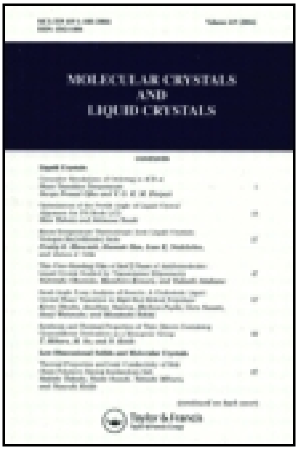

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Field Emission Property of Micro Emitter Array Fabricated from Conducting Polymer

Jungsuk Kim [a], Jungsik Choi [a], Yongkeun Son [a], Youngkwan Lee [b], Ji-Hoon Yang [c], Chong-Yun Park [c], Jae-Hong Park [d] & Ji-Beom Yoo [d]

[a] Department of Chemistry, Sungkyunkwan University, Suwon, Korea

[b] Department of Chemical Engineering, Sungkyunkwan University, Suwon, Korea

[c] Department of Physics and Center for Carbon Nanotube and Nanostructures, Sungkyunkwan University, Suwon, Korea

[d] Center of Nanotube and Nanostructured Composites, Sungkyunkwan University, Suwon, Korea

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Jungsuk Kim
Jungsik Choi
Yongkeun Son
Department of Chemistry, Sungkyunkwan University, Suwon, Korea

Youngkwan Lee
Department of Chemical Engineering, Sungkyunkwan University, Suwon, Korea

Ji-Hoon Yang
Chong-Yun Park
Department of Physics and Center for Carbon Nanotube and Nanostructures, Sungkyunkwan University, Suwon, Korea

Jae-Hong Park
Ji-Beom Yoo
Center of Nanotube and Nanostructured Composites, Sungkyunkwan University, Suwon, Korea

Micro scale emitter array was fabricated with a conducting polymer. A simple and easy way of electrochemical template polymerization was utilized in this process. In this study the template membrane was fixed onto an ITO glass electrode by using conductive composite glue. Applying electrochemical potential to the template electrode in monomer electrolyte allowed polymerization of pyrrole within the pores and thus the micro structures were grown. Cyclic voltammetry, SEM and EDAX measurements were done to characterize this emitter array. The emission current measurements were done in 10^{-7} Torr condition and results show redox state dependence emission of the polymer electrodes.

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Address correspondence to Yongkeun Son, Department of Chemistry and BK21 School of Molecular Science, Sungkyunkwan University, Suwon 440-746, Korea. E-mail: ykson@skku.edu

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INTRODUCTION

Over the past thirty years, conducting polymers have attracted a great deal of attention because they have many novel electrical and optical properties. A lot of research groups, therefore, have investigated the basic functionalities of these materials and provided numerous real applications [1–3]. However many of the recent studies in the field of conducting polymers have focused their aim on the fabrications and applications of micro- or nano-structural polymers prepared by using template synthesis, soft lithography, and etc. because many new application fields such as field emission displays (FEDs) and molecular electronics are coming to the fore [4–6].

The displays using conventional cathode ray tube (CRT) have a lot of advantages: bright emission, dynamic color images, depiction of detailed graphics and moderate price. However, with the appetite for space-saving and portable displays, the bulkiness of CRT now began to be a problem and thus flat panel displays (FPDs) are being expected to replace them [7]. FPDs with similar specification to CRT are consequently on demand. It is expected that FED among many competitors is the closest technology to replace CRT. One of the key components in FED is the cathode that emits electrons at low electric fields (typically in $1 \sim 20\,\mathrm{V/\mu m}$) with high current density (typically in $10 \sim 100\,\mathrm{mA/cm^2}$) to generate fluorescence [8]. Many research institutes in the world have concentrated to develop an effective emitter with a variety of materials. Most efforts were focused on fabricating metal cathode tips on silicon substrate by adopting the process used in micro-chip fabrications [9–11]. A lot of research work of fabricating cathode with conducting polymers have been done theses days, because the manufacturing processes are relatively simple and easy; e.g., I. Musa *et al*. used poly(3-octylthiophene), and C. Wang *et al*. used polyaniline respectively [4,5]. These groups used one of the following methods to prepare cathode tips. Gold was thermally evaporated onto the one side of membrane template and then this template was used as a working electrode for electrochemical polymerization. Otherwise the raw template was immersed in a mixed solution of monomer, electrolyte and oxidizing agents for chemical polymerization to make tips. The former case, however, involves a step of using the vacuum facilities to prepare the template electrode. In the case of the latter, it is not easy to control of the chemical polymerization reaction and to get well-aligned emitter arrays in neat shape.

