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# Oxide semiconductor nanoparticles for infrared plasmonic applications

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# Introduction

Oxide plasmonics have received much attention by many researchers as new optical phenomena with potential applications because impurity doping into oxide semiconductors can provide metallic conductivity for the creation of surface plasmon resonances (SPRs). Unlike noble metals such as silver (Ag) and gold (Au), plasmon resonance frequencies of doped oxide semiconductors can tune by changing the physical properties of a material, which creates new possibilities for plasmon manipulation of light [1-3].

There are currently many types of oxide semiconductors. On the way, very few oxide semiconductors are favorable for plasmonic applications because a high electron density  $(n_e)$ , small effective mass ( $m^*$ ) and high Hall mobility ( $\mu_{\rm H}$ ) are needed to obtain high-performance plasmonic devices. In contrast, a low  $n_{\rm e}$ , large  $m^*$  and low  $\mu_{\rm H}$  provide an increase in conductance losses resulting from high damping of surface plasmons. Table 5.1 shows various material properties of oxide semiconductors with metallic conductivity of an *n*-type carrier polarity. Conduction bands (CBs) of  $In_2O_3$  and ZnO are composed of 5s and 4s orbitals, respectively [4, 5], while d-related orbitals behave as conduction paths electron carriers in VO<sub>2</sub>, TiO<sub>2</sub> and WO<sub>3</sub> [6-8]. Oxide semiconductors with CBs of s-orbitals usually show low  $m^*$  and high  $\mu_{\rm H}$  values, while high  $m^*$  and low  $\mu_{\rm H}$  values are characteristics of oxide semiconductors with CBs consisting of d-orbitals. From **Table 5.1**,  $In_2O_3$ : Sn with the 5s-orbital can realize small  $m^*$ , high  $n_e$  and high  $\mu_H$  values. Furthermore,  $In_2O_3$ : Sn and ZnO: Ga has an ideal Drude component in the near infrared (NIR) region because of the absence of interband transitions such as those exhibited by Ag and Au noble metals. The interband transitions of  $In_2O_3$ : Sn and ZnO: Ga only show in the ultra-violet (UV) region. Accordingly,  $In_2O_3$ : Sn (ZnO: Ga) exhibit the lowest conductance losses in oxide semiconductors in the NIR range, which contribute to high-performance SPRs. In addition, In<sub>2</sub>O<sub>3</sub>: Sn and ZnO: Ga are well known as one of the solid oxide substrates of transparent electrodes and surface-sensing platforms based on electrochemical impedance spectroscopy [9, 10].

Oxide semiconductors can easily show metallic behaviors by doping with defects and/or impurities, allowing for excitations of SPRs at dielectric/oxide interfaces. The SPR properties concerning oxide semiconductors have been discussed on different types of sample structures such as films, nanorods and nanowires [11-13]. In particular, localized surface plasmon resonances (LSPRs) can also produce when confining the collective oscillations of free carriers into nanoparticles (NPs). NP samples based on oxide semiconductors have shown clear LSPRs in the near- to mid-IR range by controlling spectral positions through the careful choice of dopant concentrations [14, 15]. Recently,  $In_2O_3$ : Sn NPs have been launched as alternative plasmonic materials. Plasmonic-enhanced optical spectroscopes have been demonstrated with a view to developing new sensing platforms. Theoretical approaches have also supported in the development of plasmonic applications.

This chapter is organized as follows. In Section 2, we first give a description of optical properties of  $In_2O_3$ : Sn (ITO) NPs in the infrared (IR) range on a basis of relationship between plasmon responses and carrier modulations. Doped oxide semiconductors are useful plasmonic materials since their SPR energies can be widely controlled by altering electron densities in NPs. This provides an additional means of tuning optical properties in a manner that is not as readily available in metal NPs. To elucidate origin of plasmonic excitations in ITO NPs is valuable information for oxide plasmonic applications in the IR range. In Section 3, we focus on enhancements of near-IR luminescent properties of Er ions by assembled ITO NP sheets, wherein discussions concreate on the coupling of optically active Er ions with plasmon modes of ITO NPs in addition to the damping

mechanism. Interparticle coupling is recognized as one of the remarkable characteristics of LSPRs. ITO NP sheets have enhanced two-photon absorptions of dye molecules in the near-IR range. Moreover, theoretical contributions that explain properties of ITO NP sheets have progressed. In this study, we demonstrate an increase of near-IR luminescence using ITO NP sheets. Section 4 is devoted to discussion of solar-thermal shielding techniques of ITO NP sheets utilizing plasmonic interactions between ITO NPs towards industrial applications. In particular, we describe IR plasmonic responses in assembled films of ITO NPs. The electric-field interactions along the inplane and out-of-plane directions in the assembled films allow for resonant splitting of plasmon excitations, thereby realizing selective high reflections in the near- and mid-IR range. The ITO NP-based assembled films can be extended to large-size flexible films with high IR reflectance, which simultaneous exhibit microwave transmittance. This provides important insights for harnessing IR optical responses using plasmonic techniques for the fabrication of solar-thermal shielding applications. Finally, some concluding remakes are given in Section 5.

