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Reaction factors for photo-electrochemical deposition of metal silver on polypyrrole as conducting polymer

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ABSTRACT

Composite of metal and conducting polymer is expected for electrical application by the use of their advantages. For improvement of the composite's characteristics, it is important to control formation rate and structure of the composites obtained by simultaneous metal deposition and polymerization under photo irradiation. The purpose of this research was to reveal the effects of UV irradiation and dopant type for conducting polymer on photo-electrochemical deposition of metal. Cathodic polarization curves for silver deposition on polypyrrole doped with different types of anion at different intensity of the UV light were compared. Deposited particles were evaluated by the statistical analysis. The experimental results showed that silver deposition on polypyrrole was enhanced by UV introduction and depended on the dopant type.

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1. Introduction

Composites of organic polymer and metal are promising to be applied to various fields of electronics, catalyst, sensor, etc by taking advantages of their characteristics such as conductivity and flexibility. Although there are various selections of metal and polymer, the composites of silver and conducting polymers are attractive mainly because of their electrical characteristics [1–5]. The composites of polypyrrole as conducting polymer and metal silver had the conductivity $2.0 \times 10^4\,\Omega\,cm^{-1}$ two orders of magnitude higher than commercial conducting polymer [6] and also were mechanically flexible and strongly adhesive to various plastic substrates [7,8].

Conducing polymer/silver composites were fabricated by a single-step formation process [9–11], which is attractive in terms of time and cost for large scale production. In this process, oxidative polymerization of conducting polymer took place simultaneously together with reductive deposition of metal in one reaction system. This process was accelerated by introduction of UV light to the reaction system and the formation rate of the composite ~40 nm s^{-1} was ten times larger than that by current techniques of metal formation such as electroplating and CVD [6]. Reaction condition such as anion type for conducting polymer could change the composite structure, leading to improve the conductivity by 4 orders of magnitude in the state of thin film [8,12].

For further improvement of the composites' characteristics, it is important to reveal their formation mechanisms. So far, the acceleration mechanisms by the UV introduction were studied regarding formation of silver/polyaniline composite [9,13]. In these studies, UV irradiation might influence on the polymerization step by activating aniline monomer and nitrate ion as reaction reagents. On the other hand, there has been no reports focusing on the effect of the UV irradiation on the silver deposition step upon the formation of the composite. In addition, most reports about the structures of the composite obtained by the single-step formation process showed that silver was incorporated as a core or dispersed inside the conducting polymer [10,14–18]. In some reports, metal silver was deposited on the surface of the polymer [6,19,20]. In order to control the structure of the composite formed by the simultaneous reactions of silver deposition and polymerization under UV irradiation, it is essential to reveal the role of UV light on silver deposition. Although electroless deposition of silver on conducting polymer without any special attention to a light condition [21] and silver deposition behaviour on inorganic oxide

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semiconductor under photo irradiation [22,23] were studied, deposition behavior of metal silver on conducting polymer under the photo irradiation is still unclear as well as the role of doping anion in conducting polymer upon silver deposition.

The purpose of this study was to reveal the effect of UV irradiation and dopant type on metal deposition behaviour on conducting polymer. Deposition rates on films of polypyrrole as a conducting polymer with different types of doping anion were evaluated by electrochemical techniques under the UV irradiation with different light intensity. In addition, the statistics of deposited particles were analyzed.

2. Experimental

2.1. Preparation of conducting polymer

A film of conducting polymer was prepared by anodic polymerization with three electrode electrochemical cell. The cell was schematically illustrated in Fig. 1 and had two windows at parallel walls of the cell. One window was covered with optically transparent glass and the other was covered with the front surface of working electrode, which was faced to the electrolyte at an exposed area of 0.78 cm^2. A stainless steel SUS304 plate was used as the working electrode and was abraded with SiC paper at grit size #600, ultrasonicated in acetone for 5 min and dried by blowing nitrogen gas, followed by setting to the cell. The electrolyte was a solution containing 0.1 M pyrrole (C_4H_5N, Junsei Chemical) and 0.1 M salt in organic solvent. In this study, the salt played roles in both supporting electrolyte and supplying source of doping anion in polypyrrole. Lithium tetrafluoroborate ($LiBF_4$, Wako Pure Chemical Industries), lithum hexafluorophosphate ($LiPF_6$, Tokyo Chemical Industry) or tetra-ethyl ammonium p-toulenesulfonate ($(C_2H_5)_4NCH_3C_6H_4SO_3$, KANTO KAGAKU) was dissolved into acetonitrile and lithium nitrate ($LiNO_3$, Wako Pure Chemical Industries) was dissolved into ethanol. The counter and reference electrodes were a platinum plate and a silver wire, respectively.