For those reasons, we tried to use a simple and easy way to prepare conducting polymer emitter array in this study. After fixing a polycarbonate membrane template onto an indium-tin oxide (ITO) glass electrode with the conducting polymer composite glue (CPCG), we fabricated imbedded type micro-emitters only within pores of the template by using electrochemical polymerization that could control the polymerization reaction easily. Cyclic voltammetry was performed to characterize the electrochemical properties of micro-emitters. The shape of them was identified by using scanning electron microscopy (SEM) and field emission currents were also measured without removing the template.

EXPERIMENTAL

Chemicals and Apparatus

All chemicals used in this work were of ACS grade. These chemicals were purchased from Sigma-Aldrich Korea Ltd. and used without further purification. The templates for fabricating conducting polymer emitters were polycarbonate membranes holding pores of 2 μm size diameter (Whatman) and 10 μm (Millipore Corp.) in 10 μm thick. Transparent indium-tin oxide (ITO) glass electrode (Samsung Corning, Korea) was used as a supporting electrode after several cleaning steps. Platinum plate and Ag/AgCl (sat'd KCl) were used as counter and reference electrode, respectively. Electrochemical experiments were carried out using BAS 100B potentiostat (Bioanalytical Systems Inc., USA). Vacuum oven (VO-20X, Jeio Tech, Korea) was used for drying template/CPCG/ITO glass electrode. All SEM (scanning electron microscope) and EDAX (energy-dispersive analysis of X-rays) images were obtained by using JSM 6700F (JEOL, Japan) and JSM 7000F (JEOL, Japan), respectively.

Fabrication and Characterization of Conducting Polymer Emitters

Through the process that appears in Figure 1, we prepared the working electrode to which a polycarbonate membrane was clung. We first made CPCG that consists of poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS) and poly(vinyl alcohol) (PVA). CPCG was spin coated onto ITO glass electrode and then a piece of template was

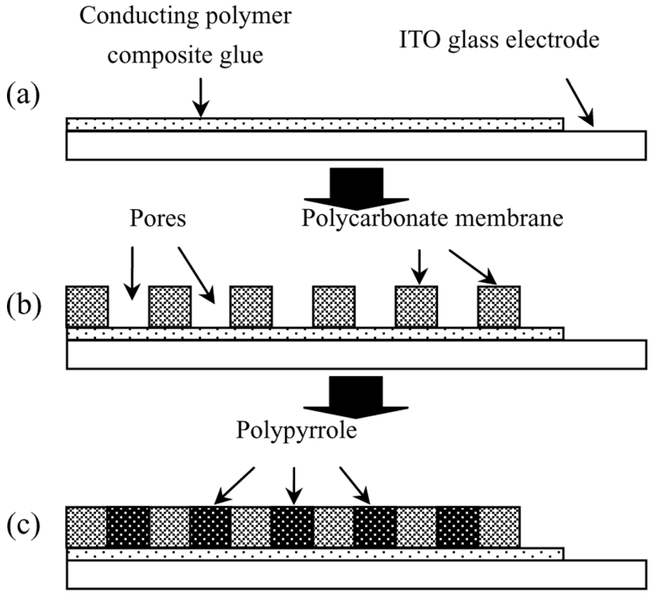

FIGURE 1 A schematic diagram for the fabrication of micro-/nano-structural conducting polymer: (a) spin casting of conducting polymer composite glue onto ITO glass electrode, (b) attaching the membrane, (c) polypyrrole synthesis by using electrochemical polymerization.

carefully attached on the electrode. This working electrode was completely dried out in vacuum oven for 24 hours. Conducting polymer, polypyrrole, was electrochemically synthesized within the pores of the template by applying external potential. The electrochemical polymerization was carried out in a solution of 0.1 M pyrrole in 0.1 M $LiClO_4/CH_3CN$. To get conducting polymer/metal composite emitters, reduced polymer electrodes were immersed in 0.01 M $AuCl_3$/nitromethane solution for 30 min. All electrochemical experiments were performed after N_2 purging for 10 min and all potential values in this paper are based on Ag/AgCl (sat'd KCl) reference electrode. Methylene chloride (MC) was used to remove the membrane after polymerization for investigating the shape of polypyrrole emitters only.

