

Phthalocyanine Monolayer-Modified Gold Substrates as Efficient Anodes for Organic Light-Emitting Diodes

Shuai Wang, Yunqi Liu,* Xuebin Huang, Gui Yu, and Daoben Zhu*

Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China

Received: June 2, 2003; In Final Form: September 23, 2003

A self-assembled monolayer (SAM) of 2,9,16-tri(*tert*-butyl)-23-(10-mercaptodecyloxy) phthalocyanine (HS-Pc) on the surface of a Au thin film has been employed as an anode in organic light-emitting diodes (OLEDs). Compared with the device without SAM, the turn-on voltage for the device with SAM decreased from 13 to 8 V and the external quantum efficiency (η_{ext}) increased ca. 27 times as a result of the improvement of hole injection ability of the SAM. In addition, the device with Au–SAM as an anode showed higher efficiency ($\eta_{\text{ext}} = 0.66$) than that of an indium tin oxide (ITO) glass anode ($\eta_{\text{ext}} = 0.33$), which is commonly used in OLEDs.

Introduction

Organic light-emitting diodes (OLEDs) are under active research because of their application in flat panel display.^{1–5} Over the past years, increasing activity has focused on improving charge injection efficiency at both OLED cathode/organic and anode/organic interfaces.^{6–9} A number of techniques, including adding injecting/transporting layers and using metals with low work functions as the cathode, have been developed to improve and balance injection.¹⁰ The insertion of phthalocyanines (Pcs) film fabricated by evaporation or sputter-grown has demonstrated excellent improvement of the hole injection.^{11,12} In contrast to ultrathin films made by traditional methods used in the fabrication of OLED, for example, vacuum evaporation and spin coating, self-assembled monolayers (SAMs) are more highly ordered and oriented and can incorporate a wide range of groups. The high-molecular-order parameter in SAMs makes them ideal as components in electrooptic devices.¹³ Our interest is combining the hole injecting property of Pcs and the stability and high degree of organization of SAM, and investigating the SAM of Pcs in the fabrication of OLEDs.

SAMs are ordered molecular assemblies that are formed spontaneously by the adsorption of organic molecules with a specific affinity of their headgroups on substrates.¹⁴ SAMs have received a great deal of attention because of their fundamental importance in understanding interfacial properties and for their potential application in molecular-based technologies and automated fabrication.^{15,16} Alkanethiols adsorbed on gold surface are the most extensively studied due to their stability and high degree of organization.¹⁷ Monolayers formed from phthalocyanines (Pcs) or their derivatives, although less studied, are interesting as surface modification reagents, because they are important functional materials. Their 18 π electron system provides the basis for their characteristic photophysical, optoelectronic, and conductometric properties. In this paper, self-assembly techniques were used to attach a monolayer of 2,9,16-tri(*tert*-butyl)-23-(10-mercaptodecyloxy) phthalocyanine (HS-Pc) to the surface of a Au electrode.

Experimental Section

The synthesis and characterizations of HS-Pc were reported in our previous work.¹⁸ The presence of a long chain spacer between the gold surface and macrocycle (Figure 1) is intended to insulate the ring electronically from the metallic substrate and to contribute to the structural organization of the molecules at the interface.¹⁷ To gauge the success of monolayer formation, X-ray photoelectron spectroscopy (XPS) and absorption spectrum (ABS) were used to characterize the SAM.

The substrates used for self-assemble consisted of ca. 500 Å vapor-deposited Au on the top of 50 Å vapor-deposited Cr, used as an adherent, on indium tin oxide (ITO) glass substrates or mica substrates. Monolayer preparation was conducted by spontaneous adsorption from chloroform solutions containing 10^{-5} M concentrations of the HS-Pc. The clean substrates were kept in the adsorption solution for 24 h to prepare the monolayer. When withdrawn from the adsorption solution, the modified gold surfaces were washed by chloroform solution to remove the non self-assembled HS-Pc molecules, and then dried in a vacuum oven for about half an hour. The self-assembled layers on mica substrates were examined by scanning electron microscopy (SEM, JEOL JSM-6301F) to characterize their profile and alignment. The Au layers coated by SAM on ITO glass substrates were used in the performance of OLEDs. LEDs were fabricated using tris(8-hydroxyquinolino)aluminum (Alq₃) as the electron-transporting and emitting layer, *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) as the hole-transporting layer, Al as the cathode, and the Au-coated SAMs, Au, or ITO as anodes. TPD, Alq₃, Al, and Au electrodes were deposited by vacuum evaporation at a pressure below 10^{-5} Torr (Figure 2). The active area of devices was about 7 mm². Electroluminescence (EL) spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer with the LED forward biased. The power of EL emission was measured using a Newport 2835-C multifunction optical meter. Current–voltage characteristics were measured with a Hewlett-Packard 4140B semiconductor parameter analyzer. To compare the performance of Au, Au–SAM, or ITO as the anodes in OLEDs, the optical transmittance in the visible range (400–700 nm) of the Au-coated ITO glass substrate was measured with an ITO glass substrate as a reference. Its maximum reached 35%, so that the

