Syntheses of Colloidal F:In$_2$O$_3$ Cubes: Fluorine-Induced Faceting and Infrared Plasmonic Response

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Abstract

Cube-shaped nanocrystals (NCs) of conventional metals like gold and silver generally exhibit localized surface plasmon resonance (LSPR) in the visible region with spectral modes determined by their faceted shapes. However, faceted NCs exhibiting LSPR response in the infrared (IR) region are relatively rare. Here, we describe the colloidal synthesis of nanoscale fluorine-doped indium oxide (F:In$_2$O$_3$) cubes with LSPR response in the IR region, wherein fluorine was found to both directly control the cubic morphology and act as an anionic dopant. Single crystalline 160 nm F:In$_2$O$_3$ cubes terminated by (100) facets and concave cubes were synthesized using a colloidal heat-up method. The presence of fluorine was found to impart higher stabilization to the (100) facets through density functional theory (DFT) calculations that evaluated the energetics of F-substitution at surface oxygen sites. These calculations suggest that the cubic morphology results from surface binding of F-atoms. In addition, fluorine acts as an anionic aliovalent dopant in the cubic bixbyite lattice of In$_2$O$_3$, introducing a high concentration of free electrons leading to LSPR. We confirmed the presence of lattice fluorine dopants in these cubes using solid-state $^{19}$F and $^{115}$In nuclear magnetic resonance (NMR) spectroscopy. The cubes exhibit narrow, shape-dependent multimodal LSPR extinction peaks due to corner- and edge-centered modes. The spatial origin of these different contributions to the spectral response are directly visualized by electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM).

Introduction

Colloidal syntheses of doped metal oxide NCs have emerged recently as new means of extending localized surface plasmon resonance (LSPR) to the infrared (IR) range, although shape control has yet to be broadly established. A wide range of morphologies have been reported for colloidal gold and silver NCs; including cubes and octopods, leading to the observation of shape-dependent LSPR and strongly enhanced electromagnetic near-fields around corners and edges. Yet, metal NCs intrinsically possess high free carrier concentrations exceeding $10^{19}$ cm$^{-3}$, so the optical response of isotropic NCs tends to be restricted to the visible region of the electromagnetic spectrum. On the other hand, controlled doping of semiconductor NCs allows lower carrier concentrations around $10^{15}$ cm$^{-3}$, resulting in IR-range LSPR. In this study, we demonstrate shape-controlled colloidal syntheses of highly faceted, fluorine-doped indium oxide (F:In$_2$O$_3$) cubes with an LSPR response in the IR range. Typically, doping strategies in plasmonic metal oxide NCs (e.g., Sn:In$_2$O$_3$, Al:ZnO, and In$_2$CdO$_5$ NCs) have focused on aliovalent cation substitution. Halogen anions, meanwhile, can act as surface capping agents that have been used for shape control of metal, metal oxide, and metal chalcogenide NCs. In some metal oxide NCs, fluorine has been incorporated as an anionic co-dopant (e.g., F:In$_2$CdO$_5$, F:Sn:In$_2$O$_3$). Very little has been reported regarding fluoride doping alone to induce LSPR, as in fluorinated TiO$_2$ NCs. Furthermore, while anionic doping in nanocrystalline F:SnO$_2$ has been demonstrated, the effects of fluorine on faceting or LSPR properties of metal oxide NCs have not been well explored. Faceted NCs give rise to shape-dependent LSPR phenomena not observed for spherical NCs, including highly enhanced near field hot spots around corners and edges that, in conventional metals, have been leveraged for plasmonic nanoantennas and surface-enhanced Raman spectroscopy (SERS). Disks and elongated NCs of copper chalcogenides have been reported, but reports are conflicting regarding shape effects on their LSPR properties, which are likely to be strongly influenced by crystalline anisotropy as well. Shape-dependent studies of LSPR in doped metal oxide NCs are few, motivating the development of new strategies for synthetic shape control.

We succeed in modulating the shape of F:In$_2$O$_3$ NCs by varying the ratio of InF$_2$ to In(acac)$_3$, precursors and observe multimodal shape-dependent LSPR extinction features. The role of fluorine in defining NC facets and inducing LSPR spectral response is attributed to the presence of fluorine on the external surfaces and internally within the NCs, respectively. Through X-ray photoelectron spectroscopy (XPS) and solid-state $^{19}$F magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy correlated with density functional theory (DFT) calculations, fluorine is found to occupy surface sites on dominantly exposed {100} facets. Fluorine dopant species internal to the NCs are probed by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), time of flight-secondary ion mass spectrometry (TOF-SIMS), and $^{19}$F MAS-NMR spectroscopy. Aliovalent substitutional fluorine doping on oxygen lattice sites leads to free carrier compensation, inducing LSPR. The local metallic environments of the sub-surface fluorine and indium atoms in the NC lattices are established by analyses of $^{19}$F spin-lattice $T_1$ relaxation times and white line $^{115}$In NMR spectra, which are shown to exhibit temperature- and frequency-dependencies that are characteristic of coupling to free (metallic) electron carriers. Arising from the free carriers and highly faceted NC shape, single NC LSPR spatial modes are directly visualized by monochromated electron energy loss spectroscopy (EELS) performed in a scanning transmission electron microscope (STEM) to assign the observed multimodal features to distinct spatial dipolar modes. The observed material characteristics lead to IR light near field localization, making F:In$_2$O$_3$ NCs a foundation material for near field enhancement applications in the IR.
Experimental Methods

Materials: Indium (III) acetylacetonate (In(acac)), 99.999%, Indium (III) fluoride (InF₃, > 99.9%), Indium (III) chloride (InCl₃, 99.999%), Indium (III) bromide (InBr₃, 99.999%), Oleic acid (OA, 90%, technical grade), Octylamine (OcAm, 99%), Trioctyltolyne (TOA, 98%) and tetrachloroethylene (TCE, ≥ 99%) were purchased from Sigma-Aldrich. Toluene (99.5%) was purchased from Fisher Chemical. All chemicals were used as received without any further purification.

Fluorine-Doped Indium Oxide (F:(InO)₃) Cube (3% InF₃) Synthesis: All synthesis procedures were carried out using standard Schlenk line techniques aided by a nitrogen-filled glovebox. For the growth of 3% doped F:(InO)₃, a mixture of In(acac)₃ (399.78 mg, 0.97 mmol), InF₃ (5.15 mg, 0.03 mmol), OA (1 ml), OcAm (0.5 ml) and TOA (3.5 ml) was loaded into a three-neck round-bottom flask in the glovebox. This precursor mixture was then stirred with a magnetic bar at 600 rpm and degassed under vacuum at 120 °C for 15 min. The mixture turned transparent during this operation signifying the formation of indium oleate. Thereafter, the flask was filled with nitrogen and further heated at a ramp rate of 15 °C/min to 320 °C. The reaction mixture turned cloudy and opaque which signified cube growths was designated as the growth reaction start time. The growth reaction was allowed to run for 5 min at 320 °C or the desired set point temperature. Subsequently, growth was terminated by removing the heating mantle and the reaction mixture was cooled by blowing an air jet on the flask. The cubes were washed and dispersed in toluene and centrifuged at 4500 rpm for 5 min. This washing process was repeated three times. The resultant cubes were dispersed in toluene for further analysis.

Varying concentrations of F doping in these NCs were achieved by controlling the molar ratio of InF₃ to In(acac), while keeping other reaction parameters identical. Aliquots (0.1 ml), at various reaction times during growth, were extracted from the reaction mixture with a nitrogen purged syringe needle and quenched into TCE for further analysis.

Indium Oxide (InO)₃ NCs Synthesis: Undoped indium oxide (InO)₃ NCs were synthesized by adding In(acac) (1 mmol) in the reaction flask without InF₃ while keeping other reaction parameters identical to the procedure described above for the F:(InO)₃ NCs.

Chlorine/Bromine Doped Indium Oxide (Cl(InO)₂, Br(InO)₂) NC Synthesis: Cl(InO)₂ (3% InCl₃) NCs were synthesized by adding In(acac) (0.97 mmol), substituting InCl₃ (0.03 mmol) precursor for In(acac) in the reaction flask, while keeping other reaction parameter identical. In a similar manner, InBr₃ (0.03 mmol) was used to synthesize Br(InO)₂ (3% InBr₃) NCs keeping other reaction parameters identical.

