Photocurrent Decay Kinetics of Acetylferrocene

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Abstract

This work deals with the investigation of the photocurrent decay kinetics in a ferrocene (FcH) derivative, acetylferrocene (AFc). A five-fold increase of current in AFc sample was observed within few seconds after exposing the sample with polychromatic light at a temperature 284 K. After switching off the light, following the initial fast decay, current reaches the initial dark current value within few minutes. In the present experiment, the kinetics of photocurrent decay in the case of AFc follows the power law. The sublinear dependence of photocurrent with time indicates the exponential type of trap distribution in this ferrocene derivative. From the slope of the decay curve the characteristic temperature (T_c) of exponential trap distribution was also calculated for AFc at this temperature. The results have been compared with the previous experiments of dark and photoconductivity of AFc.

Keywords: *acetylferrocene, photocurrent, decay kinetics, trap distribution, recombination*

1. Introduction

The first synthesized organometallic semiconductor, ferrocene (FcH) and its derivatives are drawing much attention nowadays due to their interesting physical, chemical and electrochemical properties. Their interesting physical properties along with high stability makes them highly attracting in practical applications and as a result they are used widely in different fields of science and technology [Carraher C.E., Sheets J.E. and Pittman C.U.,1982]. For instance, ferrocene and its derivatives are used widely in the development of biosensors [Sęk J.P., Kasprzak A, Bystrzejewski M., Poplawska M., Kaszuwara W., Stojek Z., Nowicka A.M., 2018], in the preparation of charge transfer complex with organic solid [Gutmann F., Keyzer H. and Lyons L.E., 1983], in the preparation of new material of higher electrical conductivity [Ozaki J., Watanbe T. and Nishiyoma Y., 1993]. In the field of organic electronics they

are used efficiently in organic solar cells [Patil Y., Misra R., Singh M.K. and Sharma G.D., 2017; Daeneke T., Kwon T.-H., Holmes A.B., Duffy N.W., Bach U and Spiccia L., 2011], in high mobility organic field effect transistor [Nar I., Atsay A., Altındal A. and Hamuryudan E., 2018] etc. The studies of photoconductivity of these materials showed some interesting results like anomalous changes in the photocurrent [Bera R.N. and Mallik B., 1998; Chakraborty A.K., Bera R.N., Bhattacharjee A. and Mallik B., 1998; Chakraborty A.K. and Mallik B., 2009], which was explained by phase transition. Such phase transition affects the trapping/detrapping and charge carrier recombination processes. In this work I studied photocurrent decay kinetics of a ferrocene derivative, acetylferrocene (AFc) at a temperature lower than room temperature. The kinetics of photocurrent decay provides us with ideas of trapping/detrapping and recombination processes.

2. Experimental

Highly pure AFc was purchased from Aldrich Chem. Co., Inc. (Milwaukee, Wisconsin, USA) in powder form and were used after further purification by recrystallization. The experiment was carried out by the conventional sandwich cell technique [Rosenberg B., Misra T.N. and Switzer B., 1968]. The pure dry powder of AFc (10 mg) was placed between an indium tin oxide (ITO) coated glass and a stainless-steel electrode and kept inside a brass chamber, fashioned with Teflon and having a quartz window at the top for the passage of light. The sample cells were prepared in air and in safe of light illumination. All the measurements were performed by keeping the sample in a controlled dry nitrogen atmosphere. Before the conductivity measurements, desorption of water vapor or any pre-adsorbed (if adsorbed during sample cell preparation) vapours/gases from the sample was ensured by repeated heating and cooling treatments of the sample, initially in vacuum and finally in dry nitrogen gas atmosphere. A d.c. bias potential 25 V across the electrodes was

