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Transient Photoinduced Charge Carrier Dynamics of Glassy Carbon Film

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Conjugated organic polymers have been intensively investigated in the past few years because of their electrical and optical properties. Of special interests are electroluminescence, photoconductivity, photovoltaic effect, and the electrical conductivity of polymers. Moreover, because of their often large nonlinear optical susceptibilities and their roles as model compounds for quasi-one-dimensional semiconductors, considerable interests have been directed to the studies of electrical and optical properties with long conjugated chain polymers, such as polyacetylenes,¹ polydiacetylenes,^{2,3} polythiophenes,^{3,4} poly(phenylenevinylene)s,⁵ poly(2,5-diethynylthiophene),⁶ etc. To understand the electrical conductivities of conjugated polymers as well as their promising optical and nonlinear optical properties, the charge carrier generation and transporting behaviors in these polymers have become the subject of interests. Also, since

the charge carrier dynamics proceed in fast-time regions, generally from femtoseconds to milliseconds,⁷ pulsed laser spectroscopy has become a powerful tool to investigate these charge carrier generation and transporting mechanisms.

Glassy carbon (GC) polymer which is investigated in the present study is the electrode material which is commercially being utilized. To our knowledge, however the detailed conduction mechanisms of GC have not been reported yet. Therefore, in this study, we have investigated the conduction mechanism of the synthesized GC film with steady-state absorption and nanosecond time-resolved transient photoconductivity (PC) measurement. The result of the transient PC measurement of the GC film shows tens of nanoseconds PC decay signal and the steady-state absorption spectrum of the GC shows a broad band structure peaked approximately at 592 nm in the visible wavelength range. To discuss these experimental results, we have compared them with the reported spectroscopic results of pyrene

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Langmuir-Blodgett (LB) film which is structurally similar to the GC film. The dimeric or excimeric complex formation in the GC film by photoexcitation is discussed by comparing the results of the GC film with those of time-resolved and steady-state fluorescences of the pyrene LB film.

Experimental

Glassy carbon (GC) film used for the experiment was prepared by applying suitable heat (200 °C) and pressure (4200 psi) to the synthesized polydiacetylene polymer following the reported synthetic procedure.⁸ The thickness of the prepared film was about 200 μm . To investigate the surface condition of the film, SEM (scanning electron microscope) photograph was taken. In the photograph, we observed a few narrow lines and pores. The lines in Figure 1 seem to come from the overlapping of a number of monolayered aromatic plates of the GC film and the pores seem to occur from the imperfect cyclization of the polydiacetylenes. In spite of all these respects, we could confirm that the condition of the synthesised film was satisfactory, which is based on the good packing of the film.

The absorption spectrum of the GC film was obtained by UV-VIS spectrophotometer (SHIMADZU, UV-160A) at

room temperature. The experimental set-up used for the transient PC measurement is shown in Figure 2. In Figure 2, the excitation source was nanosecond (fwhm: 4ns) laser pulse obtained from optical parametric oscillator (BMI OP 901) pumped by third harmonic generation (355 nm) from Q-switching Nd-YAG laser (BMI SERIE 5000). The bias voltage used for the experiment was 30 V from DC power supply (J. W. Co.). The variable neutral density filter was used to vary the excitation beam intensity and a convex lens was used to focuss the excitation beam which covers the center area between two copper wires contacted to the GC film by silver paste. The distance between two closest points of the silver paste areas was about 100 μm . The preamplifier (SRS SR 445) was used to increase the signal level during the experiment. The transient PC signal was measured with 50 Ω terminated 500 MHz digital oscilloscope (HP 54520A). Since the resolution of the digital scope was about 1 ns at the sampling rate of 1 GHz, we could expect a transient PC signal in nanoseconds time range with this experimental set-up. The instrument response function (IRF) of the detection system was obtained by measuring the shape of excitation pulse through picosecond rise photodiode (Newport 818BB-20) and the digital oscilloscope. The exponential fitting procedure of the PC decay was performed with iterative least squares deconvolution fitting method by a personal computer.⁹

Results and Discussion

As a result of the steady-state experiment, we have obtained an absorption spectrum of the GC film as shown in