Fourier Transform IR (FTIR) Spectra: FTIR spectral measurements were conducted using a Bruker Vertex 70 FTIR at 4 cm⁻¹ resolution. Aliquot solutions were diluted in TCE and loaded into a liquid cell with KBr windows for FTIR measurements. NCs dispersed in TCE were sonicated for 1 hour to prevent aggregation before loading into the liquid cell.

XRD Analysis: Samples for XRD measurements were prepared by drop-casting a 10 mg/mL dispersion of F:(InO)₃ NCs on silicon substrates. The data were collected with a Rigaku MiniFlex 600 X-ray diffractometer using Cu Kα radiation, 1.54 Å, and analyzed with GSAS-II software.²⁸

Electron Microscopy: Samples were prepared by drop-casting NC dispersions onto carbon-coated 400 mesh copper grids (Ted Pella) and the imaging was performed in a Hitachi S5500 scanning electron microscope (SEM) operating in the STEM mode at an accelerating voltage of 30 kV. NC size analysis was performed with ImageJ software with 250 NC count. High resolution transmission electron microscopy (HRTEM) images and selected-area electron diffraction (SAED) patterns were acquired with JEOL JEM-2100F transmission electron microscope (TEM) equipped with a CCD camera and a Schottky field emission gun operating at 200 kV.

Elemental Analysis: Elemental spectrum acquisition of F:(InO)₃ cubes drop-cast on silicon substrates was carried out using a Hitachi S5500 SEM with a Bruker XFlash EDX detector attachment at 5 kV. Elemental deconvolution was performed with the Bruker Quantax software reference library at zero-tick angle P/B-ZAF correction. TOF-SIMS was conducted on TOF-SIMS 5, ION-TOF GmbH with C₆⁺ sputtering at 2 kV.

Thermogravimetric Analysis (TGA): Measurements were carried out using a Mettler Toledo TGA2 thermogravimetric analyzer. Dried NC powders were loaded into alumina crucibles of 100 µL volume and heated from 25 to 1100 °C at a heating rate of 5 °C/min under nitrogen flow (50 sccm).

XPS: Samples were prepared by drop casting NC solutions on silicon substrates and the measurements were performed in a Kratos Axis Ultra DLD spectrometer with a monochromatic Al Kα source (1486.6 eV). Wide survey scans were acquired at analyzer pass energy of 80 eV and the high-resolution narrow region scans were performed at a pass energy of 20 eV with steps of 0.1 eV. Spectral acquisitions were performed with photoelectron take-off angle at 0° with respect to the surface normal and pressure in the analysis chamber was maintained at around 10⁻⁷ torr. Data analysis was performed in CasaXPS software using the Kratos relative sensitivity factor library. The binding energy (BE) scale was internally referenced to the C 1s peak (BE for C-C = 284.8 eV).

DFT Calculations: DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP) with PAW pseudopotentials in the package. The Perdew-Burke-Ernzerhod (PBE) exchange-correlation functional was used in all the DFT calculations. 3×3×1 Monkhorst-Pack k point mesh for the Brillouin zone integration was used, with a vacuum layer of 15 Å to prevent interactions between periodic images of the slab. Further details are in the Supporting Information, Text S1.

Solid-State ³¹P and ¹⁹F NMR Spectroscopy: Solid-state ³¹P and ¹⁹F MAS-NMR spectra were acquired on a Bruker ASCEND 400 MHz (9.4 T) solid-state DNP-NMR spectrometer operating at Larmor frequencies of 400.202 and 376.532 MHz for ³¹P and ¹⁹F, respectively. For the solid-state MAS-NMR measurements, the F:(InO)₃ NCs were mixed with KBr powder in a 1:1 ratio by mass. The KBr served as an internal temperature probe for accurate determination of the sample temperature under the different measurement conditions.³⁰,³¹ The ¹⁹F Hahn echo spectrum was acquired at 35 kHz MAS, at 395 K, and using a 90°-180°-t pulse sequence with rotor-synchronized t delay times of one rotor period and 100 kHz rf pulses. The ²³H¹⁺F NMR correlation spectrum was acquired using a 2D dipolar-mediated Hahn Nuclear Multiple Quantum Coherence (HMQC) pulse sequence, where the ²³H¹⁺F nuclear dipole-dipole couplings were reintroduced by using SR26,³² recoupling with 50 kHz rf power for recoupling. The ¹⁹F-spin-lattice (T₁) relaxation analyses relaxation times at different temperatures were measured by using a saturation-recovery pulse sequence with Hahn echo detection.

The solid-state ¹⁹F NMR spectrum of undoped bulk polycrystalline InO₃ (99.9% purity, Aldrich) was acquired on Bruker AVANCE-III Ultrashield Plus 800 MHz (18.8 T) narrow-bore spectrometer operating at Larmor frequency of 174.354 MHz for ¹⁹F and using a Bruker 3.2 mm broadband double-resonance H-X probehead. The solid-state ¹⁹F NMR spectrum of the F:(InO)₃ NCs was acquired on a 19.6 T Bruker DRX NMR spectrometer (National High Magnetic Field Laboratory) operating at a Larmor frequency of 182.266 MHz for ¹⁹F and using a custom-build 3.2 mm double resonance H-X probehead. The ¹⁹F NMR spectra were acquired using a quadrupolar Carr-Purcell-Meiboom-Gill (QCPMG) pulse sequence,³³ which yields manifolds of very narrow, evenly-spaced NMR signals (spikelets), which can be systematically acquired as a series that can be overlaid to map the full central transition (CT) region of the ¹⁹F NMR spectra. Each ¹⁹F NMR spectrum is presented as a mosaic overlay of 22 individual QCPMG sub-spectra (plotted in different colors) acquired at evenly spaced frequency intervals. The ¹⁹F spectra were referenced to a 1 M In(NO₃)₃ solution at 0 ppm. Further details on the ³¹P and ¹⁹F NMR analyses are provided in the Supporting Information, Text S2.

STEM-EELS: Plasmon mapping was performed in a Nikon high-energy-resolution monochromated EELS STEM (HERMES) at Oak Ridge National Laboratory operated at 60 kV and a Nikon prototype spectrometer.³⁴ Using a variable slit we choose an energy resolution of 186 cm⁻¹ (23 meV) to optimize the resolution between the plasmon peaks and the signal in the monochromated beam. For the plasmon deconvolution we use the non-negative matrix factorization routine available in the Python HyperSpy library (http://hyperspy.org/). More details can be found in the Supporting Information (Text S3).

Results and Discussion

NC Shape Control. The shapes of the F:(InO)₃ NCs were controlled by varying the molar ratio of InF₃ to In(acac); precursors during synthesis, which also determined the extent of fluorine incorporation in the resulting NCs. F:(InO)₃ NCs with well-defined morphology were produced for 1–3% InF₃ in the growth solution, as shown in Figure 1. SEM images showed that monodisperse NCs (edge length 162.1 ± 9.2 nm) with cubic morphology were obtained exclusively in the presence of InF₃ (3% in molar ratio to In(acac);) (Figure 1a, rightmost panel). By comparison, in the absence of InF₃ during the synthesis, NCs with pseudospherical morphology were observed (Figure 1a, leftmost panel), with no cubic-
shaped NCs observed. Intermediate amounts of InF$_3$ led to variations in the NC morphology, specifically forming concave cubes with edges protruding outwards for 2% InF$_3$ (Figure 1a, second from right) and 1% InF$_3$ (Figure 1a, second from left). The cube morphology persists for higher concentrations of InF$_3$ (4% and 5%) as well, until a threshold is reached at 6% InF$_3$, beyond which NCs exhibit roughened surfaces (Figure S2).

