Electronic Supporting Information: Chemically modifying the mechanical properties of core-shell liquid metal nanoparticles

Nicholas J. Morris,[ab‡] Zachary J. Farrell,[ab‡] and Christopher E. Tabor[b*]

Experimental Methods

Materials

99.9999% purity Ga shot and 99.9999% purity In shot were purchased from Indium Corporation and used to produce a slightly off-eutectic GaIn alloy(10.4 at% In, 89.6 at% Ga) as needed. The initial Ga/In ratio was varied slightly from the eutectic case (of 14.2 at% In, 85.8 at% Ga) as very small ($D_{avg} \sim 60$ nm) nanoparticles are expected to gallium deplete the core due to formation of a gallium oxide shell, as discussed in Lear, *et al.*[1] A mass balance on the basis of D=50 nm nanoparticles possessing an EGaIn core (14.2 at% In, 85.8 at% Ga) and a 3 nm thick Ga_2O_3 shell (assumed to have a density of 5.88 g/cm^3, equivalent to β-Ga_2O_3) suggested the 10.4 at% In, 89.6 at% Ga ratio used above.[2,3] The particles are generally referred to as being composed of eutectic gallium-indium (EGaIn) as at the final size the core is expected to be at the eutectic composition.

1-dodecanethiol (≥98%), 2,3,4,5,6-pentafluorothiophenol (FTP, ≥97%), 11-phosphonoundecanoic acid (11-PUA, 96%), (4-fluorobenzyl)phosphonic acid (FBPA, 99%, HPLC), n-dodecylphosphonic acid, (3-aminopropyl)triethoxysilane (99%), (3-mercaptopropyl)trimethoxysilane (95%), 2-mercaptoethanol (≥99%), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC, ≥98%), tannic acid (ACS Reagent grade), phenol (ReagentPlus, ≥99%), 30% hydrogen peroxide solution (ACS Reagent), silver nitrate (ACS Reagent, ≥99%), trisodium citrate dihydrate (ACS Reagent, ≥99%), methanol (CHROMASOLV for HPLC, ≥99%), dichloromethane (anhydrous, ≥98%, contains 40-150 ppm BHT), and chlorobenzene (ReagentPlus, ≥99%) were purchased from Sigma-Aldrich and used as received. Concentrated hydrochloric acid (certified ACS Plus) was purchased from Fisher. Ethanol (200 proof, anhydrous USP, Decon Laboratories, Inc.) was obtained from stock on hand and used as received. ITO patterned glass (15 Ω) was purchased from Luminescence Technology Corp. Mechanical-grade silicon wafers were obtained from Nova Electronic Materials.

Fabrication of EGaIn Nanoparticles

As it was desired to produce a wide variety of nanoparticles with differences in the thickness of their gallium oxide shell, a number of different particle formation approaches were utilized, as described in the following subsections.

Unfunctionalized EGaIn Particles

To make EGaIn nanoparticles with no ligands/functionalization, 0.6 mL EGaIn was placed in a standard 20 mL, 28mm OD borosilicate glass vial with 14.4 mL ethanol. The vials were then immersed (approximately half the vial height) into a chilled water bath maintained at 10 °C. A 3 mm diameter tapered microtip was then immersed in the vial contents, ∼1 cm from the bottom of the vial, followed by covering the opening between the vial mouth and microtip with Parafilm M, to the greatest extent possible. This microtip was then driven by a Sonics and Materials, Inc. VCX 500 ultrasonic processor at an amplitude of 30% for 16 hours. After probe sonication, the vial of EGaIn particles was removed, sealed, and stored until analysis or further processing was to be performed. This basic procedure also serves as the basis for producing functionalized particles, with some modifications as discussed in their respective sections.

Thiolated EGaIn Particles

Thiolated EGaIn particles are made similarly to the unfunctionalized nanoparticles by addition of 64 mM of 1-dodecanethiol prior to probe ultrasonication. Following ultrasonication, particle suspensions are washed to remove excess unabsorbed thiols via centrifugation at 2057 RCF, followed by redispersion in ethanol. This process is repeated three times. After the final centrifugation step, the nanoparticle dispersions were stored in sealed vials until performing further sample preparation or analysis.

