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Surface Chemistry

Electric-Field Enhancement Inducing Near-Infrared Two-Photon Absorption in an Indium–Tin Oxide Nanoparticle Film**

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Nanoparticles (NPs) of noble metals such as gold and silver are well-known to have strong plasmon bands in the visible region and show unique optical characteristics because of an enhanced near-field electric field at the NP surface. This near field can sense the environmental properties through optical measurements of light absorption and scattering. The plasmon resonance condition changes when the refractive index of the surrounding medium changes, which can be measured as an absorption band shift. Even a single molecule can be detected through surface-enhanced Raman scattering (SERS) when the molecule is located within the enhanced electric field. SERS enhancement factors of $>10^4$ for a spherical NP and $>10^{10}$ for a NP dimer are reported.[1–8] The SERS enhancement factor is proportional to E^4, where E is the electromagnetic field enhancement factor.

We have recently reported that indium–tin oxide (ITO) NPs have a unique plasmon property in the near-infrared (NIR) range and the peak wavelength can be easily tuned by controlling the amount of Sn doping.[9] The plasmon oscillation is generated by conductive electrons in the conduction band through doping and not by the free electrons of the metal. Because of the reduced electron densities in ITO ($n \approx 10^{21}\,\mathrm{cm}^{-3}$) compared to metals ($n \approx 10^{23}\,\mathrm{cm}^{-3}$) and other different properties of the conductive electrons, such as the effective mass and mobility, it is still not understood how large the electric enhancement factor of ITO NPs is and whether this property can be used to enhance any optical transition near the NPs, although there are recent articles on a doped metal oxide with a tuneable plasmon band in the NIR region.[10,11]

In this work, we have applied transient absorption spectroscopy to a dye-coated ITO NP film, where dye absorption is present at half the wavelength of the plasmon resonance so that two-photon-induced transient absorption can be expected. Since a two-photon process occurs only in a strong electric field, we can selectively observe the near field generated by ITO NPs.

A hexane solution of 11 nm spherical ITO NPs was prepared by a method reported previously.[9] ITO NPs doped with 10 % Sn were synthesized and used for this study because they show the strongest plasmon absorption within a doping range of 3 to 30 % of Sn. The solution gave a plasmon absorption peak at 1720 nm as shown in Figure 1. Spin-coating was applied to produce a NP film on a glass substrate. The film thickness was estimated to be about 100–150 nm using the optical density of the film, the known absorption coefficient of the ITO NPs (around $0.5\times10^{8}\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$), and SEM measurements for several selected cross-sections of the film, indicating that the film consisted of 10–15 layers of NPs. The film showed a plasmon band that shifted to a longer wavelength at 2140 nm relative to that in solution because of plasmon coupling.

A near-infrared laser dye, IR26 (Exciton), was coated homogeneously on the ITO film from an acetonitrile solution. Since ITO NPs are capped by fatty organic layers with thickness of about 1 nm, the dye layer is expected to simply overlay the ITO film. The dye layer thickness was estimated to be about 130 nm using the observed optical density (Figure 1) and an assumed IR26 molecular volume of $0.8\,\mathrm{nm}^3$ together with an absorption coefficient of about $10^4\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$. This estimation was confirmed by SEM meas-

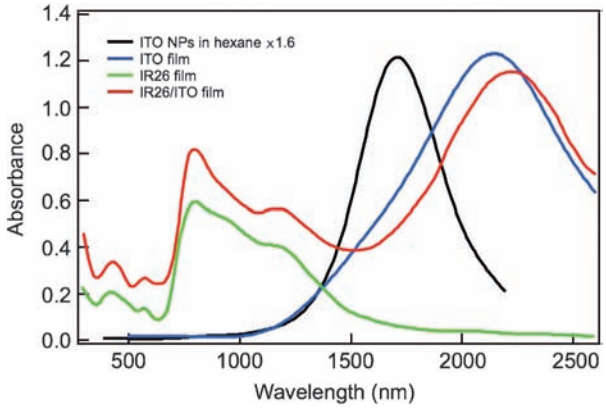

Figure 1. Steady-state absorption spectra of ITO NPs in hexane (black line), an ITO NP film (blue line), an IR26 film (green line), and an IR26-coated ITO NP film (red line).

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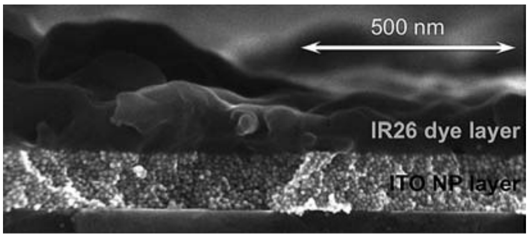

Figure 2. SEM image of IR26-coated ITO NP layer on a glass substrate.

urements (Figure 2). A control sample was prepared by coating the IR26 dye directly on the glass substrate. Both the IR26 absorption spectra of IR26/ITO and the control IR26 films showed absorption peaks at 770 nm with almost the same intensity (0.6–0.8 OD). This peak wavelength is shorter than that in solution, which derives from a dye-stacking structure like an H-aggregate. The plasmon band in the IR26/ITO film appears at 2220 nm, which is nearly identical to that of the ITO film.