The TEM images in Figure 1 show that the as-synthesized F:In$_2$O$_3$ cubes exhibit well-defined crystalline facets. Selected-area electron diffraction (SAED) confirms that the F:In$_2$O$_3$ cubes are each single crystals and allows indexing of their surface facets. A TEM image of an F:In$_2$O$_3$ cube (3% InF$_3$) is shown in Figure 1b, which exhibits a flat (100) face and a well-defined edge. The cube is terminated with (100) facets of the In$_2$O$_3$ cubic bixbyite structure, corroborated by the position of the (400) reflections in the SAED pattern (Figure 1b, right). A cube on <110> zone axis orientation exhibits (422) reflections in the SAED pattern (Figure 1c, right), corresponding to the (422) spacings observed by HRTEM (Figure 1f). Concave F:In$_2$O$_3$ cubes (1% and 2% InF$_3$) are also single crystalline as observed in SAED patterns collected down the <100> zone axis (Figure 1d, right). An HRTEM image of the elongated tip on a concave cube (1% InF$_3$) shows (022) lattice spacing (3.56 Å), along with (400) lattice spacing parallel to the facets (Figure 1g). Together, these observations indicate that the as-synthesized F:In$_2$O$_3$ cubes have cubic bixbyite {100}-dominant surface facets.

To quantify total fluorine incorporation in F:In$_2$O$_3$ NCs (Table 1), EDX spectroscopy (Figure S3) and TOF-SIMS analysis were conducted (Figure S4). Because the emitted X-rays are of high energy, EDX has an effective probe depth of about 200 nm, the entire volume of the NCs is probed and the results approximately reflect the overall F/In atomic (at.) composition ratio. However, owing to the low sensitivity of EDX to fluorine in low dopant concentration NC samples, TOF-SIMS was employed to quantify the F/In atomic ratio as a film of NCs is progressively etched. EDX with TOF-SIMS support a trend of increasing F atomic composition in F:In$_2$O$_3$ NCs, as a function of InF$_3$ concentration employed during synthesis. Syntheses with InCl$_3$ and InBr$_3$ precursors were observed to result in low halide (X = Cl, Br) incorporation instead.

![Figure 1](image-url)  
(a) SEM images showing the progressive effect of F on In$_2$O$_3$ NC morphology. Outlines are shown as guides to visualize the indicated facets. TEM images (left panels) and the corresponding SAED patterns (right panels) of (b) cube, (c) edge-oriented cube, (d) sharp concave cube, and (e) concave cube F:In$_2$O$_3$ NCs. Scale bars are 100 nm for a-c. (f) HRTEM image of a single F:In$_2$O$_3$ cube corner with NC oriented on its edge (inset). (g) Extended corner of concave cube F:In$_2$O$_3$ NC (inset). Scale bars are 2 nm in f and g, and 20 nm in the insets.

Table 1. EDX quantification of fluorine in F:In$_2$O$_3$ NCs synthesized with 1-12% InF$_3$ precursor, and halide quantification for NCs synthesized with 3% InCl$_3$ and 3% InBr$_3$ precursors. The EDX fluorine quantification in F:In$_2$O$_3$ NCs are accompanied by TOF-SIMS results.

Aliquots taken during the synthesis of F:In$_2$O$_3$ cubes (3% InF$_3$) were analyzed by FTIR spectroscopy to assess the chemical decomposition mechanism. Typically, In(acac)$_3$ and oleic acid were heated at 120 °C to form an indium oleate (In-OA) precursor. For F:In$_2$O$_3$ NCs, a ramp rate of 15 °C/min to 320 °C was used to rapidly decompose the indium precursors. In-OA and octylamine (OcAm) lead to the formation of indium monomers and amide byproducts 35,36 which lead to rapid decomposition (Figure S5). The FTIR fingerprint region shows that the precursor undergoes an aminolysis reaction with OcAm during synthesis. The metal carboxylate (1614 cm$^{-1}$ and 1582 cm$^{-1}$) peak signals 37,38 are significantly reduced in intensity after heating to 260 °C and continue to fall as the reaction progresses from 0 to 5 min, past this point. Concurrently, amide byproduct C=O stretch (1651 cm$^{-1}$) signals 39,40 increase as In-OA is decomposed (Figure S5). These observations indicate that anamolysis is a primary mechanism of growth, which entails nucleophilic attack of the amylamine on the metal-alkylcarboxylate complex, which is a common NC growth mechanism for metal oxides. 41,42 Average NC product yield was 54.3% by weight for all F:In$_2$O$_3$ NC samples. Differing from typical doped In$_2$O$_3$ NC syntheses, 31 such large sized (100 nm scale) NCs are enabled by a combination of aminolysis-driven growth and a concentrated precursor solution (0.2 mmol/ml) at high reaction temperature (320 °C). To evaluate the progression of NC shape with reaction time, SEM analyses were performed on aliquots collected during the growth of F:In$_2$O$_3$ cubes. As reaction time progresses and the precursors progressively decompose, NC size is expected to increase, accompanied by either shape retention or changes. Aliquots taken during the growth of F:In$_2$O$_3$ cubes (3% InF$_3$) show that the cube morphology is retained throughout the 5 min growth period (Figure 2a) as size increases from 35.6 ± 7.6 nm to 81.6 ± 11.4 nm (Figure 2b). This indicates [100] surface stabilization throughout growth at sufficient InF$_3$ concentration, allowing synthesis of well-defined cube-shaped NCs. Aliquots over longer reaction times (at 5 min, 30 min, 1 h, and 2.5 h) at 320 °C were also taken to
For the concave F:In₃O₅ cubes (1% InF₃), SEM images of aliquots reveal progressive growth at the corners that results in morphological evolution (Figure 2c). The initial aliquot, taken when turbidity was first observed in the reaction flask (0 min), shows cube-shaped NCs that are 81.3 ± 15.3 nm in size. SEM images show a second stage involving rapid NC size growth (Figure 2d) and observation of ledges on the faces. In the final stage, ledges converge into elongated tip extensions that project in the <111> directions, from the corners. A smooth concave surface has replaced the flat {100} cube facets in the final 5 min aliquot to form 274.0 ± 45.5 nm sized F:In₃O₅ concave cubes with elongated corners. This suggests that the {100} facets may not be as stable for this case, compared to the cubes synthesized with 3% InF₃ in the reaction mixture. At longer reaction times of 2.5 h or more, further rounding of the elongated corners occurs (Figure S6).

The synthesis of well-defined F:In₃O₅ cubes was also found to depend on the reaction temperature. For the 3% InF₃ synthesis, which produced optimally structured cubes at 320 °C, the morphological evolution was studied for reactions at temperatures between 280 and 340 °C. Strongly faceted cube shapes were produced at reaction temperatures of 340 and 320 °C (Figure S6). However, at a lower reaction temperature (280 °C), smaller rounded cubes were observed at 5 min reaction time, evolving after 30 min to more defined cubic shapes.

The concave cube morphology is more sensitive to reaction temperature. Synthesizing F:In₃O₅ NCs (1% InF₃) at an elevated reaction temperature (340 °C) resulted in irregular pseudospherical shapes with growth in randomly oriented directions (Figure S6). Apparently, the preference for growth in the <111> direction is weakened at higher growth temperatures, which is consistent with growth occurring without directional preference potentially due to enhanced monomer diffusion along the surface at high temperatures. Synthesizing F:In₃O₅ NCs (1% InF₃) at a lower reaction temperature (280 °C) resulted in rounded NCs instead of a concave cube morphology, up to 2.5 h reaction time (Figure S6).

Influences of Fluorine on NC Shape. SEM and HRTEM analyses indicate that fluorine has a facet-directing function in the growth of F:In₃O₅ NCs. The cube-shaped NCs were produced only in the presence of fluorine (Figure 1a, right), while the cubic shape is not observed in its absence (Figure 1a, left). To assess whether fluorine is unique compared to other halides as a morphology-directing agent under these synthesis conditions, InCl₃ and InBr₃ were used in place of InF₃. The bond dissociation energy is 439 kJ/mol for the In-Cl bond and 418 kJ/mol for the In-Br bond, which are lower than for In-F at 506 kJ/mol. In-F bonds, being stronger than In-O bonds (at 360 kJ/mol), are hypothesized to be highly stable at In₃O₅ NC surfaces, while weaker In-Cl or In-Br bonds are
The NC products synthesized in the presence of InCl₃ or InBr₃ were large and rounded: 246.7 ± 16.6 nm for Cl:In₂O₃ NCs and 348.3 ± 58.1 nm for Br:In₂O₃ NCs with poorly defined facets (Figure S7), whereas F:In₂O₃ cubes synthesized with the same precursor ratio had well-defined shape with edge lengths of 162.1 ± 9.2 nm (Figure S1).

