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Single-crystal Copper–Phthalocyanine Nanorods Self-assembled by a Solvent Evaporation Method

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Copper–phthalocyanine (CuPc) nanorods were prepared on a Si substrate by a solvent evaporation method. The results of XRD indicate that the CuPc nanorods were β-phase single crystals and grown along the [010] direction. The diameters of CuPc nanorods depend on the solution concentration, and the formation of CuPc nanorods is insensitive to the solvents and substrates. This implies that the growth of CuPc nanorods is dominated by the intrinsic π–π stacking between Pc rings. In addition, a p–n junction was formed between CuPc nanorod and Si substrate.

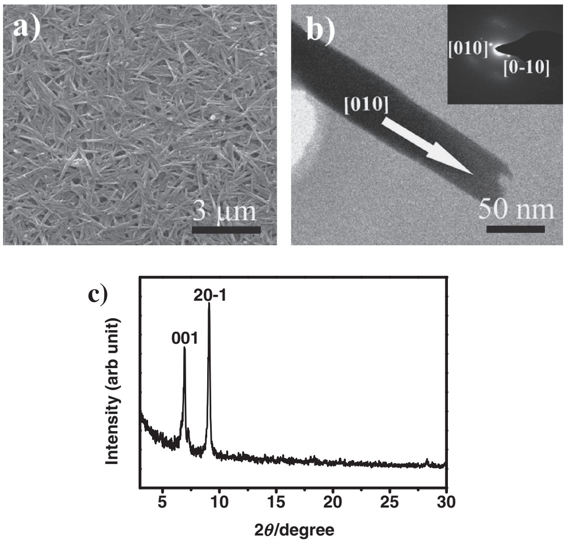

Figure 1. (a) SEM image of CuPc nanorods produced by evaporation of CuPc solution (0.25 mg mL^{-1}, ca. 10 μL) on a Si substrate. (b) TEM image of a single CuPc nanorod. The inset is the corresponding selected area electron diffraction (SAED) pattern. (c) XRD pattern of CuPc nanorods.

One-dimensional (1D) nanostructures of CuPc have been attracting great attention in recent years. This is due to their desirable optical, electrical, and catalytic properties,[1–5] which make them ideal materials in applications such as field effect transistors,[6] phototransistors,[7] and solar cells.[8] In general, 1D CuPc nanostructures are prepared by vapor transport methods (i.e., dry processes),[9,10] which are costly and complicated operations. A more convenient method is thus urgently pursued to prepare 1D CuPc nanostructures. Solution-based processes can meet this requirement because they are low cost, facile to control the structure, and feasible for operation. However, to date, only CuPc derivatives have been successfully employed to prepare 1D nanostructures.[11–13] The preparation of 1D CuPc nanostructures by using pure CuPc through a solution process is almost unexplored.

Herein, we report for the first time a solution process to prepare single-crystal nanorods of pure CuPc. In brief, CuPc solutions were prepared by ultrasonification of CuPc powder (>99.9%, Aladdin Chemical Company, China) with chloroform (>98.5%, Sinopharm Chemical Reagent Co., Ltd.) for 15–30 min. The concentration of CuPc in chloroform was ca. 0.25 mg mL^{-1}. A drop of CuPc solution was then deposited onto a (10 mm × 10 mm) Si substrate, and the solvent was slowly evaporated under ambient conditions. The samples were characterized by means of scanning electron microscopy (SEM, Quanta 400 FEG), transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin), X-ray power diffraction (XRD, X'Pert-Pro MPD), and conductive atomic force microscopy (CAFM, Dimension 3100).

Figure 1a shows a typical SEM image of CuPc nanorods formed on a Si substrate. It can be seen that the final products are rodlike structures, which are of several micrometers in length and tens of nanometers in diameter. Figure 1b shows a TEM image of a single CuPc nanorod with a diameter of ca. 45 nm. Note that with the increase of the concentration of CuPc solution, larger size nanorods can be obtained. The inset is the corresponding SAED pattern. No change of SAED pattern was observed for different parts of the same crystal, indicating that the whole nanorod is a single crystal. The SAED pattern of the nanorod can be indexed with its crystal lattice constants, and the single-crystal nanorod grew along the [010] direction, i.e, π–π interaction induced the fastest growth along this direction. As a consequence, 1D CuPc nanostructure has been obtained. This coincides with the stacking of planar CuPc molecules in the β-phase along this direction through π–π interaction.[12] Figure 1c is the XRD pattern of the nanorods. It is obvious that the nanorods were oriented. The 2θ peaks at 6.97 and 7.18° can be indexed as the (001) and $(20\bar{1})$ peaks of β-phase CuPc, respectively. This result is comparable to the literature within experimental errors.[14,15] Therefore, it is concluded that the as-prepared nanorods are β-phase single crystals of CuPc. Similar nanorods have been obtained in a variety of solvents including toluene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, chlorobenzene, 1,3-dichlorobenzene, and 1,2-dichlorobenzene for CuPc. The results demonstrate that the formation of CuPc nanorods is independent of solvents.

