

Enhancing Plasmon Quality Factor for Photonic Materials via Solvothermal Annealing in Cd₂SnO₄ Nanocrystals

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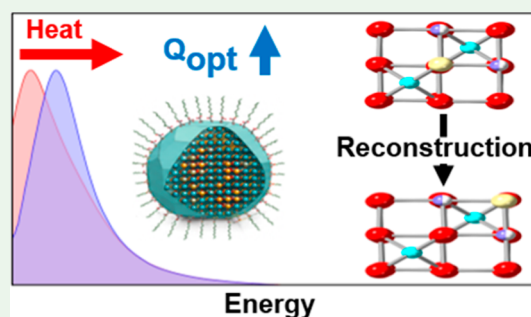
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Supporting Information

ABSTRACT: Photonic properties in a plasmonic nanocrystal are directly impacted by carrier density, carrier effective mass, and carrier damping behavior. Postprocessing of as-prepared Cd₂SnO₄ (CTO) by solvothermal annealing is shown to enhance the localized surface plasmon (LSPR) optical quality through a time-dependent LSPR shift and LSPR narrowing. The change in the LSPR is complex but postulated to be driven by surface reconstruction leading to incorporation of Sn, reduction in size, and defect evolution. The changes in the CTO produce a shift to higher frequency for the LSPR and loss of a high energy shoulder with an exponential rate of $k \sim 1.0 \text{ h}^{-1}$. The improved plasmonic quality factor is due to the overall increase in carrier density and loss of the shoulder during solvothermal annealing. During annealing, an increase in the depletion layer width and a decrease in Sn activation in CTO with $k \sim 0.5 \text{ h}^{-1}$ are also observed. Postprocessing of isolated plasmonic metal oxide nanocrystals through solvo-thermal annealing may represent a convenient strategy to enhance LSPR quality factors, providing a pathway to improving photonic properties in this class of materials.

KEYWORDS: plasmonic, magnetoplasmonic, defect engineering, metal oxide, annealing, nanocrystal, photonic



INTRODUCTION

Noble metal colloidal nanocrystals have been studied for nearly two decades for their beneficial plasmonic localized surface plasmon resonance (LSPR) behavior leading to unique optoelectronic behavior, particularly in biomolecular applications.^{1–11} Recently, plasmonic metal oxides have begun to attract attention due to their strong magneto-optical responses in the mid-infrared region to induce rotation of polarized light that can be competitive with traditional materials used in fiber optics for optical isolators or rotators.^{5,12–14} In plasmonic semiconductor nanocrystals (PSNCs), the localized surface plasmon (ω_{LSPR}) is tunable from near-IR to THz frequencies by the control of carrier density (n), carrier effective mass (m^*), and the material dielectric (ϵ_∞). The observed ω_p frequency follows the Drude–Lorentz model, such that $\omega_p = \sqrt{\frac{ne^2}{m^* \epsilon_0}}$, in which n is the charge carrier density, m^* is the charge carrier effective mass, e is the electron charge, and ϵ_0 is vacuum permittivity.^{15,16} Pineider and co-workers suggested that the strong LSPR in PSNC could be transformative in magneto-optical applications by allowing large Faraday rotations in nanocrystal films for materials that have a low m^* value with a high carrier density.^{9,12–14,17} Unfortunately, in n-type wide bandgap metal oxides, the values of n and m^* are linked reflecting band curvature of the conduction band

leading to increasing carrier mass with increasing carrier density.^{18–20} Other inherent limitations that exist in n-type plasmonic nanocrystals include the presence of a depletion layer,^{21–23} the presence of point defects (donor/acceptor levels), surface termination differences,²⁴ and nanocrystal shape effects on LSPR quality factor.²⁵ Obtaining high-performing n-type semiconductor nanocrystals for photonic applications thus represents a complex balancing of the intrinsic constraints that occur within n-type semiconductors.

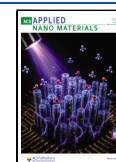
Cadmium stannate, Cd₂SnO₄ (CTO), represents a recently reported n-type plasmonic nanocrystal that was computationally predicted to have a low m^* (0.13 m_e) value. CTO forms in an inverted spinel structure, where the carriers arise from antisite occupation rather than oxygen vacancies.^{26,27} From DFT calculations^{18,20,28} and thin film studies,²⁹ CTO is anticipated to exhibit a nearly parabolic conduction band shape that should moderate the problem of increasing m^* value with

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increasing carrier densities (n). Although only a limited number of studies on CTO nanocrystals have appeared in the literature,^{28,30} CTO could represent an ideal candidate for achieving enhanced photonic performance predicted for low m^* plasmonic nanocrystals by Pineider et al.¹⁴

In a plasmonic nanocrystal, the LSPR breadth will be impacted by the presence of surface scattering, defect scattering, or the presence of a surface depletion layer.^{21,22} LSPR broadening lowers the LSPR quality (Q) factor (Q -factor = LSPR frequency/LSPR breadth) and thus the photonic performance of plasmonic nanocrystals.³¹ In CdO, reduction of oxygen vacancies (V_O) and cadmium vacancies (V_{Cd}) through thermal annealing has been reported to reduce scattering centers, improving carrier mobility, carrier concentration, and decreasing resistivity.^{32–34} While thermal annealing leads to defect evolution, improving the optical performance in thin film studies, the application of solvothermal annealing to improve the LSPR Q -factor on preisolated plasmonic nanocrystals has not been reported.

In this study, we evaluate the improvement in the LSPR Q -factor during time-dependent solvothermal annealing in 11.2 ± 1.8 nm and 10.4 ± 1.3 nm truncated octahedron-shaped Cd_2SnO_4 (CTO). Solvothermal annealing leads to a time-dependent shift to higher energy for the LSPR, an increase in the Q -factor (Q_{opt}), and a loss of a high-energy shoulder in the LSPR spectrum. Evaluation of the time-dependent changes of the LSPR, Q -factor, Sn to Cd ratio, and nanocrystal structure, morphology, and size reveals that the improvement in Q -factor during annealing can be traced to an increase in carrier density (n) and a change in the effective carrier mass (m^*). The increase in the Sn content is tentatively assigned to surface reconstruction during annealing, arising from passivating layer changes and cation exchange. The high-energy shoulder decreases in intensity with annealing time and is assigned to the evolution of defects in the CTO.

The experimental results offer a new postsynthetic strategy to enhance the Q -factor in plasmonic nanocrystals and their potential use as epsilon near-zero materials for photonics.^{14,35,36} The improved plasmonic Q -factor with low m^* value for CTO compared to reported materials may offer a new material for incorporation into nanophotonic technologies ranging from telecommunications to spintronics in addition to current sensing applications, as suggested in the magneto-optical roadmap.¹³

EXPERIMENTAL SECTION

Materials

Cadmium acetylacetonate ($Cd(acac)_2$), tin(II) acetate ($Sn(OAc)_2$), tin(II) fluoride (SnF_2), oleic acid (OA, technical grade, 90%), octadecene (ODE), toluene, isopropanol (IPA), and tetrachloroethylene (TCE) were purchased from Sigma-Aldrich or VWR. OA-passivated octahedron Cd_2SnO_4 (CTO) was prepared, isolated, and purified as described previously.¹⁷ FCTO synthesis is identical to CTO with the substitution of SnF_2 . The synthetic details for FCTO are provided in Supporting Information. The size is controlled by reducing the OA-to-Cd ratio in the reaction.