applied from the voltage source of a programmable electrometer (model 617, Keithley Inst. Inc., Cleveland, OH, USA). The current was also recorded by the same electrometer. A proportional temperature controller (model RTE 110, Neslab Inst. Inc., NH, USA) was used to control the temperature of the sample inside the chamber. The Temperature was measured by using a copper-constantan thermocouple attached at the top of the metal electrode with the help of a digital millivoltmeter. The details of the experimental set-up can be found elsewhere [Chakraborty A.K., Bera R.N., Bhattacharjee A. and Mallik B.,1998]. A 125 W mercury lamp was used as the polychromatic light source for the photoconductivity measurements. The approximate integral photon flux reaching the sample surface was about 3.0 x 10^{12} cm^{-2}. In this experiment the conductivity cell consisted of two junctions of stainless steel/AFc and AFc/ITO. To check whether the junctions were rectifying or Ohmic, the current measurements in a sandwich cell of the material were performed with forward as well as reverse bias. The values of measured current with both forward and reverse bias were almost equal which indicated that both the junctions were Ohmic in nature.

3. Results and Discussion

For the photocurrent decay kinetics study, AFc sample cell was irradiated with polychromatic light of a mercury lamp (125W). Figure 1 shows the change of current with time before irradiation, during irradiation and after irradiation at a temperature 284 K. From the Fig.1, it is clear that the current increases rapidly in the initial stage of illumination, then there is a slow rise and finally attains an equilibrium value of current. A five-fold increase in current has been observed in the present intensity of incident light. Similarly, after switching off the light, following the initial fast decay, current reaches the initial dark current value within few minutes. In the present experiment, photocurrent (I_{ph}) was measured by subtracting the dark current (I_d) i.e., current before irradiation from the total current (I_t), i.e., current during irradiation or after switching off light. The direct electron-hole recombination and recombination via shallow traps gives fast decay of photocurrent [Pal P., Ghosh D., Jain K.M., Misra T.M., 1987]. The dominant levels which have higher capture or release crossection also contribute to the fast decay of photocurrent. On the other hand exponential decay is expected when trapping of carriers freed from traps is negligible [Pal P., Ghosh D., Jain K.M., Misra

T.M., 1987]. The slow decay of photocurrent can be expressed by [Hansmeier, 1974],

$$\frac{1}{I_{ph}} = kt + c \qquad (1)$$

where, I_{ph} is the photocurrent at time t; k and c are positive constants. From Eq. (1), we get ,

$$-log\ I_{ph} = log\ (kt+c) \qquad (2)$$

If t be very large such that $kt >> c$, then Eq. (2) can be written as

$$I_{ph} \propto t^{-n} \qquad (3)$$

This is known as power low. A plot of $log\ I_{ph}$ vs $log\ t$ following Eq. (3) gives a straight line, the slope of which gives the value of n.
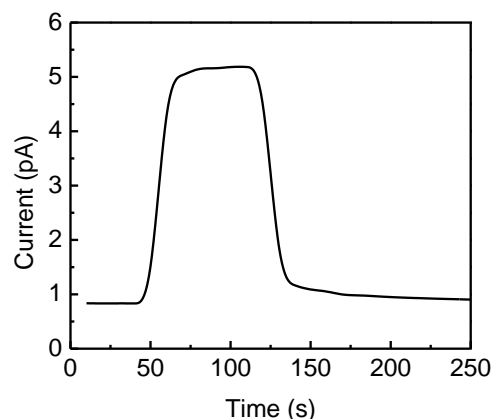

Fig. 1. Photocurrent rise and decay in acetyl ferrocene at a temperature 284 K with 25 V bias.

I studied decay of I_{ph} at a temperature of 284 K. Such decay plot in log-log scale is shown in Fig.2. Good straight line plot was noticed in log-log scale, indicating that $kt >> c$ in the present case. The value of n was calculated from the slope of the straight line and found to be 0.74. The observation of a single straight line in the measured time scale of the present investigation for a fixed temperature indicates that n is constant for the measured time scale. In the present study of slow decay, the calculated value of n is lower than 1, which indicates the presence of exponential type of trap distribution in AFc. The light intensity dependent photoconductivity study also suggested the presence of exponential type trap distribution in

this material [Bera R.N. and Mallik B., 1998]. However, from the dark conductivity measurements, single discrete level type trap distribution had been reported for AFc [Chakraborty A.K., Bhattacharjee A., and Mallik B., 1994].