Figure 3 a shows transient absorption kinetics of the IR26/ITO and the control IR26 films excited at 800 nm, where it is expected that only one-photon absorption by IR26 occurs and the excited-state dynamics is simply followed. We chose the probe wavelength at 1250 nm to observe transient bleaching signals. In both films, similar profiles were observed, namely, the bleaching recovered through a two-step decay with time constants of about 800 fs and 50 ps (the fitting function is shown by the dashed line in Figure 3 a), with almost the same amplitudes between the two samples. The observed shorter lifetime component relative to that of the IR26 dye in solution of a few tens of picoseconds[12] may be ascribed to the formation of an aggregate of dyes.[13] ITO NPs were found to have no effect on the excited-state generation and relaxation. We also confirmed that the excitation was obtained by a one-photon process, as the transient bleaching amplitude immediately after excitation was proportional to the excitation power (Figure 3 b).

Two-photon excitation of the IR26 dye at 2200 nm, which is displayed by the peak of the ITO film plasmon band, was applied to both films to examine the electric-field enhancement effect by ITO NPs. Figure 4 a shows the transient bleaching kinetics probed at 1175 nm for the two films. Whereas the control IR26 film showed very small transient bleaching signals, the IR26/ITO film showed a distinct signal immediately after excitation, surely confirming a plasmon enhancement effect. The observed recovery behavior in IR26/ITO is slightly different from that under one-photon excitation at 800 nm; namely, the rapid decay became much faster which is shown by a shift from the 800 to the 170 fs time constant and the disappearance of the 50 ps component. This accelerated relaxation may be induced by energy transfer to the ITO NPs, because dye molecules close to the NPs are considered to be selectively excited.

We have examined the power dependence of the peak amplitude of the bleaching as shown in Figure 4 b. The occurrence of two-photon excitation can be confirmed by a slope of 2 and the apparent enhancement factor for two-photon absorption was evaluated to be 30. This gives an apparent electric-field enhancement factor of 2.34 from the fourth root of 30. Since the IR26 layer is around 130 nm thick, only the vicinity of the ITO layer is considered to contribute to the two-photon absorption enhancement. Electric en-

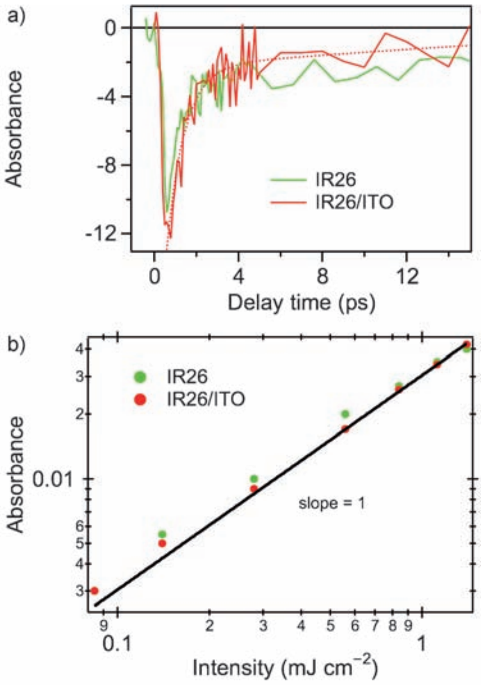

Figure 3. a) Transient absorption kinetics observed at 1250 nm after optical excitation at 800 nm of IR26/ITO and control IR26 films. b) Transient bleaching amplitudes against the excitation power.

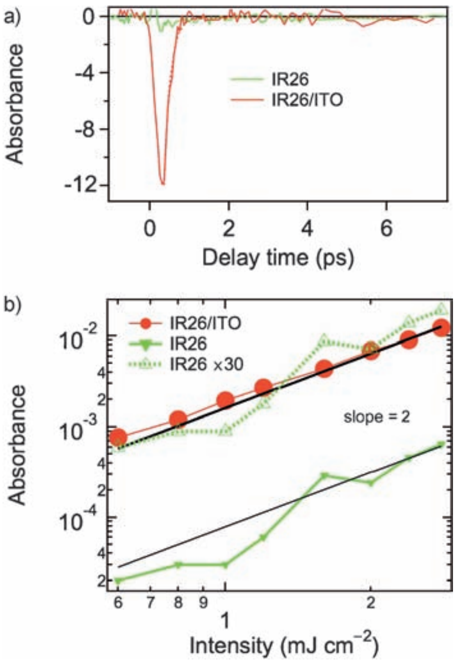

Figure 4. a) Transient absorption kinetics of IR26/ITO and control IR26 films observed at 1175 nm after optical excitation at 2200 nm, where plasmon resonance of ITO NPs exists. b) The bleaching amplitudes are plotted against the excitation laser power.