Field emission current was measured using the field emission cell. The cathode was polypyrrole emitters which were embedded in polycarbonate membrane. Another piece of ITO glass electrode was used as the anode and kept 400 μm away from the cathode by using glass spacers. This measurement was carried out in a vacuum chamber at $\sim 10^{-7}$ Torr.

RESULTS AND DISCUSSION

Micro-structures of polypyrrole were prepared within pores of the template membrane by using electrochemical polymerization of 0.1 M pyrrole in 0.1 M $LiClO_4/CH_3CN$ electrolyte solution with potential cycling between −0.50 and 1.30 V. Figure 2(a) showed the representative cyclic voltammogram (CV) for the polymerization of pyrrole. As shown in

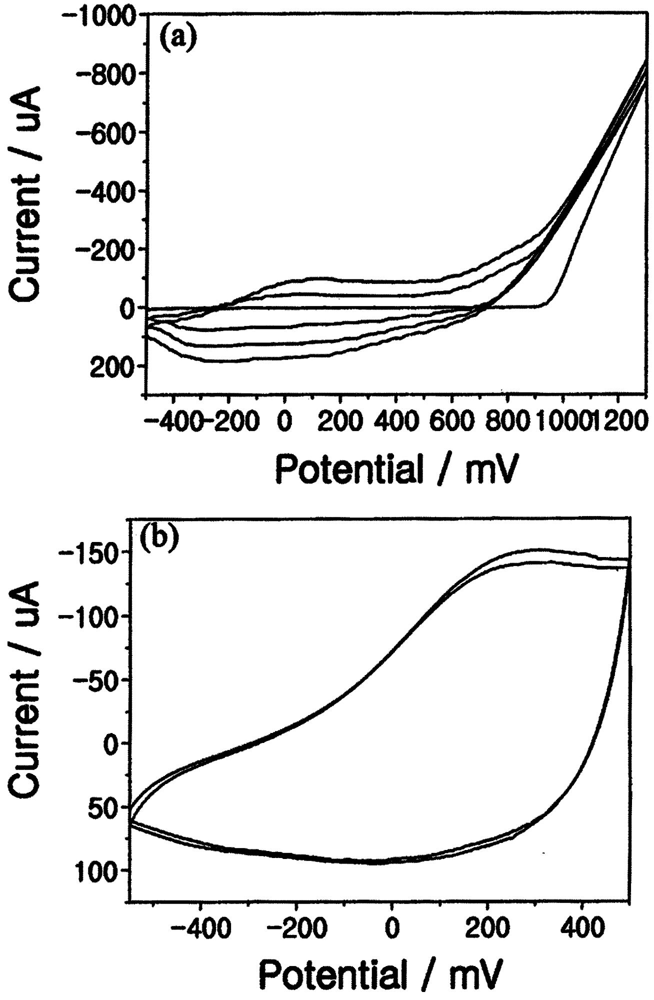

FIGURE 2 CVs of (a) electrochemical polymerization of pyrrole (in 0.1 M pyrrole in 0.1 M $LiClO_4/CH_3CN$) and (b) polypyrrole after removing the membrane (in 0.1 M $LiClO_4/CH_3CN$).

here, the oxidation current of monomer in the first anodic scan of CV rapidly increased at 0.95 V. This rapid increase mainly due to the increase in the active area of the electrode as the polymer formed on the electrode. The polymerized product began to be deposited within pores of the membrane at this stage. After the first anodic scan, the potential scan was changed to cathodic direction. This continuing cathode scan made the reduction peak (at *ca.* −0.30 V) of the polymer produced during the first oxidation process. By the successive cycles, the oxidation peak of the deposited polymer appeared at 0.15 V. The heights of peak pair due to the redox reaction of the deposited polymer were increased gradually during repeated cycles. This implied that polymer structures were being well fabricated within pores. SEM images of Figure 3 after polymerization confirmed this result. As shown in these SEM images, polymer structures in tubular shape were grown only within pores and there was no polymer on the template surface. We also observed that as the number of potential cycles was increased, pores of the membrane were filled with polymer and they finally began to appear on the membrane surface. Therefore, we need to control the number of cycles to keep polymer structures grown within pores.