---

[a] *UES, Inc., 4401 Dayton Xenia Rd, Dayton, OH 45432, USA.*
[b] *Air Force Research Laboratory, Address, Dayton, OH, USA. Tel: +1 (937) 426-6900; E-mail: christopher.tabor.1@us.af.mil*

Phosphonic Acid Grafted EGaIn Particles

Phosphonic acid functionalized EGaIn nanoparticles are produced via a post-synthetic modification of the unfunctionalized EGaIn nanoparticles discussed above. Following probe ultrasonication, a phosphonic acid is added to the vial of EGaIn particle suspension to bring the concentration to 16 mM. Phosphonic acids utilized for this were n-dodecylphosphonic acid or 11-phosphonoundecanoic acid. The sealed vials were then placed into a bath sonicator held at a temperature of 50 °C for 4 hours to drive robust attachment of phosphonic acids[4,5] After the attachment step, residual unbound phosphonic acids were removed by centrifugation at 2057 RCF for 30 minutes followed by resuspension of particles in ethanol; this process was repeated three times. The final, purified phosphonic acid functionalized EGaIn particle suspension was stored in a sealed vial until sample preparation or analysis was performed.

Hybrid Thiol/PA Functionalized Particles

To make hybrid thiolated/phosphonic acid functionalized EGaIn particles, 64 mM of FTP and 16 mM of FBPA were added prior to the start of probe ultrasonication to allow thiol attachment during the particle formation process. Additionally, chlorobenzene is used in place of ethanol in this procedure. Following probe ultrasonication, vials were removed, sealed and placed in a bath ultrasonicator for 4 hours at 50 °C to promote robust phosphonic acid attachment.[4,5] Following the bath sonication treatment, particle suspensions were centrifuged at 2604 RCF for 30 minutes and the supernatant discarded before being refilled with their respective solvents and redispersed via vortex mixing. A second and third centrifugation/wash step were carried out as above, except at 10414 RCF rather than 2604 RCF. Following the final redispersion step, particle suspensions were placed in sealed vials and stored awaiting further analysis or sample preparation.

Extremely Thick Gallium Oxide Shelled Particles

As an alternative approach to the extended periods of aging required to produce thick gallium oxide shells in EGaIn particles under ambient conditions, a chemical protocol was devised to rapidly and artificially generate a thick layer of gallium oxide on EGaIn nanoparticles. Unfunctionalized EGaIn nanoparticles are first produced as per the protocol described above. Following sonication, 5 mL H_2O_2, 50 mg phenol, and a small Teflon-coated stir bar were added to the sealed vial, which was then magnetically stirred for 24 hours. The particle suspension was centrifuged at 2057 RCF to remove unreacted H_2O_2 and phenol, followed by resuspension in ethanol. This centrifugation/resuspension process was repeated three times. The final particle suspension in ethanol was then placed in a sealed vial and stored pending sample preparation and analysis.

Synthesis of Silver Nanoparticles

Silver nanoparticles to be used as a mechanical standard for validation of the nanoindentation method were produced based on the synthetic method of Bastus, *et al.*[6] 200 mL of an aqueous solution containing trisodium citrate dihydrate (5 mM) and tannic acid (0.1 mM) was brought to boil with stirring in a 500 mL round-bottom flask in a sand bath on a hot plate. Once boiling had started, 1 mL of silver nitrate solution (50 mM) was added. A color change was near-immediately observable. Based on the original synthetic procedure, this was anticipated to produce silver nanoparticle seeds of $D \approx 15$ nm.