	In <sub>2</sub> O <sub>3</sub>	ZnO	VO <sub>2</sub>	TiO <sub>2</sub>
Conduction band	5 <i>s</i>	4 <i>s</i>	3 <i>d</i>	3d
Impurity dopant	Sn <sup>4+</sup>	Ga <sup>3+</sup>	W <sup>5+</sup>	Nb <sup>5+</sup>
Carrier density, <i>n</i> <sub>e</sub> (cm <sup>-3</sup> )	2×10 <sup>21</sup>	1×10 <sup>21</sup>	3×10 <sup>22</sup>	3×10 <sup>21</sup>
Effective mass, m*	0.3 <i>m</i> 。	$0.27m_{o}$	$1.6m_{o}$	$1.0m_{\circ}$
Hall mobility, $\mu_{\rm H}$ (cm <sup>2</sup> /V.s)	40 - 50	30 - 40	0.1-10	1-10

# TABLE 5.1 Physical properties of doped oxide semiconductors with electron carriers

TABLE 5.2

Fitted parameters for NCs with different Sn content using the classical Drude model. These values were obtained using Eqs. (1) - (3), and estimated mean free path length of free electron  $(I_m)$ . Reproduced from [16], with permission. Copyright 2014, American Institute of Physics

[Sn] (%)	$\omega_{ ho}(eV)$	<i>n</i> <sub>e</sub> (cm <sup>-3</sup> )	γ(eV)	<i>l<sub>m</sub></i> (nm)
5	2.09	1.09×10 <sup>21</sup>	0.183	10.7
1	1.52	5.78×10 <sup>20</sup>	0.164	8.78
0.5	1.22	3.67×10 <sup>20</sup>	0.146	7.76
0.1	0.76	1.42×10 <sup>20</sup>	0.142	5.08
0.05	0.50	6.27×10 <sup>19</sup>	0.138	4.27
0.02	0.42	4.42×10 <sup>19</sup>	0.140	3.30

# **Fabrications of ITO NPs**

ITO NPs with different Sn contents were grown using the chemical thermolysis method with metal complexes  $(C_9H_{22}CO_2)_3In$  and  $(C_9H_{22}CO_3)_4Sn$ . In and Sn carboxylates showing white powders were heated in a flask using a mantle heater to  $350^{\circ}C$  without a solvent in a nitrogen atmosphere. The heating temperature was kept for 4 hours, and the mixture was then gradually cooled to  $27^{\circ}C$ . The resultant mixture provided a pale blue suspension, to which excess ethanol was added to induce precipitation.



#### FIGURE 5.1

(a) XRD patterns of ITO NPs with Sn content of 0 and 5%. Inset shows low-resolution (left) and high-resolution (right) TEM images of ITO NP with a Sn content of 5%. (b) EDX spectra at the center and edge regions in the NP. Inset indicates ED patterns of the (222) plane at the center and edge. Reproduced from [16], with permission. Copyright 2014, American Institute of Physics

Centrifugation and repeated washing processes were carried out four times using ethanol, producing dried powders of ITO NPs. Finally, the NP powders were dispersed in toluene. X-ray diffraction (XRD) patterns of NPs show broad peaks characteristic of colloidal ITO NPs with a crystalline nature (Fig. 5.1a) [17]. The *a*-axis length increased from 10.087Å to 10.152Å following doping with Sn atoms. Local structures of NPs were obtained by transmittance electron microscopy (TEM). Broadening of the line-width of the XRD pattern is related to structural imperfections such as defects and strains. The difference between crystalline and particle sizes is due to the presence of structural defects in the NPs. The electron diffraction patterns revealed that the lattice interval ( $d_{222}$ ) of the (222) plane at the center region (0.301 nm) was similar to that at the edge region in the NP (0.302 nm)(inset of Fig. 5.1b). The results of energy-dispersive X-ray microscopy showed that the Sn content [Sn] at the center region (5.4%) was similar to that at the edge region (5.2%), indicating that Sn atoms in the NP were homogeneous (Fig. 5.1b).

Figures 5.2a - 2c shows Scanning-TEM (STEM) images with electron-energy loss spectroscopy (EELS) [18]. High-angle annular dark field (HAADF) image revealed that In and Sn-related impurities in the



#### FIGURE 5.2

Aberration-corrected STEM image (a), and HAADF images of In (b) and Sn atoms (c) in the NP(Sn content of 5%). (d) EELS spectra measured at vacuum (back line) and edge (red line) regions, and a STEM-acquired particle image (inset). (e) Differential EELS (black line), and optical spectra taken in the near-IR (green line). Reproduced from [16], with permission. Copyright 2014, American Institute of Physics



#### FIGURE 5.3

Absorption spectra and TEM images of ITO NPs with different Sn contents: (a) 0.02%, (b) 0.05%, (c) 0.1%, (d) 0.5%, (e) 1% and (f) 5%. Red lines indicate the results of parameter-fittings using Eqs. (1) - (3). Reproduced from [16], with permission. Copyright 2014, American Institute of Physics

NP (Sn content: 5%) were distributed homogeneously. The EELS spectra at an edge and vacuum regions on the STEM-acquired particle image exhibited a slight spectral difference in energy-loss regions from0.5 to 1.0 eV (Fig. 5.2d). From Fig. 5.2e, a differential EELS spectrum had a maximum peak at 0.7 eV that was close to the optical absorption in the near-IR, which is direct evidence of a LSP excitation on the NP surface. ITO NPs showed clear LSPRs in the near-IR range by doping homogeneously with Sn impurities into the NPs, which were suitable for alternatively plasmonic nanomaterials in the near-IR range because of relatively low carrier concentrations around  $10^{21}$  cm<sup>-3</sup>. The near-IR plasmonic responses cannot obtain using metal NPs because plasmonic properties of metal NPs exhibited within the visible range due to high carrier concentrations around  $10^{22}$  cm<sup>-3</sup>, which were higher than those of ITO NPs.