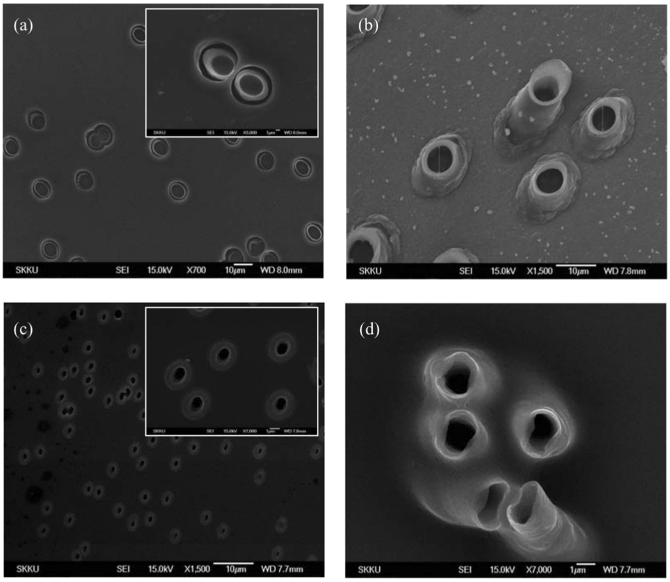

FIGURE 3 SEM images of polypyrrole emitters before and after removing of the membrane: (a) and (b); pore diameter of 10 μm, (c) and (d); 2 μm.

After polymerization, the membrane was removed with methylene chloride (MC) to investigate the electrochemical property and to observe the entire shape of polymer structures. As appeared in Figure 2(b), CV showed an oxidation peak at 0.30 V and a reduction peak at -0.15 V. The whole shape and peak positions of CV of polypyrrole emitters were well matched with other's results for polypyrrole [12,13]. EDAX analysis (not shown in here) also implied that these tips were based on polypyrrole and counter ion, ClO_4^-. From Figure 3, it can be clearly seen that these structures had the inside diameter of about $5 \sim 7$ and $1.3 \sim 1.6$ µm and the shape of structures was a primarily tubular form. This indicated that in early stage of polymerization, polypyrrole was laterally synthesized along the inside surface of pores from the circumference of pores bottom. It was interesting to note that the electrochemical synthesis of polypyrrole naturally lead to the formation of tubules while the electrochemical deposition of some metals and alloys produced wires [14,15]. It has been proposed that the electrostatic attraction between the synthesized polycationic polymer (in this case, oxidized polymer) and anionic sites along the pore walls of the polycarbonate membrane might lead to the preferential nucleation and growth of conducting polymers on the pore walls producing tubular structures instead of wires formation [16]. We also fabricated polymer structures with chronoamperometry method and they showed similar results.

The field emission characteristics of polypyrrole emitters were measured. Appling the reduction and oxidation potential with chronoamperometry method, fully reduced and oxidized polymer emitter samples were prepared. To prepare polypyrrole/Au composite emitters, we dipped reduced polypyrrole emitters in $AuCl_3$/nitromethane solution to induce the oxidation of polymer and concurrent reduction Au(III) to Au(0). In the case of fully reduced samples, almost no emitting current was observed because the polymer is in non-conducting state. Oxidized samples also showed no current response at a low electric field. However the current density rapidly began to increase at *ca.* 2.5 V/µm due to field emission and it reached to 36.3 µA/cm^2 at 4.2 V/µm, as shown in Figure 4(a). Composite emitters showed similar behavior in the low field range. Current began to increase slowly after *ca.* 3 V/µm and expressed current was 691 µA/cm^2 at 5.7 V/µm. This numerical value is about 19 times increase than that of fully oxidized polymer. This phenomenon is presumed by result that the conductivity of composite emitters is increased fairly than that of pure polymer. The insets in Figure 4 showed that Fowler-Nordheim (F-N) plot almost followed a linear relationship that proves the Fowler-Nordheim mechanism. The numbers in emission current density and turn-on