To grow these nanoparticles to a similar size regime ($D \sim 50$ nm) as the EGaIn nanoparticles which they would serve as a standard for, the iterative growth process from Bastus, et al. was used.[6] Based on 15 nm seeds, it was decided that 12 growth cycles would target approximately the desired particle size regime. Continuing after the synthesis of the silver seed particles, the reaction flask was allowed to cool to 90°C. 40 mL of silver seed particles were removed for later use; 33 mL of water was subsequently added back to the flask. For each of the 12 growth steps, 1 mL of 25 mM trisodium citrate dihydrate solution was added, followed by 1.5 mL of 5 mM tannic acid solution, followed by by 1 mL of 50 mM silver nitrate solution. 15 minutes were allowed to elapse between growth steps. After the final growth step, the reaction flask was removed from the heat and allowed to cool.

To purify and concentrate the silver nanoparticles, the entire reaction volume was divided between 6 50 mL centrifuge tubes and centrifuged at 6000 RPM for 30 minutes. After centrifugation, the supernatant was discarded and the remaining sediment redispersed using $\sim$60 mL of 2.2 mM trisodium citrate dihydrate solution. The redispersed silver nanoparticle suspensions were combined into 2 centrifuge tubes and centrifuged again at 4649 RCF for 30 minutes. The supernatant was again discarded and the sedimented nanoparticles resuspended using $\sim$ 30 mL of 2.2 mM trisodium citrate dihydrate solution; the redispersed nanoparticles were placed into a single centrifuge tube and centrifuged at 4649 RCF for 30 minutes. Following this final centrifugation step, the supernatant was discarded and the particle sediment resuspended in 20 mL of 2.2 mM trisodium citrate dihydrate solution. This final concentrated silver nanoparticle suspension was transferred to a standard 28 mm OD borosilicate vial for storage and later use.

EGaIn Particle Sizing

EGaIn nanoparticles were sized using scanning transmission electron microscope (STEM) images taken with a high-angle annular dark-field detector on an FEI Talos microscope operating at 200 keV. Using ImageJ, at least 300 nanoparticles were manually measured for each sample reported on in this paper. Following measurement, the average diameter, surface-area weighted diameter, standard deviation, and relative standard deviation were calculated and plots of the particle size distribution produced. These plots appear in the supplementary information.

To mount EGaIn particles for STEM measurements, 1-2 drops of a given particle suspension was added to 2 mL of dichloromethane. This dilute suspension was then dropped onto a TEM grid held in self-closing, anti-capillary tweezers until a single drop fell from the grid. The grids used consisted of ultrathin (3-4 nm) carbon films on 400-mesh copper grids purchased from Electron Microscopy Sciences (CF400-Cu-UL). Following deposition, a folded piece of filter paper was used to wick excess solvent from the grid underside.

XPS Measurements

X-ray photoelectron spectroscopy (XPS) measurements were taken of EGaIn nanoparticle films corresponding to films produced for nanoindentation measurements. As sample age potentially affects the gallium oxide shell thickness, XPS measurements were taken simultaneously with nanoindentation measurements. Films for XPS were produced by spin-coating a small amount of a given EGaIn nanoparticle suspension onto substrates consisting of adhesive copper foil tape affixed to a 1 cm x 1 cm piece of glass. The EGaIn nanoparticle suspension was deposited dropwise until the nanoparticle layer had thickened to the point of opacity and the copper foil was no longer visible. EGaIn suspensions used were vortex mixed immediately prior to deposition to ensure homogenaity. Samples prepared in this way were introduced into the XPS within 30 minutes, with XPS measurements commencing within 90 minutes.

XPS measurements for the unfunctionalized, DDT, and DDPA samples were collected on an SSI M-Probe using a monochromated Al source. The measurements regions were as follows: survey spectrum, high-resolution spectrum 30 eV wide centered at 19 eV BE (Ga3d, In4d, O2s), high resolution spectrum 30 eV wide centered at 445 eV BE (In3d), high resolution spectrum 20 eV wide centered at 532 eV (O1s), and a high resolution spectrum 20 eV wide centered at 1117 eV (Ga2p$_{3/2}$). The Ga3d/In4d/O2s region background was fitted with a Tougaard universal background, O1s and Ga2p backgrounds with a Shirley, and the In3d with linear. All peaks were fitted with 30% Gaussian, 70% Lorentzian line shapes and all measurements were taken with the same number of scans to ease comparison between regions.