Solvothermal Annealing

In a 3-neck 100 mL round-bottom flask, CTO (300 mg) was dissolved in 30 mL of ODE. This solution was heated to 120 °C and degassed for 20 min, followed by rapid heating to an annealing temperature of 280 °C. After the final temperature was reached, 2 mL aliquots were taken. Larger aliquots (8 mL) were taken at $t = 0, 6$, and 24 h to allow full-sample characterization (UV–vis, transmission

electron microscopy (TEM), powder X-ray diffraction (pXRD), thermal gravimetric analysis (TGA), magnetic circular dichroism (MCD), EPR) of CTO PSNCs. During annealing, metallic Cd is observed to precipitate from solution and settle at the bottom of the vessel. The aliquots are precipitated by the addition of IPA followed by centrifugation. The precipitate is dissolved in toluene, centrifuged at 3000 rpm to remove Cd(0) and isolated by the addition of IPA, followed by a final centrifugation step.

UV–Vis–NIR Spectroscopy

The experimental changes in the UV–vis–NIR spectra were measured at 0 (before annealing), 1, 2, 4, 6, 8, and 12 h during annealing to evaluate the time-dependent change in bandgap and LSPR shift. The spectral data were fit to the Simplified Extended Drude Approximation (SXDA) model, and the LSPR features were evaluated. The UV–vis–NIR spectra for the isolated aliquots of solvothermal annealed CTO samples dissolved in 1 mL of TCE were measured on a PerkinElmer Lambda 950 spectrometer. A 1 mm path length NIR quartz cuvette was used for all absorbance measurements.

Powder X-ray Diffraction

pXRD patterns were collected with a Rigaku MiniFlex powder X-ray diffractometer using a $Cu K\alpha$ source. The pXRD is calibrated using Si as a reference. The pXRD patterns were collected using a zero-background micropowder plate. Scans were collected from 15° to 70° at a rate of 7°/min and a 0.05° step size.

Transmission Electron Microscopy

HAADF-STEM and EDX measurements were performed at Rice University on a 200 kV Tecnai Osiris transmission electron microscope for the 10.4 nm sample and on an FEI Talos F200i S/TEM 200 kV aberration corrected transmission electron microscope at the University of Florida for the 11.2 nm sample. Size, size dispersity, and morphology were obtained by TEM. Samples were sonicated for 5 min and drop-casted onto lacey carbon-coated copper TEM grids (Ted Pella 01896). Elemental composition for all samples was evaluated by TEM–EDX measurements at 100,000X.

Thermal Gravimetric Analysis

TGA measurements were performed on a TA Instruments model Q600 TGA. The measurements were performed on powdered samples from 20 to 800 °C under an N_2 atmosphere.

Electron Paramagnetic Resonance

The powders were loaded into 4 mm o.d. quartz EPR tubes, sparged by N_2 for 5 min. Continuous wave X-band (9.5 GHz) EPR experiments were performed using field modulation with a phase-sensitive lock-in detection on a Bruker ELEXSYS II E500 EPR spectrometer (Bruker Biospin, Ettlingen, Germany), equipped with a rectangular TE102 resonator (Bruker ER4102ST). This type of detection results in first-derivative-type EPR spectra. Spectral simulations were performed on Matlab using the EasySpin package.³⁷

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5100 X-ray photoelectron spectrometer (Mg $K\alpha$ source) with a pass energy of 22.36 eV. Powdered CTO samples at 0 and 6 h of annealing were deposited on carbon tape. The samples were Ar^+ -sputtered using a sputtering gun at 5 keV and 1 μA prior to measurement. The XPS spectra were fitted using CasaXPS software. Samples were calibrated to the aliphatic carbon assignment (C 1s, 284.8 eV).

Magnetic Circular Dichroism

Fixed field (1.4 T) MCD at RT was measured on TCE dispersions of the NCs in the LSPR peak region, using a homemade MCD setup. Light emitted from a Xe lamp (300 W) source is monochromated (Cornerstone 260) and then passes through a Rochon linear polarizer and a photoelastic modulator, which modulates the polarization of light between left-handed and right-handed at 47 kHz. The sample is placed in an electromagnet operating at an applied field of 1.4 T, parallel to the propagation direction of light. Light transmitted by the sample is collected by an InGaAs photodiode. The signal is then

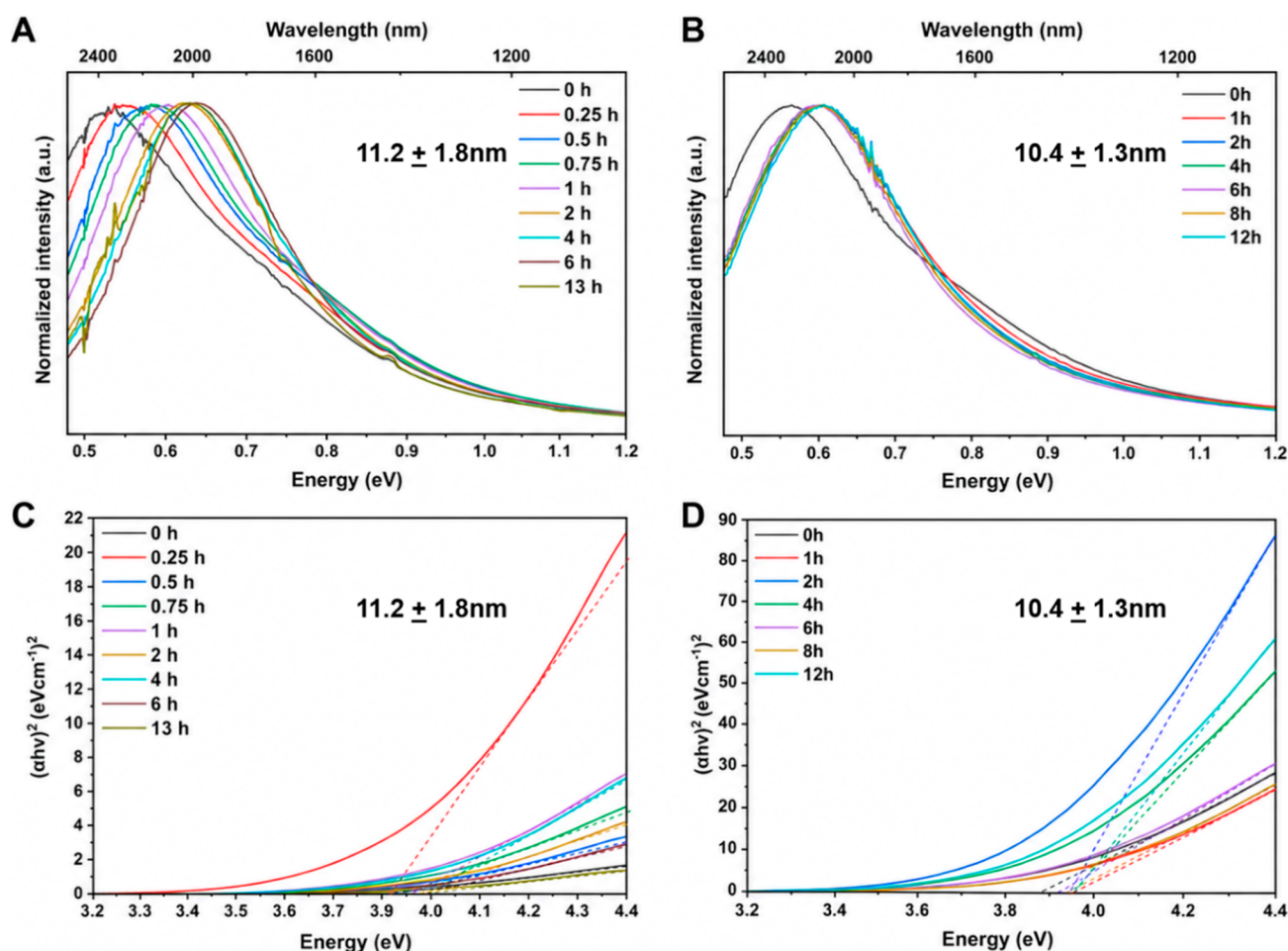


Figure 1. Time-dependent LSPR spectral changes arising following annealing of truncated octahedron morphology oleic acid passivated CTO dissolved in octadecene at 280 °C for the (A) 11.2 ± 1.8 nm CTO LSPR and (B) 10.4 ± 1.3 nm CTO LSPR. Time-dependent changes for band edge and E_g evaluated by a Tauc plot for (C) 11.2 ± 1.8 nm CTO and (D) 10.4 ± 1.3 nm CTO.

amplified and analyzed by a lock-in amplifier. Further details can be found in ref 38. Extinction and MCD spectra were recorded on the same dispersion of the NCs in TCE using a 1 mm quartz Suprasil QX cuvette.

