A novel solution-based self-assembly approach to preparing ultralong titanyl phthalocyanine sub-micron wires*

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Ultralong titanyl phthalocyanine (TiOPc) sub-micron wires have been synthesized by a novel solution-based self-assembly method. By using different solvents, changing the mass concentration and the solvent vapor pressure, the length and the shape of the wires can be adjusted. The mixed-phase properties of the TiOPc sub-micron wires were investigated by the ultraviolet–visible (UV–vis) absorption spectrum and X-ray diffraction. Organic transistors based on these wires were studied, which show the typical p-channel characteristics.

Keywords: titanyl phthalocyanine, sub-micron wire, transistor, solution method

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1. Introduction

Organic semiconductor microstructures have attracted explosive attention in the context of flexible optoelectronics[1] owing to their excellent chemical tenability. These highly ordered functional materials with characteristic structures exhibit great potentials in nanoelectric devices such as field-effect transistors,[2] sensors,[3] and photovoltaic cells.[4] Recently, it has been reported that the π-conjugated molecular packing in a highly organized microstructure facilitates the carrier transport and hence improves the performance of optoelectronic devices.[5] In this regard, various strategies have been used to fabricate organic semiconductor microstructures, including the solution method,[6] the phase transfer method,[7,8] chemical vapor deposition,[9] surface-assisted self-assembly,[10] the substitution method,[11–13] and so on. Among these methods, the solution method is the most efficient way to grow nanowires.[10] However, from the viewpoint of application, it still suffers from tedious procedures, expensive and specialized equipments, which seriously hinder its practical application.

Titanyl phthalocyanine (TiOPc) is one kind of non-planar metal phthalocyanine, which possesses high non-linear optical sensitivity[14] and excellent chemical and thermal stability. Especially, TiOPc has a large π-conjugated plane that can facilitate the electron transport,[15] which enables it as the active layer for the organic thin-film transistor (OTFT). If TiOPc can be made into a microstructure, it can effectively shrink the device size for the purpose of high integration and low-cost manufacture. Driven by this, several groups have made some progress on the synthesis of the TiPOc microstructure. For instances, Barbara *et al.*[16] prepared TiOPc nanobelts based on TiOPc/perylene phenethylimide bilayers. Brinkmann *et al.*[17] also obtained a uniform α-TiOPc nanobelt by the high-vacuum deposition of TiOPc onto an oriented poly (tetrafluoroethylene) substrate. Unfortunately, to date, microstructures of metal phthalocyanine have not been prepared by the solution method because they suffer from extreme insolubility and instability in solvents. Therefore, it is still a challenge to use the solution method to assemble the TiOPc microstructure, which is expected to exhibit excellent electric properties.[15,18]

In this paper, we firstly demonstrated a novel solution-based self-assembly method to prepare high-quality TiOPc sub-micron wires without the need for surfactants or substitution. Ultralong TiOPc sub-micron wires about 1 mm in length were successfully obtained by optimizing the experimental parameters such as the solvent types, the solvent volume, and the mass concentration. The phase analyses of ultralong TiOPc sub-micron wires were performed by techniques using the ultraviolet–visible (UV–vis) absorption spectrum and X-ray diffraction (XRD). Further, the OTFT fabricated *in situ* on a singular ultralong TiOPc sub-micron wire and its electric properties were presented.

2. Experiment

2.1. Material

TiOPc was purchased from Aldrich without further purification. Alcohol, methanol, acetone, and n-hexane were brought from Sinopharm Chemical Reagent Co., Ltd.

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2.2. Glass instruments

All the apparatus such as the weighing bottle (25 mm× 40 mm), magnon (6 mm× 10 mm), sample vial, petri dish (90 mm in diameter), and petri dish (120 mm in diameter) were cleaned with cleaner, ethanol, acetone, and deionized water step by step and dried in a drying cabinet.