Since fluorine plays an important role in the faceting of the In₃O₅ NCs, XPS was used to probe the presence of fluorine on their surfaces. XPS is sensitive to surface composition, since the escape depth of photoelectrons is only a few nanometers. The existence of fluorine on the F:In₃O₅ NC surfaces was revealed by XPS spectra acquired for the In 3d (Figure 3a) and F 1s (Figure 3b) regions. As shown in Figure 3a, the In 3d signal was deconvoluted into components that are assignable to lattice In-O (444.3 eV), In-OH (445.0 eV), and In-F (445.8 eV) species, with the peak due to the In-F species becoming more dominant as the In₃F₃ precursor concentration is increased. Furthermore, the F 1s peak at 684.6 eV, flanked by the In 3p doublet peaks, also exhibits an increase in relative intensity as the In-F precursor concentration is increased (Figure 3b). Deconvolution of the O 1s signal is shown in Figure S8, with components that are assignable to lattice oxygen (530.0 eV), oxygen adjacent to oxygen vacancies or other charged defects, such as F₃O (531.0 eV), surface hydroxyl (531.8 eV), and carboxyl (533.1 eV) species, respectively. Overall, the undoped In₃O₅ NCs are observed to have more surface-adsorbed hydroxyl and carboxyl species, as compared to F:In₃O₅ NCs which further signifies the incorporation of F species as surface-capping agents. XPS characterization thus suggests that fluorine adsorbs on the In₃O₅ NC surfaces, which may be linked to the stability and prevalence of {100} facets in cube-shaped NCs.

Fluoride anions have been described as facet-directing agents in metal oxide NCs, such as in the fluorinated synthesis of TiO₂ NCs and may also have played this role in the synthesis of F and Sn co-doped In₂O₃ NCs. Metal fluoride precursors, such as InF₃, decompose into HF in the presence of oleic acid during the reaction, releasing fluoride anions and passivating the In-O surfaces with In-F bonds. Walsh et al. determined through density functional theory (DFT) calculations that for bixbyte In₃O₆, relaxed {111} facets are energetically preferred over oxygen terminated {100} facets (γ₁₁₁ < γ₁₀₀). However, surface-passivation by F in metal oxide NCs can be expected to alter the energetic sequence of the facets: F passivation of the {100} facets results in surface energy inversion (γ₁₁₁ > γ₁₀₀). Correspondingly, F functions as a favorable {100} facet capping agent over {111} in the bixbyte In₃O₆ NCs, which we expect hinders growth at F terminate {100} surfaces due to fewer O sites available for In-OH monomer condensation to occur. We suggest that this directs the synthesis of well-defined F:In₂O₃ cube NCs (3% InF₃) wherein sufficient F passivation occurs at the {100} facets.

To understand the surface effects of fluorine on the morphology of In₂O₃, DFT calculations were conducted (details in SI, Text S1) by calculating relative formation energies of F substituting at surface O atomic sites on (100) and (111) surfaces. The (111) surface was selected for comparison with (100) as it has been reported to have the lowest surface energy in In₂O₃ without F doping. All possible F substitution sites were considered, and only the low formation energy surface configurations are shown in Figure 3a and d. F substitution is more energetically favorable on the (100) surfaces than the (111) surfaces, with F substitution at (111) surfaces yielding formation energies (2.55 eV, 2.82 eV) that are higher than the (100) surface configurations. Since growth through monomer deposition requires addition of new In/O atoms on oxygen terminated sites, it can be expected that this process is more difficult at fluorine capped (100) surfaces than on (111) surfaces. This explains why the (100) facets grow more slowly and become the dominant NC surface. NMR chemical shifts of PF₃ atoms in different configurations on the (100) surface are calculated,
with the most stable structure (Figure 3c, left) corresponding to a chemical shift of -246 ppm, to be compared below to experimental $^{19}$F NMR spectra.

The complex concave cube shape of moderately passivated F:In$_2$O$_3$ NCs (1% InF$_3$) can be rationalized through the shape control model previously described for other halide-passivated NCs.\textsuperscript{11,12} Colloidal syntheses of NCs involve both thermodynamic and kinetic effects that impact NC shape. The conceptual framework involves two monomer addition processes: deposition on facets with high surface energy (kinetic) and monomer surface diffusion to minimize total surface energy of NC facets (thermodynamic).\textsuperscript{2} The high rate of In-OA precursor decomposition, driven by aminolysis, leads to a high rate of monomer deposition onto growth-favorable NC facets at a short reaction time (5 min). During fluoro-free synthesis, undoped In$_2$O$_3$ NCs exhibit growth in all <100>, <110>, and <111> directions into irregularly shaped NCs (Figure 1a, leftmost panel). With intermediate InF$_3$ concentrations (1-2% InF$_3$), the (100) facets are partially capped by F, and In monomer deposition becomes unfavorable on (100) facets with more F capped sites. Instead, the reaction conditions are favorable for selective monomer deposition on the less F surface occupied (111) facets. Thus, F passivated (100) facets have slower growth and monomers preferentially deposit on (111) facets during NC growth.\textsuperscript{14} Through this process, elongated <111> direction tips are seen in F:In$_2$O$_3$ concave cube NCs (1% InF$_3$), with concave {100} facets (Figure 1a, second from left). Well-defined concave cube F:In$_2$O$_3$ NCs of 290.4 ± 17.9 nm size with sharp elongated <111> corners result when using a 2% InF$_3$ precursor content, showing distinct high-index quadrant boundaries on the (100) facets (Figure 1a, second from right). With higher InF$_3$ concentration (3% InF$_3$), the (100) facets become increasingly passivated by F capping, fluoride terminated (100) surface exposure is favored for minimizing total surface energy, and well-defined cube-shaped NCs result.

Although the XRD and electron diffraction patterns indicate substantial long- and short-range lattice order in the F:In$_2$O$_3$ NCs, the non-stoichiometric distributions of fluoride species introduce significant and important complexity to the NC structures that govern their growth and optical properties. The types, distributions, and electronic environments of fluoride atoms in F:In$_2$O$_3$ NCs are established by solid-state $^{19}$F MAS NMR analyses. The solid-state 1D $^{19}$F MAS NMR spectrum of F:In$_2$O$_3$ NCs (3% InF$_3$) in Figure 4a reveals four resolved $^{19}$F signals at 50, -50, -208, and -234 ppm, which are assigned on the basis of the 2D $^1$H-$^1$H NMR correlation spectrum and $^1$F spin-lattice relaxation time analyses discussed below to $^1$F nuclei in different types of chemical and electronic environments in the F:In$_2$O$_3$ NCs.

Importantly, dilute surface fluoride moieties are detected and identified in the solid-state two-dimensional (2D) $^1$H-$^{19}$F correlation NMR spectrum in Figure 4b. The spectrum is shown as a 2D contour plot, having $^1$H and $^{19}$F frequency axes (with units of ppm) on the abscissa and ordinate, respectively. Correlated signal intensities in the 2D spectrum arise only from $^1$H species that are dipole-dipole-coupled with $^{19}$F atoms over nanoscale distances (<0.5 nm for the short dipolar recoupling time, 0.96 ms, used here), thereby establishing the mutual proximities of the $^1$H and $^{19}$F species with associated signals. For comparison, a standard 1D $^1$H MAS NMR spectrum is shown above the $^1$H axis of the 2D spectrum, which exhibits signals at 0.6, 1.0, 1.7, 5.5, and 7.0 ppm that are all assigned to $^1$H moieties on the octylamine, trioctylamine, or oleate organic surfactant molecules as indicated by the labels above the respective $^1$H signals. The 2D $^1$H-$^{19}$F correlation spectrum resolves two $^{19}$F signals at -234 and -220 ppm that are correlated to $^1$H signals at 1.0 ppm from -CH$_2$- moieties on the organic surfactant molecules, unambiguously establishing the interactions and proximities of the corresponding $^1$H and $^{19}$F species at the F:In$_2$O$_3$ particle surfaces. Notably, no correlated signal intensity is observed for the relatively narrow $^{19}$F signal at -208 ppm (6 ppm full-

![Figure 4](image.png)

Figure 4. Solid state (a) 1D $^{19}$F echo and (b) 2D $^1$H-$^{19}$F) correlation MAS NMR spectra of F:In$_2$O$_3$ NCs (3% InF$_3$) diluted in 1:1 ratio by mass with KBr. Solid state 1D single-pulse $^1$H and $^{19}$F spectra acquired under the same conditions are shown along the horizontal and vertical axes of the 2D spectrum in (b) for comparison with the 1D projections. The inset shows a schematic diagram of a surface $^1$F moiety interacting with the alkyl chain of a surface-bound organic ligand, as indicated by arrows. The spectra were acquired at 9.4 T, (a) 35 kHz MAS and 395 K or (b) 25 kHz MAS and 327 K.