* Authors to whom correspondence should be addressed. E-mail: liuyq@iccas.ac.cn.

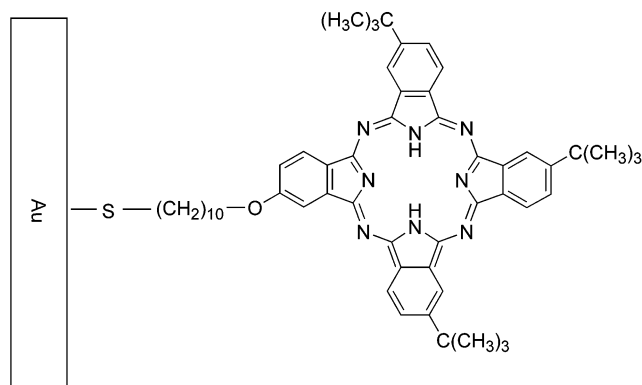


Figure 1. HS-Pc monolayer-modified gold substrate.

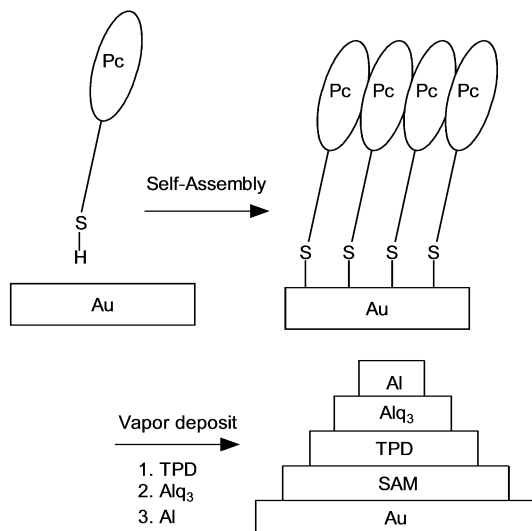


Figure 2. Procedure for the fabrication of OLEDs using SAM as the hole-transport layer.

real brightness of devices with Au or Au-SAM as anode is greatly higher than the measured. Here, we calculated the real brightness through dividing the measured brightness by 35%. All the measurements were performed under ambient atmosphere at room temperature.

Results and Discussion

XPS analysis offers direct evidence for the formation of the self-assembled monolayers. The S2p peak appearing at 161.70 eV clearly suggests that the major sulfur species present is a thiolate (RSAu).¹⁸

Figure 3a is a SEM micrograph showing the surface of a mica substrate coated by Au. The alignment of SAM of HS-Pc is demonstrated in Figure 3b. From Figure 3b, we can see that the self-assembly of HS-Pcs formed a dense monolayer film on the Au. However, the same growth conditions did not lead to the same structures of patterns, and its distribution is not uniform. Because of the dense alignment of SAM, their configurations are difficult to identify. So we performed SEM analysis on no completely self-assembled SAM (Figure 3c). In Figure 3c, different patterns are demonstrated. They included round, ellipse, strip, and other shapes. Those configurations were isolated with each other. Figure 3d is a higher magnification image of an area within the SAM, which more clearly shows this distribution. Here, the formation mode of SAM is proposed. A randomly occupied growth mechanism for these patterns is provided. At the self-assembled beginning stage, HS-Pc molecules randomly occupied the places on the surface of Au. The

effect of van der Waals force forced the followed HS-Pcs molecules to locate the position near these molecules, which led to the dense ordered packing of HS-Pcs. Before reaching the dense aligning SAM (Figure 3b), the random occupying of HS-Pc and the effect of van der Waals force resulted at all kinds of shapes with some empty spaces.

