White Light Optical Waveguide Detection of Transient Absorption Spectra in Ultrathin Organic Films upon Pulsed Laser Excitation

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(Received September 22, 2001; CL-010881)

White light optical waveguide (WOWG) method was applied to transient absorption spectroscopy of ultrathin polymer films. Tetraphenylporphinetetrasulfonic acid (TPPS) in poly(vinyl alcohol) films on the surface of OWG glass was excited with the second harmonics of a nanosecond Nd:YAG laser. The transient absorption spectrum of excited triplet TPPS was detected highly sensitively for a film with the absorbance at 532 nm of only 0.0005.

It is interesting and important to make spectroscopic studies on photoreactions and photoresponses in ultrathin organic films in view of molecular photonics and sensing application. However, it is usually not easy to measure transient spectra and their dynamics due to very small optical density at the excitation wavelength and to extremely weak changes.

Optical waveguide (OWG) is one of the essential components of advanced photonics and integrated optics. The electric fields of light propagating through the OWG layer by repeated total reflection have an exponentially decreasing value as evanescent waves beyond both surfaces of the OWG layer. Evanescent waves have been used to sensitively detect and to characterize adsorbates and thin films on the OWG glass. Recently the OWG methods have been employed for spectroscopy using white light as a probe beam.[1,2] Kato et al. measured the absorption spectra of monolayer or sub-monolayer of Cu-porphyrin on the OWG glass.[1] Ohno et al. reported the absorption spectra of cytochrome *c* adsorbed on a quartz glass or gold surface were measured with evanescent wave of the non-contacted OWG layer.[2] Ikeda et al. measured transient absorption spectra of a thin surface film spin-coated on a 1 mm thick sapphire plate by evanescent waves with attenuated total reflection method.[3] However the reflection number is much smaller than the OWG, only a few times. To the best knowledge of authors, no reports have been made to detect transient species by the WOWG method.

We have been studying highly sensitive detection of various photoreactions and photoresponses in ultrathin organic films by the use of various types of laser as a probe in the OWG method.[4–8] Photoinduced electrochromism by specific ion-pair charge-transfer complexes of 4,4'-bipyridinium in steady photolysis was detected even in a single monolayer LB film (2.7 nm thick) and also spin-coated ultrathin polymer films.[4,5,8] Transient species upon pulsed laser excitation of ultrathin polymer films and LB films was detected sensitively.[6–8] A 150 times increase was demonstrated in the sensitivity of the OWG method as compared with the conventional method. We now report, for the first time, the application of the WOWG method to transient absorption spectroscopy of ultrathin polymer films upon a nanosecond pulsed laser excitation.

OWGs were prepared by a thermal ion-exchange method from non-fluorescent glass slide (Matsunami, 24 mm × 76 mm × 1 mm) in molten potassium nitrate at 370 ± 1 °C for 60 min. Ultrathin poly(vinyl alcohol) (PVA) films containing 5, 10, 15, 20-tetraphenylporphinetetrasulfonic acid (TPPS) with a weight ratio of 1 : 200 (0.5 wt %) were prepared by spin-coating from aqueous solutions (0.025 g/mL) for 10 s at 100 rpm and 60 s at 2000 rpm. Conventional absorption spectra were measured by UV–vis spectrophotometer (Hitachi U-3500). The film thickness was estimated to be approximately 120 nm by a surface plasmon resonance method and comparison of absorbance by a spectrophotometer.

These films were excited with the second harmonics of a nanosecond pulsed Nd:YAG laser (532 nm, 8 ns, 3 mJ/pulse) from a surface normal direction. The pulsed laser beam was focused to 2 mm × 20 mm area with a cylindrical lens to excite thin films between two coupling prisms separated by 3 cm. No damage of samples was observed by repeated excitation at 532 nm. The modulated high pressure Xe lamp (150 W, 2 Hz, 1 ms) was used as the probe light. The WOWG signals were detected with a photomultichannel analyzer (Hamamatsu Photonics, PMA-50) for steady absorption spectra. A photomultiplier (Hamamatsu Photonics, R928) and a streak camera (Hamamatsu Photonics, C2830) were used for transient absorption spectra. The OWG signals were averaged 50 times measurements. The transient absorbance was calculated from the OWG signals after excitation relative to those before excitation.

Absorption spectra of TPPS/PVA film (120 nm) measured by the conventional spectrophotometer and the WOWG method are shown in Figure 1. The Q-band at 550–700 nm region was not observed clearly by the spectrophotometer, since its detection limit is about 0.0002. On the other hand, the same film measured by the WOWG method gave well-resolved four peaks of the Q-band as shown by the solid line. Comparison of the

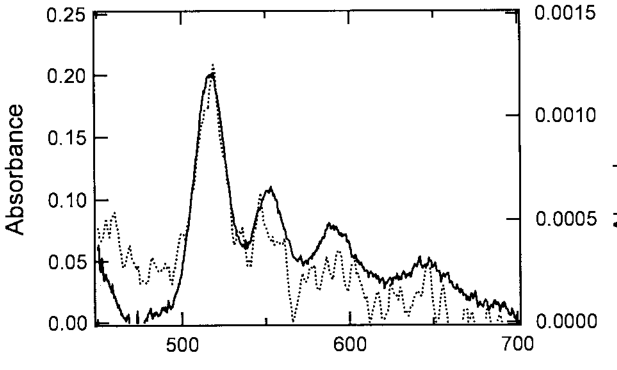

Figure 1. Absorption spectra of a spin-coated TPPS / PVA film (1 : 200) by the WOWG method (solid line, left axis) and a spectrophotometer (dotted line, right axis), respectively.