From the quantitative single-pulse 1D $^{19}$F MAS NMR spectrum (Figure S11), the $^{19}$F signals in the frequency range from -220 to -234 ppm account for only 1-2% of all the $^{19}$F signal intensity, indicating that <2% of all of the $^{19}$F species in the F:In$_2$O$_3$ NCs are in surface environments. These surface-related $^{19}$F signals in the range of -220 to -234 ppm are close to the shift values predicted by DFT calculations for the most energetically
stable $^{19}$F structure on the (100) surface (-246 ppm, Figure 3c, left). While the DFT models neglect other possible adsorbates for computational simplicity and represent an idealized subset of numerous possible surface configurations, this agreement suggests that the DFT calculations capture the main effects of fluorine on the (100) surface. The combined solid-state $^{19}$F and $^{2}$H[$^{19}$F] NMR analyses and DFT calculations, thus identify and quantify the small fraction of $^{19}$F species at the surfaces of the In$_{3}$O$_{5}$ NCs that are hypothesized to direct the NC morphology by adsorbing on (100) facet surface sites.

Fluorine as an Anionic Dopant. The discussion regarding fluorine has so far been limited to the NC surface: F$^{-}$ selectively passivate NC surfaces to influence shape. The possible impact on the crystal lattice when F$^{-}$ is incorporated into the In$_{3}$O$_{5}$ NCs is investigated by analyzing XRD as a function of fluorine incorporation. Fluorine being more electronegative than oxygen, and the crystal ionic radius$^{36}$ of F$^{-}$ (1.19 Å) being only slightly smaller than the O$^{2-}$ site (1.28 Å) in bixbyite phase In$_{3}$O$_{5}$, would allow it to easily occupy oxygen sites.$^{38,39}$ XRD patterns (Figure S12) of F:In$_{3}$O$_{5}$ NCs (1-12% InF$_{3}$) confirm the cubic bixbyite In$_{3}$O$_{5}$ crystal structure is maintained$^{39}$ and reveal that the F doping induces lattice strain. Lattice contraction relative to undoped In$_{3}$O$_{5}$ NCs is observed based on the shift in the position of the (400) diffraction reflection at low doping level (1% InF$_{3}$), which is ascribed to the smaller ionic radius of F$^{-}$ as a substitutonal dopant occupying O lattice sites not only at the surface, but also internal to the NCs (Figure S12). Lattice contraction is also observed at low dopant concentrations in Sn$_{3}$In$_{5}$O$_{11}$$^{38}$ and F:SnO$_{2}$$^{37}$ where it has been similarly ascribed to ialovalent dopants with smaller ionic radii substituting the larger ions in host lattices. Rietveld refinement$^{39}$ of the full XRD pattern was conducted to quantify this initial lattice contraction and revealed the subsequent displacements of the (400) and (222) reflections at higher concentrations of F$^{-}$ doping that correspond to lattice expansion (Figure S12). Size-induced lattice expansion or contraction, though reported in sub-10 nm metal oxide NCs, can be excluded due to the large size (100 nm or larger) of the In$_{3}$O$_{5}$ NCs considered here.$^{40}$ Undoped In$_{3}$O$_{5}$ NCs have a lattice constant of a = 10.126 Å, close to the reported bulk In$_{3}$O$_{5}$ value of a = 10.119 Å.$^{41}$ In low-doped 1% InF$_{3}$ concentration NCs, a contracted lattice constant of a = 10.083 Å was measured. However, lattice expansion occurs at higher dopant concentrations, similar to the structural changes reported in highly doped F:SnO$_{2}$ and Sn$_{3}$In$_{5}$O$_{11}$ films.$^{38,42}$ The (400) reflection shifts with F$^{-}$ incorporation to a = 10.190 in 12% InF$_{3}$ doped NCs, resulting in a maximum observed lattice expansion of 0.58 % that is attributable to dopant-screening effects from electrostatic repulsions.$^{36}$ Fluorine defect cluster phases are evident by XRD in excessively doped 12% InF$_{3}$ NCs and can likely be attributed to emergent indium fluoride (InF$_{3}$) or indium oxyfluoride (InOF) phase segregation$^{39}$ (Figure S12).

To further understand the fluorine incorporation in the synthesized NC lattice, TGA was performed, as fluorine is known to diffuse out of NCs during high temperature annealing under inert conditions.$^{43}$ TGA analysis shows initial weight loss starting at 400 °C that is ascribed to the removal of organic ligands. Upon further heating to 1100 °C, F:In$_{3}$O$_{5}$ cubes exhibit 1.3% weight reduction by fluorine liberation (Figure 5), corresponding to F/In = 9.6 % atomic composition ratio. This TGA-based quantification agrees well with F/In = 10.5 % quantified by TOF-SIMS. Concave F:In$_{3}$O$_{5}$ cubes show a 0.5 % mass reduction corresponding to F/In = 3.7 %, whereas undoped In$_{3}$O$_{5}$ NCs shown little or no weight loss that could be associated with fluorine when heated to high temperatures. SEM images reveal the F:In$_{3}$O$_{5}$ cube NCs sinter into irregularly shaped massive particles during high temperature annealing (Figure S13).

Figure 5. TGA curves for undoped In$_{3}$O$_{5}$ NCs (black curve), concave F:In$_{3}$O$_{5}$ cubes (red curve), sharp concave F:In$_{3}$O$_{5}$ cubes (orange curve), and F:In$_{3}$O$_{5}$ cubes (green curve). Photographs of the F:In$_{3}$O$_{5}$ cube sample (in alumina crucible) before (left inset) and after TGA (right inset).

Substitutional fluorine dopants incorporated in the NCs can be charge-compensated by free electrons. Fluorine is well-established as an anionic n-type dopant that induces high free electron concentrations in fluorine-doped tin oxide (F:SnO$_{2}$) transparent conductive oxide films.$^{21,37}$ The Kröger-Vink equation$^{44}$ for oxygen vacancy formation demonstrates that such defects in the In$_{3}$O$_{5}$ lattice can be charge compensated by two electrons (eq. 1).$^{44}$ Oxygen substitution by F induces one free electron per fluorine ion (eq. 2).$^{44}$

\[
\begin{align*}
\text{In}_3\text{O}_5 + 3\text{O}_2^{-} &\rightarrow 2\text{In}_3\text{O}_5 + 6\text{e}^- + 3\text{O}_2(g) \quad , (1) \\
\text{In}_3\text{O}_5 + 3\text{O}_2^{-} &\rightarrow 2\text{In}_3\text{O}_5 + 3\text{F}^- + 3\text{e}^- + \frac{3}{2}\text{O}_2(g) \quad , (2)
\end{align*}
\]

Electron paramagnetic resonance (EPR) spectroscopy provides evidence for free electrons in F:In$_{3}$O$_{5}$ NCs. The induced extra electrons are delocalized in the conduction band,$^{45,46}$ leading to an observed EPR signal at g = 2.20 in doped F:In$_{3}$O$_{5}$ cubes. By comparison, undoped In$_{3}$O$_{5}$ NCs exhibit a weak EPR signal at g = 2.00 due to a low population of oxygen vacancy-induced free electrons or shallow donors (Figure S14).$^{47,48}$ EPR spectra of the F:In$_{3}$O$_{5}$ cubes at cryogenic temperatures (100 K) showed increased signal intensity, which decreased at room temperature due to rapid free electron relaxation.$^{35}$