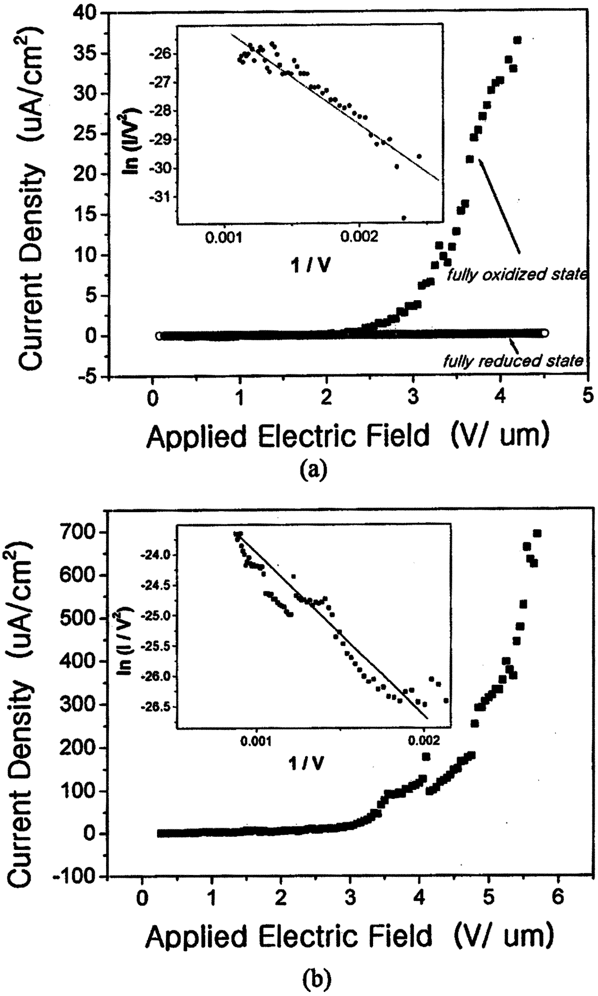

FIGURE 4 The current density plotted as a function of applied electric field strength to the emission cell: Inset: Fowler-Nordheim plot. (a) Polypyrrole and (b) polypyrrole/Au composite emitters.

voltage from our experimental results are comparable to those from other reports of conducting polymer based emitters. However, there are couple of things needed to be improved. First of all, compared to other metals such as gold, relatively low conductivity of the CPCG used in this experiment may increase the turn-on voltage. Secondly commercial polycarbonate membrane has a relatively low pore density (usually $10^5 \sim 10^8$ pores/cm^2; $10^9 \sim 10^{11}$ pores/cm^2 for aluminum oxide membrane) that may reduce the emission current density. Recently, we are trying to enhance the electrical conductivity of CPCG and the pore density through the composition change of CPCG and the use of other membranes.

As compared with the conventional methods, we fabricated the embedded type cathode tips by using an easy and simple process. Instead of metal evaporation, CPCG was used to bring membrane into contact with supporting electrode. And we could easily control the shape of polymer structures merely by the changing the electrochemical polymerization conditions such as the number of cycles and polymerization time.

CONCLUSIONS

In conclusion, conducting polymer emitters were synthesized by using the electrochemical template polymerization. In this process CPCG was used as a current collector and glue. Micro emitters showed similar electrochemical properties compared with those of the bulk. We could control the shape of emitters by varying the polymerization conditions and membrane specification. These structures were isolated from others and no polymers were found on the surface of membrane. The current density of field emission reached to 36.3 μA/cm^2 at 4.2 V/μm for oxidized polypyrrole emitters and 691 μA/cm^2 at 5.7 V/μm for composite emitter, respectively. These results showed the possibility to be used as tips for field emission display.

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