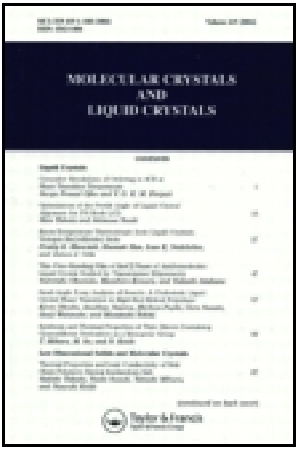

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Formation of Gold Nanoparticles During the Vapor Phase Oxidative Polymerization of EDOT Using $HAuCl_4$ Oxidant

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The thin layer of poly(3, 4-ethylenedioxythiophene) (PEDOT) on the PET film was obtained by a vapor-phase polymerization technique using $HAuCl_4$ as an oxidant. The EDOT monomer was easily oxidized by the $HAuCl_4$ oxidant while $HAuCl_4$ was reduced to form metallic Au nanoparticles. The formation of PEDOT/Au composite film was monitored by UV-vis spectra and SEM, and the formation of metallic Au was confirmed by EDAX and XPS.

Keywords: gold; PEDOT; vapor phase polymerization

INTRODUCTION

The area of conducting polymer has attracted a great deal of interest in the past 30 years following the discovery of the evolution of

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extremely high electrical conductivities of doped polyacetylene [1–2]. The conducting polymers are most commonly polyaniline, polypyrrole, polythiophene, polyphenylene, and poly(*p*-phenylene vinylene), etc. Amongst these, poly(3,4-ethylenedioxythiophene) (PEDOT) is regarded as possibly more environmentally stable and have been functionalized to facilitate aqueous solution processing using water soluble poly(styrene sulfonate) dopant [3–5]. PEDOT is a stable conjugated polymer with high transparency and high electrical conductivity in the doped (oxidized) state. However, recent reports appearing in the literature indicate that a degradation of PLEDs devices may be at least partially due to a degradation of the PEDOT [6]. So the enhancement of stability is one of the important issues on this research area.

The metal nanoparticles, such as silver and gold, have potential in technological applications and have attracted much attention due to their novelty and chemical characteristics [7]. The utilization of electrically conducting metal might offer a supplement answer for the intrinsic shortcomings of conducting polymers. Therefore, a metal/PEDOT composite formation might provide enhanced stability and conductivity compare with virgin PEDOT.

PEDOT film can be produced by direct chemical oxidation of the monomer using chemical oxidants [8–9], however, it is not trivial to obtain homogenous film using this method. In order to get the film of fine quality, a vapor-phase polymerization (VPP) has been used for making conducting polymers. The method was originally described by Mohammadi *et al*. for the polymerization of pyrrole [10]. It was later adapted for the formation of well-defined surface structure [11–12]. In our previous study, very high conductivity was obtained in the thin PEDOT films fabricated by the VPP technique using ferric toluenesulfonate (FTS) oxidant [13]. Our aim was to prepare and characterize gold nanoparticles in the conducting PEDOT films using the VPP in the presence of $HAuCl_4$ as anoxidant. In this work, the preparation and characteristics of conducting PEDOT/Au composite film are reported and compared with those of the PEDOT film polymerized on FTS oxidant.

EXPERIMENTAL SECTION

Materials

3,4-Ethylenedioxythiophene (EDOT) was supplied by Aldrich and was distilled and stored in a refrigerator. As an oxidant, 40 wt.% FTS in *n*-butanol solution from Bayer AG and $HAuCl_4$ from Aldrich were used as received.

Preparation of PEDOT Films

The PEDOT thin films were directly deposited on the PET substrate by a vapor phase polymerization technique. The oxidant solution, 30 wt.% $HAuCl_4$ or 30 wt.% of FTS in butanol was spin coated on the PET substrate which was subsequently exposed to an EDOT vapor in a reaction chamber at 50°C for 2–3 min. The resulting PEDOT films were washed with butanol and water for complete removal of residual oxidant and monomer and dried in a convection oven at 120°C for 1 h.

Characterization

Surface resistance measurements were carried out by means of the four-probe technique using a Keithley 236 current source and Keithley 617 electrometer. UV-visible spectra were obtained by spectrophotometer HP 8453. The morphology of the PEDOT film was observed using scanning electron microscopy (SEM, Phillips XL30 ESEM-FEG). An energy dispersive X-ray spectrometer (EDX, USL 30) attached to the SEM was used to determine the chemical composition of the samples. The thickness of the PEDOT film was measured using by an Alpa-step IQ (KLA Tencor Co. USA). X-ray photoelectron spectroscopy (XPS) measurements were carried out using a VG Scientific ESCA 2000 spectrometer with a Mg-Kα X-ray source operating at a power of 170 W (13 mA and 13 kV).