With using Alq₃ as the emitting layer, double-layer devices with the structure of Au-SAM/TPD/Alq₃/Al and Au/TPD/Alq₃/Al were performed. The light emission was observed when devices were operated under a forward bias (positive voltage applied to ITO electrode), demonstrating a typical diodes behavior. Their EL spectra are similar and the maximums are located at 510 nm, which indicates that the emission originates from the emission of Alq₃. Compared to the devices without the SAM, both the I-V and L-V curves of the device with SAM shift considerably to the low voltage direction. The turn-on voltage for the device with a SAM layer decreased from 13 to 8 V. To better compare the performance of Au and that of Au-SAM as the anode for OLEDs, we calculate the external quantum efficiencies by assuming Lambertian distribution of the EL emission¹⁹ according to the following equation:²⁰

$$\eta_{\text{ext}} = \frac{n_p}{n_e} = \frac{\phi_e/h\nu}{I/e_Q}$$

where η_{ext} is the external EL quantum efficiency, n_p is the number of the emitted photons per second, n_e is the number of the current electron per second, ϕ_e is the luminous power, $h\nu$ is the photon energy, I is the amount of current, and e_Q is the electric quantity of per electron. Figure 4 shows the external quantum efficiencies as a function of current density. From Figure 4, it is easily noted that the increase of external efficiencies for the device of Au-SAM/TPD/Alq₃/A is quite similar to that for the device of Au/TPD/Alq₃/Al. At the initial stage, the efficiency increases very quickly and then slows down with an increase in current density. When at high current intensity, the efficiency of three-layer device becomes stable. From the above discussion, we can deduce that there may be a similar recombination mechanism of charge carriers for these two kinds of device, and the emission originates from the radiative recombination of singlet excitons within the Alq₃. Through the addition of SAM of Pcs between the anode and hole-transporting layer, the device efficiency was enhanced by about 27 times.

Molecular modification of interfaces has been an active area of research for many years. It has been proved that small changes of the interfacial molecular structure may result in relatively large changes. In this research, to get ordered organization of HS-Pc molecules at the interface, a long chain spacer is added between the gold surface and macrocycle. The alkyl chain acts as a tether and insulates the functional groups from the gold substrate. The addition of SAM layer leads to a decrease in operation voltage and an increase in maximum luminance with highly enhanced quantum efficiency. It has been reported that insertion of a thin insulating layer between an emitting layer and cathode makes it possible to use Al as an efficient cathode. These kinds of materials include SiO₂, poly(methyl methacrylate) (PMMA), LiF, Al₂O₃, a self-assembled layer, and an ionomer.²¹ Their addition improved the emission efficiency significantly, reduced the threshold or operation voltage, and increased the maximum luminance. Similar characteristics were demonstrated in the devices incorporating the insulating alkyl layer. As a reported mechanism of reducing the effective energy barrier within the tunneling region of devices with a thin

