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Ionic liquid-assisted synthesis of ultralong nanowires of zinc octaethylporphyrin and its photoresponse

Ying Lu,[a, b] **Feng-Xia Wang,**[a] **Bo Yang**[a] , **Qing-Guo Zhang**[b] **and Ge-Bo Pan***[a]

Ultralong zinc octaethylporphyrin (ZnOEP) nanowires were successfully prepared by a facile solution-phase precipitative method and fully characterized. Specifically, ionic liquids (ILs) were employed, for the first time, as a"poor" solvent and chloroform as a "good" solvent of ZnOEP. Furthermore, the influence of the type of ILs, the volume ratio of chloroform/ILs, and the concentration of ZnOEP on the growth of nanowires were investigated. The results indicated that the as-obtained
10 **nanowires are ultralong, highly pure, and single crystalline. Both anions and cations of ILs were found to play important roles in the final morphology and aspect ratio of nanowires. In addition, the as-obtained ZnOEPnanowires were directly used for the construction of prototype photodetector and exhibited excellent performance. This advance might pave the green way for preparing nano/micro structures of organic small-molecular materials.**

Instructions

15 Functional nanomaterials made of small molecules, in particular one-dimensional (1D) ones, are of great potential use as building blocks of highly integrated miniaturized devices.[1-4] Porphyrin and its derivatives have been ideal building blocks for organic nanomaterials.[5,6] Zinc octaethylporphyrin (ZnOEP) represents
20 one of the most important metal porphyrins and is widely used in electronics and light-harvesting systems.[6-8] Moreover, ZnOEP can self-assemble into 1D nanostructures through intermolecular π-π interactions by either vapor or liquid phase methods. For instance, ZnOEP nanorods were grown by the vapor deposition
25 method, which consumes a large amount of materials and energies.[7] ZnOEP nanowires were produced via an evaporation method.[8] However, the above method is generally not suitable for large-scale production of nanowires. This drawback can be alleviated by using a solution-phase precipitative method, in
30 which a poor solvent with low solubility is simply added into a good solvent with high solubility containing targeted compounds. However, the use of high polar poor solvent of water led to a fast precipitation of ZnOEP, resulting in short nanorods.[5] It remains a challenge to set a combination of good and poor solvents to
35 fabricate the long nanowires. Note that the ultralong nanowires are highly desired in the high performance optic-electronic devices.

On the other hand, ionic liquids (ILs) composed of organic cations and organic or inorganic anions have been applied in
40 many fields due to their unusual properties.[9] Comparing to water and conventional organic solvents, they exhibit distinctive characteristics, such as almost zero pressure of saturated vapor, low flammability, excellent solvating power for organic and inorganic compounds, and adjustable structure.[10] To date, ILs
45 have been extensively used in the synthetic organic chemistry, biocatalysis, separation, and electrochemistry.[11-14] Moreover, ILs

are benign reaction media for the preparation of the inorganic nanomaterials with controllable size and morphology.[15-18] In contrast to their inorganic counterparts, to the best of our
50 knowledge, no report has described the application of ILs in controlled preparation of functional organic nanomaterials.

Herein, we report the synthesis of ZnOEP nanowires by a facile solution-phase precipitative method, in which ILs are used, for the first time, as a "poor" solvent and chloroform is as a "good"
55 solvent of ZnOEP. The influence of the type of ILs, the volume ratio of chloroform/ILs, and the concentration of ZnOEP on the formation of ZnOEP nanowires are systematically investigated. Moreover, the as-fabricated ZnOEP nanowires are directly constructed of prototype photodetector and exhibited excellent
60 performance.

Experimental sections

Chemicals. ZnOEP powder and chloroform were purchased from Aldrich and Sinopharm Chemical Reagent Co., Ltd., respectively. 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF4),
65 N-butyl-3-metylpyridinium tetrafluoroborate ([BM₃Py]BF4), N-butylpyridinium tetrafluoroborate ([Bpy]BF4), 1-butyl-3-methylimidazolium nitrate ([BMIM]NO3), 1-butyl-3-methylimidazolium bis((trifluoromethyl) sulfonyl)imide ([BMIM]NTF2) and 1-butyl-3-methylimidazolium
70 dibutylphosphate([BMIM](C4H9O)2PO2) were purchased from Shanghai Chengjie Chemical Co., Ltd. All the chemicals were used as received.

