ZnOEP based phototransistor: signal amplification and light-controlled switch†

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A phototransistor with a field-effect transistor configuration was fabricated using a single zinc octaethylporphyrin (ZnOEP) nanorod; the device showed ability in signal amplification and reversible light-controlled switching.

Owing to their abilities to convert light energy into electron motion and biocompatible properties, porphyrins and metalloporphyrins are widely used in light-harvesting systems, biocompatible applications and electronics.[1,2] For instance, bacteriochlorophyll is a crucial and essential biosystem, in which a magnesium–porphyrin composite acts as a light-harvesting center to convert light energy toward the production of oxygen and ATP.[3] Porphyrins can also be attached to semiconductor materials such as TiO_2 to increase the efficiency of dye-sensitized solar cells.[4] Various porphyrin-based nanomaterials have been prepared in recent years.[5–9] For example, Shelnutt *et al*. have fabricated porphyrin composite nanotubes by electrostatic force between two oppositely charged porphyrins.[10]

Organic phototransistors in which organic light-sensitive molecules are used can convert light into electrical energy, so that signal amplification and light detection can be realized on a single device.[11–15] In particular, phototransistors with a field-effect transistor (FET) configuration can be integrated into a large area circuit with a high density.[15] Concerning the advantages of porphyrins and phototransistors, the application of porphyrin and its derivatives in organic phototransistors is an important issue in optoelectronic devices. A remarkable photoconductivity with a rapid on/off switching rate was reported for porphyrin nanorods by Smith *et al*., demonstrating the potential of porphyrins in photosensitive devices.[16]

In this report, as a continuation of our previous study in synthesizing and fabricating porphyrin nanostructures,[7] we prepared zinc octaethylporphyrin (ZnOEP) nanorods through a physical vapor deposition (PVD) process. The structures of the ZnOEP nanorods were investigated. It was important that a phototransistor based on a single ZnOEP nanorod was successfully fabricated to investigate the photoconductivity of ZnOEP, which is the first example of a porphyrin-based organic phototransistor. The device showed a good ability in signal amplification and light-controlled switching. Such a single ZnOEP nanorod based phototransistor can be used as a light detection and conversion unit in organic optoelectronic circuits.

ZnOEP nanorods were deposited on a quartz surface by a PVD method. Fig. 1(a) is a photograph of the deposited nanorod film. Fig. 1(b)–(d) show typical scanning electron microscopy (SEM) images of the nanorods at different magnifications. In the low-magnification image Fig. 1(b) a flower-like morphology can be seen. High magnification SEM images in Fig. 1(c) and (d) indicate that these flowerlike structures are composed of nanorods with an average length of *ca*. 10 μm and a width of *ca*. 200 nm. Each nanorod has a rectangular cross-section (Fig. 1(d)). In this study, various substrates were used, including silicon, gold film and glass. The observations indicated that the substrates did not have a significant effect on the morphology of ZnOEP nanorods.

The Fourier transform infrared (FTIR) spectrum of the nanorods was measured and compared with that of the zinc

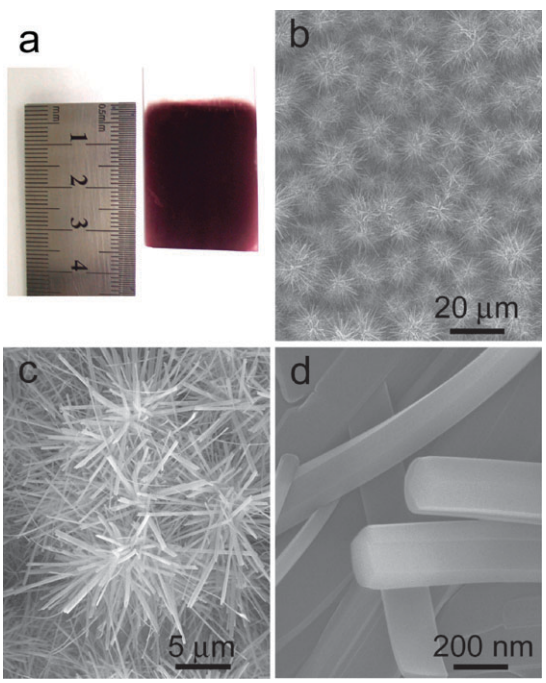

Fig. 1 (a) Photograph of ZnOEP nanorods deposited on a quartz surface (3.5 × 2.5 cm); (b)–(d) SEM images of ZnOEP nanorods at different magnifications.

