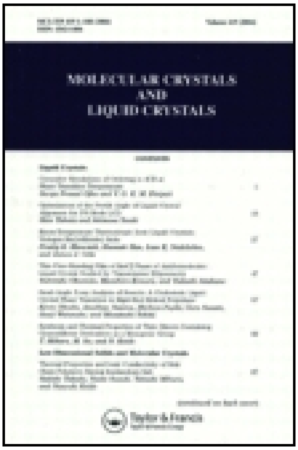

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Printed Circuit Patterns of Conducting Polymer

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Printed Circuit Patterns of Conducting Polymer

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In this work conducting polymer patterns were deposited by thermal ink jet printing technique on a plastic substrate. The poly(3,4-ethylenedioxythiophene):polystyrene sulfonic acid (PEDOT:PSS) composites were adopted as conductive inks for printing on polyester film substrate. The printed pattern has been investigated by optical microscopy and cyclic voltammetry (CV). The results have been compared to the ones obtained by other methods. No appreciable differences were noted between the electrochemical behaviors of the two samples, indicating that the thermal printing of the polymer composites did not alter appreciably the material properties. And we printed some different patterns and measure electronic properties, then metal particles were deposited onto the pattern by using direct redox reaction of the printed pattern and metal ion.

Keywords: conducting polymer; cyclic voltammetry; ink jet printing; PEDOT/PSS; polythiophene

INTRODUCTION

Electronically conductive polymers having conjugation system in their backbone have received a great deal of attention because of their unique properties related to optical, electrical, and electrochemical applications [1]. These materials are much lighter than metals and

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easy to be fabricated into various forms. These properties may be useful in the realization of a number of devices, such as for example electronic circuitry components [2], LEDs [3], sensors and biosensors [4]. In order to shape conducting polymers in well defined patterns, deposition techniques such as screen printing, soft embossing, inkjet printing, etc. [5], have been developed. Among these techniques, the inkjet printing looks like one of the most promising one for several reasons. First of all, it allows depositions of microdroplet of $2 \sim 12$ pl on any surface (plastics, metals, rubber, glass, silicon, etc.) with a very high precision. Moreover, the use of an array of ink-ejecting nozzles connected to a device-driving electronic system, which constitutes the typical configuration of a commercial print-head, permits to control the layout of a specific sequence of microdots. Finally, the absence of direct contact between the print-head and the support makes this technique particularly suitable for the deposition of materials on contact-sensitive substrates.

In this work, a conducting polymer ink was prepared and printed on a plastic and on a gold substrate by thermal ink jet printing technique. The PEDOT/PSS composite were adopted as a base material in this preparation and several surfactants and additives were also used. The printed pattern has been investigated by cyclic voltammetry, UV/VIS spectroscopy, SEM, and optical microscopy. The results have been compared to the those obtained by other methods. And we printed some different patterns and measure electronic properties. Metal particles, i.e., Au nano particles were deposited onto the pattern by using direct redox reaction of the printed pattern and metal ion.

EXPERIMENTAL

Tetrabutylammonium-tetrafluoroborate (TBABF4), 99%, polyoxyethylene-(20)-sorbitan monooleate (Tween 80), anhydrous acetonitrile (ACN) +99.9%, sodium borohydride, nitromethane and gold(III) chloride were purchased from Sigma-Aldrich and used as received. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonic acid (PEDOT:PSS) were purchased from Baytron. A three electrode cell geometry was used in all the electrochemical experiments. A thin Au film was used as working electrode. The counter electrode was a Pt plate, the reference electrode was a Ag/AgCl. BAS100B (Bioanalytical Systems, Inc) potentiostat/galvanostat interfaced with a personal computer was used in all the electrochemical measurements. Surface resistance measurements were carried out by means of the two-probe technique using a Keithley 4200 system.

PEDOT:PSS ink was prepared diluting 30 ml in distilled water until reaching 50 ml of total volume. The obtained dispersion was filtered by a 0.45 μm filter (Polytetrafluoroethylene (PTFE)) and then added Tween 80. The Tween 80 was used in order to achieve the ink surface tension characteristics necessary for the best efficiency of the thermal inkjet device [6]. The so-obtained ink was fed to a commercial thermal inkjet printer, Hewlett-Packard PSC 1210.