Synthesis. In a typical synthesis, a chloroform solution containing ZnOEP (1mg/ml, 100μl) was injected to [BMIM]BF4
75 ionic liquid (1mL). The mixture solution was stored at room temperaturefor 24 hours. The final products were centrifuged and washed with the mixture solution of distilled water and methanol for several times. Similar procedure was applied for a series of

comparative experiments, in which the type of ILs, the volume ratio of chloroform/ILs, and the concentration of ZnOEP were varied independently.

Characterization. The products were characterized by X-ray diffraction pattern (XRD) with a Bruker D8 Advance powder X-ray diffractometer. The morphology and structure were examined on a Hitachi-S4800 scanning electron microscope (SEM) and a Tecnai G2 F20 S-Twin transmission electron microscope (TEM). Selected area electron diffraction (SAED) pattern was taken simultaneously on Tecnai G2 F20 S-TEM. For SEM and TEM measurement, a drop of methanol solution with the dispersed ZnOEP nanowires was casted onto a piece of silicon and a carbon-coated Cu grid, respectively. The solvent was allowed to evaporate at room temperature in air. Energy-dispersive X-ray spectrometry (EDX) analysis was performed on the Quanta 400 FEG SEM. Diffuse reflectance UV-vis absorption spectra were performed on a Perkin-Elmer Lambda 750 equipped with a 60 mm integrating sphere. Fourier transform infrared (FTIR) spectra were acquired with a Nicolet 760 FTIR spectrometer in a KBr pellet.

Devices. The interdigitated Au electrodes with 2 fingers (width 20 μm, length 200 μm and inter finger spacing 20 μm) were fabricated by photolithography and electron beam deposition of Au on SiO2/Si substrates. The pre-patterned electrodes were cleaned using acetone, ethanol and de-ionized water. The devices were fabricated by dropping 20 μL methanol with the dispersed ZnOEP nanowires onto pre-cleaned Au electrodes and dried by vacuum-annealing at 150 °C for 30 min. Typical current-voltage curves of the devices were recorded with Keithley 4200 SCS and RF Probe Station (PE-4RF) in a shielded box at room temperature. A Xenon lamp was used as the white light source with different intensity.

Results and discussion

It can be seen that the ultralong and uniform nanowires are formed (Fig. 1a and 1b). The average diameter of nanowires ranges from 200 to 400 nm, and the length is up to 300 μm. Fig. 1b shows a typical TEM image of a single nanowire, indicating that it is solid and has uniform diameter. The crystal structure of nanowires is investigated by XRD and SAED. All the diffraction peaks in the XRD pattern (Fig. 1c) can be well indexed as a triclinic lattice. The lattice constants are a=4.692Å, b=13.185Å, c=13.28Å, α=113.94°, β=91.177°, and γ=92.157°. These values are in good agreement with the literatures.[7] Moreover; the sharp diffraction peaks of nanowires show an ideal crystalline feature. The diffraction peaks of (011^{-1}) plane of nanowires are remarkably enhanced relative to those of the source powder of ZnOEP. These results indicate that the as-obtained nanowires are highly crystalline with a preferential orientation of the nanowires perpendicular to the (011^{-1}) plane. This is confirmed by the SAED pattern (the inset in Fig. 1b) of a single ZnOEP nanowire. Moreover, the SAED pattern is consistent throughout the whole nanowire, indicating the single-crystalline nature of the nanowires. In addition, the EDX spectrum (Fig. 1d) clearly indicates the existence of C, Zn and N elements in nanowires.
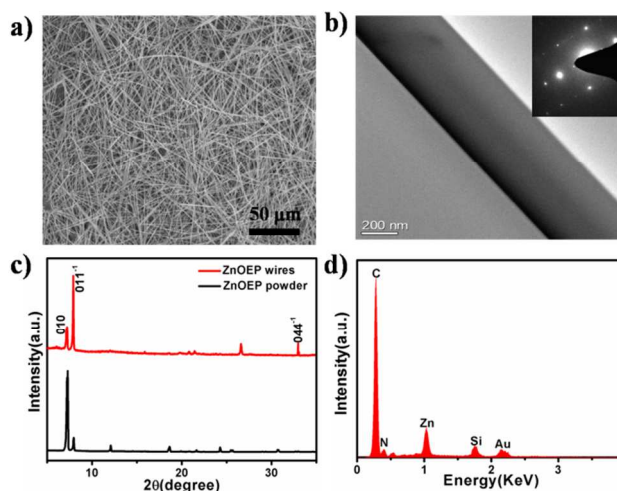