Kröger-Vink notation suggests halogen dopants with the same valency as F$^{-}$, should contribute to free-electron compensation. However, the large ionic radii of chloride (Cl$^{-}$) or bromide (Br$^{-}$) suggests that they are not suitable dopants to incorporate in In$_{3}$O$_{5}$ NCs. Doping of Cl$^{-}$ or Br$^{-}$ atoms into In$_{3}$O$_{5}$ NCs was attempted to check the viability of other halogen dopants. EDX quantification showed very low halide incorporation for these NCs, as compared to F:In$_{3}$O$_{5}$ NCs synthesized at the same dopant precursor concentration (3% In$_x$X$_{3-x}$, X= F, Cl, Br (Table 1)). Cl:In$_{3}$O$_{5}$ NCs show only Cl/In = 0.32 ± 0.11 % atomic composition ratio and Br:In$_{3}$O$_{5}$ NCs had Br/In = 2.62 ± 0.06 %, whereas F:In$_{3}$O$_{5}$ cubes show higher F/In = 11.76 ± 2.70 %. The low anionic dopant concentration observed can be attributed to Cl$^{-}$ (1.81 Å) having a much larger ionic radius than F$^{-}$ (1.19 Å), which would yield a correspondingly large ionic radius mismatch (41.4 %) with O$^{2-}$ (1.28 Å) and cause significant lattice strain in the host lattice.$^{36}$ Similarly, Br$^{-}$ (1.96 Å) is not incorporated within the In$_{3}$O$_{5}$ NC lattice, consistent with similar straining (53.1 %).$^{36}$
Based on quantitative 1D $^{19}$F MAS NMR and $^{19}$F spin-lattice relaxation time analyses, the majority of $^{19}$F atoms in the F:In$_2$O$_3$ NCs are located in metallic sub-surface environments. The 1D $^{19}$F MAS NMR spectrum in Figure 4a shows two broad $^{19}$F signals at 50 ppm and -50 ppm with FWHM signal linewidths of 66 ppm and 26 ppm, respectively. The $^{19}$F signal at -50 ppm is similar to $^{19}$F signals observed for some other metal oxyfluorides$^{76}$ and is assigned to isolated F anionic dopant species in the F:In$_2$O$_3$ NCs. By comparison, based on temperature-dependent analyses of $^{19}$F spin-lattice ($T_1$) relaxation times, the $^{19}$F signal at 50 ppm is confidently assigned to a distribution of $^{19}$F species in metallic environments in the F:In$_2$O$_3$ NCs. In metallic materials, including degenerately doped semiconductors,$^{77}$ nuclear spins and conduction band electrons in $s$-like orbitals couple through Fermi contact interactions. These interactions give rise to two characteristic effects that are manifested in the $^{19}$F NMR spectra of F:In$_2$O$_3$ NCs: a frequency displacement of the $^{19}$F NMR signals called the Knight shift,$^{77,78}$ and a Korringa-type temperature-dependence of the rate of $^{19}$F nuclear spin-lattice relaxation.$^{79,80}$ For the ideal case of isolated nuclear spins coupled to a degenerate gas of electron spins, the Korringa contribution to the relaxation rate, $T_{1K}^{-1}$, is related to the Knight shift, $K$, by the well-known Knight-Korringa relation$^{78,80}$

$$T_{1K}(K,T) = \frac{\gamma_e^2}{\gamma_n} \frac{4\pi k_B T}{h} K^2 ,$$

where $\gamma_e$ and $\gamma_n$ are the gyromagnetic ratios of the nuclear and electron spins, respectively, $k_B$ and $h$ are the Boltzmann and Planck constants, and $T$ is the absolute temperature. The Knight-Korringa relation shows that the $T_{1K}^{-1}$ values for nuclear spins in metallic environments are proportional to both temperature, $T$, and the square of the Knight shift, $K^2$. Fluorine species in metallic environments may therefore be identified on the basis of analysis of the $^{19}$F $T_{1K}$ values as functions of both NMR frequency position and temperature.

Analyses of the 1D $^{19}$F MAS NMR spectra and $T_{1K}$ relaxation rates at temperatures of 276–395 K, shown in Figure 6, reveal that the broad $^{19}$F signal at 50 ppm in Fig. 4a corresponds to $^{19}$F dopant atoms in metallic environments within the F:In$_2$O$_3$ NCs that exhibit Korringa-type relaxation behavior. By comparison, the $^{19}$F signal at -50 ppm, which also manifests a broad distribution of $^{19}$F environments, exhibits no Korringa-type temperature-dependencies in its spin-lattice relaxation behavior, consistent with its assignment to a distribution of isolated $^{19}$F dopants in the In$_2$O$_3$ lattice that experience chemical and/or paramagnetic shifts, but not metallic Knight shifts. The $^{19}$F frequency axis in Figure 4a is normalized in Figure 6a such that the signal from isolated F dopant species (-50 ppm in Figure 4a) is set to a Knight shift $K$ of 0 ppm. As shown in Figure 6a, the broad $^{19}$F signal distribution at $K = 100$ ppm (50 ppm in Figure 4a) from $^{19}$F species in metallic environments does not change significantly in width or position over the temperature range 276–395 K, consistent with the expected temperature-invariance of Knight shifts for heavily-doped semiconductors.$^{78}$ The $^{19}$F $T_{1K}$ values were measured by $^{19}$F saturation recovery experiments, and the $T_{1K}^{-1}$ values for each isochromat across the $^{19}$F Knight-shifted signal distribution were extracted by subtraction of the temperature-independent contribution ($T_{1O}^{-1}$) from the overall relaxation rate, $T_{1K}^{-1}$:

$$T_{1K}(K,T) = T_{1O}^{-1}(K,T) - T_{1K}^{-1} ,$$

where $T_{1O}^{-1}$ and $T_{1K}^{-1}$ are the temperature- and shift-independent terms, respectively. The Knight-Korringa relaxation and the extraction of the $T_{1O}^{-1}$ and $T_{1K}^{-1}$ terms are provided in the Supporting Information (Figure S15). The square root of
the temperature-dependent relaxation term, $T_{1,\text{R}}^{-1}$, is plotted as a function of $K$ for the $K = 50$ to 175 ppm region (boxed region in Figure 4a) in Figure 6b. At temperatures of 395 K (red) and 276 K (blue), the measured $T_{1,\text{R}}^{-1}$ values show excellent agreement across the entire $^{19}$F Knight shift distribution with the theoretical values predicted by the Knight-Korringa expression at the different temperatures (dotted lines), which notably has no adjustable parameters and is derived from first principles. Additionally, the Knight-Korringa relation holds across the entire temperature range of 276-395 K. The Korringa-type plot in Figure 6c shows a plot of the $T_{1,\text{R}}^{-1}$ values extracted at the maxima of the $^{19}$F Knight shift distribution ($K = 100$ ppm), as a function of temperature, revealing excellent agreement with the Knight-Korringa relation over the entire temperature range. This corroborates the conclusion that the broad $^{19}$F signal at 50 ppm in Figure 4a arises from a distribution of Knight shifts that manifest a range of couplings of $^{19}$F nuclei to conduction band electrons in regions of the F:In$_2$O$_3$ NCs with different extents of metallic character. The $^{19}$F atoms, acting as anionic n-type dopants, therefore are sufficiently dense that their associated unpaired electrons form a conductive network within the heavily-doped In$_2$O$_3$ lattice.

Furthermore, based on the quantitative single-pulse $^{19}$F NMR spectrum of the F:In$_2$O$_3$ NCs (3% InF) (Figure S11), approximately 82 ± 1% of all of the $^{19}$F species are in sub-surface metallic environments in the In$_2$O$_3$ lattice, 17 ± 1% in residual InF, and <1% at isolated dopant sites in the In$_2$O$_3$ lattice. The combined solid-state 2D $^4\text{H}(^{19}\text{F})$ NMR correlation and $^{19}$F $T_1$ relaxation analyses establish that only a small percentage (1-2%) of $^{19}$F species are at the surfaces of the F:In$_2$O$_3$ NCs. The majority of $^{19}$F species are incorporated into the F:In$_2$O$_3$ NCs in sub-surface metallic domains, consistent with F as an anionic dopant within the In$_2$O$_3$ lattice.

