Int. J. Electrochem. Sci., 8 **(2013)** 8623 - 8631

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Phthalocyanine Nanoribbons Fabricated by Template-Free Electrophoretic Deposition

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Received: 30 March 2013 / *Accepted:* 9 May 2013 / *Published:* 1 June 2013

A simple method of constructing organic phthalocyanine nanoribbons by template-free electrophoretic deposition is provided. Copper phthalocyanine molecules in low protonation degree driven under electric field enable the intermolecular ordered assembling at the approaching electrode surface which is proven by the formation of their one dimensional structures at the surface of anode aluminum oxide template electrode. Similar results are also obtained using electrode with different surface morphology which supports the proposed mechanism. This method could be applied to the same type of phthalocyanine molecules. Such studies provide possible venues for achieving controllable molecular assembling structures.

Keywords: Phthalocyanine; nanoribbon; template-free electrophoretic deposition

1. INTRODUCTION

Phthalocyanines are compounds with great potential for serving as components of molecular materials that possess unique electronic [1] and optical properties [2,3]. A specific interaction between phthalocyanine molecules is highly required in order to express their function to a maximal level and for this reason it is important to construct arrays in which phthalocyanine molecules are organized in well-defined geometries with respect to their neighbors [4,5]. The ordered phthalocyanine assemblies can be commonly controlled by evaporation processes and accompanied annealing process using vacuum deposition method [6-8].

On the other hand, solution-processible methods [9-13] have demonstrated technological importance in preparing organic semiconductor structures at room temperatures, which makes them desirable for achieving low-cost, large-area integrated electronic devices on flexible substrates. Among many organic species studied for device applications, copper phthalocyanine (CuPc) is known to have, however, poor solubility in commonly used solvents. Trifluoroacetic acid (TFA), as one of solution-processible procedures, has been used to protonate the meso-bridging aza nitrogen atoms of CuPc which enables directional movement of the molecules to negative electrode under direct current (DC) electric field [14]. Based on this method organic thin film of CuPc molecules was fabricated by electrophoretic deposition (EPD) [14,15]. Furthermore, the combination of anode aluminum oxide (AAO) template and EPD technique made CuPc capable of deposition in the one dimensional (1D) pore channel of AAO template [2].

Template-free fabrication of one dimensional structures of CuPc molecules by EPD could be a promising method to achieve controllable organization of this kind of molecular materials into highly ordered low dimensional assembling structures using less complicated processing procedures. In the paper presented here TFA was found to play a key role in tuning the intermolecular ordered assembling of CuPc at the approaching electrode surface. CuPc molecules in low protonation degree driven under electric field enable the intermolecular ordered assembling at the approaching electrode surface which is proven by the formation of their one dimensional structures at the surface of AAO template electrode. Similar results are also obtained using electrode with different surface morphology which supports the proposed mechanism. The 1D structures of same type of unsubstituted phthalocyanine molecules are achieved by this method as well.

2. EXPERIMENTS

2.1 Materials

29H, 31H-phthalocyanine (Pc) and CuPc were purchased from Sigma-Aldrich. Chloroform ($CHCl_3$) and TFA were analytical grades without further purification before use. AAO template was purchased from Whatman Int. Ltd. Two kinds of EPD equipments were constructed as follows: (I) AAO template (deposition of gold film on one side) or (II) indium tin oxide (ITO) coated glass plate served as negative electrode and platinum plate served as positive electrode; the distance between electrodes was kept at 1.0 cm. The detailed structures for cells used in the electrophoretic deposition were given in Fig. S1 of supplementary materials. The cell diameter was 0.6 cm for (a) and 3.0 cm for (b), respectively.

2.2 Preparation of phthalocyanine ribbons

Excessive CuPc powder was dissolved in TFA / $CHCl_3$ mixed solution (the ratio of TFA / $CHCl_3$, 10 μL / 1.5 mL). The solution was ultrasoniced for 30 min and then centrifuged for 10 min. CuPc solution of 10^{-4} M was obtained by discarding unsolved CuPc powder. Solution with different ratio of TFA / $CHCl_3$ was prepared by adding an amount of TFA into as-prepared 10^{-4} M CuPc solution. A 2 mL solution (the ratio of TFA / $CHCl_3$, 20 μL / 1.5 mL) was used for the equipment (I) and a 40 mL solution for the equipment (II). The direct current (DC) voltage applied between electrodes for both equipments was ranged from 0.5 to 30 V in order to optimize the deposition condition. Control experiment with high ratio of TFA / $CHCl_3$ (300 μL / 1.5 mL) was performed with the equipment (I). The identical procedures were also carried out for Pc assemblies. A 40 mL Pc solution (ratio of TFA / $CHCl_3$, 20 μL / 1.5 mL) was used for the equipment (II).