2.3. Sample preparation

A heavily doped n-type silicon wafer with 300 nm thick SiO_2 was used as the substrate. The substrate was cleaned with acetone, alcohol, and deionized water respectively and dried in a drying cabinet. In a typical process, 1.5 mg of TiOPc was added to 2 ml organic solvent hosted in a weighing bottle (25 mm×40 mm) with a small magnon (6 mm×10). After that, the bottle was put into an ultrasonic cleaner for 25 min to smash the slug gathered TiOPc particles into smaller ones. Taking into account the uniform distribution of the solute in the solvent, magnetic stirring with a rotation speed of 700 rpm was applied for 12 h on digital heating units at the temperature of 45 °C. Subsequently, the solution was filtered by a syringe through a 0.22 μm filter into another clean sample vial. The filtrate was then dropped on the substrate, which was placed onto petri dish 1 (90 mm in diameter). Petri dish 1 was put into a larger one (120 mm in diameter) filled with an appropriate volume of the same solvent, which was used to configure the solution to provide a solvent vapor atmosphere. With the atmospheric temperature at 21 °C, TiOPc aggregates could be observed on the substrate 48 h later. All samples were then dried in the drying cabinet at 110 °C for 12 h.

2.4. Device fabrication

A TiOPc sub-micron wire was first synthesized on the silicon dioxide using the above solution process and dried. Then a sample mesh (used for TEM bearing samples, 500 meshes) was used as the shadow mask to evaporate the Al source and drain electrode, defining the channel length of 16 μm and channel width of 500 nm. The sample mesh was stuck firmly on the substrate by high temperature tape and could not move during the deposition. The single TiOPc sub-micron wire served as the active layer.

2.5. Measurement

The optical graph was obtained with a Leica DM2500M, the XRD and the UV–vis absorption spectrum were measured by an X-ray analytical instrument (Rigaku Corporation, 18KW, D/ MAX2500V+/PC) and a UV spectrophotometer (Hitahi Corporation, U-3990H), respectively. All the samples were placed on a cryogenic probe station (Lakeshore Company) and measured by a semiconductor parameter analyzer (Alight technology 4155C) to gain the electronic characteristics.

3. Results and discussion

As illustrated in Fig. 1(a), the dish-in-dish setup was designed to confine the synthesis of ultralong TiOPc sub-micron wires inside a finite space. The heavily doped n-type silicon wafer with 300 nm thick SiO_2 acted as the substrate for the self-assembly of TiOPc wires. The substrate with an alcohol solution the TiOPc precursor dropped on was placed onto a small petri dish. Afterwards, the small petri dish was put into a larger petri dish, which was filled with appropriate alcohol to provide a solvent vapor atmosphere. Finally, the system was held at atmospheric temperature (21 °C) for 48 h and TiOPc nanoparticles were self-assembled into ultralong sub-micron wires on the substrate. During the process of self-assembly, the hydrogen from the O–H bond of the alcoholic solvent combined with the oxygen from TiOPc to form a new kind of OH bond. This OH bond can promote the attraction between TiOPc molecules, which is favorable for the formation of ultralong TiOPc wires.

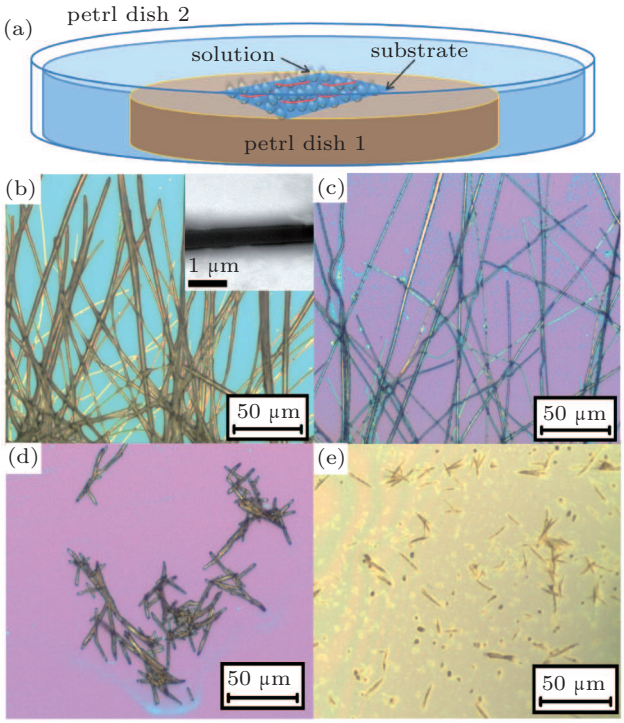


Fig. 1. (color online) (a) Schematic diagram of the static relative position of substrate and two different petri dishes. Optical micrographs of TiOPc sub-micron wires fabricated by using four different solvents: (b) alcohol, (c) methanol, (d) acetone, (e) n-hexane. Inset in panel (b) shows TEM morphology of a single TiOPc sub-micron wire.