Variable field MCD (VH-MCD) measurements performed at the intraband energy on a home-built system coupled to an Oxford Instruments HelioxTL Superconducting Spectromag. A Newport Xe Arc Lamp is used as the light source in combination with a Thorlabs Glan–Taylor linear polarizer (GLB-10) to linearly polarize the incident light, followed by using a HINDS Instruments photoelastic modulator (PEM-100) for subsequent circular polarization. To ensure the PMT is operating in the linear range, the lamp intensity was adjusted via a PID circuit. A Hamamatsu PMT amplified with a Femto current amplifier (LCA-200 K-20M) is used to measure the UV–vis spectra from 1.4 to 2.4 eV. Temperature was monitored and controlled through a Keck-Clamp fiber cable routed through the sample probe and mounted adjacent to the sample substrate. A positive and negative field sweep scan from 0 to 6 T was performed for the thin film samples at 32 ± 0.1 K in 1 T intervals. The collected spectra were corrected by subtracting the 0 T scan to reduce artifacts from polarization effects, using the $\pm$ fields to correct for background, CD features, or magnetic field inhomogeneity, and other anomalies during spectral measurements.

The analysis of the MCD data follows the fitting protocol described in Kuszynski et al.³⁹ In a plasmonic n-type semiconductor, the MCD signal for the LSPR and intraband will exhibit A-term behavior for a degenerate excited state. The carrier effective mass (m^*) is extracted by fitting the Zeeman splitting of the optical transition. To accomplish the fit of the data, the linear absorption feature is fitted with a

Gaussian function over the relevant spectral window (LSPR or intraband). The Gaussian amplitude, center energy, and FWHM are used to analyze the change in $\Delta A/A$ for fields between -6 and 6 T, allowing the extraction of the Zeeman splitting energies ($E_{\text{Zeeman}} = \text{ELCP} - \text{ERCP}$). The slope of the plot of E_z as a function of the applied field (B) allows extraction of the effective mass from the cyclotron relation. The MCD-derived m^* values were used as input parameters for the optical fitting used to extract carrier density, following the expression $E_{\text{Zeeman}}/\hbar = \omega_c = \frac{eB}{m^*m_e}$.

RESULTS AND DISCUSSION

In Figure 1, the time-dependent spectral evolution of the localized surface plasmon (LSPR) and band edge, plotted as a Tauc plot, for a 11.2 ± 1.8 nm and 10.4 ± 1.3 nm truncated octahedron oleate passivated CTO nanocrystal annealed in octadecene at 280 °C is shown. The observed LSPR shifts to higher energy, narrows, and loses a high-energy shoulder during annealing. A shift to higher energy for the band edge is observed during annealing. The shift in the LSPR is accompanied by cadmium metal precipitation during annealing, as evidenced by pXRD on the precipitate (Supporting Information Figure S1). SEM–EDX analysis shows the composition to be 98.2% Cd and 1.8% Sn.

In Figure 2, a plot of the time-dependent shift in the Δ_{LSPR} , $\Delta_{\text{LSPR(FWHM)}}$, and ΔE_g , Q_{opt} ($Q_{\text{opt}} = E_{\text{LSPR}}/\text{LSPR}_{\text{FWHM}}$). The time-dependent changes of Δ_{LSPR} , $\Delta_{\text{LSPR(FWHM)}}$, and ΔE_g , Q_{opt}

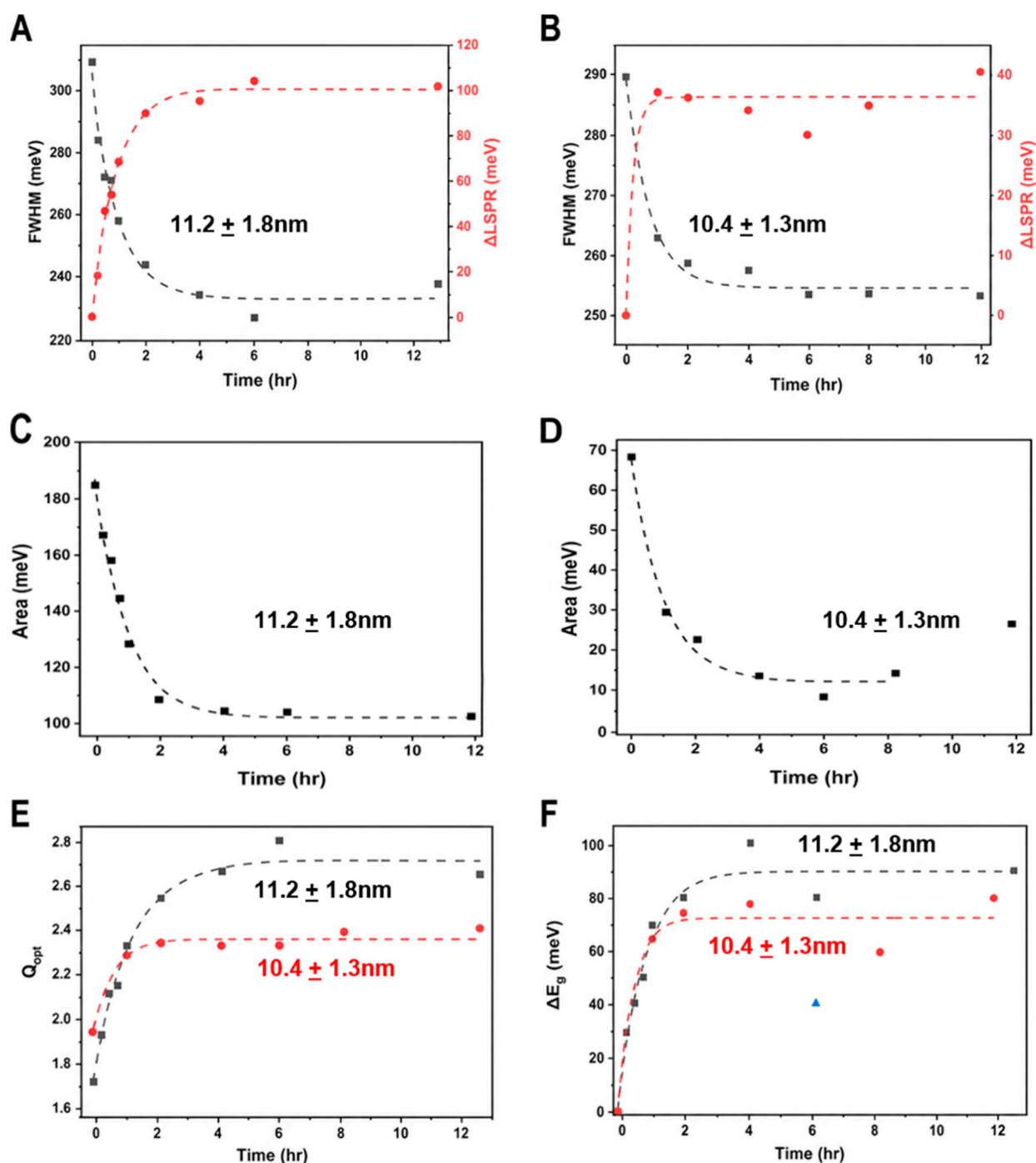


Figure 2. Time-dependent shift in the LSPR energy (ΔLSPR) and LSPR FWHM for (A) 11.2 ± 1.8 nm CTO and (B) 10.4 ± 1.3 nm CTO. The change in the data is fit to an exponential function. Decay of mode-2 area for (C) 11.2 ± 1.8 nm and (D) 10.4 ± 1.3 nm CTO samples, (E) the change in the Q_{opt} value of 11.2 ± 1.8 nm (black) and 10.4 ± 1.3 nm (red) CTO. The data are fit to an exponential function. (F) The change in the bandgap energy evaluated from a Tauc plot (ΔE_g) for 11.2 ± 1.8 nm (black) and 10.4 ± 1.3 nm (red) CTO. The data are fit to an exponential function. The blue triangle in (F) was not included in the fit.