XPS measurements for the EDC/11-PUA, FTP/FBPA, and H_2O_2/phenol samples were collected with a Kratos Axis Nova using a monochromated Al anode operated at 10 mA and 12 kV. For all samples, the following measurement regions and widths were used: a survey spectrum, high-resolution spectrum 30 eV wide centered at 19 eV (Ga3d, In4d, O2s), a high-resolution spectrum 20 eV wide centered at 534 eV (O1s), a high-resolution spectrum 30 eV wide centered at 448 eV (In3d), and a high-resolution spectrum 20 eV wide centered at 1116 eV (Ga2p$_{3/2}$). The Ga3d/In4d/O2s region was fitted with a Tougaard universal background; O1s, C1s, and In3d$_{3/2}$ regions were fitted with a Shirley background. All peaks were fitted using a 80% Lorentzian, 20% Gaussian lineshape and all high-resolution scans were taken with the same number of passes to simplify comparison between analysis regions. In the cases of the Ga3d and In4d peaks, both the 5/2 and 3/2 components were fitted. For Ga3d, the peak area of the 3/2 component was constrained to 66.6% of the area of the 5/2 component, FWHMs of the peaks were constrained to be equal, and the distance between peaks was taken to be 0.46 eV.[7] For In4d, the peak area of the 3/2 component was constrained to 66.6% of the area of the 5/2 component, FWHMs of the peaks were constrained to be equal, and the distance between peaks was taken to be 0.8 eV.[8]

XPS Calculation of Gallium Oxide Shell Thickness

To calculate the absolute thickness of the gallium oxide shell surrounding the EGaIn core, the approach previously put forward by Farrell and Tabor (based on Cant, *et al.*) is used.[9,10] The particle sizes as determined in the previous section were reweighted to provide a surface-area weighted average which was used in these calculations. The core was assumed to be EGaIn (14.2 at% In, 85.8 at% Ga) based upon the size/material considerations described previously.[2,3] The gallium oxide shell was assumed to be stoichiometric and the organic outer shell was assumed to have an atomic number of $Z = 4$ as per Seah.[11]

Nanoindentation Particle Film Preparation

Unfunctionalized Silicon Substrates

To form thin films of EGaIn nanoparticles on unfunctionalized silicon, 1 cm x 1 cm mechanical grade silicon wafer squares were first plasma cleaned (air) for 1 minute. The cleaned wafer squares were then pressed onto a cured PDMS substrate (∼3 cm x ∼3 cm) which was then placed on a spin coater and spun at 2200 RPM. 1-2 drops of an EGaIn nanoparticle sample which had been diluted six-fold (0.1 mL EGaIn/15 mL solvent) was then dropped onto the spinning wafer. After ∼10 seconds to allow the film to dry, the spin coater was stopped and the wafer square removed. This film preparation process was used for the unfunctionalized, 1-dodecanethiol treated, n-dodecylphosphonic acid treated, and 1-dodecanethiol/n-dodecylphosphonic acid hybridized nanoparticles.

Silanization of Silicon/ITO Substrates

To permit attachment of particles with certain functionalities silicon or ITO substrates were silanized with (3-aminopropyl)triethoxysilane (APTES) or (3-mercaptopropyl)trimethoxysilane (MPTMS), respectively.

In the case of silicon/APTES, 50 mm diameter mechanical-grade silicon wafers were air plasma cleaned for 1 minute, followed by immersion in a 1:1 v:v solution of HCl:methanol for 30 minutes. The wafers were then rinsed with deionized water and placed into an 80 °C vacuum oven at 25 mmHg overnight. The next day, the wafers were placed into a solution of 1% v:v APTES:ethanol for 30 minutes, followed by removal of the wafer and sonication in fresh ethanol five times to remove unreacted APTES. The wafers were then placed back into the 80 °C, 25 mmHg vacuum oven for three hours to evaporate any remaining ethanol. The wafers were then diced into $\sim$1 cm x $\sim$3 cm long strips for later use and stored in a nitrogen-purged dessicator until used.

