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Photothermal and optical absorption studies of electrodeposited polyaniline

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Abstract: Photothermal spectroscopy using thermistor is applied to study the heat generation by nonradiative processes in electrodeposited polyaniline together with the optical absorption. Although the optical absorption spectra showed several peaks, photothermal ones showed monotonous changes against photon energy. It shows that the increase of signal intensity of heat generation is different from that of optical absorption.

1. INTRODUCTION

Polyaniline is a very attractive conducting polymer because it exhibits good stability and the redox mechanisms involve the exchange of protons and electrons[1]. Also, it has attracted much attention because of fundamental interest and possible applications such as batteries, electrochromic displays and others as well[2,3]. However, the recent literature on this material is not clear and subject to controversy. Although several investigations have been carried out on the optical absorption[1,4], there are few investigations on the photothermal spectroscopy of polyaniline. In general, photothermal spectroscopy will offer useful information on electron-phonon interactions. We present here the experimental results of photon energy dependence of the direct detection of temperature changes resulting from nonradiative processes in electrodeposited polyaniline together with optical absorption using a simple photothermal spectroscopy apparatus (PTS) by Brilmyer et al[5].

2. EXPERIMENTAL

Polyaniline films were deposited on ITO glasses by constant-potential electrolysis (+0.7 V versus Ag/AgCl electrode (RE)) in aqueous solution containing 0.5 M aniline in 1.0 M HCl(1-5 min.). NaOH was added in order

to investigate the pH dependence of PTS and optical absorption on polymerization. Then the potentiostatic oxidation was carried out at +0.6 V versus RE (2.5 min.) in 0.1 M HCl following the reduction at -0.2 V versus RE (2.5 min.). The films exhibit a granular morphology except 1 min. polymerization sample which exhibits a fibril morphology and the thickness is approximately $0.5 \mu\text{m}$ for all the samples. The cell for PTS is described elsewhere [5-7]. PTS measurements were carried out by two thermistors in a differential arrangement (one for the sample and the other for reference) which was compensated for changes in ambient temperature. The thermistor has a nominal resistance of $12 \text{ k}\Omega$ and a sensitivity of $480 \Omega/\text{K}$ at 20°C . The signals were measured as the difference of resistance between working and reference thermistors, since temperature changes in the sample resulted in an unbalance of a Wheatstone bridge powered by a dc 1.0 V. The light source was a 500 W short arc xenon lamp. The light beam was focused on the sample through a monochromator with light impinging on an area of 0.16 cm^2 . Neither thermistor was irradiated by the exciting beam during the experiment. PTS measurements were carried out at room temperature over the wavelength range from 320 nm to 900 nm. The PTS signal intensity was always divided by the light intensity measured by PTS of carbon for normalization. The optical absorption and reflection were measured by conventional methods.

3. RESULTS AND DISCUSSION

Fig. 1 shows the PTS signal intensities of electrodeposited polyaniline films without potentiostatic oxidation in $\text{pH} = 1.0$ for different polymerization times as functions of photon energy. They show monotonous changes and the peaks at 4.0 eV. The total rates of optical energy absorption, $1-T-R$ (T: transmittance; R: reflectance), in polyaniline films without potentiostatic oxidation are plotted in Fig. 2. Fig. 2 shows that there are minima at 2.5 eV photon energy for different polymerization time. In order to compare the increases and changes of both PTS and $1-T-R$, PTS signals were divided by $1-T-R$ ($\text{PTS}/(1-T-R)$). Fig. 3 shows the

Fig. 1. Photon energy dependence of PTS of polyaniline films without oxidation for different polymerization times ($\text{pH}=1.0$).

Fig. 2. Photon energy dependence of 1-T-R of polyaniline films without oxidation for different polymerization times (pH=1.0).

Fig. 3. Photon energy dependence of PTS/(1-T-R) of polyaniline films without oxidation for different polymerization times (pH=1.0).

photon energy dependence of the PTS/(1-T-R) for polyaniline films without potentiostatic oxidation for different polymerization times. The result indicates that the increases and changes of PTS are identical with those of the total rate of optical energy absorption except the case for 1 min. polymerization. Fig. 4 shows the PTS signal intensity of electrodeposited polyaniline films with oxidation as a function of photon energy for different pH values. They show monotonous changes and the peaks at 4.0 eV. The slope of the decreasing of the PTS signal between 1.5 eV and 3.0 eV is depend on the pH values. 1-T-R of polyaniline films are plotted in Fig. 5. Fig. 5 shows that there are two peaks (~ 2.1 eV, $\sim$

Fig. 4. Photon energy dependence of PTS of polyaniline films with oxidation for different pH values.

Fig.5. Photon energy dependence of 1-T-R of polyaniline films with oxidation for different pH values.

Fig.6. Photon energy dependence of PTS/(1-T-R) of polyaniline films with oxidation for different pH values.

4.0 eV) and another peak (~ 3.0 eV) for pH = 3.0 and 4.0. The spectra of 1-T-R are different from those of the PTS. Fig.6 shows the photon energy dependence of the PTS/(1-T-R) for polyaniline films with oxidation. The result indicates that the increases and changes of the PTS are different from those of the total rate of optical energy absorption, 1-T-R, and depend on the pH values. Fig.6 suggests that there is a different yield of thermal deactivation and it is related to the polymerization processes of electrodeposited polyaniline with oxidation.

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