The inkjet deposition of the film was made on a thin Au film. The deposition was repeated 10 times over the same surface and the sample compared to the ones obtained by drop-coating. These samples have been investigated by cyclic voltammetry. Some different patterns were deposition on polyester film for 10 times over the same surface and measure electronic properties. Then metal particles (Au particles by 0.01 M $AuCl_3$/Nitromethane solution) were deposited onto the pattern by using direct redox reaction of the printed pattern and metal ion after reducing the pattern polymer by using saturated $NaBH_4$/ethanol solution).

RESULTS AND DISCUSSION

The PEDOT/PSS film was inkjet printed onto a thin Au film electrode, thereafter a successive electrochemical characterization was done for the deposed film sample. First of all a serial deposition was performed to examine the ink performance on an Au substrate and on a PET substrate. The ink shows good printing performance with an everyday-use ink jet printer. Results are presented in the Figures 2 and 6. A 10×10 mm film was obtained by ten successive printings over the same surface area of the Au substrate in order to realize a thick multi-layered film. In order to evaluate the thermal stress effect which was imparted by the printer head to the printed polymer, electrochemical properties of the multi-layered film were examined and compared to those from a film prepared by a drop-coated method as a reference sample. Cyclic voltammetry of the sample films were registered in 0.1 M TBABF4/ACN solution in 50% water was illustrated in Figure 1. The voltammetric path was obtained in the potential range from -0.8 to $+0.8$ V and the scan rate was 50 mV/s. Figure 1(a) shows the current response of the drop-coated film. A broad and large anodic current peak is appearing at 0.32 V and a cathodic peak is standing at -0.49 V vs. Ag/AgCl(sat'ed KCl) respectively. This type of CV is a well known electrochemical redox behavior of the PEDOP/PSS films [7]. A similar voltammertic path was obtained form the ink-jet printed film as appeared in Figure 1(b). Also in this case a cathodic peak was observable at a potential of 0.46 V with a corresponding anodic peak