2.3 Measurements

Absorption properties were measured with Perkin Elmer Lambda 950 UV-vis spectrometer. A Hitachi S-4800 field emission scanning electron microscope (SEM) was employed to depict the morphology of phthalocyanine assembling structures. X-ray diffraction (XRD) analysis was carried out on a Rigaku D/Max-2500 using filtered Cu K_α radiation.

3. RESULTS AND DISCUSSION

Two factors, the ratio of TFA / $CHCl_3$ and the voltage applied between electrodes at fixed distance, contribute together to the final deposition morphology of charged phthalocyanines. An interesting observation is that CuPc ribbons could be formed at the surface of AAO template at relatively low ratio of TFA / $CHCl_3$ (20 μL / 1.5 mL) and low applied voltage. Fig. 1 demonstrates the effect of varying voltages on CuPc assemblies at the surface of AAO template at fixed low ratio of TFA / $CHCl_3$ (20 μL / 1.5 mL). In contrast to the common expected behavior, CuPc molecules are not filling into the pores of AAO template but accumulated and assembled into 1D structure on top of the template. At the low voltage of 0.5 V a few scattered short thin CuPc nanoribbons appear at the surface of AAO template (Fig. 1a). Much more grown-up nanoribbons distribute at the surface of AAO template as the voltage is increased to 5 V (Fig. 1b). At the up to 30 V voltages individual nanoribbons are observed to conglomerate into large particles above the pores (Fig. 1c). According to the deposition results at different voltages the optimized condition of 5 V for 1 h is chosen to obtain CuPc nanoribbons which distribute uniformly on top of AAO template (Fig. 2a). From the magnified SEM image flatten 1D assembling structures are distinctly discerned with average length of 4.0 μm and width of 100 nm (Fig. 2b) In addition, the SEM observation of inner AAO template is to further confirm that the 1D CuPc assemblies are not grown from the inside pores of AAO template but formed above them (Fig. S2). While at the high ratio of TFA / $CHCl_3$ (300 μL / 1.5 mL) the pores of AAO template are just filled with CuPc molecules like the reported results [2], and if the AAO template removed only amorphous film is obtained. The observation indicates that the concentration of TFA is a crucial parameter for the formation of CuPc ribbon structures.

It is known that CuPc molecule has four meso-bridging aza nitrogen atoms which could be partial protonated depending on $[H^+]$ of solution. The UV-vis spectroscopy experiment of CuPc in TFA / $CHCl_3$ mixed solution is carried out to investigate the role of $[H^+]$ in the electrophoretic deposition process. The absorbance of CuPc solution between 320 – 800 nm is recorded with increased concentration of TFA ranging from 0.043 to 2.7 M (Fig. 3). Each curve is normalized respect to the absorption at the wavelength of maximum absorbance (λ_{max}) for the convenience of comparison. The peak values of CuPc absorption at 320 nm and 600 – 700 nm (Q band) decrease gradually with increased concentration of TFA and simultaneously red-shift of the peak positions occurs. A prominent red-shift of 20 nm at λ_{max} is observed as the concentration of TFA is increased to 0.81 M, which is indicative of acceptance of H^+ ion by more meso-bridging aza nitrogen atoms of CuPc molecules. The concentration of TFA used for fabrication of CuPc ribbon structures is 0.086 M far below the prominent red-shift level. CuPc molecules in solution should exist in low protonation degree (+1) which suggests that CuPc molecules with low charge number play a key role in the electrophoretic deposition of 1D assembling structure. By contrast, previously reported results [14,15] showed that the TFA concentration was far above the prominent red-shift level which resulted in CuPc with high charge number (+2 and above).