It is well documented that the solvent polarity plays a crucial role in the self-assembly process.[19] In the present work, the effect of different solvents on the formation of TiOPc sub-micron wires was studied. Figure 1 shows the optical micrographs of TiOPc sub-micron wires prepared with different solvents. When alcohol was used as the solvent, TiOPc wires as long as 1 mm were observed (Fig. 1(b)). A close examination revealed that these wires were about 500 nm–2 μm in width (inset of Fig. 1(b)). So the aspect ratio of the wires could reach

2000. When methanol was used, the length of the wires was almost the same, however, the width was decreased (Fig. 1(c)). In the case of acetone, the length of TiOPc wires was reduced to only 30 μm (Fig. 1(d)). When n-hexane was used, a few wires with the length of about 15 μm were observed. It is obvious that alcoholic solvents are favorable for achieving long TiOPc wires.

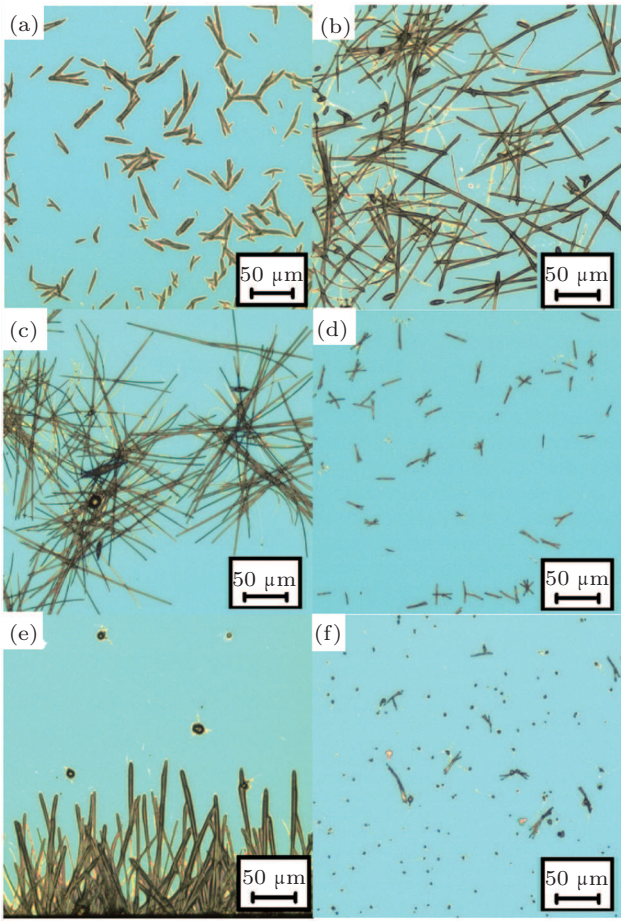


Fig. 2. (color online) Optical micrographs of TiOPc sub-micron wires fabricated from 0.45 mg·mL^{-1} solution (TiOPc/alcohol) exposed at different volumes of alcohol solvent: (a) 0 mL; (b) 5 mL; (c) 10 mL; (d) 15 mL; (e) 20 mL; (f) 25 mL.