# **Carrier-dependent plasmonic properties of ITO NPs**

The plasmonic responses in metal NPs have been the subject of extensive research with regard to study concerning the damping processes of LSPRs. Above all, radiation and surfaces scattering of electron carriers are recognized as significant damping factors in metal NPs, in addition to the presence of interband and intraband damping from the viewpoint of electronic structure [19 - 21]. On the other hand, carrier-dependent damping is a specific point of plasmonic properties of ITO NPs. Unfortunately, no systematic examination has been reported regarding the relationship between LSPR excitations and electron densities from a plasmon damping. Investigations of the carrier-dependent plasmonic responses are required for the design of plasmonic nanomaterials based on oxide semiconductors. The purpose of this session is to examine the light interactions of carrier-controlled NPs. We discuss on the carrier-dependent plasmonic response. A rigorous approach to the analysis of the optical properties allows us to present a quantitative assessment of the electronic properties in the NPs.

Optical absorptions and TEM images of ITO NCs with different Sn content have been examined (Fig. 5.3). Optical measurements in the mid-IR range have been carried out using a FT-IR spectrometer with a liquid-cooled MCT detector. From Fig. 5.3a, an ITO NP with the lowest Sn content of 0.02% showed two absorption peaks (A) and (B), which gradually shifted to high photon energies with



#### FIGURE 5.4

(a) Extinction spectra of spherical ITO NCs with different  $n_e$  calculated using Mie theory: (1)  $1.5 \times 10^{19}$  cm<sup>-3</sup>, (2)  $5.6 \times 10^{19}$  cm<sup>-3</sup>, (3)  $1.1 \times 10^{20}$  cm<sup>-3</sup>, (4)  $3.8 \times 10^{20}$  cm<sup>-3</sup>, (5)  $5.1 \times 10^{20}$  cm<sup>-3</sup>, and (6)  $1.2 \times 10^{21}$  cm<sup>-3</sup>. Peak energy (b) and intensity (c) of absorption (B) as a function of electron density (black dots). Comparative data (red line) was extracted from the calculated extinction spectra in Fig. 5.2a. Reproduced from [16], with permission. Copyright 2014, American Institute of Physics

increasing Sn content (Figs. 5.3b - 3f). Although an ITO NP with the highest Sn content of 5% exhibited a single absorption at 0.73 eV (Fig. 5.3f).

Absorption spectra of ITO NPs with different  $n_e$  were calculated using Mie theory. The simulated absorption spectra revealed that LSPR peaks shifted to high photon energies with increasing  $n_e$  (Fig. 5.4a).On the other hand, the  $n_e$  of ITO NPs was extracted by utilizing the free-electron Drude term with a damping constant ( $\gamma$ ), which can be described by the following equations [22, 23]:

(1) 
$$\varepsilon_p(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$$

 $\varepsilon_{\rm p}(\omega)$  is the particle dielectric function and  $\gamma$  represents a damping constant. The plasma frequency  $(\omega_{\rm p})$  is given by  $\omega_{\rm p}^2 = n_e e/\varepsilon \varepsilon_0 m^*, \varepsilon$  is the high-energy dielectric constant, and  $\varepsilon_0$  is the vacuum permittivity. Theoretical optical absorption  $(\sigma_{\rm A})$  in the quasi-static limit has been employed:

(2) 
$$\sigma_{A}(\omega) = 4\pi k R^{3} \operatorname{Im} \left\{ \frac{\varepsilon_{p}(\omega) - \varepsilon_{H}}{\varepsilon_{p}(\omega) + 2\varepsilon_{H}} \right\}$$

where  $k = 2\pi (\varepsilon_{\rm H})^{1/2} \omega/c$  with c being the speed of light, and *R* is the particle radius.  $\varepsilon_{\rm H}$  indicates the host dielectric constants of toluene. The effective dielectric function ( $\varepsilon_{\rm eff}$ ) was used to obtain real nanoparticle dispersions by the Maxwell-Garnett effective medium approximation [24]:

(3) 
$$\frac{\varepsilon_{eff}(\omega) - \varepsilon_H}{\varepsilon_{eff}(\omega) + 2\varepsilon_H} = f_v \frac{\varepsilon_p(\omega) - \varepsilon_H}{\varepsilon_p(\omega) + 2\varepsilon_H}$$

where  $f_v$  is the particle volume fraction, and since this was in the order of  $10^{-5}$  because near-field coupling between adjacent NPs in the medium was neglected. Fitted absorption spectra were used with specific parameter values ( $\varepsilon_H = 2.23$ ,  $\varepsilon_{\infty} = 3.8$  and  $m^* = 0.3m_0$ ) to determine  $\varepsilon_p(\omega)$ , which would be reasonable for ITO NCs (red lines in Figs. 5.3a). As shown in Table 5.2, the estimated  $n_e$  changed markedly with changing Sn content. Peaks and intensities of absorption (B) were similar to those predicted using Mie theory (Figs. 5.3b and 3c), and were identified as belonging to LSPRs. For the ITO NP with the lowest Sn of 0.02%, a LSPR peak was located at 0.16 eV. Above the Mott critical density ( $N_c = 6 \times 10^{18}$  cm<sup>-3</sup>) of ITO. LSPRs support up to longer wavelengths in the mid-IR. On the other hand,