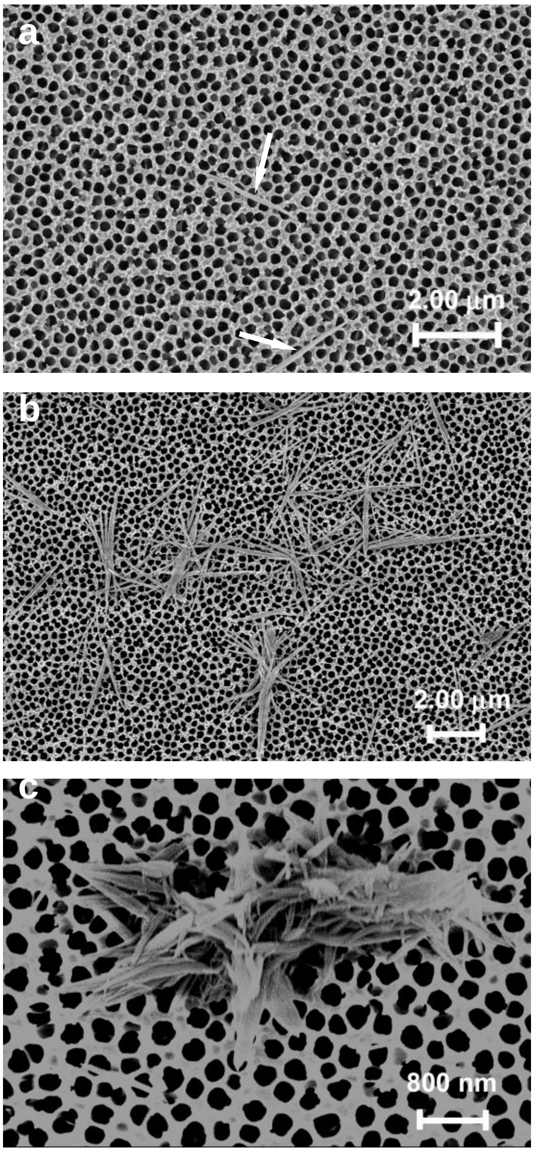

Figure 1. Formation of CuPc nanoribbons at the surface of AAO template with 200 nm pore diameter at applied voltages of (a) 0.5 V, (b) 5 V and (c) 30 V, respectively.

The mechanism for the growth of CuPc nanoribbons is proposed according to the data collected from EPD and UV-vis experiments (Fig. 4). The deposition process could proceed in two states based on the charge number of CuPc. CuPc with high charge number is controlled mainly by the electric force and migrates quickly to negative electrode. The intermolecular force in the course of migration should be minor on this condition. As a result the molecules on the electrode lack highly ordered stacking and exist in polycrystalline or amorphous form. As to CuPc with low charge number, electric force as well as intermolecular force function together to promote the formation of 1D CuPc ribbons. In this state CuPc molecules move along the direction to negative electrode in a low rate. The intermolecular force becomes prominent when CuPc molecules approach the electrode surface because the probability of collision between enriched CuPc molecules near the negative electrode could be remarkably enhanced. It is this kind of intermolecular force that leads to the nucleation and growth of CuPc molecules via π-π interaction and van der Waals force in the vicinity of electrode surface.

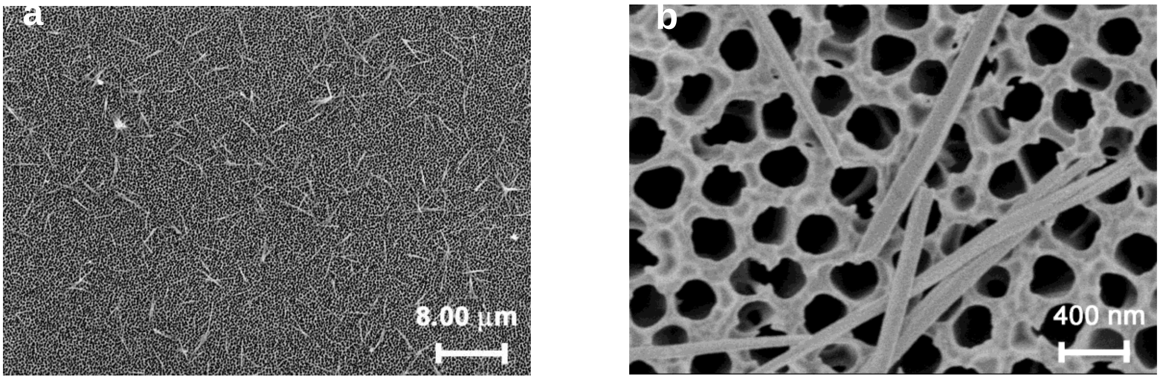

Figure 2. (a) CuPc nanoribbons deposited on AAO template with 200 nm pore diameter under optimized condition of 5 V for 1 h. (b): Magnified part of (a).