for the 11.2 nm sample are well fit by an exponential function with $k = 1.1 \pm 0.08 \text{ h}^{-1}$ (ΔLSPR , $R^2 = 0.99$), $k = 1.1 \pm 0.14 \text{ h}^{-1}$ (FWHM, $R^2 = 0.98$), $k = 1.3 \pm 0.14 \text{ h}^{-1}$ (ΔE_g , $R^2 = 0.96$), and $k = 0.9 \pm 0.14 \text{ h}^{-1}$ (Q_{opt} , $R^2 = 0.99$). While the fits are on the same order of magnitude for the 10.4 ± 1.3 nm sample in Figure 2, the rates are not reported due to poor statistics reflecting the limited data set. The fit parameters for the 11.2 ± 1.8 nm sample are available in the Supporting Information.

The TEM–EDX analysis of Sn and Cd atomic percent during the time-dependent solvothermal annealing can be correlated to changes in the LSPR energy. From the change in the Sn content and carrier density (n), heterogeneous ensemble Drude approximation (HEDA) allows insight into carrier depletion layers. In Table 1 and Supporting Information, the LSPR is fit and parametrized by three comparative models including the SXDA, HEDA, and discrete dipole approximation (DDA). SXDA, originally developed by

Table 1. Time-Dependent Changes in CTO LSPR Properties for Mode-1 and Mode-2 Evaluated Using SXDA Modeling

set	time (h)	size (nm)	mode-1						mode-2					
			ω_{LSPR} (eV)	ω_{p} (eV)	m^* ^a	n (10^{20} cm ⁻³)	Q_{opt} ^b	FWHM (eV) ^b	ω_{LSPR} (eV)	ω_{p} (eV)	m^* ^a	n (10^{20} cm ⁻³)	Q_{opt} ^b	FWHM (eV) ^b
10.4	0	10.4	0.55	1.61	0.16	3.02	2.32	0.25	0.76	2.23	0.16	5.78	3.13	0.25
	1	9.3	0.59	1.74	0.22	4.83	2.38	0.25	0.78	2.24	0.22	8.02	3.13	0.25
	2	9.3	0.59	1.74	0.22	4.85	2.38	0.25	0.78	2.24	0.22	8.02	3.13	0.25
	4	9.3	0.59	1.73	0.22	4.80	2.38	0.25	0.77	2.28	0.22	8.08	3.13	0.25
	6	9.3	0.59	1.73	0.22	4.78	2.37	0.25	0.76	2.25	0.22	8.07	3.13	0.25
	8	9.3	0.59	1.74	0.22	4.85	2.38	0.25	0.76	2.25	0.22	8.07	3.13	0.25
	12	9.3	0.59	1.74	0.22	4.85	2.38	0.25	0.77	2.25	0.22	8.02	3.13	0.25
11.2	0	11.2	0.52	1.54	0.16	2.73	2.45	0.22	0.67	1.96	0.16	4.478	1.79	0.39
	0.25	11.2	0.54	1.58	0.22	4.00	2.73	0.20	0.68	2.01	0.22	6.431	2.19	0.32
	0.50	11.2	0.55	1.64	0.22	4.30	2.93	0.19	0.71	2.10	0.22	7.015	2.33	0.31
	0.75	10.9	0.57	1.69	0.22	4.57	2.97	0.20	0.72	2.14	0.22	7.316	2.51	0.30
	1	10.6	0.59	1.73	0.22	4.79	3.07	0.19	0.73	2.15	0.22	7.360	2.66	0.28
	2	9.8	0.61	1.79	0.22	5.13	3.26	0.19	0.73	2.15	0.22	7.364	3.00	0.25
	4	9.7	0.61	1.82	0.22	5.26	3.45	0.18	0.73	2.16	0.22	7.414	3.13	0.24
	6	9.6	0.62	1.82	0.22	5.39	3.64	0.17	0.73	2.14	0.22	7.331	3.37	0.22
	13	9.6	0.61	1.81	0.22	5.23	2.95	0.21	0.69	2.03	0.22	6.604	2.29	0.31

^a m^* values are extracted from MCD measurements shown in Figure 4. ^b Q_{opt} and LSPR_{FWHM} are extracted by fitting the experimental extinction spectra.

Milliron⁴⁰ and co-workers, fits the LSPR spectrum to a Drude model with a radial distribution of aliovalent dopants producing carriers and incorporates damping terms. The fits are provided in Supporting Information Figures S2–S4. The SXDA model is coded to account for a 2-mode fitting to distinguish the time-dependent changes in the main LSPR feature from the high-energy feature observed in the LSPR in Figure 1. HEDA, developed by the Milliron group,⁴⁰ is a refinement of a classical Drude-based model that accounts for nanocrystal heterogeneity in the metal oxide nanocrystals. An advantage of HEDA is it can estimate the depletion layer that arises in n-type semiconductors due to band bending. HEDA is not able to independently fit the two features in the LSPR spectrum due to coupled terms in the code, and thus the HEDA fit only accounts for the main LSPR feature. The DDA model is a computational electrodynamics approach used to model how electromagnetic radiation interacts with particles whose size is comparable to or smaller than the wavelength. The DDA model can predict the LSPR spectra for nanocrystals with complex shapes (sphere, cube, truncated octahedron). The computationally predicted LSPR spectrum utilizes carrier densities from the SXDA model for the DDA model. In the Drude models, the m^* value is calculated by fitting MCD data at 0 h and 6 h of annealing to a field-dependent Zeeman A-term behavior (see below and Supporting Information). For LSPR fitting, the m^* value was assumed to be constant for the 10.3 ± 1.3 nm sample and 11.2 ± 1.8 nm sample, as the carrier densities are similar.