Since alcohol is non-toxic and accessible, herein we chose alcohol as the solvent and changed its volume to modulate the solvent vapor pressure with the other experimental parameters unchanged. Figure 2 shows the optical micrographs of the samples prepared with different volumes of alcohol solvent. As can be seen, without alcohol (0 mL), there were a few wires with 40 μm in length scattered on the substrate (Fig. 2(a)). When the alcohol volume was increased to 5 mL, submicron wires about 80 μm long were observed (Fig. 2(b)). When the alcohol volume was further increased to 10 mL, 200–250 μm wires were obtained. With the alcohol volume further increased to more than 15 mL, the cases were apparently changed. For the alcohol volume of 15 mL, there were only a few short wires with about 30 μm in length on the surface of the Si/SiO_2 substrate (Fig. 2(d)). When 20 mL alcohol was used, some 150 μm long wires were found to self-assemble just on the edge of the substrate (Fig. 2(e)). When the alcohol volume was increased up to 25 mL, a few short wires and many particles were observed on the surface of the Si/SiO_2 substrate (Fig. 2(f)). Having these experimental results in mind and considering that the volume of the petri dish with 120 mm in diameter is 250 mL, we can conclude that a small volume of solvent (below 4% of the volume of the 120 mm petri dish) in a big petri dish is favorable for inducing the self-assembly structure. It is because a small volume of solvent forms a relatively lower solvent vapor pressure, which could improve the π–π stacking of the TiOPc units during the volatilization process. So the TiOPc units can self-assemble sufficiently and form the general morphology of TiOPc micron-wires. When a large volume of solvent (over 4% of the volume of the 120 mm petri dish) is used, the evaporation rate of the TiOPc solution is slowed down, which then decreases the growth rate of the TiOPc unit and thus reduces the yield of the wires. Therefore, we believe that the solvent vapor pressure, which is closely related to the solvent volume, can affect the formation of TiOPc sub-micron wires during volatilization.

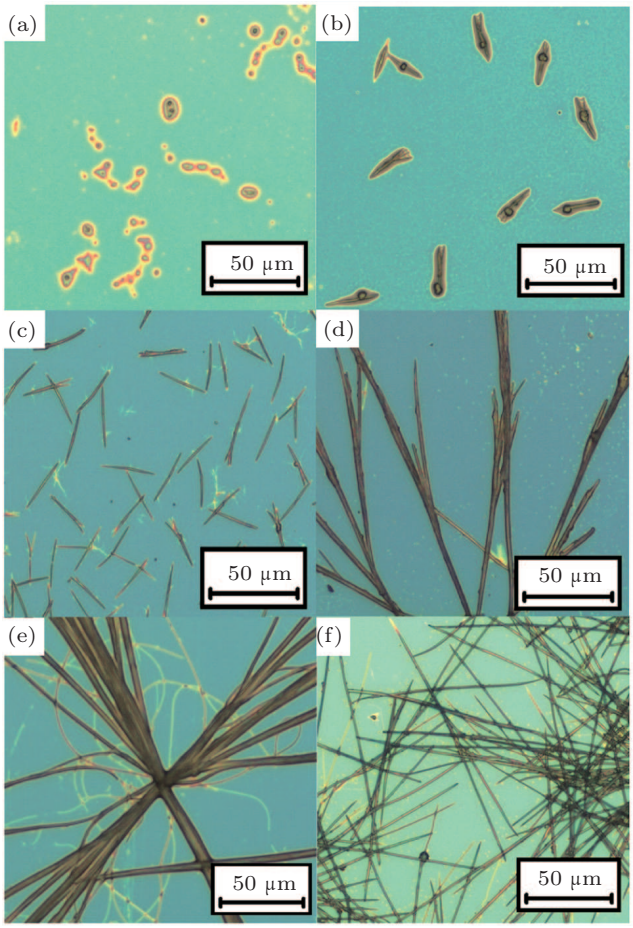


Fig. 3. (color online) Optical micrographs of TiOPc sub-micron wires fabricated from solutions (TiOPc/alcohol) of different mass concentrations: (a) 0.15 mg·mL^{-1}; (b) 0.3 mg·mL^{-1}; (c) 0.45 mg·mL^{-1}; (d) 0.6 mg·mL^{-1}; (e) 0.75 mg·mL^{-1}; (f) 0.9 mg·mL^{-1}.