hancement occurs only in the vicinity of NPs. Assuming that a 5–10 nm layer is effective, the actual electric-field enhancement factor can be calculated to be 5.24–4.41, indicating that an enhancement factor of about 400–700 for SERS can be expected. This calculation was done using the following equation in the case of a 5 nm active layer: $5A^4 + 125 = 130 \times 30$, where A is the enhanced electric factor. Thinking of possible field distribution within the effective layer, the highest enhancement factor on a local level may be larger.

Using the FDTD calculation (Fujitsu, Poynting for Optics), we have simulated the electric field in the vicinity (0.6 nm away from a single ITO NP) based on the Drude model with a reported refractive index and extinction coefficient of ITO.[14] The electric field of a femotosecond pulse (150 fs full width at half maximum, FWHM) at the plasmon resonance wavelength was found to increase by a factor of around 10, indicating an approximate agreement with the experimental result. Also, we have extended the calculation to obtain an electric field distribution around the 11 nm ITO NP as shown in Figure 5, where the electric field of the incident light (propagating in the y-axis) is found in direction of the z axis with an amplitude of 1 mV m^{-1}. Electric-field enhancement occurs up to about 5–10 nm from the ITO surface.

Despite the about two orders of magnitude smaller electron density of ITO relative to the densities of noble metals, the electric enhancement property of ITO NPs was confirmed experimentally. Also, their absorption coefficients are not small. For example, a gold NP of 10 nm in diameter has a molar absorption coefficient of around $10^8\,\text{M}^{-1}\,\text{cm}^{-1}$. These properties may be ascribed to the small effective mass of the electrons in ITO, which is about 0.3 m_e and smaller than in gold by a factor of around 3. Also, we anticipate that the longer plasmon lifetime of the electrons in ITO may be another reason, because the band width (FWHM) of an ITO solution is 0.2 eV, whereas typical gold NPs show a band width > 0.3 eV.[15] Although further understanding of the optical properties of ITO NPs is necessary for future material development, here we have successfully shown the NIR light enhancement effect of ITO NPs.

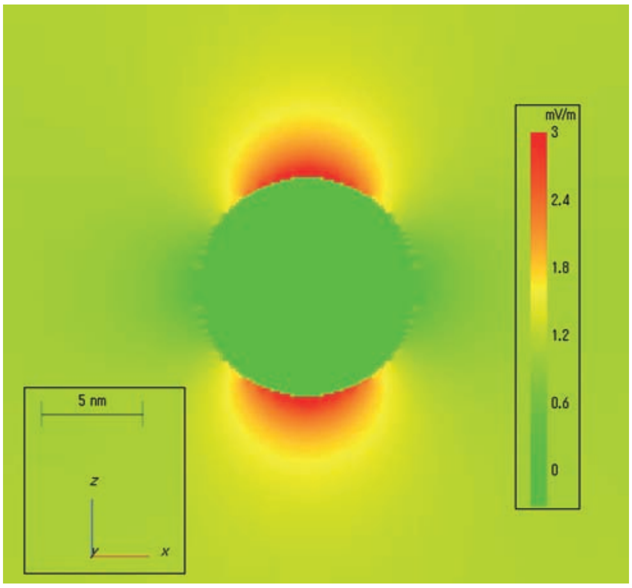

Figure 5. Calculated electric field around a single ITO NP upon incident of a femtosecond laser pulse propagating in direction of the y axis. The incident electric field in direction of the z axis is 1 mV m^{-1}.

In conclusion, the electric enhancement property of an ITO NP film has been evaluated by measuring transient bleaching of a surface IR26 dye layer induced by NIR two-photon excitation at 2200 nm, which is the peak of the plasmon resonance. It was found that the dye molecules were excited much more efficiently in the presence of an ITO NP layer by a factor of 30 compared to the control sample without ITO NPs. The results show that NPs of transparent conductive metal oxides can possibly be applied in plasmonic sensors and solar cells, because in general NIR light interacts weakly with chemical substances in the wavelength window ranging from the UV/Vis electronic transition region and the IR vibrational region.

Experimental Section

In femtosecond transient absorption measurements, an amplified Ti:sapphire laser system (Spectra-physics, Hurricane) combined with two optical parametric amplifiers (Quantronix, TOPAS) to generate pump and probe pulses were used, details of which were already reported previously.[16] The excitation laser spot size at the sample was about 0.3 mm in diameter. Measurements were performed at 22 °C in air.

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