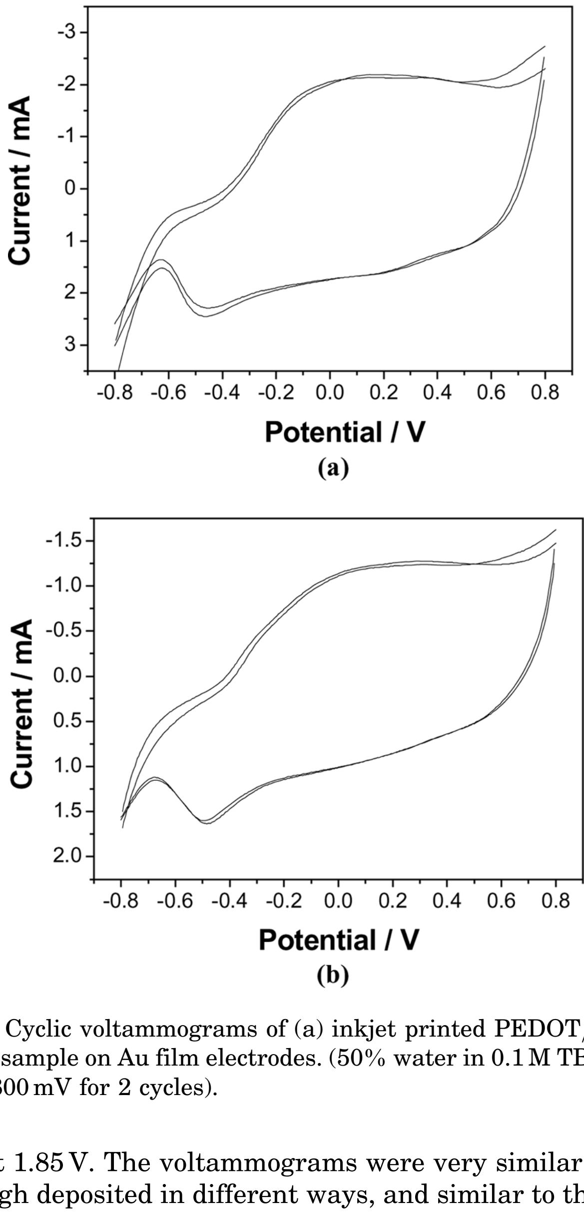


FIGURE 1 Cyclic voltammograms of (a) inkjet printed PEDOT/PSS and (b) drop-coated sample on Au film electrodes. (50% water in 0.1 M TBABF4/ACN, –800 mV ~800 mV for 2 cycles).

centered at 1.85 V. The voltammograms were very similar for the two films, though deposited in different ways, and similar to that reported in literature [7]. No appreciable differences in shape were detected between the voltammetric behavior of the two samples.

Draw patterns were made by using a commercial drawing software to obtain a printed patterns are in Figure 2(a). Printed patterns using the polymer ink are in (b) of the same figure. The printed patterns

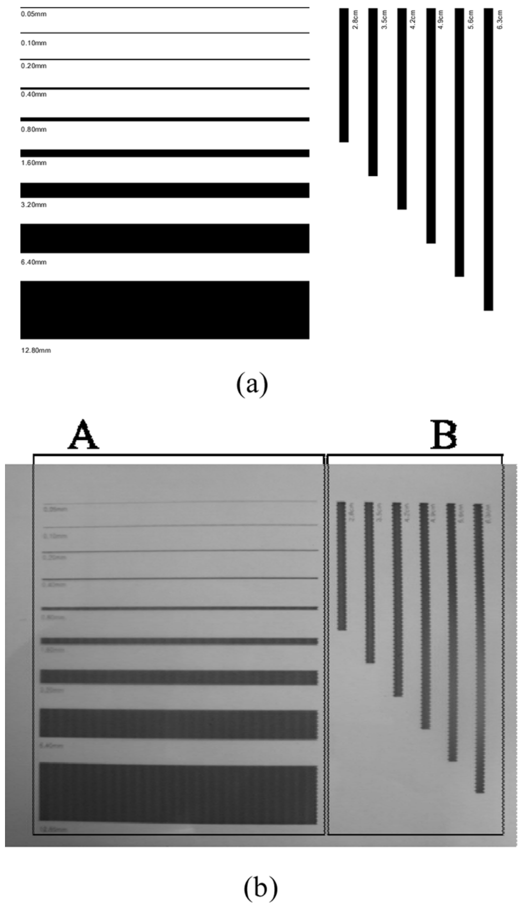
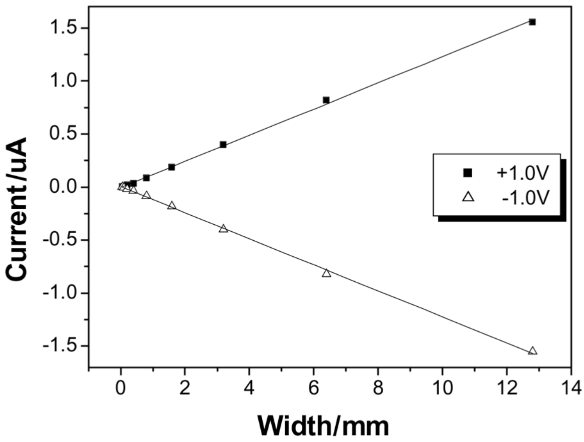
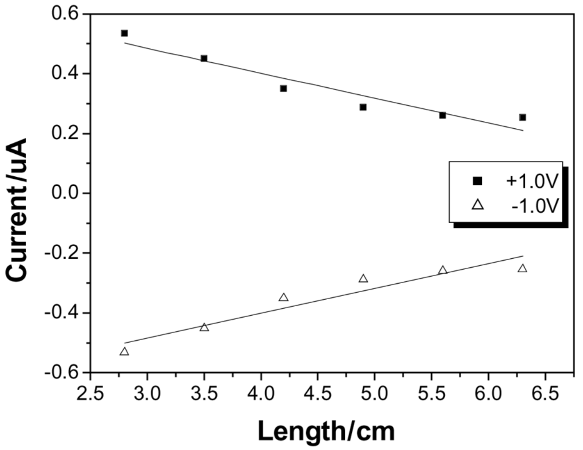