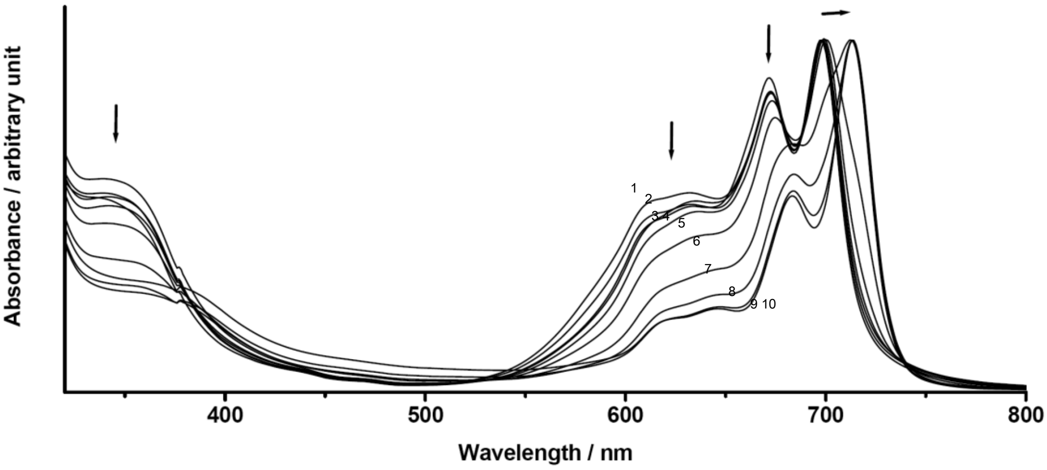

Figure 3. UV-vis absorbance of CuPc in $CHCl_3$ with increased concentration of TFA ranging from 0.043 (1), 0.065 (2), 0.086 (3), 0.13 (4), 0.21 (5), 0.42 (6), 0.81 (7), 1.2 (8), 1.9 (9) to 2.7 M (10).

Therefore adjusting the concentration of TFA would greatly influence the electric force of CuPc molecules suffered and further the time needed to grow. At low concentration of TFA there is enough time to permit the construction of CuPc nanoribbons due to the slow mobility while at high concentration the molecules already arrive at the electrode before their self-assembly

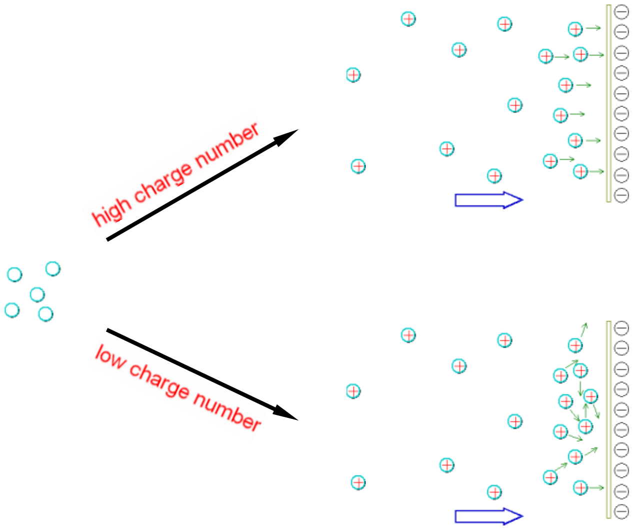

Figure 4. Schematic representation of electrophoretic deposition of CuPc molecules with two different charge numbers on negative electrode.