#### FIGURE 5.5

(a) Dependence of quality factor Q on electron density. Experimental data (black dots) are compared with theoretical data (red line) extracted from the calculated absorption spectra. (b) Mobility ( $\mu_{\rm H}$ ) as a function of electron density ( $n_{\rm e}$ ). The  $\mu_{\rm H}$  is compared with those obtained using ionized impurity scattering (red line). Reproduced from [16], with permission. Copyright 2014, American Institute of Physics

absorption (A) peaks were close to the photon energies where the real part of the permittivity,  $\varepsilon(\omega)$ , in ITO films crosses zero, Re [ $\varepsilon(\omega)$ ] = 0. According to Mie theory, bulk plasmon absorption (BPR) appears as the real part of the permittivity crosses zero. The absorption (A) peak was not derived from LSPR peaks. Plasmon quality ( $Q = E_{res} / \gamma$ ) is evaluated by the damping factor ( $\gamma$ ) and LSPR energy ( $E_{res}$ ), which is related to the quality factor of LSPR [22]. The experimental Q value increased with increasing  $n_{\rm e}$  (Fig. 5.5a). For the ITO NP with the highest  $n_{\rm e}$  of  $1.1 \times 10^{21}$  cm<sup>-3</sup>, the experimental Q value was two times lower than the theoretical Q value of 8.2 predicted using Mie theory. However, experimental Q values were close to theoretical Q values for low  $n_e$  below  $10^{20}$  cm<sup>-</sup> <sup>3</sup>. A difference in Q value has been only found for high  $n_e$  above 10<sup>20</sup> cm<sup>-3</sup>. This can be attributed to an increase in  $\gamma$  with increasing  $n_e$  (see Table 5.2). For metal NPs, electron-surface scattering is known to act as an additional damping effect, which is taken into account by the Drude term. The damping factor ( $\gamma = \gamma_{\rm IB} + \gamma_{\rm s}$ ) is described by intraband damping ( $\gamma_{\rm IB}$ ) and surface scattering ( $\gamma_{\rm s} =$  $Av_{\rm F}/I_{\rm sc}$ ) for a small nanoparticle [23], where A is a material constant, and  $v_{\rm F}$  is the Fermi velocity [ $v_{\rm F}$  $= \hbar/m^{*}(3\pi n_{e})^{1/3}$ ]. The surface scattering length ( $I_{sc}$ ) is defined by  $I_{sc} = 4V/S$  where V is the volume and S is the surface area of the particle. For our ITO NPs,  $l_{sc}$  was calculated as 24 nm, which is longer than the electron free path length of ITO [25, 26]. Damping related to surface scattering is only effective if a particle size is smaller than  $I_{\rm m}$ . Thus, size- and interband transition-related damping is excluded in our ITO NPs. Therefore, we consider a carrier-dependent damping factor as follows. Carrier-dependent plasmon response can be divided into two  $n_{\rm e}$  regions. Region I comprises low  $n_{\rm e}$ below 10<sup>20</sup> cm<sup>-3</sup>, in which coherence of plasmon oscillations in ITO NPs is not always disturbed by electron-impurity scattering. Electron-impurity scattering mainly becomes a damping factor in oxide semiconductors. The spectral features of LSPRs comprise narrow line-widths and symmetric lineshapes, which are suitable for Mie theory given the absence of additional damping factors. However, the quality factor is relatively small since a short mean free path length ( $I_m = v_F / \gamma$ ) determines the coherence of plasmon oscillations in the NPs (Table 5.2). This situation is due to insufficient conduction paths derived from overlap of electrons from the viewpoint of electron transport. Region-II comprises high  $n_e$  above  $10^{20}$  cm<sup>-3</sup>, in which LSPR excitations become more effective with increasing  $I_m$  as a consequence of increased  $n_e$ . However, LSPR excitations are strongly influenced by electron-impurity scattering. This generated the asymmetric line-shapes, resulting in restricted enhancement of the quality factor of LSPRs. Degenerate metals on doped oxide semiconductors are generally realized by extrinsic and/or intrinsic dopants. Therefore, electronimpurity scattering dominates the optical properties of LSPRs in the high  $n_e$  region. The quality factor of LSPRs can enhanced by controlling the crystallinity and impurities in ITO NPs and would result in high plasmonic performance in the near- to mid-IR regions.

# Plasmon-enhanced near-IR luminescence

For the studies of metal NPs, the use of sheet structures fabricated by assembly of metal NPs provides powerful methods in surface-enhanced Raman and fluorescence spectroscopes [27, 28]. When metal NPs are placed in close proximity to one another, coupling of LSPRs occurs in the nanogap between NPs. The magnitudes of LSPRs increase with the strength due to interparticle coupling, relating to collective plasmonic excitations [29]. This phenomenonis expected for a photoluminescent (PL) enhancement, as observed using heterostructures of metal NPs and InGaN/GaN quantum wells [30]. On the way, LSPR energies on metal NP sheets are limited within the visible range. Herein, the use of oxide semiconductor NPs is applied to longer wavelengths in the near-IR and mid-IR range. Above all, plasmon coupling to light emissions at 1.54  $\mu$ m from Er ions is important towards the developments of optical communications [31]. In this section, we describe on the coupling of Er PL to plasmon modes of ITO NP sheets in the near-IR range. A remarkable change of luminescence from Er ions located at around NP sheets is observed in this work.