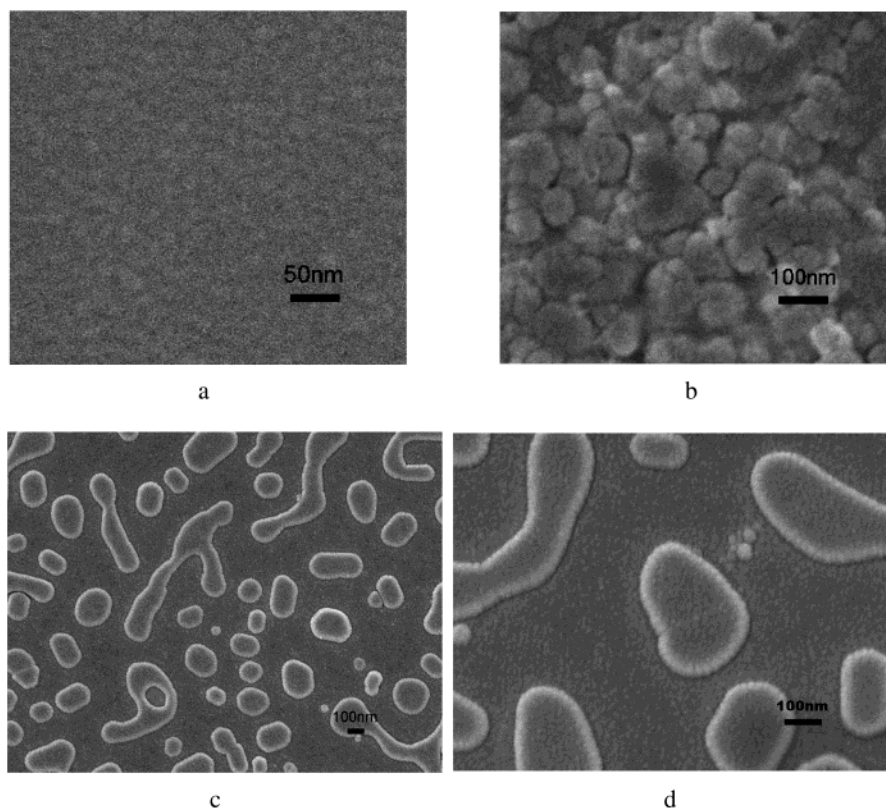


Figure 3. SEM images of the mica coated with Au layer (a) and SAM of HS-Pc on the mica coated with Au layer (b). A SEM image of no completely self-assembled SAM on a mica coated with Au layer (c) and a higher magnification image of an area of this SAM (d).

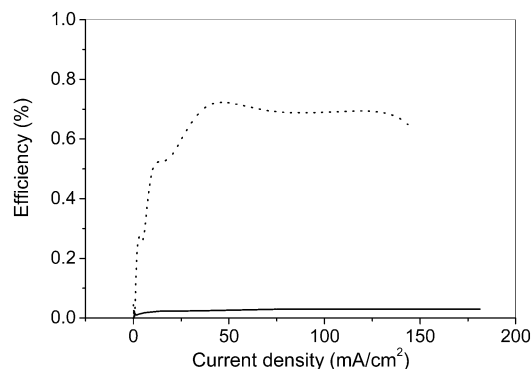


Figure 4. The hole-transporting effect of the self-assembled HS-Pc. External quantum efficiency vs current density plots for Au/TPD/Alq₃/Al (solid line) and Au-SAM/TPD/Alq₃/Al (dot line).

insulating layer between an emitting layer and cathode,^{22–24} the insulating layer in the devices with SAM layer may lower the effective energy barrier height between the TPD and ITO anode resulting from the large voltage drop across the insulating layer. It had also been reported that insertion of a thin phthalocyanine layer between the ITO and hole-transport layer enhanced the hole injection, reduced the operational voltage, and resulted in higher efficiency.²⁵ In this study, a highly enhanced quantum efficiency is achieved in the EL device with a SAM layer, which might originate from a combination of several different factors favorable for hole injection: the good compatibility with the anode at the interface, and the lowering of the effective energy barrier between the TPD and the anode because of the addition of the insulating layer and Pc layer.

To improve charge injection, many low work function metals (e.g., Ca, Mg) and combinations with other atmospherically stable metals (e.g., Ag, Al) have been implemented as cathodes. In contrast, relatively few materials have been explored as

alternatives to ITO as OLED anodes.²⁶ As the widely used anode material in OLEDs, ITO also has some disadvantages as revealed in the previous literature, such as the diffusion into the organic materials and the defects formed on the surface.²⁷ So finding anode materials with good properties becomes necessary both in foundational research and in practice. If the molecular modification on the Au interfaces can result in efficient hole injection, the Au-SAM may be used as the anode in OLEDs in some conditions.