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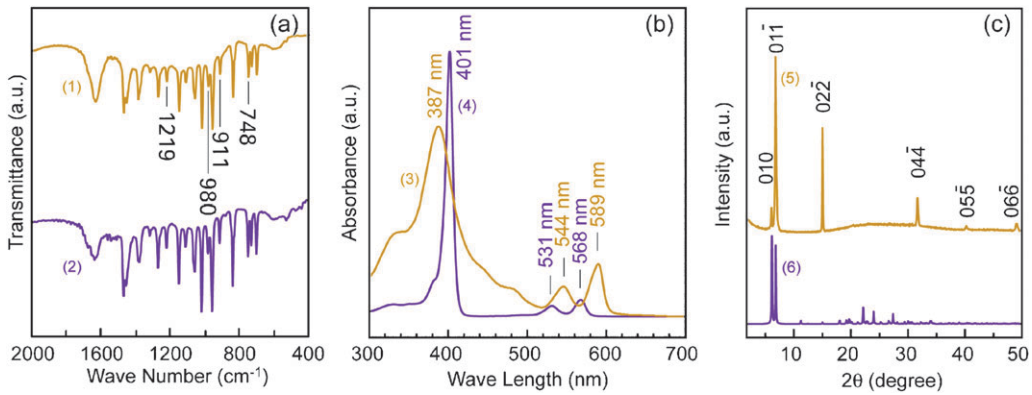

Fig. 2 (a) FTIR spectra of ZnOEP nanorods (1) and ZnOEP starting material (2) in KBr pellet. (b) UV–Vis absorption spectra of ZnOEP nanorods deposited on a quartz substrate (3) and ZnOEP monomers in ethanol solution (4). (c) XRD patterns of ZnOEP nanorods deposited on a glass substrate (5) and simulated XRD pattern (6) from published single crystalline data (CCDC, Refcode: ALOKOB).

octaethylporphyrin (ZnOEP) starting material, as shown in Fig. 2(a), to investigate the chemical composition of the nanorods. It is clear that the FTIR spectrum of the nanorods has the same characteristic IR absorptions as that of the ZnOEP starting material. Four metal-sensitive IR bands of octaethylporphyrin at 748, 911, 980 and 1219 cm^{-1}, respectively, prove that ZnOEP did not undergo decomposition or other chemical reactions during the PVD process.[17]

The crystal structure of the ZnOEP nanorods was investigated by UV–Vis spectroscopy and X-ray diffraction. Fig. 2(b) shows typical absorption spectra of ZnOEP nanorods deposited on quartz and ZnOEP monomer in ethanol solution. All absorption bands are broadened in the solid nanorods, in contrast to the sharp peaks from the solution sample. The *Q* bands at 544 and 589 nm are red-shifted while the *S* band at 387 nm is blue-shifted. In addition, two weak bands on the low-energy tail of the *S* band appear. These changes of absorption spectrum are consistent with that reported by Bard *et al.*,[18] which can be attributed to highly ordered molecule-packing in ZnOEP nanorods. The increased blue-shift of the *S* band is due to the decrease in interchromophore spacing as well as the decrease in the tilt angle of the porphyrins in the packing column.[18] The crystal structure of the ZnOEP nanorods was analyzed by comparing the X-ray diffraction pattern of the ZnOEP nanorods with that simulated from published single crystalline data.[19] As shown in Fig. 2(c), the peaks in the XRD pattern of the ZnOEP nanorods are very sharp and can be well indexed according to the simulated pattern from the crystal structure reported by Balch *et al.* (CCDC, Refcode: ALOKOB).[19] The diffraction peaks of $(0k\bar{k})$ planes are significantly enhanced relative to the simulated pattern. These results prove that the ZnOEP nanorods are highly crystalline with a preferential orientation of the nanorods perpendicular to the $(01\bar{1})$ plane.

A phototransistor based on a single ZnOEP nanorod was fabricated. ZnOEP nanorods were first transferred onto Si/SiO_2 (300 nm) substrates. Then gold gap electrodes were fabricated by thermal evaporation with a copper grid as a mask. A schematic illustration and a typical photograph of the phototransistor are shown in Fig. 3(a). It can be seen that the two ends of a single ZnOEP nanorod are firmly connected to two metallic electrodes with a channel length of *ca.* 5 μm.

Fig. 3(b) shows the output of the ZnOEP nanorod based device under white-light irradiation at various light intensities. The device shows a large increase in current, I_{SD}, when the light intensity is enhanced, demonstrating that the output of the transistor can be controlled by incident light, and its output characteristics are similar to those of other organic FETs.[20,21] When light with a photon energy equal to or higher than the band-gap energy of the ZnOEP nanorod is absorbed by the ZnOEP nanorod, a large number of charge carriers are generated, leading to an increase in I_{SD}.[13,14] This result suggests that light can act as an additional terminal to control the output of the transistor for signal magnification.