In the case of indium tin oxide/MPTMS, 2 cm x 3 cm ITO on glass slides were air plasma cleaned for 1 minute. As HCl would dissolve the ITO layer, hydroxylation of the ITO surface was promoted by heating in a high humidity setting. The cleaned ITO slides were placed into a vacuum oven at 60 °C with 200 mL of water in a beaker. Vacuum was pulled to 25 mmHG and the vacuum valve closed. After 16 hours, the ITO slides were removed from the water-vapor saturated oven, rinsed with acetone, and blown dry with an N_2 stream. The slides were then immersed in a 10% v:v MPTMS:ethanol solution for 2 hours. After removal, the slides were rinsed with ethanol, then placed in a beaker with ethanol and sonicated for 10 minutes. The ethanol was discarded and replaced with fresh ethanol before being sonicated another 10 minutes; this sonication step was carried out a total of five times. The MPTMS-coated slides were stored in a nitrogen-purged dessicator until their layer use.

EDC Coupling of 11-PUA Functionalized EGaIn Nanoparticles with APTES-Functionalized Silicon

To obtain nanoindentation samples with no more than one layer of EGaIn nanoparticles, EDC was used to crosslink 11-PUA functionalized EGaIn nanoparticles with APTES-functionalized silicon substrates, based on a method published by Interchim.[12] This approach enabled generation of a single-particle thick layer as the amide bonds formed during this process are chemically and mechanically durable, which permits uncrosslinked particles to be removed by washing at the end of the crosslinking process, leaving only a single layer of particles on the substrate. First, 11-PUA functionalized EGaIn particles were produced by post-fabrication treatment of unfunctionalized EGaIn nanoparticles with 0.064 mg 11-PUA at 50 °C for 4 hours, as described in a previous section. Next, the particles were washed via centrifugation (as described above) to remove any excess 11-PUA which could interfere with the EDC coupling before being dispersed in 20 mL of ethanol. 25 mg EDC was then added to the 11-PUA EGaIn nanoparticle suspension and dissolved via sonication. An approximately 1 cm x 3 cm piece of APTES-functionalized silicon was placed vertically into the vial, which was then sonicated in a bath sonicator at 30 °C for 16 hours. Following this, the crosslinked 11-PUA/APTES substrate was removed, rinsed with ethanol, and then placed in a beaker of fresh ethanol in a bath sonicator. This was repeated three times before a final rinse step with ethanol.

Adsorption of FTP/FBPA Functionalized EGaIn Nanoparticles to MPTMS-Functionalized ITO

FTP/FBPA functionalized EGaIn nanoparticles were produced as described in a previous section. 1.5 mL of the final, washed FTP/FBPA-EGaIn suspension (containing $\sim$0.06 mL EGaIn) was placed into a 28 mm OD scintillation vial with 18 mL chlorobenzene and 100μl 2-mercaptoethanol. The MTPMS-coated ITO slides were scored and snapped into pieces with dimensions approximately 1 cm x 3 cm and placed vertically into the vial of diluted FTP/FBPA EGaIn nanoparticles. A small stir bar was placed into the vial and it was sealed and left to stir for 16 hours at ambient temperature. After 16 hours, the ITO piece was removed from the vial and while holding vertically in tweezers, gently blown dry from the top using a dry nitrogen stream. Samples were tested the same day as they were produced in this manner.

Adsorption of Silver Nanoparticles to APTES-Functionalized Silicon

Citrate-protected silver nanoparticles were produced as described in a previous section. APTES-functionalized silicon substrates were cleaved into pieces approximately 1 cm x 3 cm and placed vertically into the undiluted silver nanoparticle suspension in a 28 mm OD scintillation vial. The vial was sealed and sonicated in a bath sonicator held at 30 °C overnight. The substrate was removed after 16 hours and washed via bath sonication in fresh ethanol three times. Samples produced in this way were stored in a nitrogen purged dessicator until nanoindentation testing was performed.