SXDA fit of the data for the 10.4 ± 1.3 nm and 11.2 ± 1.8 nm data is available in Supporting Information Figure S2. SXDA fitting allows the time-dependent change in n and extraction of the mode area of the main LSPR feature (mode-1), and the high-energy shoulder (mode-2) is tabulated in Table 1. The SXDA fit of the LSPR spectrum to two Lorentzian-shaped modes in SXDA has R^2 values of 0.99. The carrier densities are observed to increase with the annealing time for mode-1 and mode-2, but the intensity of mode-2 decreases at longer times. For the SXDA fitting $\epsilon_{\infty} = 4.2$ (CTO), $\epsilon_{\text{TCE}} = 1.505$, ϵ (OA) = 1.46, path length = 1 mm, and

the carrier effective mass was measured by magnetic-circular dichroism (reported below). The time-dependent change in the area of mode-2 (Figure 2C,D) identified in the SXDA fit is observed to follow an exponential trajectory with $k = 1.06 \pm 0.09 \text{ h}^{-1}$ ($R^2 = 0.99$) for the 11.2 ± 1.8 nm sample. The change in mode-1 area is identical to the ΔLSPR plot exponential trajectory in Figure 2. The observed carrier density at 0 h for mode-1 is 2.7×10^{20} carriers/cm³ and 4.8×10^{20} carriers/cm³ for mode-2 in the 11.2 ± 1.8 nm CTO sample. For the 10.4 ± 1.3 nm sample, the observed carrier density at 0 h for mode-1 is 3.0×10^{20} carriers/cm³ and for mode-2, it is 5.8×10^{20} carriers/cm³. The increase in carrier density would produce the LSPR shift according to the Drude model that relates $\omega_{\text{p}} = (C \times n/m^*)^{1/2}$, where $C = e^2/\epsilon_0$, and the high-frequency dielectric constant, $\epsilon_{\infty}^{\text{(CTO)}} = 4.2$. The increase in carrier density would also explain the shift of the bandgap (E_{g}) (Figure 2) and the similarity in the rates for ΔLSPR and ΔE_{g} . An increase in carrier density will lead to a shift to higher energy for E_{g} according to the Burstein–Moss (BM) effect, which predicts a shift to higher energy with the population of unoccupied states above the Fermi level. The Burstein–Moss model predicts a change in the optical bandgap with increasing carrier density, such that $\Delta E = E_{\text{g}}^{\text{Sn antisite}} - E_{\text{g}}^{\text{CTO}} = (\hbar^2/2m^*)(3\pi^2n)^{2/3}$, where $E_{\text{g}}^{\text{Sn antisite}}$ is the bandgap evaluated by a Tauc plot on samples exhibiting a plasmon mode arising from Sn antisites, $E_{\text{g}}^{\text{CTO}}$ is the bandgap for CTO with no antisite occupation, and n and m^* are the carrier density and effective mass of the free carrier, respectively.⁴¹

Changes in CTO size, shape, and Sn-to-Cd ratio during annealing were evaluated by TEM, TEM–EDX, and pXRD performed on the samples at selected time points during annealing. The TEM (size, size distribution) and pXRD are provided in Supporting Information Figure S5. TEM imaging reveals a reduction in size of 1.6 nm (0.8 nm per facet) in the 11.2 ± 1.8 nm sample and 1.1 nm (0.55 nm per facet) in the 10.4 ± 1.3 nm sample. Concomitant with the reduction in size, TEM–EDX data reveal an increase in the Sn/Cd ratio with annealing time. The TEM images exhibit rounding of the truncated octahedron facets and an increase in the Sn content

with increasing annealing times. Inspection of the pXRD patterns reveals a slight narrowing in the pXRD reflections with increasing time, which can be interpreted as a decrease in strain based on the smaller measured TEM size with an increasing annealing time. pXRD does not exhibit secondary phases during annealing. In Figure 3, a plot of the size change

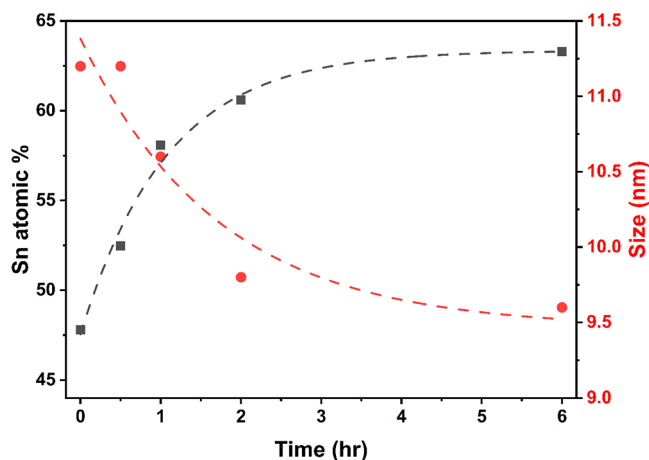


Figure 3. Plot of the change in the size of the CTO and Sn concentration during annealing for the 11.2 ± 1.8 nm CTO sample.

and Sn atomic percent evaluated at selected time points is shown for the 11.2 ± 1.8 nm sample. Data at 0, 6, and 24 h (24 h as an infinite time sample to ensure no long-term evolution) were analyzed for 10.4 ± 1.3 nm and for 0, 0.5, 1, 2, and 6 h for the 11.2 ± 1.8 nm CTO sample are provided in Supporting Information Figure S5. The change in size with time can be fitted to an exponential function with a $k = 0.59 \pm 0.34 \text{ h}^{-1}$ (R^2

$= 0.91$), while the Sn atomic percentage follows an exponential trajectory with $k = 0.93 \pm 0.2 \text{ h}^{-1}$ ($R^2 = 0.99$).

The observed shift in the LSPR, E_g , and improvement in Q_{opt} during annealing are postulated to primarily reflect the observed change in the Sn/Cd ratio. The speculation is supported based on a Drude model interpretation that an increase in the Sn content will increase the carrier density (n) and would lead to the observed LSPR shift to higher energy during annealing. While an alternative explanation could include size and shape changes, as reported for the LSPR in CdO nanocrystals due to an increase in oxygen vacancy with increasing surface to volume ratio,²⁴ the role of size effects is not believed to account for the LSPR change or the shoulder intensity since (i) the CTO carriers arise from Sn antisites, which are not anticipated to scale with the surface to core ratio, (ii) the CTO data in Figure 1 are nearly identical to the previously reported 19 nm CTO sample having the same Sn content,²⁸ and (iii) ITO does not exhibit a size-dependent shift with nanocrystal size from 10 to 100 nm at a constant Sn concentration.²⁵ The argument for the shift in LSPR not arising from a change in size is further supported by evaluation of the size-dependent shift in LSPR for F-doped CTO (FCTO, Supporting Information Figure S6B) over sizes ranging from 7.9 to 11.3 nm, where the magnitude of the LSPR shift is much smaller than observed during solvothermal annealing.

While size changes alone are unlikely to explain the observed LSPR evolution, the possibility of metal oxide shape changes should also be considered. As reported in ITO, a truncated octahedron compared to a sphere will lead to a splitting of the LSPR mode into a high-energy shoulder, a shift in the main LSPR peak position to lower energy, and a broadening of the main LSPR feature (lowering of Q_{opt}).²⁵ To evaluate the validity of the above supposition, the observed LSPR features can be assessed by fitting the experimental and hypothetical

