

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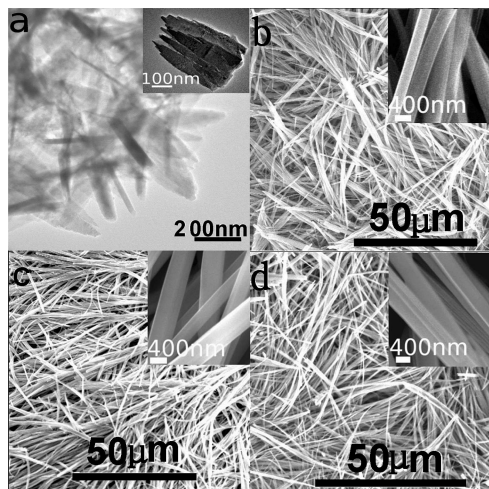


Figure 5. (a) TEM image of the CuPC products synthesized for 10 h. (b–d) SEM images of the CuPC products synthesized for 15 h and 3 days. The upper right insets are the enlarged images taken from each product, respectively. All of the products are obtained by a water-phase reaction at 150 °C.

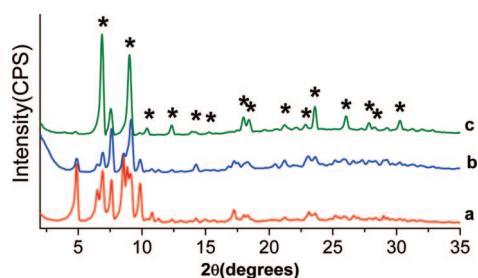
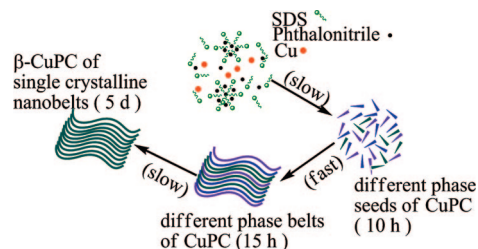


Figure 6. XRD patterns of CuPC nanobelts produced at 150 °C for (a) 10 h, (b) 15 h, and (c) 3 days. The β phase is labeled with asterisks (*).

Scheme 1. Schematic Illustration of the Formation Mechanism for the CuPC Single-Crystal Nanobelts



Finally, a detailed time-dependent morphology and crystal-phase evolution were studied at 150 °C. The product obtained after 10 h contained arrowhead-like particles with a width of 100 nm and a length of 400–500 nm (inset of Figure 5a). It further gave nanobelts with a width of 400–500 nm and a length of tens of micrometers when the reaction time was prolonged to 15 h (Figure 5b). For reaction times of 3 and 5 days, the morphology of the nanobelts was almost the same as that obtained for 15 h, except for a longer length (Figure 5c,d). Meanwhile, XRD analysis (Figure 6) showed that all peaks of β -CuPC can be found in the three XRD patterns, while the crystal phases of CuPC gradually transformed to β -CuPC after 10 h. β -CuPC was previously reported to be

the main thermodynamically stable crystal phase in theory among the eight crystal phases of CuPC, while the other phases tended to transform to a β phase under some conditions.¹⁴ In the XRD patterns of CuPC obtained after 10 h (Figure 6 a), there were many peaks that could not be designated by a single phase of CuPC, which suggested that the product in this stage consisted of multiple phases. For the sample obtained after 15 h and 3 days (Figure 6b,c), the peaks of the β -CuPC phase were strengthened while other peaks were weakened or disappeared. The XRD patterns became very similar to the standard β -CuPC phase. After 5 days, the sample was completely transformed to β -CuPC according to its XRD pattern (Figure 2). These results implied that there were multiple crystal phases of CuPC in the initial reaction and β -CuPC was the only stable crystal with prolonged time under the reaction conditions.

Based on the results and discussion above, the formation mechanism for the CuPC single-crystal nanobelts was demonstrated as follows (Scheme 1):

1. In the synthetic process, SDS acted as the emulsion agent, providing a microenvironment, while the copper powders acted as the nucleating agent for the synthesis of CuPC. The cooperative effect of the surfactant and copper powder promoted the formation of CuPC.

2. After 10 h, CuPC arrowhead-like particles were formed as different crystal-phase seeds.

3. In the next 5 h, these seeds with different crystal phases grew quickly to form nanobelts.

4. After 5 days, these different crystal nanobelts transformed gradually to β -CuPC single-crystal nanobelts through a crystal-phase transition.

In summary, uniform β -CuPC single-crystal nanobelts have been successfully synthesized through a water-chemical route. Various experimental conditions, including surfactant, copper powders, and reaction time, for the growth of the β -CuPC single-crystal nanobelts were investigated. Based on the results of electron microscope images and XRD patterns, the formation mechanism of the β -CuPC single-crystal nanobelts has been discussed. The cooperative effect of the SDS and copper powder was found to be of vital importance to the formation of the CuPC molecules and the nanobelts were obtained through a self-assembly process. A phase transition took place and, finally, resulted in the formation of β -CuPC single-crystal nanobelts. With the present growing concern about organic functional materials, this direct, mild, and simple method should be worth further exploration for other organic nanomaterials.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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