Plasmon coupling to an Er light emission has been carried out using a structure comprising an ITO NP sheet and ZnO: Er layer (Er content: 1%). A 80 nm-thick ZnO: Er layer was grown on a *c*-face sapphire by pulsed laser ablation. ArF excimer laser pulses have been focused on ZnO: Er targets located 3.5 cm from the substrate in an  $O_2$  flow of  $10^{-3}$  Pa. The 300 nm-thick NP sheet was fabricated on the ZnO: Er layer with a SiO<sub>2</sub> spacer, and then heat-treated at 250°C (Fig. 5.6a). Scanning electron microscopy (SEM) revealed that the surface morphology of the NP sheet exhibited a closed-packed structure with a slight size distribution (Fig. 5.6b). From a TEM image, the gap length between NPs was about 2 nm, and the spatial separation distance between the NP sheet and ZnO: Er layer was 10 nm (Fig. 5.6c). The plasmon-enhanced PL is dependent on the separation distance between the emitting layers and metal nanostructures. It is reported that plasmon-enhanced PL on metal-emitter systems such as Au-CdSe QDs and Ag-Eu<sup>3+</sup> emitters, has been obtained with separation distances of around 10 nm [33 – 35]. Accordingly, a separation thickness of 10 nm between the NP sheet and ZnO: Er layer the NP sheet and ZnO: Er layer has been chosen for experiments.



#### FIGURE 5.6

(a) Cross-section TEM image of a hybrid structure consisting of an NP sheet and ZnO: Er layer. (b) Surface SEM morphology of the NP sheet. (c) Cross-section TEM image of the hybrid structure focused on the interface between the NP sheet and ZnO: Er layer. (d) Er PL spectra at 10 K of coated (red line) and uncoated (black line) ZnO: Er layers. Inset indicates an energy-level diagram of the Stark levels of Er emission. Reproduced from [32], with permission. Copyright 2014, American Institute of Physics

Near-IR luminescence has been measured by a 30-cm single monochromator with a liquid-nitrogencooled InGaAs detector. A He-Cd laser has been used as the excitation source. PL excitation and luminescence collections were performed from the substrate side. A ZnO: Er layer without the NP sheet (uncoated ZnO: Er) showed a maximum peak of 0.811 eV at 10 K (black line in Fig. 5.6d), indicating energy transitions from the excited  ${}^{4}I_{13/2}$  to ground  ${}^{4}I_{15/2}$  states of Er ions. Furthermore, a shoulder structure at 0.798 eV has been identified to Stark splitting with the several sub-bands because Er ions in ZnO are located in six-fold configurations with bonding to neighboring oxygen atoms [36]. On the other hand, the PL peak of the ZnO: Er layer with the NP sheet (coated ZnO: Er) showed a redshift of 13 meV compared to that of the uncoated ZnO: Er layer (red line in Fig. 5.6d), and was close to an energy interval of the Stark sub-band. The PL intensity of the coated ZnO layer was four-fold higher than that of the uncoated ZnO layer. Above all, a strongly increased spectral composition compared to that of the uncoated ZnO: Er layer has been obtained in the low photon energy region of the spectrum. This indicated that the proximal NP sheet modulated the luminescent transitions in the Stark sub-bands of Er ions.



#### FIGURE 5.7

(a) Extinction spectra of the NP sheet with a thickness (t) of 300 nm. Experimental data (black) are compared with theoretical data (red) calculated using the FDTD simulation. Inset indicates extinction spectra of the NP sheet with different thicknesses on glass substrates. (b) *E* intensities at the gap (black) and interface (red) as a function of photon energy. Electric field distributions at photon energies of 0.58 eV and 0.80 eV are shown in (c) and (d), respectively. Reproduced from [32], with permission. Copyright 2014, American Institute of Physics

It has been investigated the optical response of the NP sheets fabricated on glass substrates (inset of Fig. 5.7a). We could no peak structure in the spectra in the near-IR range at 21 and 98-nm-thicknesses. In contrast, a 260 nm-thick NP sheet showed a clear peak at 0.58 eV and a shoulder component at around 0.80 eV. Similar spectra have also been observed on the NP sheet on the ZnO: Er layer (black line in **Fig. 5.7a**). Furthermore, we studied an excitation process of the NP sheet using a finite-difference time-domain (FDTD) simulation.

The modeled NP sheet has a hexagonally packed structure with an interparticle length of 2.0 nm. The dielectric constants of NPs were taken from ellipsometric data of an ITO layer. The refractive index (n = 1.437) of capric acid was applied to the medium between the NPs since capric acid was used for the organic ligands on the NP surfaces [37]. The modeled structure was illuminated with light directed in the *Z*-direction from the ZnO: Er layer side. The direction of the electric field was perpendicular to the light and parallel to the *X* direction. The hybrid structure was simulated using periodic boundary conditions along the *X* and *Y* axes. The electric field distribution was simulated at the *XZ* plane. The calculated extinction spectrum of the NP sheet was dependent on the number of NP layers. For a model of a NP sheet with 22 NP layers, the calculated extinction spectrum was similar to the experimental extinction spectrum (red line in Fig. 5.7a). We theoretically succeeded to reproduce an extinction spectrum of the NP sheet in the near-IR range.