Based on photo-generated charge carriers, a phototransistor can work under two different effects, a photoconductive effect and a photovoltaic effect.[13,14,22] When the gate voltage (V_G) is lower than the threshold voltage (V_{Th}), the device is in the turned-off state and works mainly under the photoconductive effect. On the other hand, when the gate voltage is higher than the threshold voltage, the device works under the photovoltaic effect.[22] In this study, the device is operated without gate voltage, thus the photocurrent must originate from the photoconductive effect. To verify this hypothesis, the output current (I_{SD}) is plotted as a function of incident light intensity (Fig. 3(c)). The photocurrent induced by the photoconductive effect in a device can be described as:[22]

$$I_{ph} = (q\mu_p pE)WD = BP_{opt}$$

where q is the electronic charge, μ_p is the charge carrier mobility, p is the charge carrier concentration, E is the electrical field in the channel, W is the gate width, D is the depth of the absorption region, B is the fitting parameter and P_{opt} is the incident light intensity. In this case I_{ph} is linearly proportional to P_{opt}. As shown in Fig. 3(c), the current (I_{SD}) is linear with light intensity in the range of 0.7 to 8.9 mW cm^{-2}, indicating that the single ZnOEP nanorod based phototransistor works under the photoconductive effect. When light reaches the surface of the photoconductor, the number of charge carriers in the photoconductor increases, resulting in an increase of conductivity ($\sigma = nq\mu_p$, where σ is the conductivity, n is the number of charge carriers, μ_p is the carrier mobility of ZnOEP, and q is the electronic charge).

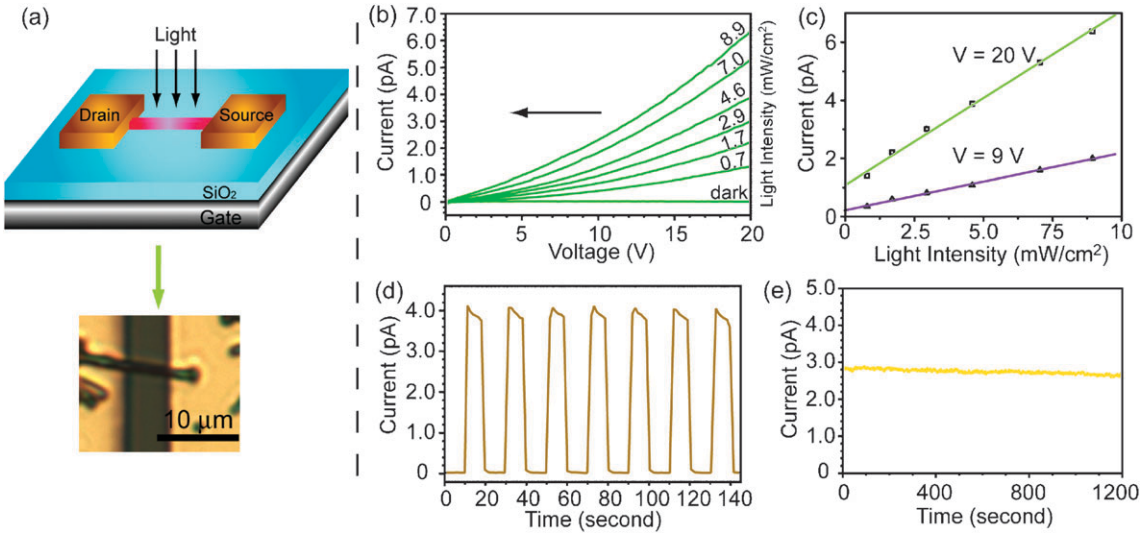

Fig. 3 (a) Schematic depiction and photograph of a phototransistor based on a single ZnOEP nanorod. (b) The signal amplification characteristic of a ZnOEP phototransistor by using light irradiation instead of gate voltage. The light intensity is tuned from 0 to 8.9 mW cm^{-2}. (c) Photocurrent as a function of light intensity under different voltage bias. (d) Photo-detection property of a ZnOEP phototransistor, which can be switched on/off rapidly by illumination. The on/off switching ratio is *ca.* 100 under white-light intensity of 8 mW cm^{-2} and voltage bias of 20 V. (e) Stability of ZnOEP phototransistor under sustained white-light intensity of 4.5 mW cm^{-2} and voltage bias of 20 V.