Fig.1 (a) SEM image of ZnOEP nanowires. (b) TEM image of a single ZnOEP nanowire. The inset is an SAED pattern recorded with a single ZnOEP nanowire. (c) XRD pattern of the nanowires and source powder of ZnOEP. (d) EDX spectrum of ZnOEP nanowire. The volume ratio of chloroform and [BMIM] BF4 was 1:10 for the synthesis of the ZnOEP nanowires.

The chemical composition of nanowires is analyzed by FT-IR (Fig. 2a). It is clear that the FT-IR spectrum of nanowires has the same feature as the source powder of ZnOEP. Four metal-sensitive IR characteristic bands of octaethylporphyrin are observed at 747, 910, 980 and 1214 cm^{-1}, implying that ZnOEP does not undergo decomposition or other chemical reactions during the IL-assisted synthesis. Fig. 2b shows typical UV-vis absorption spectra of nanowires deposited on quartz and ZnOEP monomer in chloroform solution. Similar to the monomers, the nanowires have three characteristic adsorption bands, labelled S, Q_1, and Q_2. It is noted that the bands of nanowires are broadened in comparison with the sharp peaks from the monomers. Moreover, the Q bands are red-shifted, whereas the S band is blue-shifted. This can be attributed to the highly ordered molecule-packing in ZnOEP nanowires.
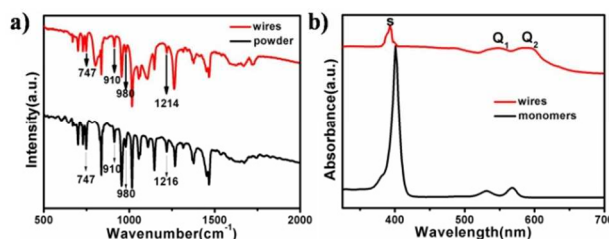

Fig. 2 (a) FTIR spectra of nanowires and source powder of ZnOEP. (b) UV-vis absorption spectra of ZnOEP nanowires on a quartz substrate and ZnOEP monomers in chloroform solution. The volume ratio of chloroform and [BMIM] BF4 was 1:10 for the synthesis of the ZnOEP nanowires.

The influence of the volume ratio of the chloroform solution and [BMIM]BF4 on the nanostructures of ZnOEP was investigated and shown in Fig. 3. It can be seen that the length of nanowire of ZnOEP increases with the decrease of the ratio. At the volume ratio of 1:1, the average length of nanowires is 50~80

μm, and the average diameter is 200~400 nm (Fig. 3a). Upon reducing the volume ratio to 1:5 and 1:10, the average length of nanowires reaches to ~300 μm, while the average diameter is about 0.5~1 μm at 1:5 (Fig. 3b) and 200~400 nm at 1:10 (Fig. 3c).
5 However, at the volume ratio of 1:20, these nanowires more easily cross-links together and the average diameter is about 1 μm (Fig. 3d). The above results demonstrate the volume ratio of chloroform solution and [BMIM]BF$_4$ effectively modulates the diameter and length of ZnOEP nanowires. In addition, the
10 influence of concentration on the growth of ZnOEP nanowires was also investigated. The results indicate that a lower or higher concentration (0.5 mg/ml or 2 mg/ml) did not lead to the growth of uniform ZnOEP nanowires.
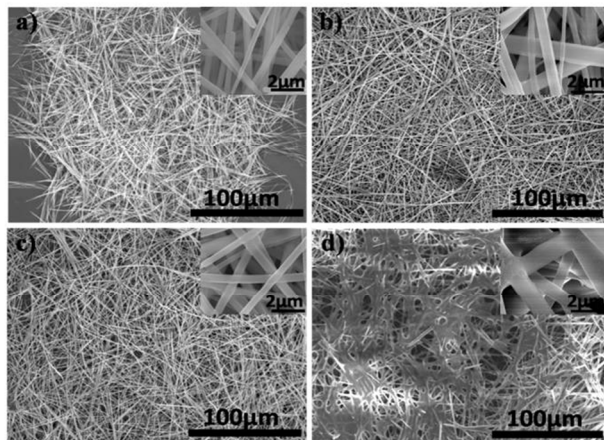

15 **Fig. 3** SEM images of ZnOEP nanowires obtained with different volume ratio of chloroform and [BMIM]BF$_4$: (a) 1:1, (b) 1:5, (c) 1:10and (d) 1:20. The insets are the SEM images of the corresponding samples at higher magnification.