It is well known that the solute concentration is crucial for the nucleation of solid materials in solution chemistry. To understand the effects of the mass concentration on the length of the TiOPc wire, we performed a series of comparative experiments. We changed the mass concentration of TiOPc in alcohol solvent and made the other experimental parameters unchanged. For a low mass concentration of 0.15 mg·mL^{-1}, TiOPc particles were aligned closely in line and no wires were observed (Fig. 3(a)). With the mass concentration increased to 0.3 mg·mL^{-1} and 0.45 mg·mL^{-1}, sub-micron TiOPc wires 20 μm and 50 μm in length were observed, respectively (Figs. 3(b) and 3(c)). When the mass concentration was further increased to 0.6 mg·mL^{-1}, the length of the sub-micron TiOPc wires increased to 250 μm and the aspect ratio of the wires exceeded 300 (Fig. 3(d)). Some individual wires were twisted with each other and formed a broom-like structure. Excitingly, it is possible to fabricate TiOPc sub-micron wire devices, which was never accessible previously. With the mass concentration increased to 0.75 mg·mL^{-1}, some star-like sub-micron wires appeared (Fig. 3(e)). When the mass concentration was increased up to 0.9 mg·mL^{-1}, the broom-like or star-like sub-micron wires disappeared and there were only some individual 200 μm long wires accumulated together (Fig. 3(f)). From the above results, it is confirmed that the mass concentration has a great influence on the length of the TiOPc wire. The mass concentration of 0.75 mg·mL^{-1} seems to be an optimized one for the growth of TiOPc wires since several shape-like aggregates can be obtained.

Based on the above experimental results and the SEM observation results (Figs. 4(b)–4(e)), we propose a possible self-assembly mechanism for the TiOPc wires. Figure 4(a) shows the schematic diagram of evolution of different shaped TiOPc aggregates. At 0.75 mg·mL^{-1}, accumulating TiOPc wires appear on some areas of the substrate. The wires are very uniform with a length of almost 60 μm (Fig. 4(b)). Besides, some Y-shaped aggregates are also observed (Fig. 4(c)). We find that each Y-shaped aggregate has a dot, which can be called the original dot (OD) as indicated by red circles 1 and 2. So we can assume that if the TiOPc particles are small enough and distributed uniformly on the substrate, one TiOPc unit serves as the OD, from which the other particles begin to self-assemble and one single wire appears (Fig. 4(a-1)). A Y-shape aggregate (Fig. 4(a-2)) appears when the OD is on an individual wire 1, then wire 2 grows in a different direction. If several wires share the same OD, we can observe a star-shape aggregate (Fig. 4(a-3)). Obviously, if some TiOPc particles germinate from the tops of a star-shape aggregate, a broom-shaped aggregate is obtained finally. The tops will then turn into the heads of the broom-shaped aggregate and the bottom will become the tail. The results of our experiments are quite consistent with the above theory, as shown in Figs. 4(c) and 4(d). A zoom-out photon of one head (Fig. 4(e)) shows that it contains lots of Y-shape structures.