The single ZnOEP nanorod based device can also be used as a photo-switch, as shown in Fig. 3(d). By switching the light on/off every 20 s, the device was turned on/off rapidly and reversibly, with an on/off ratio of about 100 under sustained DC voltage of 20 V and illumination intensity of 8 mW cm^{-2}. The device also exhibited a high stability under white-light illumination. No obvious on/off ratio decrease was observed after 10 cycles of switch experiments. Furthermore, sustained DC voltage and illumination of 20 min (Fig. 3(e)) did not degrade the device. These results suggest that the ZnOEP nanorod based device can be integrated into micro-/nano-electronic circuits as a photo-detection unit or a photo-controlled electrical switch.

In summary, a PVD technique was developed to prepare highly crystalline zinc octaethylporphyrin nanorods. A single ZnOEP nanorod was employed to fabricate a phototransistor, which works under the photoconductive effect and shows promising potential in signal amplification and photo-controlled switches. The light induced functions on the nanorods are reversible and reproducible. Future work will focus on the application of porphyrins in low-cost, ultrahigh density organic photoelectrical integration.

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Notes and references

1 K. Kadish, K. M. Smith and R. Guilard, *The Porphyrin Handbook*, Academic Press, New York, 1999–2003.
2 T. Hasobe, H. Imahori, P. V. Kamat, T. K. Ahn, S. K. Kim, D. Kim, A. Fujimoto, T. Hirakawa and S. Fukuzumi, *J. Am. Chem. Soc.*, 2005, **127**, 1216.
3 J. Deisenhofer and J. R. Norris, *The Photosynthetic Reaction Center*, Academic Publishing, San Diego, 1993.
4 W. M. Campbell, A. K. Burrell, D. L. Officer and K. W. Jolley, *Coord. Chem. Rev.*, 2004, **248**, 1363.
5 A. D. Schwab, D. E. Smith, C. S. Rich, E. R. Young, W. F. Smith and J. C. de Paula, *J. Phys. Chem. B*, 2003, **107** 11339.
6 T. Kojima, R. Harada, T. Nakanishi, K. Kaneko and S. Fukuzumi, *Chem. Mater.*, 2007, **19**, 51.
7 J. S. Hu, Y. G. Guo, H. P. Liang, L. J. Wan and L. Jiang, *J. Am. Chem. Soc.*, 2005, **127**, 17090.
8 M. C. Lensen, K. Takazawa, J. Elemans, C. Jeukens, P. C. M. Christianen, J. C. Maan, A. E. Rowan and R. I. M. Nolte, *Chem.–Eur. J.*, 2004, **10**, 831.
9 T. N. Milic, N. Chi, D. G. Yablon, G. W. Flynn, J. D. Batteas and C. M. Drain, *Angew. Chem., Int. Ed.*, 2002, **41**, 2117.
10 Z. C. Wang, C. J. Medforth and J. A. Shelnutt, *J. Am. Chem. Soc.*, 2004, **126**, 16720.
11 S. R. Forrest and M. E. Thompson, *Chem. Rev.*, 2007, **107** 923.
12 Q. X. Tang, L. Q. Li, Y. B. Song, Y. L. Liu, H. X. Li, W. Xu, Y. Q. Liu, W. P. Hu and D. B. Zhu, *Adv. Mater.*, 2007, **19**, 2624.
13 A. Madjar, P. R. Herczfeld and A. Paolella, *IEEE Trans. Microwave Theory Tech.*, 1992, **40**, 1681.
14 M. A. Romero, M. A. G. Martinez and P. R. Herczfeld, *IEEE Trans. Microwave Theory Tech.*, 1996, **44**, 2279.
15 Y. Y. Noh, D. Y. Kim and K. Yase, *J. Appl. Phys.*, 2005, **98**, 074505.
16 A. D. Schwab, D. E. Smith, B. Bond-Watts, D. E. Johnston, J. Hone, A. T. Johnson, J. C. de Paula and W. F. Smith, *Nano Lett.*, 2004, **4**, 1261.
17 K. D. Stanley, L. Luo, R. L. Delavega and J. M. E. Quirke, *Inorg. Chem.*, 1993, **32**, 1233.
18 B. A. Gregg, M. A. Fox and A. J. Bard, *J. Phys. Chem.*, 1989, **93**, 4227.
19 A. Ozarowski, H. M. Lee and A. L. Balch, *J. Am. Chem. Soc.*, 2003, **125**, 12606.
20 J. Zaumseil and H. Sirringhaus, *Chem. Rev.*, 2007, **107**, 1296.
21 Q. X. Tang, H. X. Li, M. He, W. P. Hu, C. M. Liu, K. Q. Chen, C. Wang, Y. Q. Liu and D. B. Zhu, *Adv. Mater.*, 2006, **18** 65.
22 S. M. Sze and K. K. Ng, *Physics of Semiconductor Devices*, Wiley, New York, 3rd edn, 2007.