Galvanostatically anodic polarization was carried out to prepare polypyrrole films at constant electrical charge of 60 mC cm^{-2} (typically applying current at 10 $\mu A\,cm^{-2}$ for 100 min) with a potentiostat/galvanostat (HOKUTO DENKO CORP., HZ-5000).

2.2. Electrochemical deposition of silver

Deposition of silver on the polypyrrole electrode was carried out by using the same electrochemical cell as explained above (see Fig. 1). After preparation of polypyrrole, the cell was rinsed out with acetonitrile. Therefore the working electrode was a film of polypyrrole with different types of doping anion prepared on the stainless plate explained above. The electrolyte was 0.1 M of silver nitrate ($AgNO_3$, Wako Pure Chemical Industries) in acetonitrile. The counter and reference electrodes were a platinum plate and a silver wire, respectively. The potentiostatic polarization was carried out for 300 sec at −50 mV versus Ag/Ag^+ electrode potential. The UV light was introduced to the front surface of the working electrode through the electrolyte and the optical glass at the opposite side of working electrode. The light source was a super high pressure mercury lump (Ushio SX-UI502HQ-STC, USHIO INC., emission lines: 436, 405 and 365 nm in wavelength). The light intensity was adjusted 0–50 mW cm^{-2} at the surface of the working electrode. After the reaction, the substrate with deposit was removed from the solution, rinsed out carefully with acetone and dried at ambient temperature.

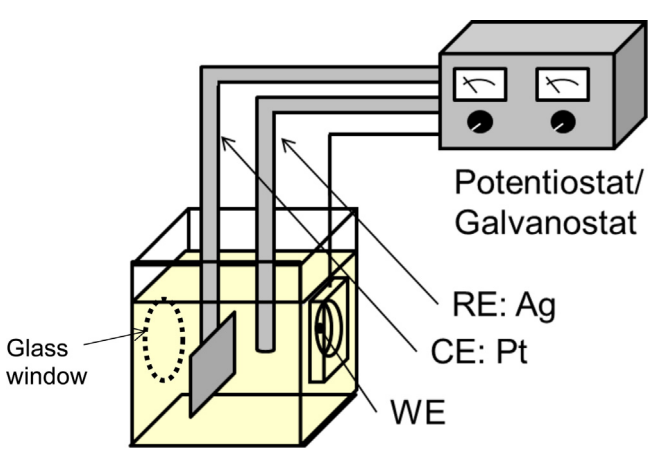

Fig. 1. Schematic illustration of electrochemical cell.

2.3. Characterization of specimens

The surface morphology of the specimens was observed by scanning electron microscopy (SEM, Hitachi High-Technologies Corporation SU-8000 and S-4800). The electrical resistance of the specimens was measured by using an instrument of Mitsubishi Chemical Analytech Co., Ltd. (Loresta GP MCP-T610), referring to the Japanese industrial standard (JIS) K 7194:1994 about testing method for resistivity of conductive plastics with a four-point probe array.

3. Results and discussion

3.1. Effect of light intensity on silver deposition behaviour

Fig. 2 shows changes in current with time obtained on the electrode of polypyrrole doped with BF_4 during potentiostatic polarization at −50 mV versus the Ag/Ag^+ reference electrode in the dark and under UV radiation with different light intensity. Current at a certain potential was increased with the light intensity. Here, the current observed was considered to correspond to the rate of silver deposition caused by cathodic polarization according to the following equation,

$$Ag^+ + e^- \rightarrow Ag^0. \quad (1)$$

Therefore, the increase in current with the light intensity indicated that deposition of silver was accelerated by UV radiation. On the other hand, spontaneous deposition of silver by reduction without cathodic polarization under UV irradiation did not seem to take place on the polypyrrole electrode. This is because the electrode potentials for oxidative decomposition of polypyrrole as the electrode and of CH_3CN and NO_3^- involved mainly in the electrolyte are too high to inhibit oxidation as the paired reaction

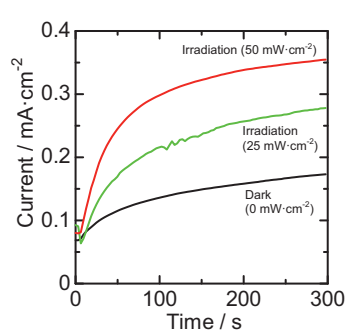

Fig. 2. Changes in cathodic current with time on polypyrrole doped with BF_4 during potentiostatic polarization at −50 mV versus Ag/Ag^+ with different intensity of UV light.

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