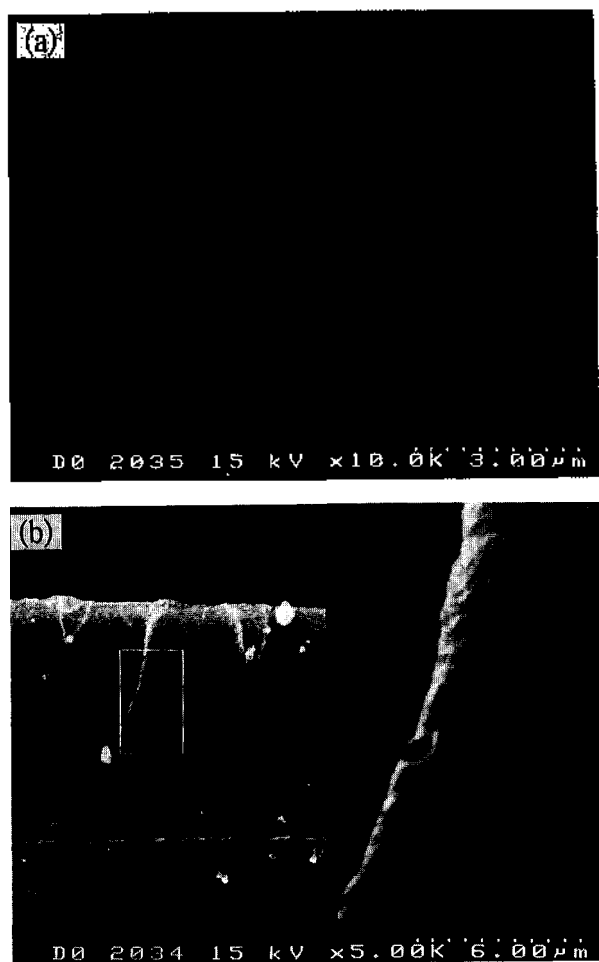


Figure 1. SEM (scanning electron microscope) photograph of the GC film. (a) upper view (b) side view and magnification. The upper part of the film was used for the experiment.

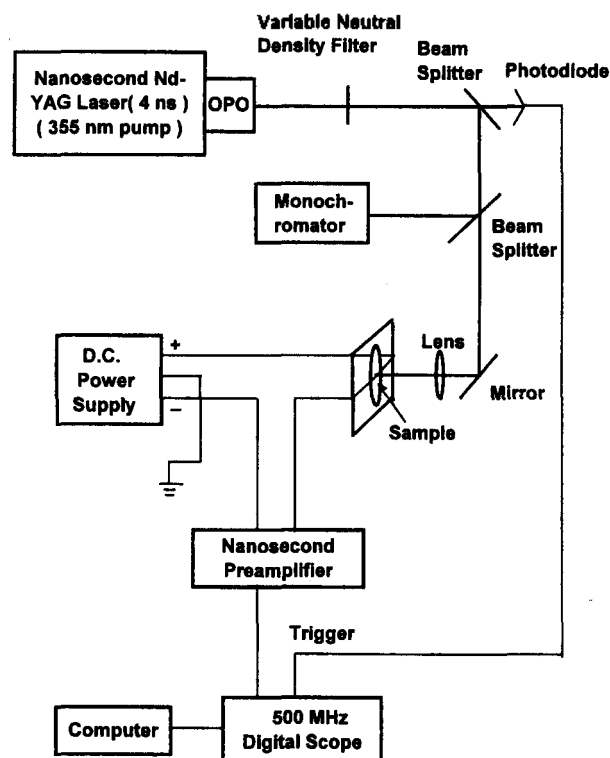


Figure 2. Experimental set-up for nanosecond transient photoconductivity measurement.

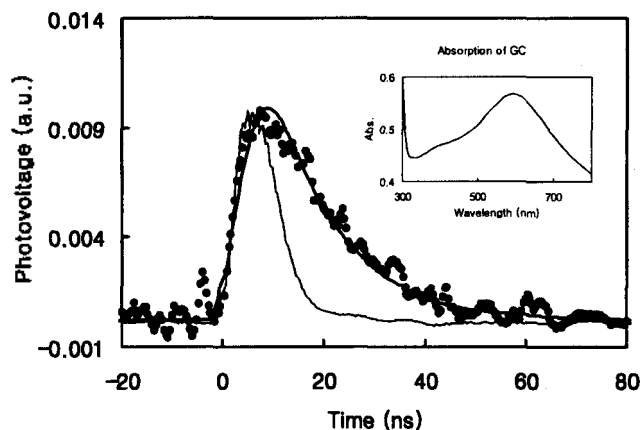


Figure 3. Transient PC decay of the GC film; IRF (—), decay (\bullet), fit (---) and steady-state absorption spectrum of the GC (inset).