For exponential trap distribution the value of power *n* can be expressed as [Tiedji T. and Rose A., 1981]

$$n = 1 - \frac{T}{T_c} \qquad (4)$$

where, T_c is a constant known as characteristic temperature for exponential trap distribution. T_c gives the rate at which trap density falls with energy. The value of T_c was calculated following Eq. (4) and the calculated value is 1092 K in the present investigation.
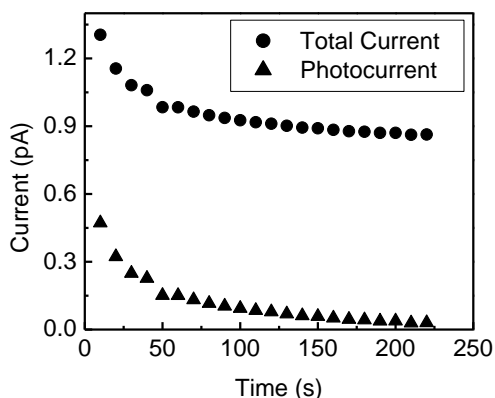

Fig. 2. Total current and photocurrent in acetylferrocene after switching of the light.

There are two coplanar cyclopentadienyl rings in an AFc molecule, which are lying above and below an iron centre. The two cyclopentadienyl rings may rotate with respect to each other as if the metal acts as a "ball-bearing" in between them [Medina J.C., Li C., Bott S.G., Atwood J.L. and Gokel G.W., 1991]. Due to this "ball-bearing" motion, an AFc molecule may have various thermally accessible conformations at a fixed temperature. Illumination by light may changed the conformations of this molecule significantly. The intermolecular interactions among AFc molecules in solid state have also play a crucial role in the photoconductivity change. It is reported that the orientational motion of an AFc molecule may be hindered in solid state due to the intermolecular interactions with neighbouring molecules [Sato K., Katada M., Sano H. and Kono M., 1984]. The changes in conformational motion in the presence

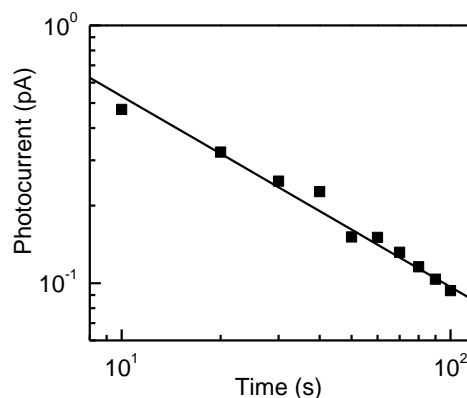of light might be responsible for changing of trap distribution in AFc in the presence of light.

Fig. 3. Dependence of photocurrent on time after switching off the light in acetylferrocene (AFc) at a temperature 284 K.

4. Conclusions

Kinetics of photocurrent decay of a ferrocene derivative, acetyl ferrocene (AFc), was studied in order to investigate the trap distribution in this material. A five-fold increase in photocurrent was observed within few seconds of illumination of the sample with the light from a 125 W mercury lamp. After switching off the light, the current decreases rapidly at the initial stage, then a slow decay of photocurrent was observed with time and finally attains the initial dark current value within few minutes. The kinetics of photocurrent decay in the case of AFc follows the power law. The sublinear dependence of photocurrent with a slope of 0.74 in log-log plot indicates the exponential type of trap distribution in this ferrocene derivative. The characteristic temperature (T_c) of exponential trap distribution was also calculated and found to be 1092 K.

Acknowledgement

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