The spatial distribution of the electric field (*E*-field) was dependent on the excitation photon energy. The *E*-field (I) at 0.58 eV was strongly localized in the gap between the NPs (Fig. 5.7c). This was due to plasmon coupling between the NPs, as characterized by the redshift observed for the LSPR energy of the isolated NPs. In contrast, the *E*-field (II) at 0.80 eV appeared at an interface between the NP sheet and ZnO: Er layer (Fig. 5.7d). Figure 5.7b shows *E*-field intensities at the gap and interface as a function of photon energy. The maximum *E*-field at the gap was obtained at 0.58 eV, while the *E*-field at the interface showed a maximum peak at 0.80 eV.



#### FIGURE 5.8

(a) Temperature dependence of Er PL spectra in the NIR range for uncoated (a) and coated (b) ZnO: Er layers.
(c) Er PL peak energy as a function of temperature for uncoated (black) and coated (red) ZnO: Er layers. (d) Dependence of Er PL intensity on temperature for uncoated (black) and coated (red) ZnO: Er layers. Reproduced from [32], with permission. Copyright 2014, American Institute of Physics

The NP sheet exhibited different *E*-fields at both the gap and interface in the NIR range, which could account for the two optical components in the extinction spectrum. Accordingly, the magnitude of *E*-field (II) at the interface contributed to the enhancement of Er PL. The plasmon mode of the thick NP sheets was effective for an increase in optically active Er ions, which was demonstrated using the three-dimensional FDTD simulations. The coupling of Er emission to the NP sheet will be discussed in relation to the temperature-dependent Er PL spectra (Figs. 5.8a and 8b). The PL peak positions of the coated ZnO: Er layer moved to low photon energies with the increase of temperature, which was close to that observed for the uncoated ZnO: Er layer at 50 K (Fig. 5.8c). Moreover, the enhanced PL intensity at 10 K of the coated ZnO: Er layer gradually weakened with increasing temperature, and then returned to the PL intensity of the uncoated ZnO: Er layer at 50 K (Fig. 5.8d). The spectral modifications of Er PL were simultaneously induced with PL enhancement. Energy coupling of transition dipoles of emitters and plasmons of metal NPs is dependent on the quantum yield of the emitter, which has been reported for metal NPs combined with light emissions from QDs and QWs. In the Persson model, the energy coupling efficiency ( $\phi_{ET}$ ) can be written by the separation distance (*d*) between the ZnO: Er layer and the NP sheet as follows [38]:

(4) 
$$d_0 = \left(\frac{0.225c^3\Phi}{\omega^2\omega_F k_F}\right)$$

(5) 
$$\phi_{ET} = \frac{1}{1 + (\frac{d}{d_o})^4}$$

where *c* is the speed of light.  $\Phi$  and  $\omega$  (4.1×10<sup>6</sup> s<sup>-1</sup>) are the quantum yield and emission frequency of the Er PL, respectively.  $\omega_{\rm F}$  (8.3×10<sup>15</sup> s<sup>-1</sup>) and  $k_{\rm F}$  (3×10<sup>9</sup> m<sup>-1</sup>) are the Fermi frequency and Fermi wave vector of the ITO NP, respectively.  $\phi_{\rm ET}$  is only dependent on the  $\Phi$  value of the Er PL because the *d* value was set to 10 nm in the hybrid structure. It has been thought that the coupling of Er PL to the NP sheet was only observed at low temperatures below 50 K where Er PL with high  $\Phi$  values could be realized, while a low  $\Phi$  weakened plasmon coupling to Er PL at the high temperatures. These results showed the possibility of alternatively plasmonic materials on doped oxide semiconductor NPs.

# Solar-thermal shielding applications

For plasmonic applications of NPs based on oxide semiconductors, the assembled films consisting of ITO NPs are applied to optical enhancement of near-IR light emissions, which are attributed to *E*-fields induced on the surfaces of the assembled ITO NP films [39, 40]. The high *E*-fields localized between NPs are dependent on interparticle gap [41]. In particular, a gap distance down to sizes less than the diameter of a NP produce remarkable enhancements of *E*-fields [42]. In addition, it is difficult to control the interparticle gap between NPs. However, it is beneficial that large-area fabrications at costs make NP assemblies attractive for industrial development.

Recently, plasmonic properties on oxide semiconductors have received much attention for thermalshielding applications. In our study, ITO NPs are chosen as a concrete example. The purpose of this work is to apply the plasmonic properties of assembled films of ITO NPs to satisfy recent industry demands for a material with thermal-shielding ability. Their requirements include the fabrication of flexible sheets with high heat-ray reflections, as well as visible and microwave transmissions. To date, the IR optical responses have been investigated mainly in terms to transmittance and extinction spectra of composites and films utilizing oxide semiconductor NPs [43 - 46]. Accordingly, no previous paper has reported reflective performances in assemblies of NPs in spite of the desire for thermal-shielding to cut IR radiation not by absorption, but through reflection properties. Herein, we present the IR plasmonic properties of assembled films of ITO NPs from theoretical and experimental aspects. IR reflectance in the assembled NP films is discussed specifically following elucidation of their structure and corresponding plasmonic properties. 3D interactions of *E*-fields along the in-plane and out-of-plane directions in the films play an important role in obtaining high





#### FIGURE 5.9

(a) Experimental and (b) simulated transmittance spectra of 3D NP films.(c) Experimental and (d) reflectance spectra of 3D NP films. (e) Cross-section SEM image of a 96 nm-thick film sample. Inset is a FFT pattern. (f) A simulated model of a 3D NP film. The modeled NP sheet was illuminated with light directed in the *Z*-direction from the air side. The direction of the *E*-field was perpendicular to the light and parallel to the *X*-direction. Reported from [42], with permission. Copyright 2016, American Chemical Society

In this section, we provide new insights for enhancement of thermal-shielding ability through plasmonic techniques based on oxide semiconductor NPs.