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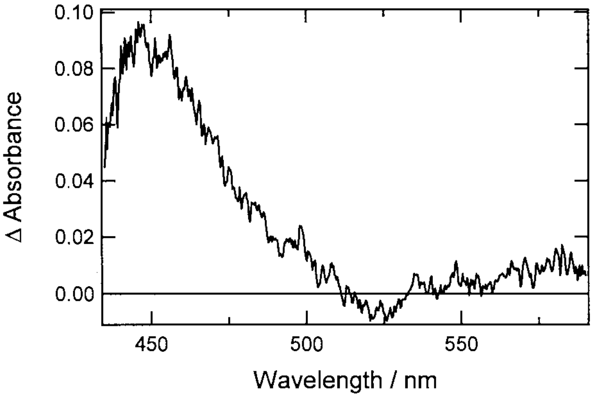

Figure 2. Transient absorption spectrum of the TPPS / PVA (120 nm) film 50 μs after excitation with a 532 nm nanosecond laser.

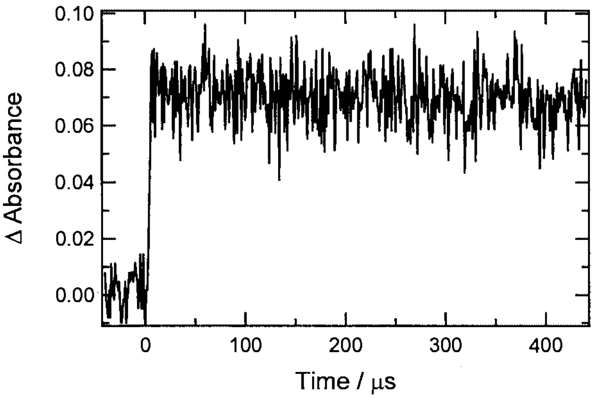

Figure 3. Time profile of transient absorption at 450 nm of the TPPS / PVA film (120 nm), excited with a 532 nm nanosecond laser.

results shown in Figure 1 indicated the WOWG method is about 160 times more sensitive than the conventional method.

Transient absorption spectrum of the spin-coated TPPS/PVA film (120 nm) observed 50 μs after excitation with a nanosecond Nd:YAG laser at 532 nm is shown in Figure 2. The absorbance of the polymer film at the excitation wavelength was about 0.0005 as shown in Figure 1. No transient absorption was observed by the conventional normal incidence laser flash photolysis. Similar absorption spectra were observed by the conventional laser flash photolysis on aqueous solutions and much thicker cast films, which were attributed to the excited triplet state of TPPS. When the OWG thickness is 2.5 μm, the reflection number is about 100 times/cm. These results clearly demonstrated that transient absorption spectrum of excited triplet state of TPPS was observed sensitively with fairly good S/N ratio in ultrathin films with absorbance at the excitation laser less than only 0.0005 by the WOWG method. Time profile of transient absorption at 450 nm is shown in Figure 3 for this TPPS/PVA film. The lifetime was found to be much longer than that in aqueous solutions ($\tau_{1/e}$ = 530 μs), which is caused by inhibition of rotations and vibrations. It was, however, difficult to estimate it precisely because the probe light pulse width is 1 ms.

Tran-Thi et al. reported the transient absorption measurements in LB films containing heterodimer of cationic porphyrin and anionic phthalocyanine observed upon excitation with pulsed laser.[9,10] They prepared LB films with 150–400 monolayer on each side of a substrate to achieve with high optical density (about 0.3) at the excitation wavelength. The observed maximum changes in transient absorption or photobleaching were only about 0.02–0.08. The absorption change observed on the TPPS/PVA film by the WOWG method shown in Figure 3 is almost the same as these data.

The WOWG method was shown to be useful for extremely high sensitive measurement of transient absorption spectra in ultrathin films upon laser excitation. It is expected to give spectroscopic and kinetic information on chromophores in organized thin film, which is essential to construct molecular photonics and electronic devices.

Authors greatly appreciate Dr. N. Matsuda and Dr. K. Kato, National Institute of Advanced Industrial Science and Technology, for valuable comments at the initial stage of the present work. This study was partly supported by the Grand-in-Aid for Scientific Research on Priority Areas “Molecular Synchronization for Design of New Materials System” (No. 11167242, 13022230) from the Ministry of Education, Science, Sports, and Culture, Japan.

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