RESULTS AND DISCUSSION

Here we report the use of $HAuCl_4$ as an oxidant for the chemical synthesis of the PEDOT film containing gold nanoparticles. The conductivity of the PEDOT film from FTS and $HAuCl_4$ was 400 and $50\,S\,cm^{-1}$, where their thickness was 100 and 150 nm, respectively. So the higher conductive film was obtained by using FTS oxidant at same reaction condition. Figure 1 shows the UV-vis spectra of PEDOT films polymerized by $HAuCl_4$ and FTS as an oxidant respectively. The PEDOT film prepared with FTS shows a very broad absorption at >900 nm, suggesting the polymer structure is bipolaronic state indicating the formation of sufficient charge carriers [14–15]. The PEDOT film initially polymerized with $HAuCl_4$ followed by a subsequent treatment with FTS was also shown. The spectrum of PEDOT film using FTS fits well with the spectrum reported for electrochemically oxidized PEDOT at potentials around 1 V [16]. The spectrum of the PEDOT film using $HAuCl_4$ has a minor absorption peak at >700 nm and an increasing absorption in the visible range but no significant similarity to spectra reported for the oxidized PEDOT.

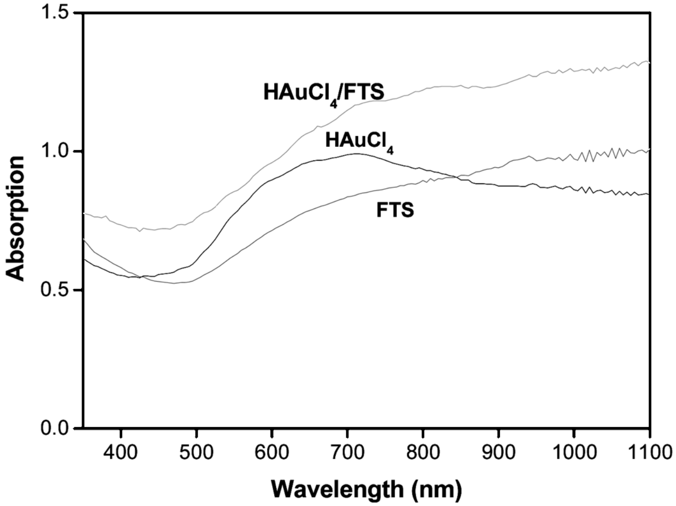
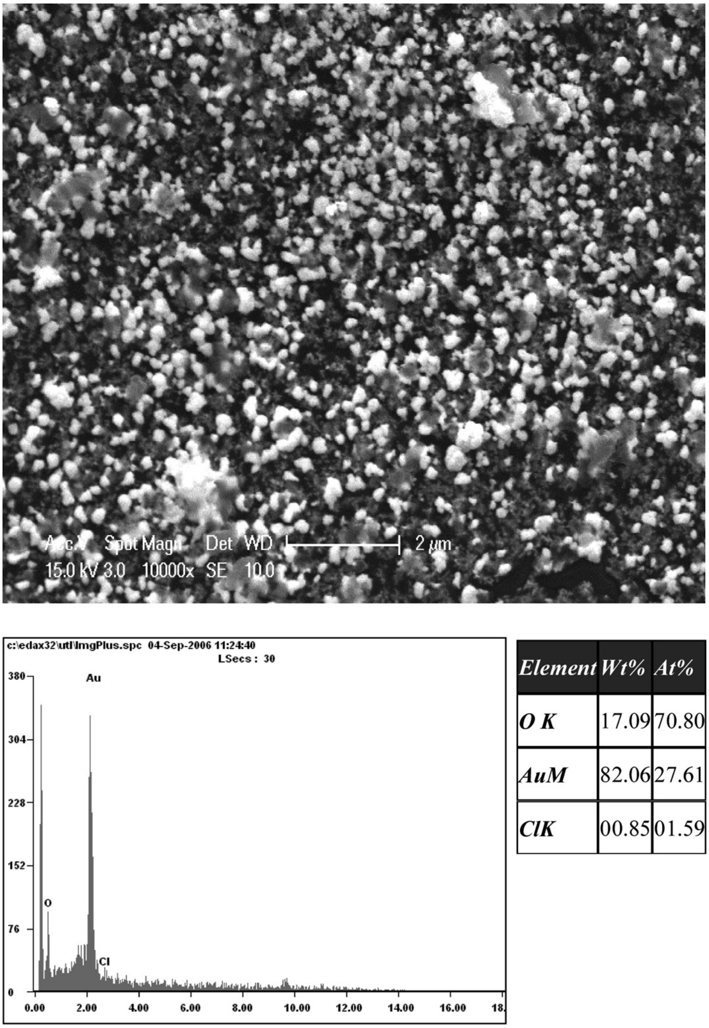


FIGURE 1 UV-vis spectra of PEDOT films polymerized on $HAuCl_4$, FTS, and post-Ox, respectively.