the inset of Figure 3. It shows a broad band structure peaked approximately at 592 nm. The high background in the absorption spectrum is due to weak transparency of the film. The wavelengths of 492, 550 and 630 nm were used as excitation beams in order to investigate wavelength dependences of the PC decay. The PC decay did not show any wavelength dependent characteristics like other previously reported results.¹⁰ It indicates that the decay of transient PC is independent of the photon energy for excitation at energies above the band gap. From the time-resolved PC experiment of the GC film, we obtained a PC decay in the range of tens of nanoseconds as shown in Figure 3. In Figure 3, the gaussian shape of photodiode signal shows the instrument response function (IRF) of our experimental detection system. The transient PC signal of the GC film is shown as a form of exponential in tens of nanoseconds time range. From the deconvolution fitting of this PC decay, we obtained a single exponential decay time of 11 ± 0.5 ns. In order to understand the PC decay time of 11 ± 0.5 ns of the GC film, we have investigated the reported charge carrier mechanisms of other π -conjugated polymer samples. Among them, the results of pyrene Langmuir-Blodgett (LB) films revealed the comparable trends to our data as follows.¹¹⁻¹⁴

According to the spectroscopic results of pyrene LB film, the pyrene molecules in their increased concentrations can be aggregated with each other, resulting in dimeric or excimeric complexes in the LB film. And these aggregated complexes show absorption band peaked at 346 nm and broad fluorescence bands peaked at 450 nm and 470 nm corresponding to dimeric and excimeric complexes respectively, and their fluorescence lifetimes are tens of nanoseconds, depending on the pyrene concentrations in the LB films.¹²⁻¹⁴ Also, the results indicate that the excimer fluorescence of pyrene LB film comes from the relaxation of excimer excitons.¹¹

As shown in Figure 4, a monolayered aromatic plate of GC and a pyrene molecule have similarities in their molecular structures, that is, a monolayered aromatic plate of GC can be considered as a spatial extension of pyrene molecule. Also, since the molecular structure of GC is the overlapping type of a number of monolayered aromatic plates which are consisted of a number of benzene rings, its structure is com-

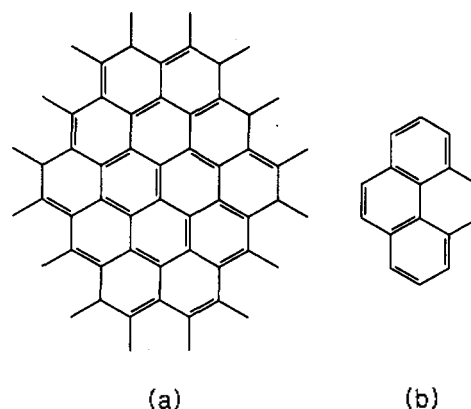


Figure 4. The molecular structures of (a) a monolayered aromatic plate of GC film and (b) a pyrene molecule. The GC film is the overlapping type of a number of monolayered aromatic plates.

parable to that of pyrene LB film which is 50 monolayered film consisted of pyrene and fatty acid molecules.¹² And since time-resolved fluorescence lifetime and transient PC decay time are comparable concepts in the respect of relaxation energy dynamics,¹⁵ the fluorescence lifetime of the pyrene LB film can be compared with the PC decay time of the GC film. From these comparable results of the GC film and the pyrene LB film, our 11 ± 0.5 ns transient PC decay time of the GC film can be considered as the relaxation time of the excimer excitons in the excited state of the GC molecules. In other words, the holes or electrons produced from one monolayered aromatic plate of the GC to the other neighboring monolayered aromatic plate, resulting in the excimer excitons between these two layers. The broad absorption band of 592 nm in the inset of figure 3 would be resulted from the formation of these excimer excitons. The PC of the GC film may occur by electrons passed through these excimer exciton defect states. The retention time in this state of photoexcited electrons is suggested to be 11 ± 0.5 ns.