As the selection of substrate is crucial for application, different substrates such as silica, glass, and aluminium foil are examined by evaporating the solvent of CuPc solution at room temperature. Similar nanorods are observed in the SEM and TEM images (not shown here) from all these substrates. This indicates that the formation of CuPc nanorod is independent of substrate. It is known that Pc is a macrocyclic π-conjugated compound consisting of 18π electrons in the center. The π–π stacking between Pc rings might play a dominant role in the formation of CuPc nanorods.[12] It is also worth mentioning that,

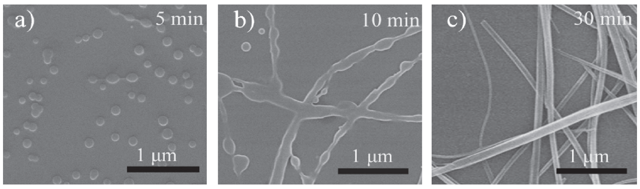

Figure 2. SEM images for the growth of CuPc nanorods at different evaporating time. (a) 5, (b) 10, and (c) 30 min. The drop volume of CuPc solution is ca. 2 μL.

in the present experiments, CuPc nanorods can be obtained in ca. 30 min by evaporating the solvent of CuPc solution. This is shorter than that of the traditional method[16] and is useful in the practical world for its convenient, timesaving operation.

The effect of the drop volume of CuPc solution on the formation of rodlike structures is also studied by depositing different volumes of CuPc solution on a Si substrate. At small drop volume (ca. 2 μL), nanorods of CuPc are found to spread separately over the Si substrate. The formation of separated nanorods allows us to study the growth mechanism of CuPc nanorods in the following section. Further increase of the drop volume results in the increase in the number of CuPc nanorods. For instance, when the drop volume is increased to ca. 10 μL, a compact film is formed (Figure 1a). This is possibly because a large volume of CuPc can provide more nuclei per area.

In addition, to reveal the growth mechanism of CuPc nanorods, a sudden-evacuation method has been proposed, by which the different growth stage of CuPc could be halted. Figure 2 shows a set of three sequential SEM images acquired by evaporation of CuPc solution for 5, 10, and 30 min. The samples are then put into a vacuum chamber and suddenly evacuated. The process leads to the fast precipitation of CuPc and hinder their diffusion. As a result, the growth of CuPc was interrupted and frozen. It is clear that CuPc precipitates in the form of particles with a diameter of about 200 nm when chloroform evaporates for 5 min (Figure 2a). Increasing the evaporating time to 10 min, chainlike morphology is formed (Figure 2b). In the case of Figure 2c, rodlike structures of CuPc are observed. The nanostructures shown in three images of Figure 2 can be regarded as snapshots of different stages in the whole process of CuPc precipitation and self-assembling. This new method of sudden evacuation has potential application in research of self-assembling process.

For CAFM measurements, the Si substrate is connected to the conductive sample directly and forms the back contact. All the measurements are performed at ambient conditions, and commercial etched Si tips coated with metal Co/Cr are used. Figure 3a show a typical AFM image of a single CuPc nanorod. Figures 3b and 3c are the corresponding CAFM images. The electrical contrast clearly indicates a phase difference between CuPc nanorod and surroundings in conduction. The dark feature in Figure 3b and the bright feature in Figure 3c can be attributed to the conductivity of CuPc nanorod. The reason for higher conduction achieved in CuPc nanorod/Si substrate with 5 V dc tip bias and lower conductive achieved with -5 V dc tip bias is that a p–n junction has formed between the Si substrate and CuPc nanorod. This feature is of potential in organic/inorganic hybrid devices. A detailed investigation on the rectification at Co/CuPc/Si junctions is under way.

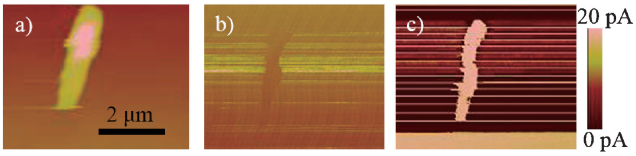

Figure 3. (a) AFM image of a single CuPc nanorod. (b) Corresponding CAFM image (-5 V dc tip bias); (c) Corresponding CAFM image (5 V dc tip bias).

In summary, CuPc nanorods have been prepared by a solvent evaporation method and characterized by SEM, TEM, XRD, and CAFM. The results indicate that the nanorods are β-phase single crystals of CuPc and grow along the [010] direction. The growth of CuPc nanorods is insensitive to the solvents and substrates, indicating that the nanorod growth is dominated by the intrinsic π–π stacking between Pc rings. In addition, the CAFM results indicate that a p–n junction can be formed between single-crystal CuPc nanorod and Si substrate.

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