Nanoindentation Measurements

Nanoindentation experiments were performed using a Nano XP™(MTS) Nanoindentation system with flat punch diamond tips with diameters of 10 and 50 μm (Micro Star Technologies). EGaIn particle-coated silicon wafer chips were mounted directly onto flat, 1-inch diameter aluminum sample stubs. Scotch tape was placed on the edges of the samples to secure them to the aluminum stub, while maintaining sample flatness. Indents were run in load-control mode with a constant loading rate of 1 mN/min to various maximum applied loads between 0.5 and 250 mN. An approach velocity of 10 nm/s at a distance of 1000 nm were used with a surface detection stiffness threshold sensitivity of 10%.

The average particle coverage for each sample was estimated using SEM images taken near the indentation sites. Image analysis software (ImageJ, NIH) was used to measure the percentage of substrate area covered with sub-monolayer particle films. This percentage of area covered with particles was then used to normalize stiffness measurements to a per particle domain, based on average number of particles loaded by the indenter tip.

In Situ Electrical Resistance Measurements

To characterize the critical load associated with particle rupture and resultant release of the liquid EGaIn core, nanoindentation experiments were conducted with an electrically conductive, flat punch doped-diamond tip (ρ=0.04 ■·m, diameter = 10 μm). A digital multimeter and datalogger (Keithley 2700) measured the *in situ* resistance between the conductive ITO-patterned glass and the nanoindenter head housing the conductive tip during indentation experiments.