FIGURE 2 Patterns for printing (a), printed patterns from polymer ink on polyester film (b).

were also printed ten times over the same surface on polyester film to get multi-layered thick film. Printed patterns in ‘A’ part have same length with difference width, and ‘B’ patterns had different length with same width. Each width of ‘A’ patterns is 0.05, 0.10, 0.20, 0.40, 0.80, 1.60, 3.20, 6.40 and 12.80 mm. Each length of ‘B’ patterns is 28, 35, 42, 49, 56 and 63 mm. The difference in shapes between (a) and (b) is due to the art effect of using small lens digital camera in taking image of the printed pattern. Electrical resistances of these patterns have been measured with Keithley 4200 system with the applied voltage of $-1.0\,V$ and $+1.0\,V$. Figure 3(a) shows, when the current



(a)



(b)

FIGURE 3 Current measurements as a function of width and length of the printed pattern with 1 V bias. From printed patterns ‘A’ (a) and patterns ‘B’ (b).

plotted as a function of width, the linear relationship is appeared. The linear increase in reverse direction is observed with reversed bias was used. The data conform well to conventional conductive materials. The resistances of these patterns are reported in Figure 4. The resistance change as a function of the width or length shows that it simply follows Ohms law.

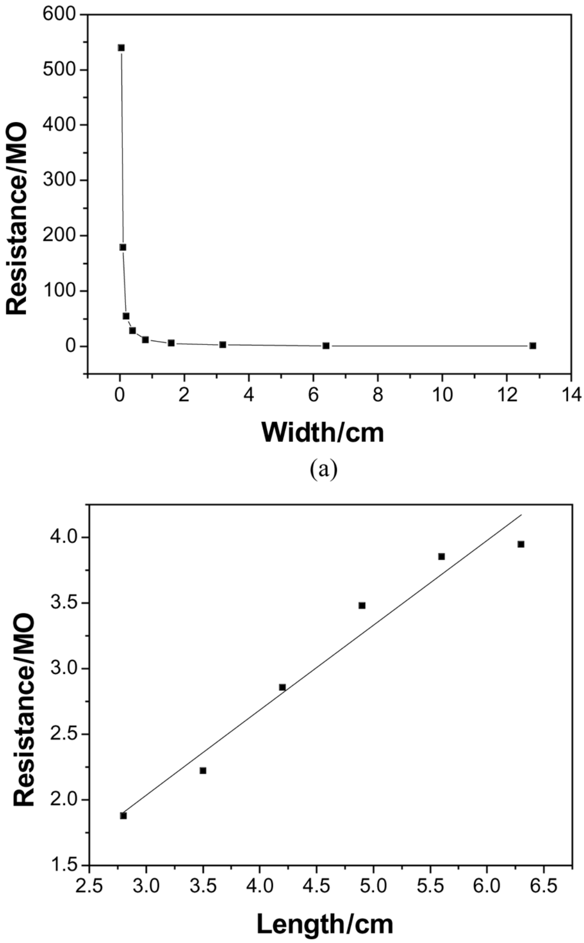


FIGURE 4 Resistance of printed pattern 'A' (a) and pattern 'B' (b).

On these patterns, gold particles were deposited by using direct redox reaction of the printed pattern and metal ion. The ink polymer is in its oxidized state, so this polymer should be reduced to induce the intended redox. First, all patterns as printed reduced by saturated $NaBH_4$/ethanol solution for 10 minutes. The UV/VIS spectra in Figure 5 shows a large absorption band over the 800 nm up near IR region of the oxidation state and after reduction treatment the appearance of an absorption band at 600 nm, which is due to the π–π^*