The metallic domains are also manifested by evidence of conduction band electron influences on local $^{115}$In environments in the F:In$_2$O$_3$ crystal lattice. Specifically, analyses and comparison of the solid-state wide-line $^{115}$In NMR spectra in Figure 7 of undoped bulk In$_2$O$_3$ and F:In$_2$O$_3$ NCs show differences that are characteristic of the coupling of $^{115}$In nuclei to free electrons. Acquisition of solid-state $^{115}$In NMR spectra has been exceedingly challenging in the past due to the highly quadrupolar character of $^{115}$In nuclei ($I = 9/2$), which often exhibit very broad (several MHz) and poorly resolved $^{115}$In NMR signals. Very few solid-state $^{115}$In NMR spectra of inorganic materials have been reported, with emphases primarily on materials with $^{115}$In atoms in symmetric environments, such as cubic zirconia and semiconductors like InP and InN, which yield narrower and more tractable line shapes. Nevertheless, recent wide-line NMR techniques enable the detection and analysis of very broad NMR signals, even for quadrupolar nuclei in paramagnetic or conductive materials.

Here, the frequency-stepped quadrupolar Carr-Purcell-Meiboom-Gill (CQPMG) technique was used to measure the solid-state $^{115}$In NMR spectra of bulk undoped polycrystalline In$_2$O$_3$ and F:In$_2$O$_3$ NCs (Figure 7). The CQPMG pulse sequence yields manifolds of very narrow, evenly spaced NMR signals (spikelets) that cannot cover the entire $^{115}$In spectral range of these materials, but can be systematically acquired as a series that can be overlain to map the full ~2 MHz broad central transition (CT) region of the $^{115}$In NMR spectrum. For example, the $^{115}$In NMR spectrum in Figure 7a of bulk undoped In$_2$O$_3$ is presented as a mosaic overlay of 22 individual CQPMG sub-spectra (plotted in different colors) that were acquired at evenly spaced frequency intervals. Though detailed analysis of the $^{115}$In NMR line shapes is complicated by overlap of the numerous $^{115}$In satellite transitions (STs) of the quadrupolar $^{115}$In nuclei, the sensitivity and resolution of the wide-line $^{115}$In CQPMG spectra is sufficient to simulate the $^{115}$In CT regions and estimate the quadrupolar coupling constant ($C_Q$), asymmetry parameter ($\eta$), and isotropic shift ($\delta_{\text{iso}}$) for the bulk In$_2$O$_3$ (Table S1). Such NMR parameters are highly sensitive to the chemical and electronic environments of $^{115}$In species in In$_2$O$_3$ and to our knowledge have never previously been measured or reported.

![Figure 7](image-url)

Figure 7. Solid-state 1D $^{115}$In NMR spectra of (a) undoped microcrystalline In$_2$O$_3$ and (b) F:In$_2$O$_3$ NCs (3% InF) acquired at 295 K, under static conditions, and at magnetic field strengths of (a) 18.8 T and (b) 19.6 T. The spectra are an overlay of 22 different sub-spectra (shown as different colors) acquired at evenly-spaced frequency intervals. Simulated $^{115}$In NMR line shapes generated using the parameters in Table S1 are shown offset above the experimental $^{115}$In NMR spectra. Signal intensities arising from $^{115}$In in satellite transitions are indicated by “ST”.

Compared to bulk In$_2$O$_3$, the $^{115}$In NMR spectrum of F:In$_2$O$_3$ NCs is displaced and broadened, consistent with the coupling of $^{115}$In nuclei to unpaired conduction band electrons. Both undoped polycrystalline In$_2$O$_3$ (Figure 7a) and F-doped In$_2$O$_3$ NCs (Figure 7b) exhibit very broad spectral features in the ~4000 to 4000 ppm range that arise from the CT of $^{115}$In nuclei in the different materials. The $^{115}$In CT regions for both materials are reproduced by a single simulated $^{115}$In line shape with $C_Q \approx 130$ MHz and $\eta = 1$, though with different isotropic shifts (Figure 7, black spectra, see also Table S1). The bulk undoped In$_2$O$_3$ (cubic bixbyite phase by XRD, Figure S16) exhibits an isotropic $^{115}$In shift of 170 ppm, consistent with diamagnetic $^{115}$In environments in the In$_2$O$_3$ lattice. By comparison, the $^{115}$In spectrum of F:In$_2$O$_3$ NCs (3% InF) exhibits an isotropic $^{115}$In shift of 1400 ppm, displaced more than 1200 ppm from the position for diamagnetic In$_2$O$_3$. This displacement provides evidence that the majority of $^{115}$In species in the F:In$_2$O$_3$ lattice experience substantial Knight shifts arising from interactions with unpaired conduction band electrons associated with the F dopant species. The $^{115}$In Knight shifts corroborate the $^{19}$F NMR and $T_1$ spin-lattice relaxation time analyses discussed above. The $^{115}$In NMR spectrum of the F:In$_2$O$_3$ NCs is also broadened compared to that of bulk undoped In$_2$O$_3$, indicating a large distribution of chemical
shifts, Knight shifts, and/or quadrupolar parameters (Table S1). The continuous distributions of signal intensity extending to higher and lower frequencies in both of the $^{19}$F NMR spectra in Figure 7 arise from the very broad and overlapping $^{19}$F satellite transitions, which are expected to span frequency regions of tens of MHz. To the best of our knowledge, the solid-state $^{115}$In NMR spectra presented here are the first $^{115}$In NMR analyses of In$_2$O$_3$, and evidence the sensitivity of $^{115}$In NMR to different electronic environments in technologically important In$_2$O$_3$ materials. The solid-state $^{115}$In and $^{19}$F NMR analyses together provide complementary and consistent evidence for metallic $^{115}$In and $^{19}$F environments in the heavily-doped F:In$_2$O$_3$ lattice.

**Optical Properties.** Considerations of charge compensation accompanying fluorine doping (eq. 2) as well as the NMR analyses of the $^{19}$F and $^{115}$In species show that the anionically doped F:In$_2$O$_3$ NCs contain substantial free electron populations leading to LSPR response. By eye, doped F:In$_2$O$_3$ NCs in solvent dispersions appear blue, in contrast to clear or white undoped F:In$_2$O$_3$ NCs (Figure S17). Liquid-cell FTIR spectra confirm that the F:In$_2$O$_3$ NCs exhibit IR range LSPR, with an absorption tail towards the visible region that is responsible for their blue appearance. The role of fluorine as an anionic dopant is apparent even in rounded F:In$_2$O$_3$ NCs (1% InF$_3$) synthesized at 280 °C. These NCs have a mean diameter of 338.0 ± 51.0 nm with 4.6 ± 0.4 at% F by EDX, and exhibit an LSPR extinction peak at 3497 cm$^{-1}$ (Figure 8). For comparison, undoped pseudospherical In$_2$O$_3$ NCs show a low energy LSPR peak located at 1370 cm$^{-1}$, consistent with a low concentration of free electrons induced by the presence of oxygen vacancies (eq. 1)\(^8\) (Figure 8). In both Cl:In$_2$O$_3$ and Br:In$_2$O$_3$ NCs however, the LSPR peak is at 1743 cm$^{-1}$, indicating low free electron concentrations compared to F:In$_2$O$_3$ NCs due to low dopant incorporation (Figure 8). These comparative observations demonstrate that fluorine is a uniquely effective anionic halide dopant for In$_2$O$_3$ NCs to induce LSPR in the IR region.

![Figure 8](image-url) **Figure 8.** Liquid-cell FTIR spectra for spherical F:In$_2$O$_3$ (green line), Cl:In$_2$O$_3$ (orange line), Br:In$_2$O$_3$ (red line), and In$_2$O$_3$ NCs (black line). Spectral bands saturated by ligand absorption are shown as blank regions. (Inset) SEM images showing F:In$_2$O$_3$ (green), Cl:In$_2$O$_3$ (orange), and Br:In$_2$O$_3$ (red) NCs. Scale bars are 200 nm.