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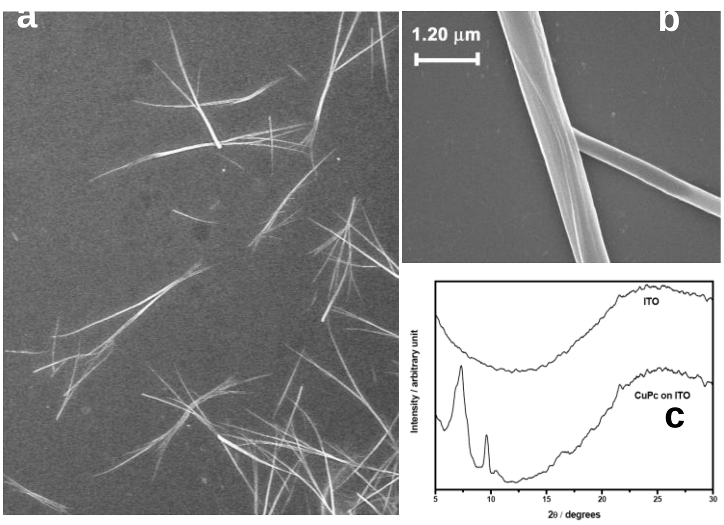

Figure 5. CuPc ribbons with branches deposited on ITO coated glass plate at 5 V for 3 h (a, b). X-ray diffraction of CuPc ribbons deposited on ITO coated glass plate (c).

Based on the above analysis one can infer that 1D CuPc structure should also be able to grow on other types of electrodes irrespective of the electrode morphology. Similar to the procedures using AAO template as negative electrode, the ITO coated glass plate is chosen as negative electrode to verify the effect. The solution volume used in the electrophoretic deposition is 40 mL, 20 times larger than that in the AAO template experiments. From the SEM images the branched CuPc ribbons with average length of 50 μm and width of 600 nm are also successfully constructed at the surface of ITO coated glass plate at 5 V for 3 h (Fig. 5a). The magnified image (Fig. 5b) displays flatten 1D structure resembling that on AAO template. The defect in the CuPc ribbon suggests layered growth mode. The branches of CuPc ribbons are formed probably because of stacking dislocation after long time deposition. X-ray diffraction analysis (d=1.2, 0.9 nm, Fig. 5c) showed □ crystallization of CuPc ribbons at ITO electrode surface. The evidence on ITO coated glass does support the mechanism of 1D CuPc structure formation.

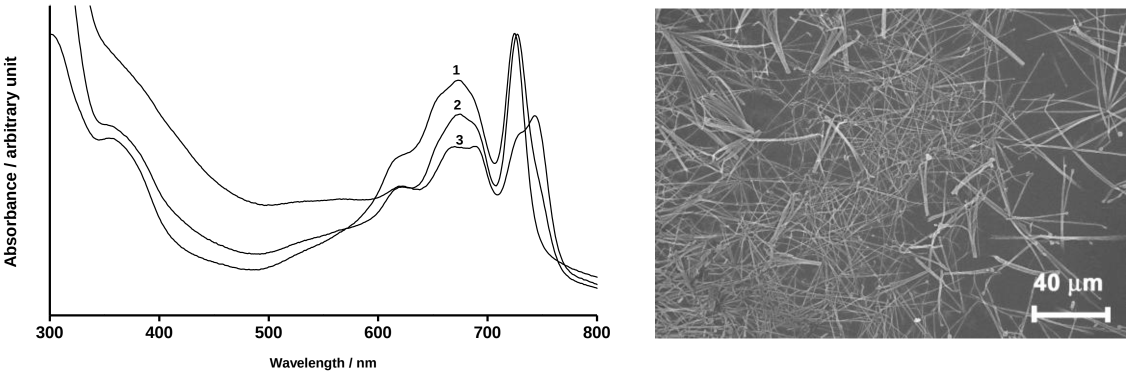

Figure 6. (a): UV-vis absorbance of Pc in $CHCl_3$ with increased concentration of TFA ranging from 0.086 (1), 0.85 (2) to 2.76 M (3). (b): Pc ribbons deposited on ITO coated glass plate on the condition resembling that in CuPc deposition experiment.

This method could also be applied to the same type of unsubstituted phthalocyanines to construct 1D structure due to the structure similarity. 29H, 31H-phthalocyanine (Pc) is used as another example to fabricate 1D structure on ITO electrode by template-free EPD method. Before the electrophoretic deposition the absorption spectroscopy of Pc with increased concentration of TFA is recorded (Fig. 6a). The red-shift of Q band (650-750 nm) of Pc occurs as $[H^+]$ is increased. At higher $[H^+]$ (3 in Fig. 6a) the Q band is split due to the decreased symmetry induced by the coordination of protons to the aza nitrogen atoms [16]. The condition in low protonation degree (1 in Fig. 6a) is chosen to succeed in constructing Pc ribbons on ITO coated glass plate. The results shown in Fig. 6b confirm that controlling the concentration of TFA should be a general method to form 1D structure for this kind of molecular materials via template-free EPD method.