Moreover, the influence of the type of ILs on the growth of
20 ZnOEP nanowires was investigated (Fig. 4 and Fig. 5). Fig. 4 shows a set of SEM images of ZnOEP nanowires formed in ILs with different alkyl length. It can be seen that the diameter and length of nanowires have hardly changed with the increase of alkyl length of ILs. As we know, the viscosity of ILs enhances
25 with the increase of the alkyl length. Above results indicate that the viscosity of ILs is not the main factor in the self-assembly process.[19] In addition, the effects of different cations in ILs on the nanostructures are investigated and shown in Fig. 5. It can be seen that nanowires are formed when [BPy]BF$_4$ and [BM$_3$Py]BF$_4$
30 are employed as a poor solvent. This indicated that the interaction between the ILs and ZnOEP molecular play an important roles in the self-assembly process of one-dimensional nanostructure.[20] Moreover, the average diameters of ZnOEP nanowires are 1~2 μm in above two ILs, which is much larger than those (200~400
35 nm) obtained in [BMIM]BF$_4$.These differences in the nanowires formed in ILs can be attributed to the different π-πinteraction and diffusion between the ILs and ZnOEP. The above observation implies that the cations of ILs play an important role in controlling nanowires morphology. On the other hand, only pink
40 solutions are obtained when [BMIM]NO$_3$, [BMIM]NTF$_2$ and [BMIM](C$_4$H$_9$O)$_2$PO$_2$ are employed as a poor solvent. This is mainly because ZnOEP has a larger solubility in these ionic liquids.
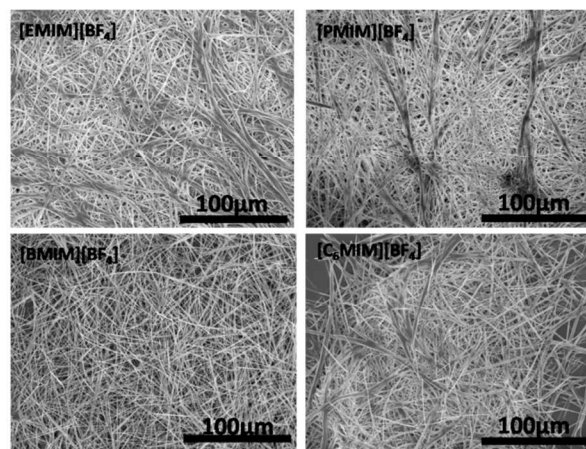

45 Fig. 4 SEM images of ZnOEP nanowires fabricated at different ILs with different alkyl length in [1-R-3-methylimidazolium]BF4.
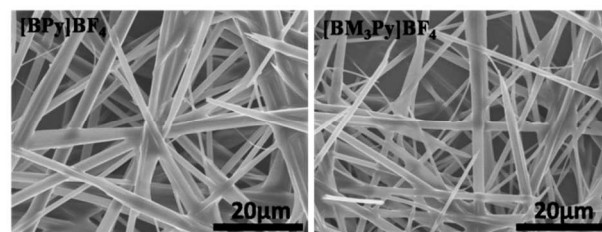

Fig. 5 SEM images of ZnOEP nanowires obtained in different ionic liquids.

