Gigantic optical Pockels effect in water within the electric double layer at the electrode-solution interface

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We have obtained the experimental evidence for the Pockels effect of water, which is placed in the electric double layer (EDL) on the interface between the bulk water and a transparent electrode. The electric-field induced energy shift was observed for the visible interference fringes in a 300-nm indium-tin-oxide (ITO) electrode layer. The signal was shown to originate from a negative (positive) refractive index change of water in the EDL for the positive (negative) bias. The refractive index change was as large as $\Delta n = -0.1$ for the 2-nm thick EDL. The Pockels constants of water in the EDL were determined to be $r_{13} = (2.0 \pm 0.3) \times 100$ pm/V and $r_{33} = (2.5 \pm 0.6) \times 100$ pm/V. At the same time, the ITO showed blue shifts of both the band gap in the UV and the plasma frequency in the near infrared due to the band population effect in the space charge layer. Both shifts lead to a negative refractive index change in the visible region of the ITO, but their effect on the interference fringe shifts in the visible region was estimated to be much smaller than that of water in the EDL.

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A liquid-solid interface provides a field for a large variety of chemical reactions. Especially, an electric double layer (EDL) of a nanometer scale is formed at the water-electrode interface and an extremely high electric field is concentrated there. Since a majority of electrochemical reactions take place in the EDL, the information and understanding of the electronic and structural properties of water in the EDL is vitally important.

The structural properties of interfacial water have been extensively studied by a surface selective infrared (IR) spectroscopy2–5 as well as by a surface x-ray scattering.6,7 It is reported that the water in the EDL has an orientational order; orientational contribution to the polarizability is quenched while the vibrational and electronic contribution is order; orientational contribution to the polarizability is quenched while the vibrational and electronic contribution is restricted to a nanometer scale so that an intense electric field, as high as $10^9$ V/m, is readily applicable. In addition, macroscopic centrosymmetry is broken at the interface to meet the condition of the second-order nonlinearity. Experimentally, similar attempts known as the electrolyte method have been performed extensively for electroreflection spectroscopy,14 but it has been difficult to separate the electro-optic effect of each layer from the other.

We have recently reported the first experimental evidence for the effect.15 However, there were several problems left to be solved. First, the signal expected for indium-tin-oxide (ITO) in an infrared region was not detected. Second, the refractive index change of water was estimated to have extremely large anisotropy. Third, the potential of zero charge (PZC) of ITO was assumed to be 2 V, but this was not experimentally confirmed. Fourth, the applied voltage drops in the EDL and SCL were not estimated precisely. These must be carefully examined for the solid determination of the Pockels constants of water. In this Rapid Communication, we have determined the Pockels constants of water without leaving the ambiguity in any relevant experimental parameters. We successfully reproduced the results by a simulation applicable by using laser pulses while there has been no experimental report on the Pockels effect of water. This is because a high dc electric field cannot be applied and because the bulk water has macroscopic centrosymmetry insensitive to the second-order optical nonlinearity. The study on the Pockels effect of water is important since it may exploit a new possibility of water as electro-optic material and a new sensitive probe for the electronic properties of the water-solid interface. By applying the external electric field, an EDL on the water surface and a space charge layer (SCL) on the electrode surface are formed. Their thicknesses are restricted to a nanometer scale so that an intense electric field, as high as $10^9$ V/m, is readily applicable. In addition, macroscopic centrosymmetry is broken at the interface to meet the condition of the second-order nonlinearity. Experimentally, similar attempts known as the electrolyte method have been performed extensively for electroreflection spectroscopy,14 but it has been difficult to separate the electro-optic effect of each layer from the other.

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FIG. 1. (a) Transmission spectrum of the 300-nm thick ITO on the glass substrate placed in air (thick solid curve) and the first derivative of the transmission spectrum with respect to wavelength (thin solid curve). (b) Difference transmission spectrum normalized by the transmission spectrum for the ITO in 0.1 M NaCl aqueous solution at the incidence angle of $\theta=0^\circ$. (c) The results of calculation with the complex refractive index change for both ITO and water (thick solid curve), with only for ITO (thin solid curve), and with only for water ($\Delta n_w=-0.1$, dashed curve). Inset: the calculated spectra from 400 to 800 nm are magnified. (d) The complex refractive index change ($\Delta n_{ITO}$) of the SCL in the ITO assumed for the calculation of the thick and thin solid curves in (c).

without the need for a large PZC for ITO and showed that the anisotropy of the Pockels effect is not as large as reported in Ref. 15.

