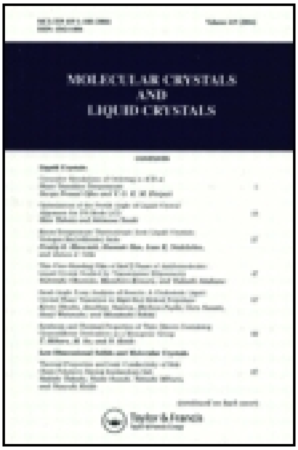

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

IN-SITU FORMATION OF GOLD NANOPARTICLE/CONDUCTING POLYMER NANOCOMPOSITES

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Version of record first published: 15 Jul 2010

To cite this article: M. Lee, B. W. Kim, J. D. Nam, Y. Lee, Y. Son & S. J. Seo (2003): IN-SITU FORMATION OF GOLD NANOPARTICLE/CONDUCTING POLYMER NANOCOMPOSITES, Molecular Crystals and Liquid Crystals, 407:1, 1-6

To link to this article: http://dx.doi.org/10.1080/744819006

Mol. Cryst. Liq. Cryst., Vol. 407, pp. 1/[397]–6/[402], 2003

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390261949

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Poly(3,4-ethylenedioxythiophene)/gold (PEDOT/Au) nanocomposites were prepared by in-situ redox reaction using PEDOT in the neutral state and $AuCl_3$ as an oxidant. $AuCl_3$ had a sufficient power to oxidize the neutral PEDOT film while it reduced to form gold nanoparticles in the polymer matrix. It was observed that the rate of redox reaction was strongly influenced by the solvent. Finally, the formation and coalescence of gold nanoparticles was clearly demonstrated by SEM and XPS experiments, and a rapid drop in film resistance was also monitored during the redox reactions.

Keywords: electrochemical oxidation; nanocomposite; XPS

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 easy to be fabricated

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This work was supported by the Advanced Materials and Process Research Center for IT at Sungkyunkwan University. (Grant No. R12-2002-057-03004-0).

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into various forms. However, they do exhibit not only limited conductivity compared to metal, but also instability upon ultraviolet irradiation, heat, and other environmental conditions. These drawbacks cause serious problems in practical applications of conducting polymers. In this work, conducting polymer/metal nanocomposites were prepared anticipating an answer in overcoming the fundamental shortcomings of conducting polymers. It is also expected that the metal nanoparticles in the composites might exhibit unique optical, electrical, magnetic, and catalytic properties [2]. In the composite preparation, poly(3,4-ethylenedioxythiophene) (PEDOT) and gold were selected for each components. PEDOT stands out for its high degree of visible light transmissivity and high environmental stability in the conducting state, along with a propensity toward multiple redox switches due to its ease of oxidation [3]. In order to confer suitable mechanical properties on PEDOT, a hybrid film was prepared by using inorganic silicate network by *in-situ* sol gel reactions as shown in literature [4].

In the preparation of PEDOT/gold nanocomposites, PEDOT films in the neutral state react with $AuCl_3$ producing oxidized PEDOT film, where the Au nanoparticles are collectively deposited by *in-situ* redox reaction. In this communication, the synthetic methodology and physical properties such as, electrical, electrochemical and morphological properties of nanocomposite are described in detail.

EXPERIMENTAL

PEDOT Film Fabrication

In order to provide mechanical strength on PEDOT film, inorganic silicate was incorporated by *in-situ* sol gel reactions. The silicate sol was prepared by dissolving 6 g of Tetraethylorthosilicate (TEOS) and 4 g of Mercaptopropyltrimethoxysilane (MPS) into the cosolvent of 4 g of H_2O and 86 g of isopropanol. MPS was used for the stabilization of gold nanoparticles. Nitric acid was added for hydrolysis catalyst and the solution pH was adjusted as 1.5. During the composite film formation, a suitable amount of EDOT and Ferric Toluene Sulfonate (FTS) oxidant were added into silicate sol, and the mixed solution was spin cast and finally baked in convection oven for 1 hr at 130°C for complete gellation. The resulting film was washed with *n*-butanol and deionized water to remove residual oxidants.

Preparation of PEDOT/Gold Nanocomposite

In order to prepare the PEDOT/gold composite, the PEDOT/silicate hybrid films were chemically doped by using $AuCl_3$ doping solution. The conducting PEDOT film was immersed in aqueous NH_4OH solution for 2 hrs for complete reduction. Then, the film was immersed in $AuCl_3$ solution. The doping solutions were prepared by adding $AuCl_3$ to acetonitrile(ACN) or nitomethane(NM) to have final concentration of 4 mM(ACN) and 2 mM(NM) respectively. The doping process was started with adding 4 mL of each doping solution in a quartz cell mounted on a UV/VIS spectrometer and then PEDOT or hybrid film was dip into the doping solution. The absorption spectral changes of the polymer films were recorded as a function of time after removing reference electrode by using of HP8453 diode array type spectrophotometer.