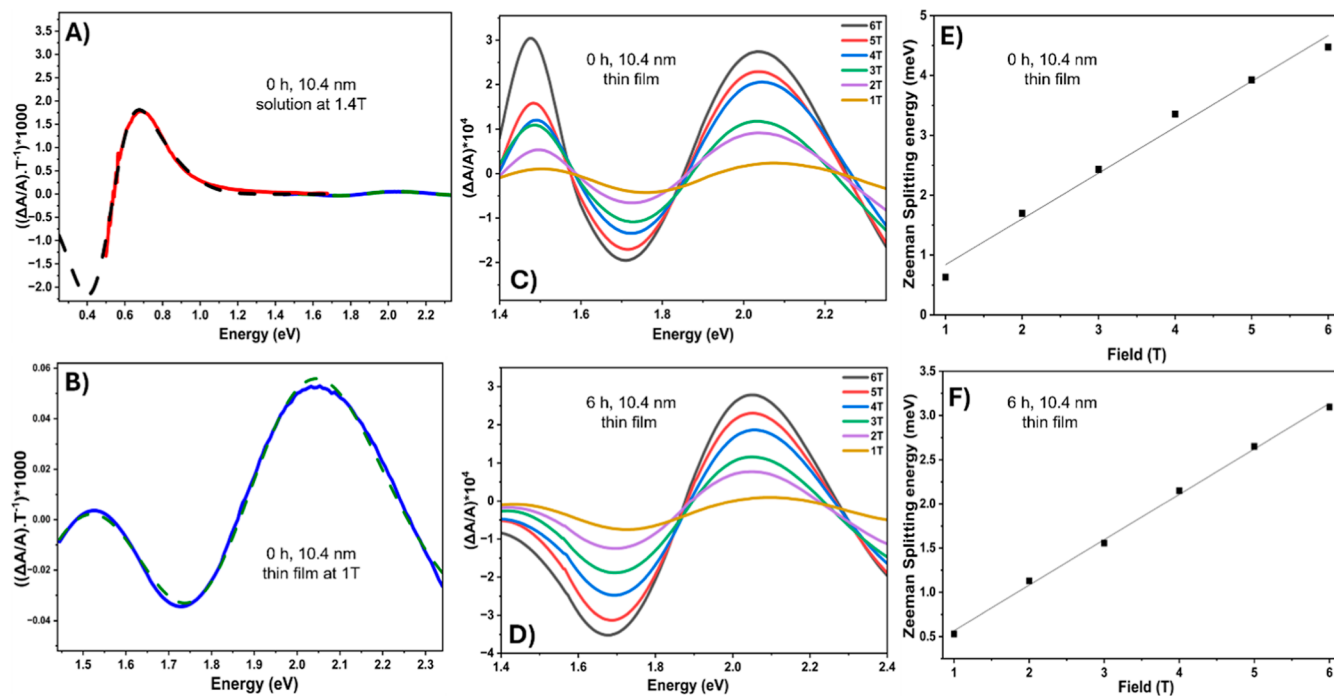


Figure 4. Magnetic circular dichroism spectra for 10.4 ± 1.3 nm CTO at (A) for 0 h in solution (normalized to 1 T) and (B) a thin film at 0 h measured for the intraband (normalized to 1 T). Field-dependent MCD measurements on a thin film at the IB energy (C,E) $t = 0$ h and (D,F) $t = 6$ h.

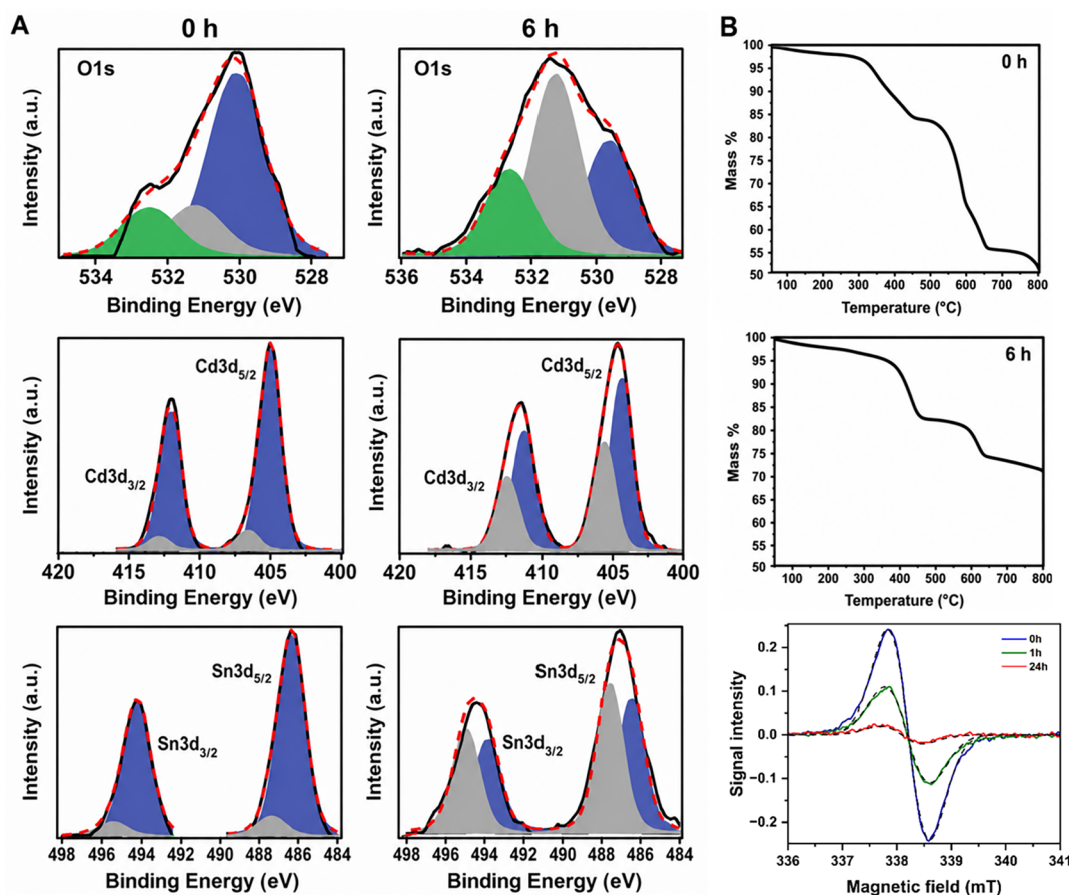


Figure 5. Selected time point analysis of the 10.4 ± 1.3 nm CTO sample. (A) XPS spectra at 0 h (left) and 6 h (right), (B) TGA data at 0 h and 6 h, and (C) EPR data measured on powdered 10.4 nm CTO samples at 0 h, 1 h, and 24 h time points by X-band. The data exhibit a loss in the intensity of $V_{O}^{\bullet\bullet}$ centers.

LSPR data to the DDA simulation of a sphere, truncated octahedron, and a cube (Supporting Information Figure S4). The DDA simulation predicts that the LSPR should not exhibit a shoulder or a shift in energy for the isolated CTO sizes and aspect ratios imaged by TEM during annealing. From the selected TEM time point images, it appears that minimal rounding of the truncated octahedron has occurred; thus, a change in shape is not anticipated to produce the observed LSPR shift nor the enhancement of Q_{opt} . As a final note of support, the FCTO that exhibits a truncated octahedral shape does not exhibit a shoulder in the LSPR spectrum, supporting the assumption that the shoulder observed in Figure 1 is not due to the truncated octahedron shape of CTO in this size range.

The effective carrier mass for an n-type semiconductor is dependent on the shape of the conduction band such that $m^* \propto dk^2/d^2E$.^{18,20} In the case of a nonparabolic conduction band, as expected for CTO,²⁸ the m^* value will increase with increasing carrier density or in effect the Fermi level of the semiconductor. Field-dependent MCD at the LSPR can be used to evaluate m^* by measuring the Zeeman splitting of the LSPR features since the carrier will exhibit A-term behavior, allowing the relationship $E_z/\hbar = \omega_c = qB/(m^* \times m_e)$ to be used.^{42–45}

In Figure 4, the MCD spectra at the LSPR and intraband (IB) energies in solution are shown. The Zeeman terms for the LSPR and the high-energy shoulder are fit to 2-modes shown

in Supporting Information Figure S7. Comparison of the solution LSPR to the thin film data measured at the intraband (IB) MCD for 0 h normalized to field is shown in Figure 4A,B, while the field-dependent data for the IB at 0 and 6 h are shown in Figure 4C,D, respectively. The value of m^* for the 0 and 6 h samples was evaluated by fitting the Zeeman energy splitting (Figure 4E,F). The LSPR mode for a solution of CTO in TCE at 0 h (1.4 T) can be fit to the two modes resulting in an effective mass of $0.15m_e$ for mode-1 and $0.16m_e$ for mode-2. At 6 h, the high-energy feature is not present in the LSPR. For completeness, the IB transition was fit to a single mode for MCD data at 0 h and 6 h at 1–6 T. Fitting to a single mode for the transition of IB was chosen due to the breadth of the transition resulting in a statistically poor fit. The IB MCD data yield a value of $0.16m_e$ at 0 h and $0.22m_e$ at 6 h by evaluating the slope of the Zeeman energy (E_z) vs magnetic field (Figure 4). The evaluation of m^* as a function of field provides a more accurate value of m^* , confirming that the MCD signal originates from itinerant carriers rather than paramagnetic centers, which would exhibit Brillouin-type nonlinearity.⁴⁶ The MCD-derived m^* values were used in evaluating the carrier density in SXDA in Table 1.