We used electrodes made of ITO (In$_2$O$_3$ doped with SnO$_2$) thin films on glass substrates (Geomatec). The ITO is an $n$-type semiconductor and is nearly transparent in the visible region. Its thickness, resistivity, and carrier density are 300 nm, $1.3 \times 10^{-4}$ $\Omega$·cm, and $1.2 \times 10^{21}$ cm$^{-3}$, respectively. A detailed description of the experimental methods is given in Ref. 15. One electrode was grounded and an ac voltage of 2 V (peak amplitude) was applied to the other at the frequency $f=1$ Hz. The collimated probe light beam from a Xe lamp was made $s$ or $p$ polarized by a polarizer to be incident into the voltage-applied ITO electrode immersed in 0.1 M NaCl aqueous solution in a quartz cell at various incidence angles. By the use of the collimated beam, accuracy in the polarization dependence of the signal was improved compared to Ref. 15. The transmitted probe light was detected through a monochromator with a 128-channel lock-in detection system. For the measurements in the visible and UV regions, the avalanche photodiodes were used while in the IR region, an InGaAs photodiode was used with a single lock-in. All the measurements were performed at room temperature.

Figure 1(a) shows the transmission spectrum of the ITO and its first derivative with respect to wavelength. There are interference fringes which are due to the ITO layer of 300-nm thickness. Low transmission in the near UV and near IR regions is due to the absorption edge of the ITO$^{16}$ and due to metallic reflection caused by the highly doped carriers, respectively. Figure 1(b) shows the normalized difference transmission spectrum $\Delta T/T$ at the normal incidence for the ITO immersed in the solution. The interference pattern in $\Delta T/T$ is similar to the first derivative of the transmission spectrum shown by the thin solid curve in Fig. 1(a). This indicates a blue shift of the interference fringes as a result of a negative refractive index change in the relevant layers for the positive bias. The dependence of $\Delta T/T$ on the incidence angle is shown in Figs. 2(a) and 2(b) for both $s$ and $p$ polarizations.

One should note that there is a net transmission increase around 300 nm and a net decrease around 1300 nm. Since water is almost dispersion free in this wavelength range, the signals should originate from the ITO. With the positive bias applied, both the conduction and valence bands bend to the lower energy at the surface, leading to the increase in the carrier density in the SCL. The absorption edge then shifts to the higher energy due to the population increase in the conduction band. This is the field-induced Burstein–Moss shift or the band population effect.$^{18}$ At the same time, the plasma frequency should increase in the SCL such that the reflection edge blueshifts. This is the first experimental observation of the plasma frequency shift due to the band population effect. It is known from the Kramers–Kronig relations that both shifts in the absorption and reflection edges induce a negative refractive index change in the visible.

We studied the ionic strength dependence of the signal as shown in Fig. 3. The $\Delta T/T$ signal intensities follow roughly the $1/M$ dependence both for 300 and 800 nm, where $M$ is the ionic strength. This is because the layer thickness of the EDL is proportional to $1/\sqrt{M}$ such that the electric-field strength is proportional to $\sqrt{M}$. Since the signal at 300 nm is considered to originate from the SCL, the results in Fig. 3 indicate that the electric-field strength in the SCL is closely correlated with that in the EDL. Therefore it is difficult to discriminate the contribution of EDL and of SCL to the visible signal by the ionic strength dependence.
GIGANTIC OPTICAL POCKELS EFFECT IN WATER... PHYSICAL REVIEW B 77, 241401(R) (2008)

FIG. 3. Ionic strength dependence of $\Delta T/T$ signal (closed squares) at 300 nm (a) and at 800 nm (b) for experiment with 125 nm ITO (1.3 $\times$ 10$^{-4}$ $\Omega$-cm and 1.62 $\times$ 10$^{21}$ cm$^{-3}$) at normal incidence. The dashed curve shows an appropriately scaled square root function of the electrolyte concentration. The calculated results (open circles) reproduce the experimental results better than the square root function. The results are similar also for 300-nm ITO.