For comparison between the performance of Au-SAM and that of ITO as an anode for OLEDs, ITO/TPD/Alq₃/Al was also performed. Figure 5a and Figure 5b show the current and luminance characteristics for ITO/TPD/Alq₃/Al and Au-SAM/TPD/Alq₃/Al. The brightness of ITO/TPD/Alq₃/Al reached 4229 cd/m² at 17 V, while Au-SAM/TPD/Alq₃/Al possessed a brightness of 10085 cd/m² at 18 V. External efficiencies at different current density were also calculated. The maximum external efficiencies changed from about 0.33% for the device of ITO/TPD/Alq₃/Al to 0.66% for the device of Au-SAM/TPD/Alq₃/Al (Figure 5c). Internal quantum efficiency is the one that most closely relates to the physics of device. External quantum efficiency is a factor of $2n^2$ smaller than internal quantum efficiency. The n is a refractive index of refraction at an interface between the emissive layer and air.¹⁹ We assume that light is isotropically emitted within the Alq₃ layer, and that the negative contact is perfectly reflecting. The uniform layers of Alq₃, TPD, Au, SAM, ITO, and glass have no effect on the angle of emission of the light into air, and we can therefore simply consider the refraction at the interface between the emissive layer and air. The increase of internal quantum efficiencies for the two kinds of devices is similar to the increase of external quantum efficiencies for these devices. The Au-SAM shows higher performance than ITO as the anode for OLED. The OLEDs with ITO as anode have poor adhesion between anode

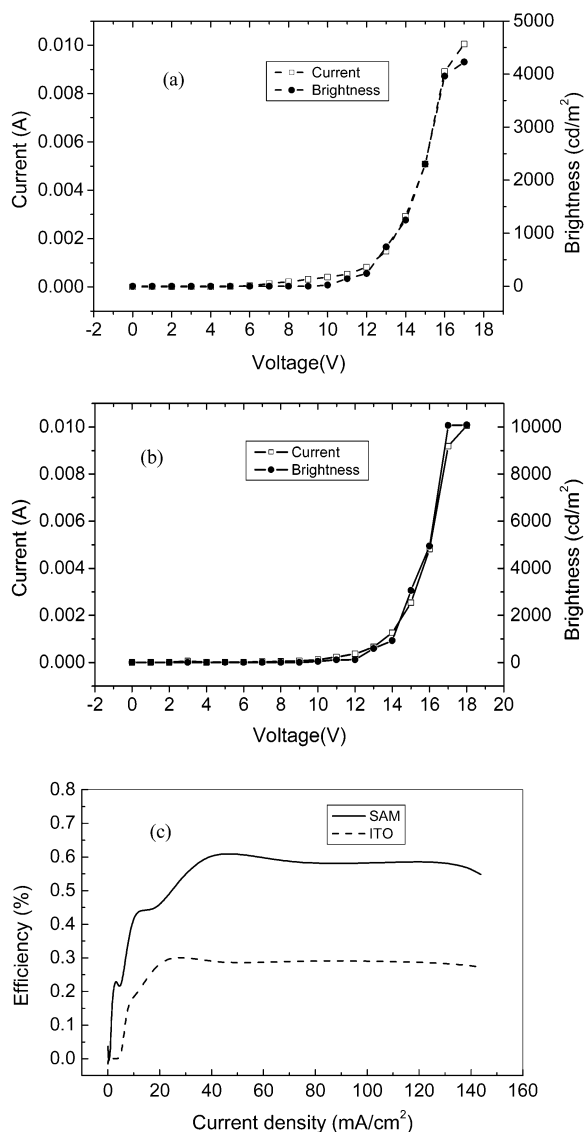


Figure 5. Current, and forward light output vs voltage plots for ITO/TPD/Alq₃/Al (a), and Au-SAM/TPD/Alq₃/Al (b). External quantum efficiency vs current density plots for Au-SAM/TPD/Alq₃/Al and ITO/TPD/Alq₃/Al (c).

and organic materials, as a result of addition of HS-Pc, OLEDs with Au-SAM as anode possess improved interface property and efficient hole injection, which leads to an efficient anode.

Conclusions

In conclusion, the self-assembly of HS-Pc was studied and its application as a hole injection material in OLEDs demon-

strated. The insertion of a SAM of HS-Pc between Au and hole-transport layers enhances the hole injection, which increases device efficiency and decreases the operation voltage. Phthalocyanine monolayer-modified gold substrates demonstrated high efficiency as anodes for organic light-emitting diodes.

Acknowledgment. The authors gratefully acknowledge financial supports from the National Science Foundation of China, the Major State Basic Research Development Program and the Chinese Academy of Sciences.