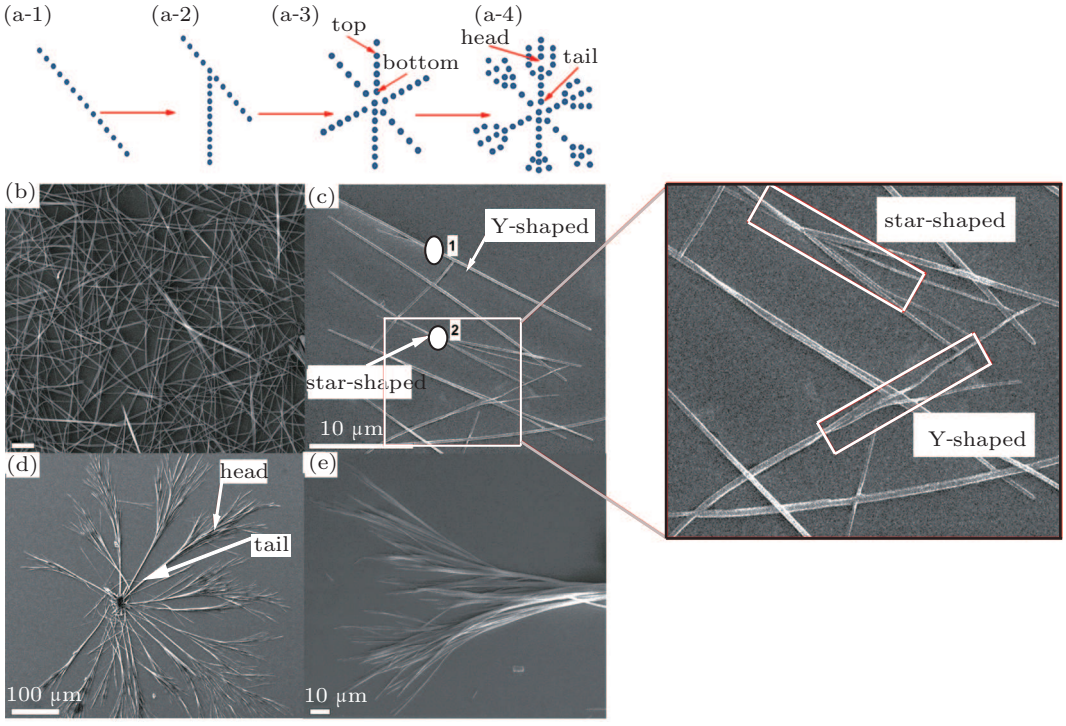


Fig. 4. (color online) (a) Schematic diagram of evolution of different shape-like TiOPc aggregates; SEM images of different shapes of TiOPc sub-micron wires obtained at 0.75 mg·mL^{-1}: (b) accumulation of a large number of individual TiOPc wires; (c) Y-shaped aggregate and star-shaped aggregate; (d) broom-shaped aggregate; (e) zoom out of the head of a broom-like aggregate.