3D assemblies of ITO NPs provided a remarkable change in optical properties, which were clearly observed from transmittance and reflectance spectra (Figs. 5.9a and 9b). Transmittance with a resonant peak at 2.20  $\mu$ m decreased to a level close to zero with increasing film thickness. In contrast, reflectance was enhanced at a close proximity of 0.6 in association with the film thickness. The single peak of a 22 nm-thick 3D NP film was separated into lower and higher wavelengths with the film thickness. (Fig. 5.10a). For a 216 nm-thick 3D NP film, two types of peaks (-I and -II) were positioned 2.13 and 4.02  $\mu$ m in the near- and mid-IR range, respectively. The ratio (*R*/*A*) of reflectance (*R*) and absorbance (*A*) increased quickly to a large value with increasing film thickness. (Fig. 5.10c). As a result, the 3D NP films provided reflectance-dominant optical responses.

FDTD simulations were performed to clarify the above optical properties. A cross-section SEM image of a 3D NP film (96 nm-thickness) showed a close-packed structure (Fig. 5.9e). The modeled 3D NP layers are based on a HCP structure with an interlayer distance of 2.0 nm along the *Z*- (out-of-plane) direction (Fig. 5.9f). The systematic change in the number of NP layers from 1 to 20 was capable of reproducing the experimental data (Figs. 5.9c and 9d). The applied model was satisfactory in describing the optical responses of the 3D NP films. The increase in number of NP layers provided the resonant dips in transmittance and peak separations in reflectance, which matched reasonably well with the experimental data (Figs. 5.10a and 10b). However, the reflectance for peak-I was smaller than that for peak-II in the case of simulations, resulting in a difference of *R*/*A* ratio between experimental and simulation data (Fig. 5.10c). This behavior indicated that the high electron density in the NPs was indispensable for realizing high reflectance from the 3D assembled NP films.



#### FIGURE 5.10

(a) Resonant wavelengths and (b) reflectance of peaks I and II as a function of film thickness (bottom horizontal axis) and number of NP layers (upper horizontal axis). Red color indicates simulated results of FDTD simulations. (c) Experimental and simulated R/A ratios evaluated at peak positions related to peak-I. R and A indicate reflectance and absorbance, respectively. Reported from [47], with permission. Copyright 2016, American Chemical society

Reflectance

The resonant origins of peaks I and II in the reflectance have theoretically been examined as a function of interparticle gap between the NPs. Figure 5.11a shows simulated reflectance spectra of 3D NP layers (20 NP layered model) at different *L*. Reflectance gradually enhanced with decreasing *L*. When decreasing *L* from 10 to 1 nm, peak-II exhibited a monotonous red-shift to longer wavelengths, while peak-I almost remained unchanged (Fig. 5.11b). This suggests a difference in the origin of plasmon resonance between peaks I and II. The localized *E*-field from each metal NP usually overlaps when metal NPs are closely positioned, and plasmon coupling occurs as a consequence. In the plasmon hybridization model, the plasmon coupling can be categorized into bonding and anti-bonding states [48]. The bonding state provides a red shift of a resonant peak with decreasing interparticle gap, while a slight blue-shift of a resonant peak results from the antibonding states, respectively. *E*-field distributions and their charge vectors were analyzed at wavelengths of peaks I and II (Figs. 5.11c and 11d). For the mid-IR reflectance at peak-II, a resonant mode consisted of individual dipolar plasmons oscillating in-phase along the direction of incident



### FIGURE 5.11

(a) Simulated reflectance spectra of 3D NP films with different inter-particle gaps. (b) Resonant wavelengths of peaks I and -II as a function of inter-particle gap. (c) Images of electric field distributions. (d) Images of charge vectors at peaks I and peak-II. Reported from [47], with permission. Copyright 2016, American Chemical Society

polarization. The E-fields between the NPs were only localized along the in-plane X-direction. In contrast, field analysis of the near-IR reflectance at peak-I revealed that the dipolar plasmons in the NPs oscillate out-of-phase, resulting in a net dipole moment of nearly zero. Their E-fields interacted with surrounding NPs along the out-of-plane and in-plane directions. The mode splitting of plasmon resonances was caused by three-dimensional stacked assemblies of NPs, which produced quadrupole and dipole modes ascribed to peak-I and peak-II, respectively. These behaviors became naturally pronounced with an increase in film thickness. For the above reason, the differences in reflectance between experimental and simulation data could be explained in terms of a local structure and plasmon mode as follows. A dipole mode can be strongly observed in precise closepacked NP assemblies. Ideally, each NP is indistinguishable and this should apply to all of its neighbors. Hence, the simulated reflectance in models of 3D NP layers with ideal HCP structures was mainly dominated by the dipole mode. In contrast, the reflectance observed in the experiment was strongly suggestive of the quadrupole mode rather than the dipole mode, indicating the dominant appearance of quadrupole coupling to the symmetry-forbidden nature of dipole coupling and symmetry-allowed quadrupole characteristics [49]. These situations were realized in the 3D NP films with increasing thickness, and they were related to the inhomogeneous arrangement of NPs from the SEM images (inset of Fig. 5.9e).