The change in size is believed to be associated with surface reconstruction and/or cation exchange reactions between Sn(II)-oleate species and Cd(II) centers at the surface of the CTO, leading to Sn incorporation and Cd loss. Evidence for loss of a metal-oleate passivation layer during solvothermal

annealing can be visualized by inspection of XPS data at selected time points (0 h and 6 h) for the 10.4 ± 1.3 nm CTO sample. The XPS assignments are made compared to literature reports for CdO,^{47,48} SnO₂,^{49,50} metal oxides,^{51,52} and metal-oleates.^{53–55} In the XPS data (Figure 5A), a comparison of 0–6 h data in the 10.4 ± 1.3 nm CTO sample is made. In the XPS data, a decrease in the Sn-oleate feature at 486 eV and an increase in the Sn(IV/II) feature at 487 eV for the Sn–O 3d_{5/2} feature during annealing are observed. The Cd-oleate feature at 407 eV is likewise reduced in intensity compared to the Cd–O 3d_{5/2} feature following annealing. The experimental data are consistent with the loss of Cd and Sn oleate from the surface of CTO during annealing. Inspection of the O 1s spectra is more complicated as features arising from O–Cd, O–Sn, and the metal-oleates contribute to the spectra. Based on literature reports, the feature at 530 eV is assigned to the metal–O, the feature at 531 eV is assigned to Sn–oleate, and the feature at 533 eV is assigned to Cd–oleate. The change in the spectra from 0 to 6 h is a reduction of the metal–O intensity and an increase in the metal oleate intensity. While the data set is limited and the assignments for O 1s are speculative, the XPS results for Sn, Cd, and O are in good agreement with measurements obtained in the TGA and TEM–EDX data. The XPS results are consistent with the observed precipitation of metal during the annealing. Since SEM–EDX showed primarily Cd metal (98.2:1.8 Cd/Sn), the surface reconstruction is most likely driven by Sn(II) to Sn(IV) reactions at the surface of the CTO. Mechanistically, the precipitation of Cd⁰ from Cd(II) is reasonable if cation exchange leads to Sn(II)–Sn(IV) conversion.

Thermogravimetric analysis (TGA) data on selected samples at 0 and 6 h annealing on the 10.4 ± 1.3 nm sample shown in Figure 5B provide further support of changes in the metal-oleate layer. In the TGA data, at 0 h, mass loss is observed at 381 °C (12% mass loss), 497 °C (23% mass loss), and 605 °C (7% mass loss), while the 6 h TGA data show a mass loss at 384 °C (13% mass loss) and 604 °C (7% mass loss). The mass loss at 380–390 °C in both cases has an $\sim 13\%$ mass loss and can be assigned as the breaking of the delocalized X-type metal-oleate bond ((O=C–O)[–]–M²⁺) based on reports for TGA analysis of SnO₂,^{56,57} CeO₂,⁵⁸ Fe₃O₄,⁵⁹ and CdS,⁶⁰ where the metal-coordinated oleate is released below 500 °C. The cleavage of the oleate is reported to result in the formation of an oxide surface following cleavage. The transition at 497 °C is only observed in the 0 h sample with a mass loss of 23%. The large mass loss is tentatively assigned to the cleavage of Z-type metal-oleate complexes (M(oleate)₂), where M is Cd(II) or Sn(II). The transition at around 604 °C observed in both samples with a 7% mass loss is assigned to cleavage of an L-type metal-oxo bond $\mu_2\text{-(HOC=O)}\text{-(M)}_2$ on a mixed metal-oxo surface. The assignment is based on the high temperature peak in the TGA. The data support a model where the size change observed in the TEM arises from surface reconstruction following the metal-oleate passivation layer cleavage during annealing.

Since cation exchange of Sn(II) to the Cd(II) site may result in incorporation of Sn(II) or Sn(IV), as well as a surface depletion layer may impact the carrier densities generated by Sn incorporation during annealing. To evaluate carrier activation, the LSPR was fit to the HEDA model, derived by Milliron and co-workers,⁴⁰ at each isolated time point to extract the time-dependent changes in the experimental carrier

density and depletion layer thickness (w_d) for the 11.2 ± 1.8 nm sample. The time-dependent changes in the experimental carrier density calculated by HEDA fitting of the LSPR (Supporting Information Figure S3) are reported in Supporting Information Table ST1 for the 10.4 ± 1.3 nm and the 11.2 ± 1.8 nm CTO samples.

The theoretical carrier density is calculated using a core–shell model, assuming a spherical nanocrystal. From the TGA, the mass fraction of the metal-oleate passivating layer lost can be delineated from the mass fraction for the CTO. The mass loss fraction can be converted into a volume fraction using the density of CTO ($d_{\text{CTO}} = 7.0$) and the density of the metal-oleate passivation (shell) layer ($d_{\text{oleate}} = 1.06$). The core–shell approach allows an estimate of the fraction of the total nanoparticle volume that corresponds to the CTO core and the passivating layer shell thickness. The measured Sn cation percentage from TEM–EDX allows an estimate of the amount of antisite Sn and therefore carrier density in CTO since antisite occupation of Sn⁴⁺ onto a Cd²⁺ site donates two electrons. The theoretical maximum carrier density can be calculated from the number of Cd₂SnO₄ formula units per cm³ using the CTO density and molar mass. Multiplication of the carrier density by the oxide volume fraction allows the theoretical carrier density averaged over the full nanoparticle volume. From the theoretical carrier density, the percentage of carrier activation is calculated by ratioing the experimental carrier density obtained by HEDA fitting relative to the theoretical carrier density.

In Figure 6, the time-dependent change in Sn activation is plotted along with the HEDA-calculated depletion width (w_d).

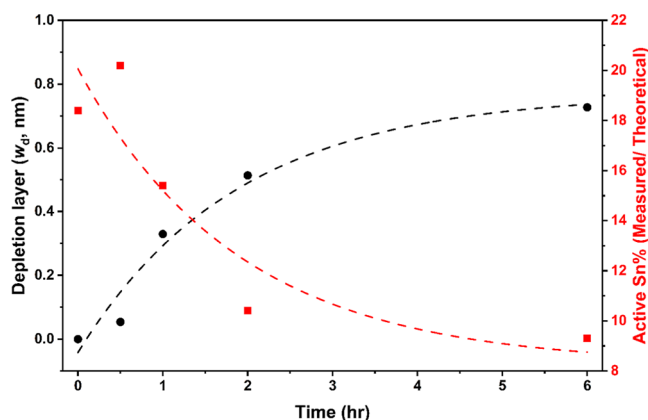


Figure 6. Time-dependent change in an 11.2 ± 1.8 nm CTO sample depletion layer (w_d , black) evaluated from HEDA analysis and the change in active Sn percentage (red) evaluated by ratioing the Sn atom percentage evaluated by TEM–EDX to the number of carriers extracted from HEDA, assuming two carriers per Sn(IV) occupying an antisite in CTO.