Conclusion

From the steady-state absorption and the transient PC decay measurement of the GC film, we obtained the 11 ± 0.5 ns PC decay time of the GC film. This 11 ± 0.5 ns PC decay time is the comparable value with the fluorescence lifetime of the pyrene dimer or excimer in the LB film. Thus, we could suggest the photoelectron transporting mechanism within the GC film by comparing the results of the GC film with those of pyrene LB films. That is, the electrons and the holes produced in the GC film by photoexcitation are altered into the excimer excitons through the interchain electron hopping process between the monolayered aromatic plates of the GC film. The PC of the GC film may occur by electrons passed through these excimer exciton defect states. The lifetime or the PC decay time due to the relaxation of these excimer excitons is suggested to be 11 ± 0.5 ns.

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Molybdenum(VI)- and Tungsten(VI)- Dioxo Complexes with Schiff Base Ligands

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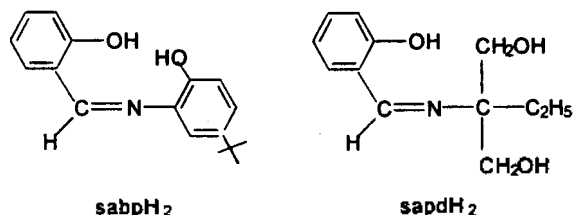
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Oxo-transfer chemistry of molybdenum and tungsten is of topical interest. Molybdenum has a special place in this type of chemistry owing to the biological relevance of the model reaction (1) involving oxo-transfer molybdoenzymes.¹



The oxo-transfer ability of MoO_2^{2+} core depends on the functionalities present in the ligands. It is well-known that the active sites of oxo-transfer molybdoenzymes involve a sulfur, oxygen, and nitrogen atoms.² In relation to these studies, we have taken up N-salicylidene-2-amino-4-*t*-butylphenol and N-salicylidene-2-amino-2-ethyl-1,3-propanediol as a trifunctional (ONO) dianionic Schiff base ligands.



These ligands are important because their complexes with the MO_2^{2+} or MO^{2+} core could be of the form MO_2L or MOL ($\text{M}=\text{Mo}, \text{W}$), possessing one or two "open" coordination sites that can be utilized for substrate binding. It has been also reported that the phenyl substituents play an important role whether the isolated molybdenum(VI)-dioxo complexes are discrete monomers, $[\text{MoO}_2\text{L}(\text{D})]$ ($\text{D}=\text{MeOH}$ or EtOH) or polymeric species, $[\text{MoO}_2\text{L}]_n$, containing $\cdots(\text{O})\text{Mo}=\text{O} \rightarrow \text{Mo}(\text{O})=\text{O} \cdots$ chains in $[\text{MoO}_2(\text{tridentate})]$ species.³

The electron-releasing substituent yield a polymer, whilst electron-withdrawing substituents favour the formation of monomers. In this relation study, the control effect of the ligands on the structures and chemical and spectroscopic properties of the molybdenum-oxo complexes studied here may help to identify the presence of different fragments or substituents attached to the active sites of relevant molybdoenzymes. In this work, we report some new monomeric or polymeric molybdenum(VI)-dioxo and tungsten(VI)-dioxo complexes of schiff base ligands with ONO donor system. Tungsten(VI)-dioxo complexes are very limited, because it is the non-availability of a suitable starting material. Spectroscopic properties and electrochemical behavior of the complexes have been discussed.

Experimental

Materials. Molybdenyl acetylacetonate, $[\text{MoO}_2(\text{acac})_2]$ was obtained from Tokyo Kasei Chem. Ind. Co. Ltd. Tungstenyl acetylacetonate, $[\text{WO}_2(\text{acac})_2]$ was prepared by literature method.⁴ Salicylaldehyde, 2-amino-4-*t*-butylphenol, and 2-amino-2-ethyl-1,3-propanediol were obtained from Aldrich Chem. Co. Ltd. The schiff bases were prepared under Ar gas by the literature methods,⁵ but was not isolated from methanol solution. All other chemical used for this work were of reagent grade and were employed without further purification. Reagent grade solvents were dried and distilled before use.

Physical measurements. C. H. N. for the complexes were analyzed by using a Carlo-Erba EA-1106R. The m.p.