4. CONCLUSIONS

Nanoribbons of unsubstituted phthalocyanines could be constructed by template-free EPD method. Phthalocyanine molecules with low charge number driven under electric field permit the intermolecular ordered stacking before their reaching electrode surface. This method could be applied to the same type of phthalocyanines. Such efforts provide possible venues for controlled organization of molecular materials into low dimensional assembling structures.

ACKNOWLEDGEMENTS
Financial support from the National Science Foundation of China (No. 21171040) and Anhui Province Office of Education (No. KJ2011B123， No. 2011SQRL101) is gratefully acknowledged.

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SUPPLEMENTARY MATERIALS

The detailed structures for cells used in the electrophoretic deposition were given in Fig. S1. The cell diameter was 0.6 cm for (a) and 3.0 cm for (b), respectively. The SEM observation of inner AAO template (Fig. S2) proved that the 1D CuPc assemblies were not grown from the inside pore channels of AAO template but formed above them. The image in Fig. S3 showed the branched structures of CuPc ribbons on ITO electrode surface.

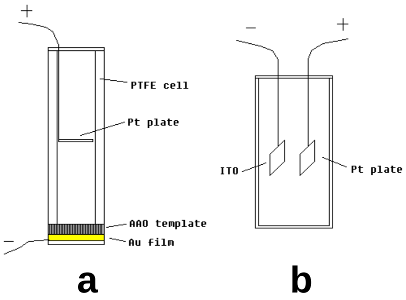

Figure S1. The structures of two kinds of cells used in the EPD. (a) The cell using AAO template as negative electrode and (b) the cell using ITO coated glass plate as negative electrode.

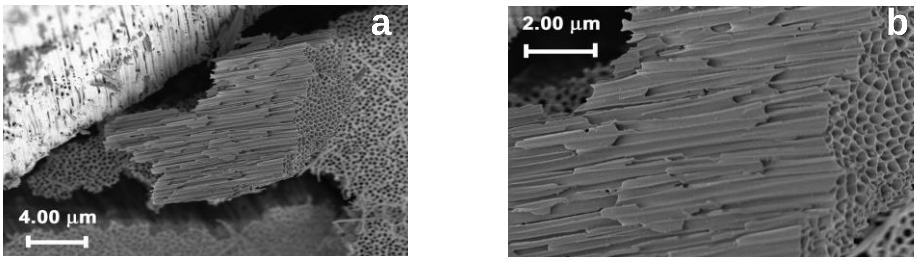

Figure S2. The inner pore channels of AAO template with CuPc nanoribbons at the surface.

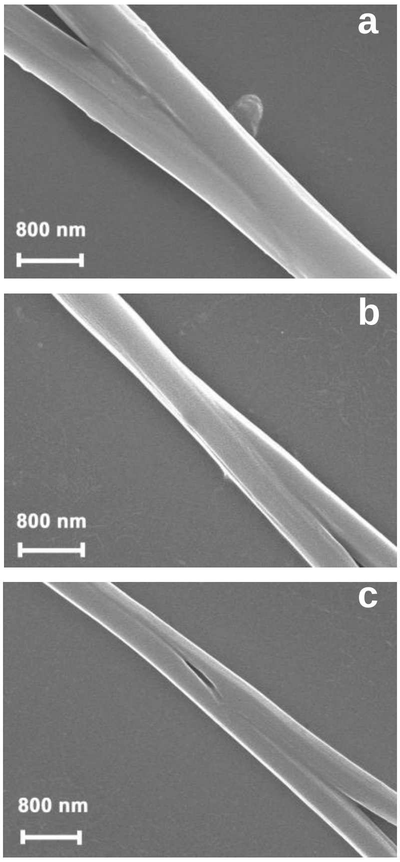

Figure S3. The branched structures of CuPc ribbons deposited on ITO coated glass plate at 5 V for 3h.