The Sn activation in CTO is observed to decrease with the annealing time, while the depletion layer width is observed to increase. The observed Sn activation is within the range of activation observed in In/CdO where the carrier activation is 8–26%.^{21,23} The data can be fitted to an exponential function with a $k_{\text{wd}} = 0.53 \pm 0.19 \text{ h}^{-1}$ ($R^2 = 0.97$) and $k_{\text{Sn activation}} = 0.53 \pm 0.46 \text{ h}^{-1}$ ($R^2 = 0.83$). The correlation of the rates supports a model where a higher density of Sn may reside in the depletion layer following solvothermal annealing, defect evolution, and localization near the surface following migration, or merely a

change in the dielectric constant following surface reconstruction. The observed narrowing of the LSPR, decrease in Sn activation, and widening of the depletion layer during annealing support the role of defect evolution.

One possible defect that can migrate in an oxide lattice is oxygen vacancies, which can be observed by EPR, which selectively probes paramagnetic $V_O^{\bullet\bullet}$ centers.^{61–63} At $t = 0$ h, a well-defined EPR signal centered at $g \approx 2.004$ is observed in the 10.4 nm CTO sample (Figure S3). The sharp feature is characteristic of $V_O^{\bullet\bullet}$ defects in metal oxides. The assignment of the g -value is performed by fitting the differential in easy-spin at the field strength of the magnet (X-band). Upon annealing, the intensity of this signal decreases, with a pronounced reduction evident by 1 h that correlates with the loss of the LSPR shoulder and complete disappearance after 24 h. Independent confirmation of the presence of $V_O^{\bullet\bullet}$ impacting the spectral properties of as-synthesized CTO can be made by comparison of the EPR and LSPR spectra for FCTO since fluorine is known to preferentially occupy $V_O^{\bullet\bullet}$ centers.³⁹ The fluorine-doped CTO (FCTO) was synthesized under identical conditions to CTO, with SnF_2 substituted for $\text{Sn}(\text{OAc})_2$ as the tin precursor. Detailed synthesis is provided in Supporting Information. The resulting FCTO nanocrystals exhibit no $V_O^{\bullet\bullet}$ EPR signal, retain an octahedral morphology with an average size of 11.2 ± 1.8 nm but exhibit a single, narrow Voigt-shaped LSPR without a high-energy shoulder. FCTO shows no LSPR shoulder but exhibits a 117 nm shift of the LSPR during annealing, consistent with surface reconstruction. Measurement of the FCTO LSPR reveals a single Voigt-shaped LSPR that has a ω_{LSPR} of 0.61 eV, a ω_p of 1.87 eV, and a carrier density of $n = 7.38 \times 10^{20} \text{ cm}^{-3}$ with an m^* value of $0.29m_e$ from the LSPR measured at 1.4 T in solution at 298 K.

The observed changes in LSPR, Q_{opt} , depletion width, and Sn activation for the annealed CTO when compared to FCTO support a model where defect evolution or migration impacts the plasmonic properties of the CTO. A model is developed in Figure 7 by analyzing the data within the assumption that size and shape effects are minimal contributors to optical changes in CTO. The model assumes that CTO forms as an inverted spinel lattice ($Fd\bar{3}m$ (No. 227)).²⁸ The A_2BO_4 inverted spinel lattice with the A-sites representing Cd(II) and the B-sites being Sn(IV). In the inverted spinel, Cd(II) occupies 100% of the T_d sites and 50% of the O_h sites, while Sn(IV) occupies the remaining O_h sites. Carriers are generated by Sn(IV), replacing Cd octahedral sites and generating Sn_{Cd} antisites that contribute two electrons into the conduction band per antisite.

The model is developed by correlating experimental observations that show (i) the LSPR and E_g shifts to higher frequency with annealing time, (ii) the Sn atomic percentage increases with annealing time, (iii) the size of the CTO decreases by almost 1 nm, (iv) cadmium precipitates with no detectable Sn alloying, (v) a decrease in Sn activation correlated with an increase in depletion layer width, and (vi) the OA passivation layer decreases with annealing time. The changes in ligand density evaluated by TGA coupled to cadmium metal precipitation and the change in metal-oleate content from the XPS during annealing suggest that the observed increase in $[\text{Sn}]$ could arise from cation exchange of Sn(II) oleate Z-type passivating moieties, leading to a nanocrystal surface passivation by L-type or X-type oleates with reduction of Cd(II) to Cd⁰ and conversion of Sn(II) to Sn(IV). While the surface reconstruction model is speculative, surface cleavage of metal-oleates has been observed previously

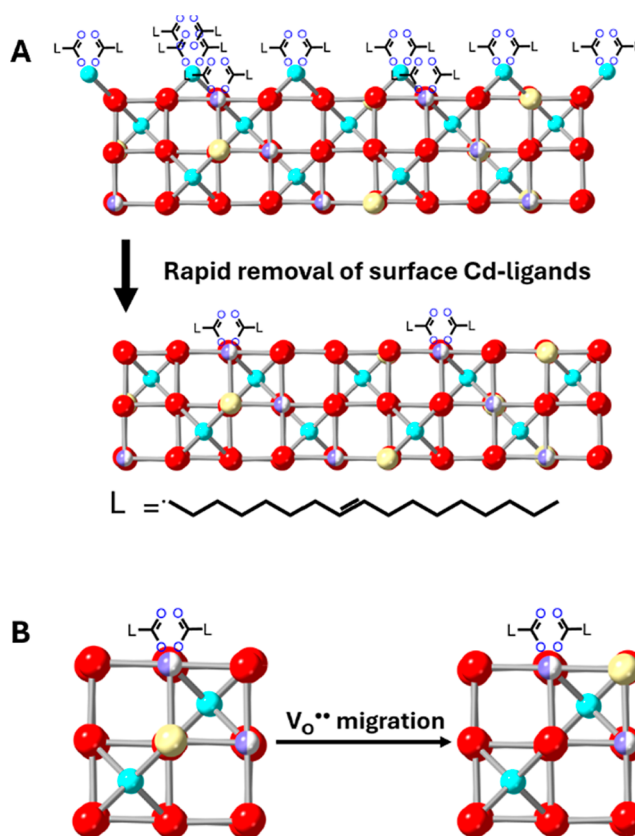


Figure 7. Proposed model to explain the evolution of the LSPR spectra during solvothermal annealing arising from (A) surface reconstruction with the loss of metal-oleate and Sn cation exchange and (B) defect evolution shown as migration and pinning at the surface for the V_O .

in nanocrystals,⁶⁴ and the precipitation of cadmium metal would explain the increase in the Sn content. Further studies are needed to fully substantiate the speculative surface reconstruction mechanism that leads to the change in the Sn/Cd ratio and the observed LSPR shift during annealing.

CONCLUSION

Thermal annealing of as-prepared CTO samples showed improved plasmonic properties. The change in the LSPR spectrum for the as-synthesized CTO can be assigned to surface reconstruction and thermodynamically driven defect evolution. The proposed model, while speculative, is consistent with the observed changes in optical spectra, Sn/Cd ratio, carrier density, carrier effective mass, nanocrystal size, nanocrystal shape, and ligand densities. The annealing studies enhance our tools for improving the plasmonic response in heavily doped metal-oxide nanocrystals. The understanding of the defect evolution dynamics in CTO PSNCs may guide future improvements in material design by performing selective annealing during the early stages, yielding improved LSPR properties for electronic and optical applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnm.6c01447>.

Optical data for CTO and FCTO, LSPR fitting by SXDA, HEDA, and DDA, and time-dependent annealing for selected time points of the 10.4 and 11.2 nm CTO samples measured using TEM and PXRD (PDF)

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Notes

The authors declare no competing financial interest.

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