In order to determine the voltage applied to each layer, EDL and SCL, the impedance of each layer was experimentally determined by the frequency dependence of the signals. The signal intensity increases with decreasing frequency because of the impedances involved in the equivalent circuit, which is the reason why the modulation frequency $F=1$ Hz was chosen. From the calculations in Fig. 1(e), it is known that the $\Delta T/T$ signals at 315 and 600 nm exclusively originated from the (complex) refractive index changes in the SCL and EDL, respectively. Therefore, the impedances of the SCL and EDL were independently determined by different frequency dependence of the signals at 315 and 600 nm to derive the voltage drops of $V_{\text{EDL}}=0.85$ V and $V_{\text{SCL}}=0.15$ V.

Finally, we have obtained the Pockels constants of water from $\Delta n_{\text{p, e}}$ and the estimated voltage drop as $r_{33}=3.0 \times 100$ pm/V and $r_{13}=2.0 \times 100$ pm/V, where pm is picometer. The errors were estimated to be within 20% from the degree of the agreement between the experimental and calculated curves shown in Fig. 4. Note that the values are an order of magnitude larger than those for typical electro-optic crystal LiNbO$_3$ ($r_{33}=30.8$ pm/V and $r_{13}=8.6$ pm/V). At the same time, the Pockels constants of the SCL of the ITO were also determined to be $r_{33}=r_{13}=1.6 \times 100$ pm/V at 500 nm. The estimated layer thicknesses may contain substantial errors but they have little effect on the evaluated Pockels constants; the $\Delta T/T$ signal intensity is proportional to $\Delta n_{\text{p, e}}$ and $\Delta n_{\text{d}}=n_{\text{d}}E_{\text{d}}=n_{\text{d}}V$. For a constant applied voltage $V$, the signal intensity divided by $V$ is proportional to the Pockels coefficient, which is not dependent on $d$.

There is a possibility that the small oscillatory feature observed in the $p$-polarization signal at $\theta=60^\circ$ comes entirely from cross-talk of the $s$ polarization due to slight imbalance in the alignment. This is because for $s$ polarization, the depth of the interference fringes increases with the incidence angle while it is vice versa for $p$ polarization. If this is the case, we should take $r_{33}=2.0 \times 100$ pm/V, complete isotropy.
Let us consider the microscopic origin of the Pockels effect of water. It was experimentally determined that for the positive (negative) bias, the refractive index of water decreases (increases) in all directions of the optical-field polarization. In addition, water in the EDL at zero external fields is bulk water in the first approximation. This is because the PZC of the ITO was measured to be within $\pm 0.01$ V and the experimental results were well reproduced with the bulk refractive index in the EDL at zero fields. The model for the origin of the Pockels effect must be consistent with these experimental findings.

Let us assume that the effect of the external field is only to induce an orientational order of water. Then, the polarization $\alpha_{ij}$ of the water molecule can contribute to the nonlinear optical effect. If water molecules are randomly oriented before the field application, a field-induced birefringence is produced, which is the third-order optical nonlinearity. The Pockels effect arises only when the interfacial water has some orientational order (broken centrosymmetry) before field application. Even if this is the case, however, the refractive index change in one of the principal axes should be compensated by that in the others such that the signs of $r_{13}$ and $r_{15}$ should be different. Therefore, the purely rotational effect originating from $\alpha_{ij}$ is excluded.

It is likely that oxygen atoms in the surface layer of the ITO interact with water molecules via hydrogen bonding, although this is beyond the approximation of bulk water at zero fields. In this case, the average dipole moment of water is not completely antisymmetric with respect to the polarity change in the external field. Accordingly, there should exist some parameter that is correlated with the refractive index and that changes linearly as the bias voltage is varied from negative to positive. One of the possible candidates for the parameter is the density of water. In fact, change in the density is reported for Ag and RuO$_2$ interfaces. For both cases, however, the expected refractive index change does not agree with the present result. Here, it is suggested that for the positive bias, the negative charges of oxygen atoms on the ITO surface may decrease and weaken the hydrogen bond with water molecules, causing the decrease in the density of water, and vice versa for the negative bias.

There are a few more remarks about the origin. The first hyperpolarizability $\beta_{ijk}$ of the water molecule or clusters can contribute to the effect if the centrosymmetry is initially broken by some orientational order. It is also important to consider a nonlocal optical response: the polarization of water in the EDL is caused by the electric field in the SCL.

In summary, the Pockels constants of water in the electric double layer were experimentally determined. They are more than ten times larger than those for the standard electro-optic crystal, LiNbO$_3$. The presence of the interface is essential for the Pockels effect of water so that the Pockels constants will be a new sensitive probe for the electronic structure of interfacial water.

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