RESULTS AND DISCUSSION

PEDOT films were fabricated with inorganic silicate network to provide superior mechanical properties. In the PEDOT/silica film formation, a suitable amount of EDOT and ferric toluene sulfonate (FTS) oxidant were added into silicate sol, and the mixture was spin-cast and finally baked in convection oven for 1 hr at 130°C for complete gellation. The silicate sol contains an optimum amount of mercaptopropyltrimethoxysilane (MPS) which has an –SH group for stabilizing gold nanoparticle [5]. These films were electrochemically or chemically reduced to yield neutral PEDOT and subsequently oxidized by the reaction of $AuCl_3$. $AuCl_3$ has sufficient power to oxidize PEDOT film to conducting state while it reduces itself to Au.

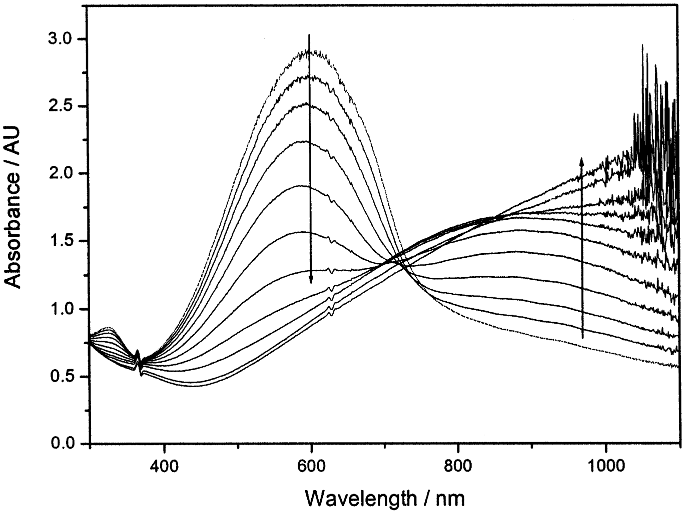

FIGURE 1 UV-Vis spectra of PEDOT during electrochemical oxidation (−0.8 ~ 0.8 V).

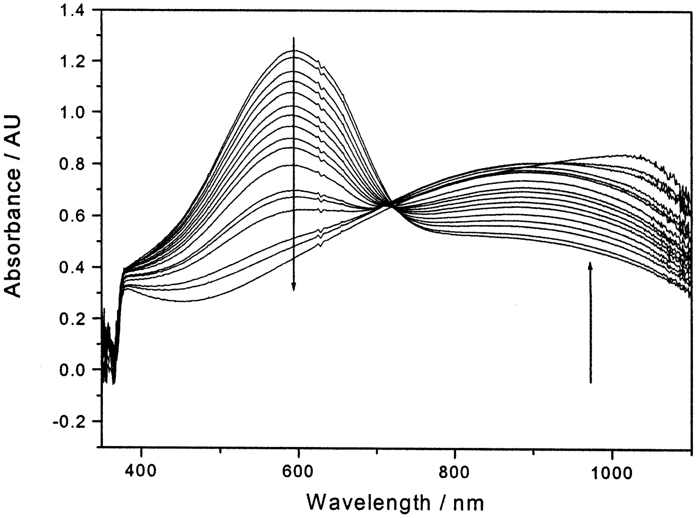

FIGURE 2 UV-Vis Spectra of PEDOT during chemical oxidation by $AuCL_3$ (for 1000 sec).

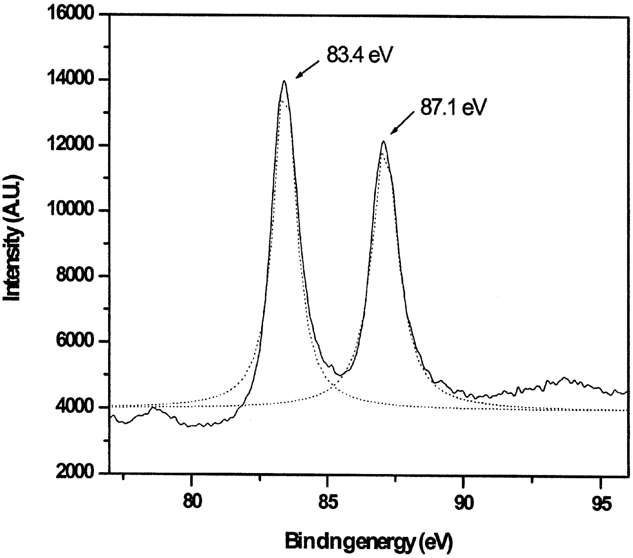

FIGURE 3 X-ray photoelectron spectroscopy spectra of PEDOT/Gold composite film.