In the F:In$_2$O$_3$ cubes, the highly defined corners and edges are expected to result in multimodal LSPR extinction peaks in the IR spectral range. F:In$_2$O$_3$ cubes (3% InF$_3$) have highly pronounced plasmon peaks at 3496 cm$^{-1}$ (FWHM 1157 cm$^{-1}$) and 5469 cm$^{-1}$ (Figure 9a, green), respectively ascribed to corner- and edge-dominated LSPR modes, by comparison to analogous modes observed for silver cubes.\(^8\) Lower fluorine-doped F:In$_2$O$_3$ concave cube NCs exhibit changes in LSPR peak shape due to NC shape effects. Sharp concave cubes (2% InF$_3$) show well-defined modes with LSPR peaks at 2974 cm$^{-1}$ and 5378 cm$^{-1}$ (Figure 9a, orange). Concave cubes (1% InF$_3$) with elongated <111> directional corners, exhibit a complex LSPR response centered at 3030 cm$^{-1}$ (Figure 9, red). Previous literature on plasmonic octopod Ag NCs has described the breakdown of simple cubic LSPR modes due to elongated corners.\(^10,11\) By contrast, no multimode LSPR peaks are observed for rounded F:In$_2$O$_3$ NCs.

![Figure 9](image-url) **Figure 9.** (a) Liquid cell FTIR spectra of F:In$_2$O$_3$ NCs with corresponding SEM images. F:In$_2$O$_3$ cube (green), F:In$_2$O$_3$ concave cube (orange), and F:In$_2$O$_3$ concave cube (red). Scale bars are 100 nm. Spectral bands saturated by ligand absorption are shown as blank regions. (b) F:In$_2$O$_3$ (3% InF$_3$) cube (top), F:In$_2$O$_3$ (2% InF$_3$) concave cube (middle), and F:In$_2$O$_3$ (1% InF$_3$) concave cube (bottom) EELS maps for corner mode frequencies (around 3900 cm$^{-1}$, left, orange) and edge mode frequencies (around 5100 cm$^{-1}$, right, blue) LSPR mode. Scale bars are 200 nm.
NCs (1% InF$_2$) grown at 280 °C due to their mostly spherical shape (Figure 8, green). During the growth of F:In$_2$O$_3$ NC cubes (3% InF$_3$), FTIR of aliquots demonstrate retention of both edge- and corner-mode LSPR peaks (Figure S18). The edge-mode LSPR at higher wavenumber range is observed at 5690 cm$^{-1}$ and retained during 1-4 min reaction time. The corner-mode LSPR peak is also retained at 3340 cm$^{-1}$ until the end of the growth reaction (2-4 min). It is observed that the F:In$_2$O$_3$ cube aliquot dopant composition is steady at F/In = 11.8 ± 0.4 % throughout the growth reaction. This suggests that incorporation of sub-surface fluorine species, as detected by $^{19}$F NMR, is sustained during NC growth.

To definitively assign the contributions to the multimodal FTIR peaks observed in faceted F:In$_2$O$_3$ NCs, we perform STEM-EELS mapping of individual cubes. Optical FTIR excitation in the FTIR only allows ensemble far-field extinction measurements of cubes, where the incidence IR excitation wavelength (1250-10000 nm) is within the LSPR quasi-static limit range. The sub-Angstrom diameter probe available in the STEM can directly sample and map the near-field localization of LSPR modes, and thanks to recent advances in monochromation these mid-infrared frequencies are now accessible using EELS. The spatial maps are acquired through spectrum imaging (SI), where the beam is rastered across the region of interest and a spectrum is acquired at each probe position resulting in a three-dimensional dataset with two spatial-dimensions and one spectral dimension. From here, individual plasmon modes are deconvoluted through the non-negative matrix factorization (NMF) method to produce spatially resolved EELS maps of individual LSPR modes. For each structure spatially- and spectrally-distinct corner and side modes can be observed and mapped through the deconvolved spectrum imaging, which are plotted in Figure 9b. The corner modes of F:In$_2$O$_3$ cube (3% InF$_3$), sharp concave cube (2% InF$_3$), and concave cube (1% InF$_3$) NCs, are observed at 4201 cm$^{-1}$, 3926 cm$^{-1}$, and 3752 cm$^{-1}$ respectively, with the side mode resonances centered at 5382 cm$^{-1}$, 5173 cm$^{-1}$ and 4861 cm$^{-1}$. It is important to note that for the side modes, the NMF-deconvolution results in a spectral component with multiple peaks, likely corresponding to spatially overlapped edge and face modes. The reported peak center is the average of these face and edge modes. Details of the deconvolution and the EELS experiments are presented in greater detail in Supporting Information, Text S3.

While FTIR samples the ensemble behavior and EELS samples individual structures, the match is strong enough to determine the modal nature of the FTIR peaks from the EEL-SI. The STEM analysis support that the high energy FTIR peaks correspond to the edge and face modes, while the lower energy peaks correspond to the corner modes. As in FTIR, in EELS the edge mode is observed at higher energy for the cube (3% InF$_3$) than for the sharp concave cube (2% InF$_3$). The frequencies of the corner modes do differ significantly between FTIR and EELS, which can be understood as originating from differences in the dielectric function in the liquid-cell FTIR experiments and the SiN/ultra-high-vacuum environment in the STEM. The observed blueshift in the EELS mode relative to the FTIR spectrum is attributed to the lower refractive index ($n=1$) of surrounding vacuum in STEM, as compared to the TCE solution medium ($n=1.5$) in the liquid-cell optical measurement.

Conclusion

Fluorine plays a dual role as a dopant, influencing preferential growth of certain crystal facets and directing morphology of colloidally synthesized In$_2$O$_3$ NCs, as well as inducing IR range LSPR by aliovalent doping within the In$_2$O$_3$ NC lattice. In this study, we have demonstrated that introducing fluorine precursors in a typical heat-up method colloidal synthesis yields highly faceted F:In$_2$O$_3$ cube NCs with shape-dependent LSPR response. Morphological control is demonstrated for the formation of concave cubes by adjusting the dopant concentration during F:In$_2$O$_3$ NC synthesis. Small percentages (1-2 at.%) of fluorine species are shown to be at the surfaces of the F:In$_2$O$_3$ NCs and hinder growth of (100) facets, as determined by combined XPS, solid-state 2D $^{19}$F NMR and DFT analyses. By comparison, the majority of fluorine species are incorporated into subsurface metallic environments in the F:In$_2$O$_3$ lattice, consistent with F acting as an anionic dopant, as revealed by variable-temperature analyses of $^{19}$F spin-lattice relaxation times and comparison to the Knight-Korringa relation. Complementary analyses of wide-line $^{19}$F NMR spectra show that the majority of $^{19}$F species in the F:In$_2$O$_3$ species interact with unpaired conduction band electrons, providing corroboratory evidence that the F:In$_2$O$_3$ NC lattice is heavily doped beyond the metal-insulator transition. Arising from the combined effects of dopant-induced free-carriers and highly-faceted NC shapes, multimodal LSPR extinction features are observed in the IR. Single-NC LSPR near-field modes spatially localized around sharp morphological features are directly observed by STEM-EELS.

With this understanding of the role played by fluorine both on the NC surface and in the lattice, F:In$_2$O$_3$ NCs provide a valuable platform material for exploring properties and applications of LSPR-active NCs. Analogous to Ag nanocubes that exhibit visible LSPR, well-defined In$_2$O$_3$ nanocubes are able to be colloidally synthesized, with shape-dependent LSPR in the IR spectral range. Near-field localization of IR light will make these highly faceted F:In$_2$O$_3$ NCs a platform material to evaluate near-field enhancement effects and explore applications unique to the infrared, including coupling LSPR to molecular vibrational modes and IR emissive excitons. To meet these demands, control of NC sizes and LSPR spectral tunability need be advanced. Further synthetic advances, such as the systematic incorporation of co-dopants, may lead to additional LSPR tuning by increasing free electron compensation in In$_2$O$_3$ NCs. However, synthetic questions remain to fully understanding cationic co-dopant incorporation in metal oxides in the presence of anionic dopants. The understanding of the dual role of fluorine as an anionic dopant in F:In$_2$O$_3$ NCs is expected to provide a foundation for addressing these questions and challenges, and further improving the properties of these versatile materials.

Associated Content

The Supporting Information is available free of charge on the ACS Publications website.

Details of nanocrystal characterization (SEM, EDX, TOF-SIMS, XPS, EPR, TGA, and XRD), nanocrystal aliquots (time and temperature series SEM, FTIR), solid-state NMR details (quantitative $^{19}$F NMR, Knight-Korringa relation, simulated lineshape parameter), DFT simulation (supercell, DFT calculation), and details of monochromated EELS (background subtraction, non-negative matrix factorization, and modal deconvolution).

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Notes
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