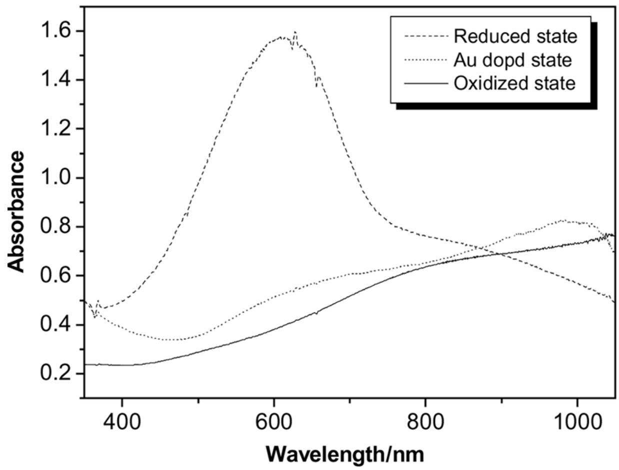


FIGURE 5 UV/VIS spectra of inkjet printed patterns of PEDOT/PSS before and after Au deposition.

transition of polymer in its neutral form is recognizable [8]. Then the gold particles were deposited by placing this reduced film into in 0.01 M $AuCl_3$/nitromethane solution for 1 hour. This film has been investigated by SEM, and surface images are shown in Figure 6. The reduced metal particles were identified as Au with EDAX analysis (not shown). This metal deposition may be able to enhance electrical conductivity. Research work related to the enhancement by metal doping is in the course at this laboratory.

CONCLUDING REMARKS

A continuous film of PEDOT/PSS was inkjet printed by means of a commercial thermal printer, and compared to another film of the same polymer deposed by drop-coating. No appreciable differences were noted between electrochemical characteristics of both films, indicating that the thermal and shear stress felt by the polymer did not alter appreciably the material properties. The printed patterns in different dimensions follow the Ohm's law. The printed pattern could be reduced chemically with $NaBH_4$. The reduced film was directly reacting with $AuCl_3$ to form Au particles on the film. These findings show that thermal inkjet printing may be an efficient and clean choice for the controlled deposition of thin films of PEDOT/PSS, and possibly also of other conjugated polymers. And we successfully deposited gold particles onto the printed patterns by using direct redox reaction.

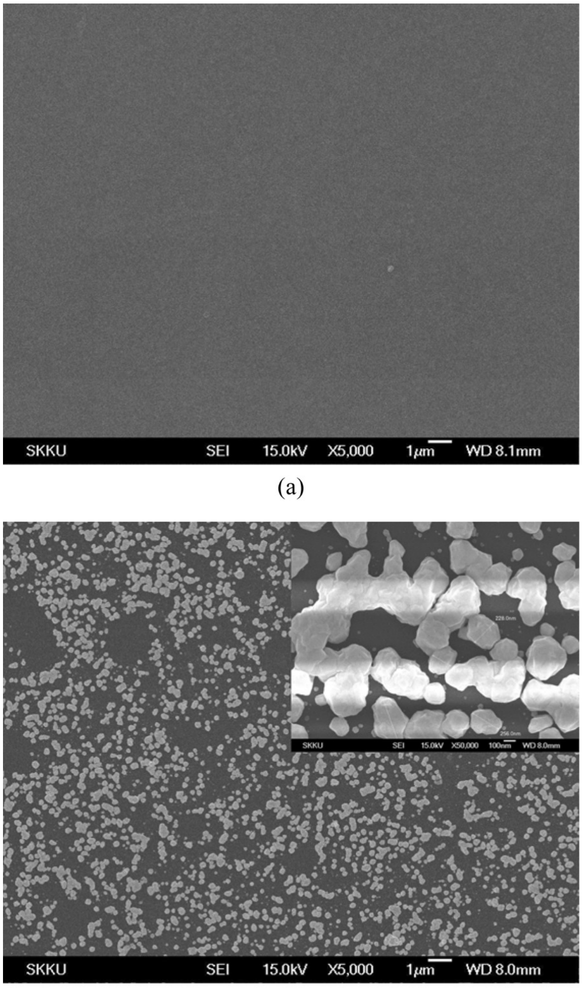


FIGURE 6 SEM images of surface before (a) and after (b) Au doping.

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