50 A photodetector based on ZnOEP nanowires was fabricated. Finger electrodes with a length of 200 μm, width of 20 μm, and distance of 20 μm were fabricated by photolithography and electron beam deposition of Au on a Si substrate covered with 300 nm thick SiO$_2$. ZnOEP nanowires were first transferred onto
55 the Au electrodes and to remove the solvent thoroughly, the device was annealed at 150 $^{\circ}$C for 30 min. The typical SEM image of the as-constructed device was shown in inset of Fig. 6a. It can be seen that the nanowires have been connected to two Au electrodes. Fig.6a shows the typical I-V curves of the device in
60 the dark and under continuous white light illumination with varying intensity. It is clear that the nanowires are hardly conductive in the dark, showing a relatively low current of 4.8 pA at an applied bias of -20 V. Even under a low power irradiation of 1.57 mW cm^{-2} upon the white light illumination, the current is
65 remarkably increased and a high current of 267 pA is obtained, which can be comparable to that reported in the literature.[8] This value can be larger when higher power irradiation is employed for the photocurrent measurement. The current reaches 740 pA under a high power irradiation of 12.05 mW cm^{-2}, producing a
70 photocurrent on/off ratio of 154. Fig. 6b shows a typical I-t curve recorded continuously over 500 s in dark and under illumination. It can be seen that the photocurrent degrades slowly at -20 V, while the current in dark nearly holds steady. After 500s, the current under light only decreases by 5.3 %. This is mainly
75 because the traps and other defect states in the semiconductor nanomaterials as reported literature.[21]
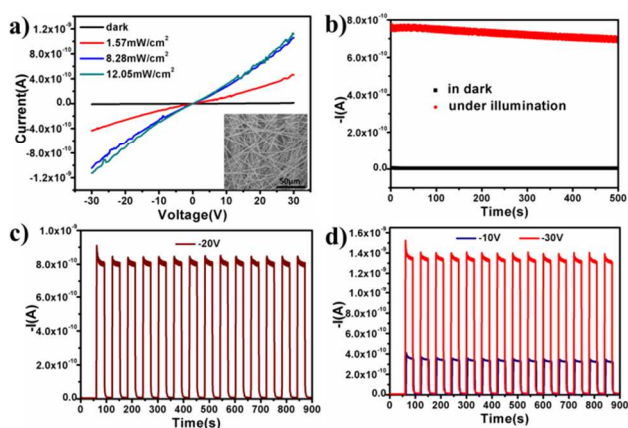
Fig. 6 (a) Dark current and photocurrents at different incident power densities. (b) Stability ofZnOEP photodetector in dark and under illumination over 750s. (c) and (d) Time-dependent on/off switching of device based on the ZnOEP nanowires. The stability and time-dependent were measured under a power density of 12.05 mW cm^{-2}. The volume ratio of chloroform and [BMIM] BF$_4$ was 1:10 for the synthesis of the ZnOEP nanowires.

In addition, the time-dependent photoresponse of devices is measured by periodically turning on and off the white light. Fig. 6c shows the typical on/off characteristics recorded and an applied bias of -20V. It is clear that by switching the light on or off every 30 s, the current of the devices shows two distinct states, a "low" current state in the dark and a "high" current state. After 14 cycles of switch experiments, no obvious current decrease was observed, showing excellent stability. Moreover, it is found that the photoswitching properties of the devices are depended on the applied voltage (Fig. 6 c and d). With the increase of the applied voltage, the current in dark hardly changes, while the photocurrent and the I_{on}/I_{off} ratio increase. The above excellent performance can be attributed to the mesh-like nanowires with the ratio of the length/diameter, due to the formation of the nanowire-nanowire and nanowire-electrode junction barriers. As a result, a significant band bending is induced near the surface of nanowires, and an electron transport occurs through the junctions.[8] These results suggest that the promising application of ZnOEP nanowiresin photodetector devices.

Conclusions

In summary, ZnOEP nanowires were prepared by ILs-assisted solution-phase precipitative method and fully characterized. Specifically, ILs was employed, for the first time, as a "poor" solvent and chloroform as a "good" solvent of ZnOEP. This method was highly efficient and scalable for large scale synthesis. Furthermore, the influence of the type of ILs, the volume ratio of chloroform/ILs, and the concentration of ZnOEP on the growth of nanowires were investigated in detail. The results indicated that the as-obtained nanowires were ultralong, highly pure, and single crystalline. Both anions and cations of ILs were found to play important roles in the final morphology and aspect ratio of nanowires. In addition, the as-obtained ZnOEP nanowires were directly used for the construction of prototype photodetector and exhibited excellent performance. This advance might pave the green way for preparing nano/micro structures of small-conjugated molecules.

Notes and references

aSuzhou Institute of Nano-tech and Nano-bionics, Chinese Academy of Sciences, 215123 Suzhou, P. R. China, Fax: 86-512-62872663; E-mail: gbpan2008@sinano.ac.cn.
bDepartment of Chemistry, Bohai University, 121000 Jinzhou, P. R. China.

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