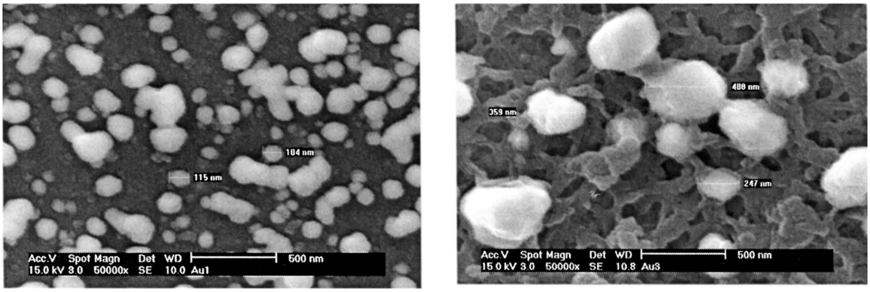

FIGURE 4 SEM images of gold nanoparticles; (a) after 10 sec, (b) ater 100 sec oxidation in nitromethane.

Figure 1 shows UV-VIS spectra of PEDOT films during the electrochemical oxidation process at the applied potential of −08 to 0.8 V. Upon oxidizing, the absorption band at 580 nm disappeared while the band responsible for the bipolaronic species at >800 nm appeared. A single isosbestic point is clearly appeared at 700 nm.

The oxidation process of neutral PEDOT using nitromethane solution of $AuCl_3$ was monitored by UV-Vis spectroscopy. The ***in-situ*** UV-Vis spectra captured during the oxidation process are shown in Figure 2. The absorption maximum at 570 nm decreases and the absorption band at >800 nm increases as the reaction proceeds. This behavior seems to be

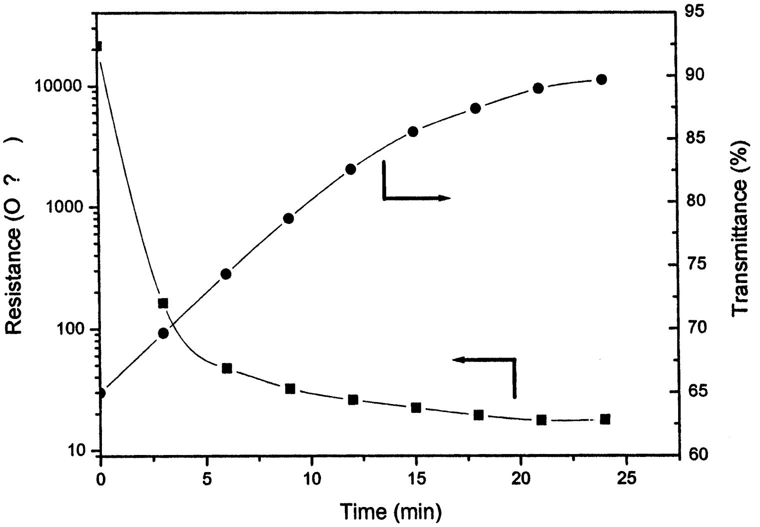

FIGURE 5 Resistance and transparency of PEDOT/gold nanocomposite film during doping reaction.

quite similar to the electrochemical doping process as already shown in Figure 1. The formation of gold particle was also confirmed by the X-ray photoelectron spectroscopy (XPS) (Figure 3). The XPS spectrum of oxidized PEDOT film shows the presence of gold species of which binding energies are 83.1 and 87.3 eV [6]. It was also revealed that the kinetics of oxidation reaction of $AuCl_3$ strongly depended on the reaction medium. Nitromethane allowed much faster reaction than acetonitrile. The formation of gold nanoparticles during the doping reaction of the PEDOT/silicate hybrid film containing MPS was demonstrated by SEM in Figure 4(a) and (b).In the early stage of doping, it can be seen that the gold particles are small and well dispersed, but the small particles starts to coalesce after 100 sec. During the doping process, the rapid drop in resistance as well as enhanced light transparency were also monitored as shown in Figure 5.

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