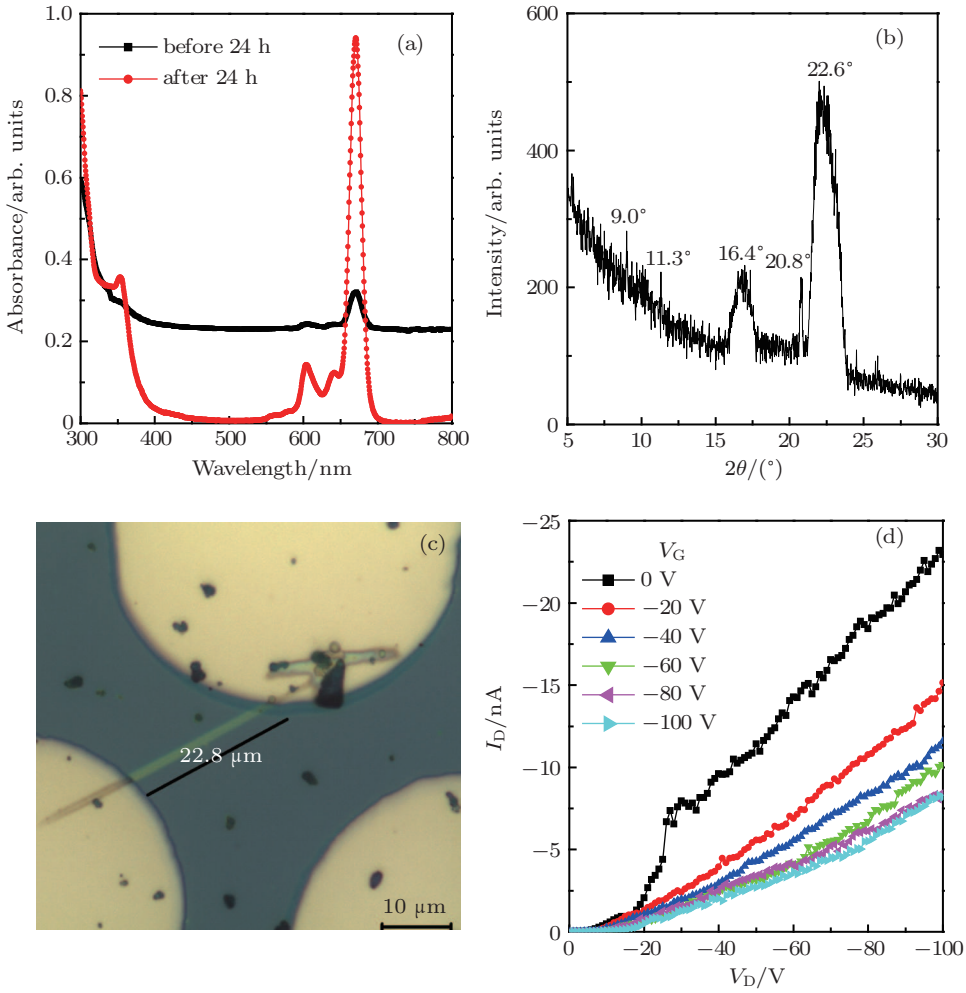


Fig. 5. (color online) (a) UV–vis absorption spectra of filtrate of TiOPc suspended in alcohol (0.75 mg·mL^{-1}) for different times; (b) X-ray diffraction pattern of TiOPc sub-micron wires; (c) optical picture of a bottom-contact TiOPc sub-micron wire transistor; (d) electronic characteristic of the single TiOPc sub-micron wire device.

To study the phase composition of TiOPc sub-micron wires, UV–vis absorption spectrum and XRD analyses were performed. Figure 5(a) shows the UV–vis absorption spectra of the filtrate of TiOPc after being suspended in alcohol (0.75 mg·mL^{-1}) for different times. It is seen that, for the sample being suspended in alcohol for less than 24 h, there are two characteristic bands, which are located at the regions of 300-400 nm and 650–700 nm, respectively. The former is known as the Soret band and the latter is the Q band.[20] The spectrum is similar to that of TiOPc dispersed in chloronaphthalene[21] and the electronic absorption spectrum of PcH2 in solution.[20] Comparatively, for the sample being suspended for more than 24 h, the relative intensity of the peak at 670 nm increases greatly and new peaks appear at around 354 nm and 640 nm. The peaks at 354 nm and 670 nm are both ascribed to the π–π^* transitions from a_{1u} to e_g and from a_{2u} to e_g,[22] and the peak at 640 nm is attributed to the α phase of the TiOPc wires.[23] Figure 5(b) shows the XRD pattern of the TiOPc wire. It is found that there are two major peaks appearing at $2\theta = 16.4°$ and 22.6°, which are attributed to the diffraction peaks of (1-11) and (21-2) faces of the α phase,[17] respectively. The diffraction peaks at 23.9° and 20.8° can be indexed to be the β phase.[24] The result clearly indicates that the TiOPc wire is mixed-phase instead of single-phase, which is totally different from those reported previously[17] where an amorphous-like diffractogram for TiOPc was found.

Thanks to the ultra-long length of the TiOPc sub-micron wire, single TiOPc wire devices were successfully fabricated. Figure 5(c) shows the optical picture of a bottom-contact TiOPc sub-micron wire transistor. The device exhibited a depletion mode in which the drain current decreased with the increase of the gate voltage, as shown in Fig. 5(d). This is possible because the intrinsic charges in TiOPc wires can be depleted by applying a negative voltage. Further optimization of the OTFT is in progress. The electric signal response has clearly indicated that the TiOPc wires can be used to fabricate organic electric devices.

4. Conclusion

A novel solution-based self-assembly method has been demonstrated to prepare TiOPc sub-micron wires with lengths

up to 1 mm. By a comparative study, the alcohol solvent was found to be the most favorable solvent for the synthesis of TiOPc wires. The length of sub-micron wires could be easily tuned by the solvent vapor pressure and the mass concentration. UV–vis absorption spectra and XRD data showed that the ultralong TiOPc sub-micron wire is a mixture of α phase and β phase. The electric characteristics of an OTFT based on a single TiOPc sub-micron wire showed that a depletion mode can be achieved, and further optimization is in progress. Our synthetic strategy represents a versatile alternative for the preparation of organic semiconductor microstructures and should be applicable to other metal phthalocyanines.

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