The lack of absorption band above 700 nm shows that the density of the polaronic states, which in oxidized PEDOT gives rise to a broad absorption above 600–700 nm, is low, which corresponds with the fact that the PEDT films obtained from $HAuCl_4$ are poor conductors. The reduced PEDOT has an absorption peak at around 600 nm corresponding to excitation of electrons across the band gap of the delocalized, semi-conducting states. It seems that, in some reason, Fe(+3) ions might be able to oxidize PEDOT species more easily than Au(+3). In order to confirm the facile oxidation of ferric ion, the PEDOT film prepared from Au(+ 3) was also treated with FTS in which the absorption at assigned to a polaron formation was disappeared and a new bipolaron band was emerged.

Figure 2 shows a representative energy dispersive X-ray analysis spectrum (EDAX, 30 mm^2) obtained from the PEDOT/Au films doped $HAuCl_4$. The spectrum shows peaks for Au (82 wt.%) and O (17 wt.%). The residual Cl signal is attributed to a few Cl^- that remain in the PEDOT films. The spectra proved that the chemical state of the gold incorporated into the PEDOT film was a metallic gold. The size of gold nanoparticles was determined from the SEM-image and was ca. 50 nm in diameter. These results may offer a new method of preparing conducting polymer-gold films as a new electrode.

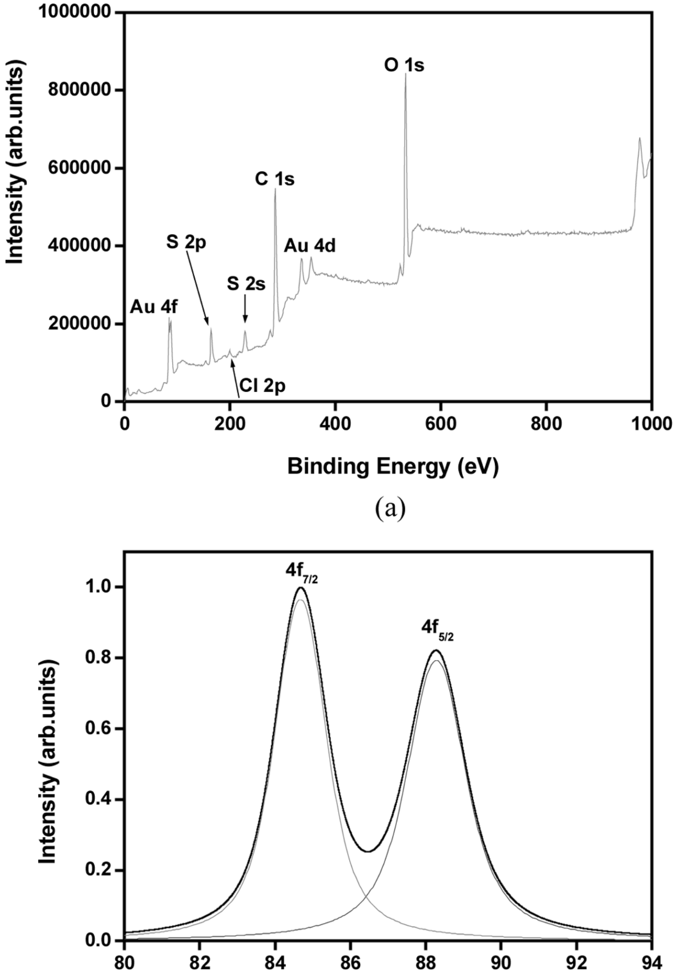
XPS confirmed the presence of zero-valent gold in the PEDOT film. Figure 3(a) clearly shows the detection of a strong pair of



Element	Wt%	At%
O K	17.09	70.80
AuM	82.06	27.61
ClK	00.85	01.59

FIGURE 2 SEM-image and EDS analysis of PEDOT/Au film doped $HAuCl_4$.

doublets at ca. 86 and 360 eV. These were assigned to Au 4f and Au 4d energy levels respectively. A close inspection of the peak-fitted Au 4f line spectrum [see Fig. 3(b)] revealed two strong signals due to electrons from the $4f_{5/2}$ and $4f_{7/2}$ energy levels. The $4f_{7/2}$ peak was centered at ca. 84.3 eV and the accompanying $4f_{5/2}$ peak was centered at ca. 88.1 eV. This doublet is characteristic of zero-valent gold [17].



(a)

(b)

FIGURE 3 XPS spectra of the PEDOT/Au film: (a) wide spectrum of PEDOT/Au film and (b) Au 4f line spectrum.

CONCLUSION

Gold containing PEDOT film can be simply prepared by oxidative polymerization of EDOT using a $HAuCl_4$ as an oxidant. It was shown that the oxidation power of Au(+3) ion is rather inferior to Fe(+3) oxidant. The formation of gold nanoparticles in the PEDOT film is proved by the EDAX spectra and the SEM-images.

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