References and Notes

- (1) Lee, C. L.; Lee, K. B.; Kim, J. J. *Appl. Phys. Lett.* **2000**, *77*, 2280.
- (2) Title, Y. A.; Hung, L. S.; Mason, M. G. *Appl. Phys. Lett.* **2001**, *78*, 3732.
- (3) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402.
- (4) Tang, C. W.; Vanslyke, S. A.; Chem, C. H. *J. Appl. Phys.* **1989**, *65*, 3610.
- (5) Tao, X. T.; Miyata, S.; Sasabe, H.; Zhang, G. J.; Wada, T.; Jiang, M. H. *Appl. Phys. Lett.* **2001**, *78*, 279.
- (6) Jabbour, G. E.; Kawabe, Y.; Shaheen, S. E.; Wang, J. F.; Morrell, M. M.; Kippelen, B.; Peyghambarian, N. *Appl. Phys. Lett.* **1997**, *71*, 1762.
- (7) Bliznyuk, V.; Ruhstaller, B.; Brock, P. J.; Scherf, U.; Carter, S. A. *Adv. Mater.* **1999**, *11*, 1257.
- (8) Ho, P. K. H.; Granstrom, M.; Friend, R. H.; Greenham, N. C. *Adv. Mater.* **1998**, *10*, 769.
- (9) Malinsky, J. E.; Jabbour, G. E.; Shaheen, S. E.; Anderson, J. D.; Richter, A. G.; Armstrong, N. R.; Kippelen, B.; Dutta, P.; Peyghambarian, N.; Marks, T. J. *Adv. Mater.* **1999**, *11*, 227.
- (10) Yu, W. L.; Pei, J.; Cao, Y.; Huang, W. J. *Appl. Phys.* **2001**, *89*, 2343.
- (11) Kim, S. C.; Lee, G. B.; Choi, M.; Roh, Y.; Wang, C. N.; Jeong, K.; Lee, J.; Kim, S. *Appl. Phys. Lett.* **2001**, *78*, 1445.
- (12) Brütting, W.; Riel, H.; Beierlein, T.; Riess, W. *J. Appl. Phys.* **2001**, *89*, 1704.
- (13) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.
- (14) Zhu, L. H.; Tang, H. Q.; Harima, Y.; Yamashita, K.; Hirayama, D.; Aso, Y.; Otsobu, T. *Chem. Commun.* **2001**, 1830.
- (15) Duan, L. L.; Garrett, S. J. *Langmuir* **2001**, *17*, 2986.
- (16) Li, D. Q.; Lütt, M.; Fitzsimmons, M. R.; Synowicki, R.; Hawley, M. E.; Brown, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 8797.
- (17) Peng, Z. Q.; Dong, S. J. *Langmuir* **2001**, *17*, 4904.
- (18) Huang, X. B.; Liu, Y. Q.; Wang, S.; Zhou, S. Q.; Zhu, D. B. *Chem. Eur. J.* **2002**, *8*, 4179.
- (19) Greenham, N. C.; Friend, R. H.; Bradley, D. D. C. *Adv. Mater.* **1994**, *6*, 491.
- (20) O'Brien, D.; Bleyer, A.; Lidzey, D. G.; Bradley, D. D. C. *J. Appl. Phys.* **1997**, *82*, 2662.
- (21) Yoon, J.; Kim, J.-J.; Lee, T.-W.; Park, O.-O. *Appl. Phys. Lett.* **2000**, *76*, 2152.
- (22) Li, F.; Tang, H.; Andereg, J.; Shinar, J. *Appl. Phys. Lett.* **1997**, *70*, 1233.
- (23) Kim, Y.-E.; Park, H.; Kim, J.-J. *Appl. Phys. Lett.* **1996**, *69*, 599.
- (24) Lee, T.-W.; Park, O. O. *Appl. Phys. Lett.* **2000**, *76*, 3161.
- (25) Kim, S. C.; Lee, G. B.; Choi, M.-W.; Roh, Y.; Whang, C. N.; Jeong, K. *Appl. Phys. Lett.* **2001**, *78*, 1445.
- (26) Cui, J.; Wang, A. C.; Edleman, N.; Ni, J.; Lee, P.; Armstrong, N.; Marks, T. *Adv. Mater.* **2001**, *13*, 1476.
- (27) Zhou, X.; He, J.; Liao, L. S.; Lu, M.; Xiong, Z. H.; Ding, X. M.; Hou, X. Y.; Tao, F. G.; Zhou, C. E.; Lee, S. T. *Appl. Phys. Lett.* **1999**, *74*, 609.