#### FIGURE 5.12

(a) Reflectance spectrum of a 3D NP sheet on a PET substrate. Inset shows a photograph of the fabricated sheet sample made using a roll-coating method. (b) Shielding effectiveness (SB) in the range 0.5 to 40 GHz for a 3D NP sheet (red open circles) and sputtered ITO film (black open circles). Reported from [47], with permission. Copyright 2016, American Chemical Society

Electromagnetic (EM) properties of 3D NP films in the microwave range 0.5 to 40 GHz, which is an important frequency range for telecommunications. Transparent solar-thermal shielding is effective techniques to prevent room heat in order to realize comfortable environment in vehicles. However, it is strongly required for vehicles to transmit EM waves in the microwave range through windows to carry out radio communications such as an "Electronic Toll Collection System (ETC)" and "Information traffic system (ITS)" in addition to "Advanced Driver Assistant System (ADAS)". Therefore, it is important to measure EM properties of 3D NP sheets based on ITO in addition to evaluate optical properties in the IR range. For microwave measurements, a 250 nm-thick 3D NP sheet ( $40 \times 30$  cm) was deposited on a flexible sheet of PET using a roll-coating technique [inset of Fig. 5.12a]. High reflectance with a close proximity of 0.6 was also reproduced [Fig. 5.12a]. The shielding effectiveness (*SE*) of the 3D NP film was almost zero, which largely differed from that of a

sputtered 127 nm-thick ITO film (Fig. 5.12b). The difference between the two materials concerns electrical conductance ( $\sigma$ ) in the films, which was in the order of 10<sup>-5</sup> and 10<sup>3</sup> S/cm for the 3D NP film and sputtered film, respectively. If the shielding material is thin, *SE* can be determined by reflection, as follows:

$$SE = 20\log(\sqrt{2}\eta_0/2R)$$

where  $\eta_0^2$  is  $\mu_0 / \varepsilon_0$  ( $\mu_0$ : absolute permeability of the vacuum, and  $\varepsilon_0$ : dielectric constant of the vacuum), and *R* is the sheet resistivity (=  $1/\sigma$ ) [50]. The significant obstruction of carrier transport between NPs produced low electrical conductance due to the presence of surface ligands on the NPs, and realized the high microwave transmissions.

ITO NPs were used to create 3D assembled films with small interparticle gaps due to the presence of surface ligands. This situation induced effective *E*-field interactions along the in-plane and outof-plane directions, which caused the splitting of plasmon resonances for the quadrupole and dipole modes. This plasmon coupling induced in the 3D NP films played an important role in producing the high reflectance in the near- and mid-IR range, which was theoretically supported using FDTD simulations that showed agreement with experimental results. In addition, the *E*-field enhancements between NPs simultaneously caused a remarkable reduction of electrical contacts between the NPs, which contributed to the high microwave transmissions. The plasmonic control in 3D assemblies of NPs represents promising potential for structural and optical designs used to fabricate a flexible thermal-shielding sheet with a reflection-type based on transparent oxide semiconductors. The knowledge gained in this study can be applied to 3D NP films utilizing inexpensive ZnO and WO<sub>3</sub> for large-size coating films of transparent windows.

# **Conclusion Remarks**

Optical properties of LSPRs in oxide semiconductor NPs were investigated using ITO NPs with different impurity contents in section 2. The plasmonic resonances of ITO NPs were clearly observed in the near-IR range from the viewpoints of optical and EELS techniques. In particular, electron-impurity scattering contributed towards plasmon damping as one of a factor that is absent in metal NPs from a systematic correlation between LSP excitations and electron carriers. A threshold electron density from a damping dominated regime to a quenched damping regime appeared at around  $10^{20}$  cm<sup>-3</sup>. It was found that electron carriers enhanced LSPRs with simultaneous damped plasmon excitations.

In section 3, Near-IR luminescence was remarkably enhanced by using ITO NP sheets. Experimental measurements and modeling cleared the presence of different *E*-fields in the NP sheets. The local *E*-field at the interface between the NP sheet and Er emitting layer of ZnO contributes for the spectral modifications of Er PL, which was attributed to the energy transfer between Er transition dipoles in ZnO and the surface plasmon modes on the NP sheet.

Finally, we described IR plasmonic applications in ITO NP sheets for solar-thermal shielding technology. Above all, the *E*-field interactions between NPs produced interesting plasmonic coupling because of the creation of narrow crevices in the interparticles. Three-dimensional field interactions along the in-plane and out-of-plane directions provided high light reflections in the near- and mid-IR regions, which were satisfied with the industrial requirements. Furthermore, ITO NP sheets could be extended to obtain large-size flexible films, which simultaneously showed microwave transmittance essential for telecommunication.

The above results provided important insights for basic science and practical applications based on plasmonic techniques utilizing oxide semiconductor NPs. However, plasmonic properties and applications are stand still-points. Hereafter, it will be needed to study plasmonic phenomena on oxide semiconductor NPs towards new concepts concerning optical manipulations in the IR range.

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