Nanoparticle STEM Images and PSDs

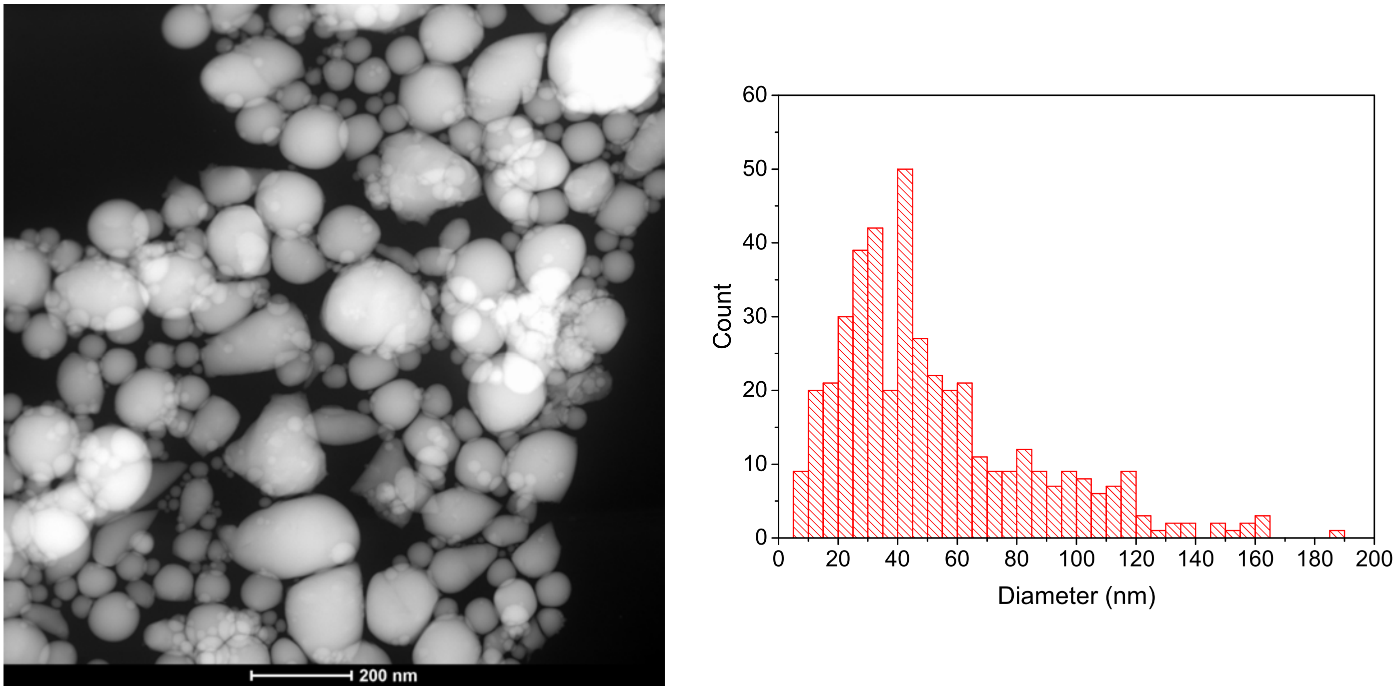

Figure 1 A representative STEM image of unfunctionalized EGaIn nanoparticles and their corresponding particle size distribution.

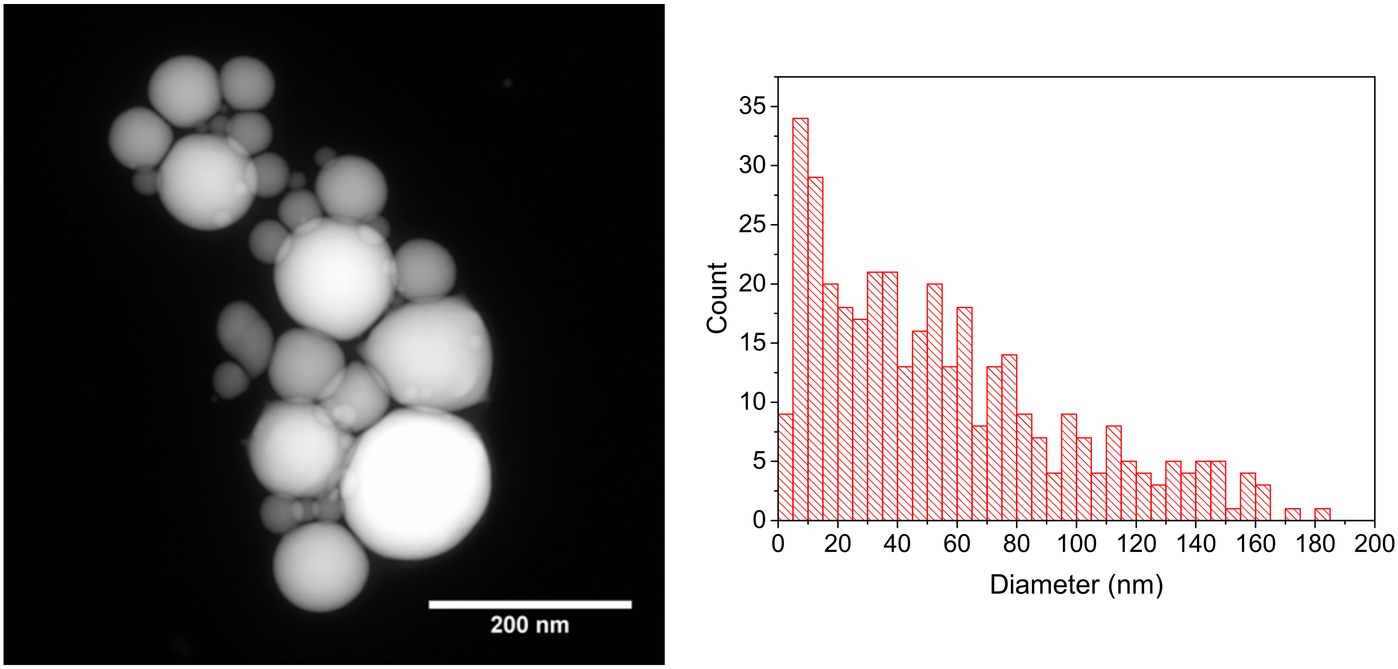

Figure 2 A representative STEM image of DDT-functionalized EGaIn nanoparticles and their corresponding particle size distribution.

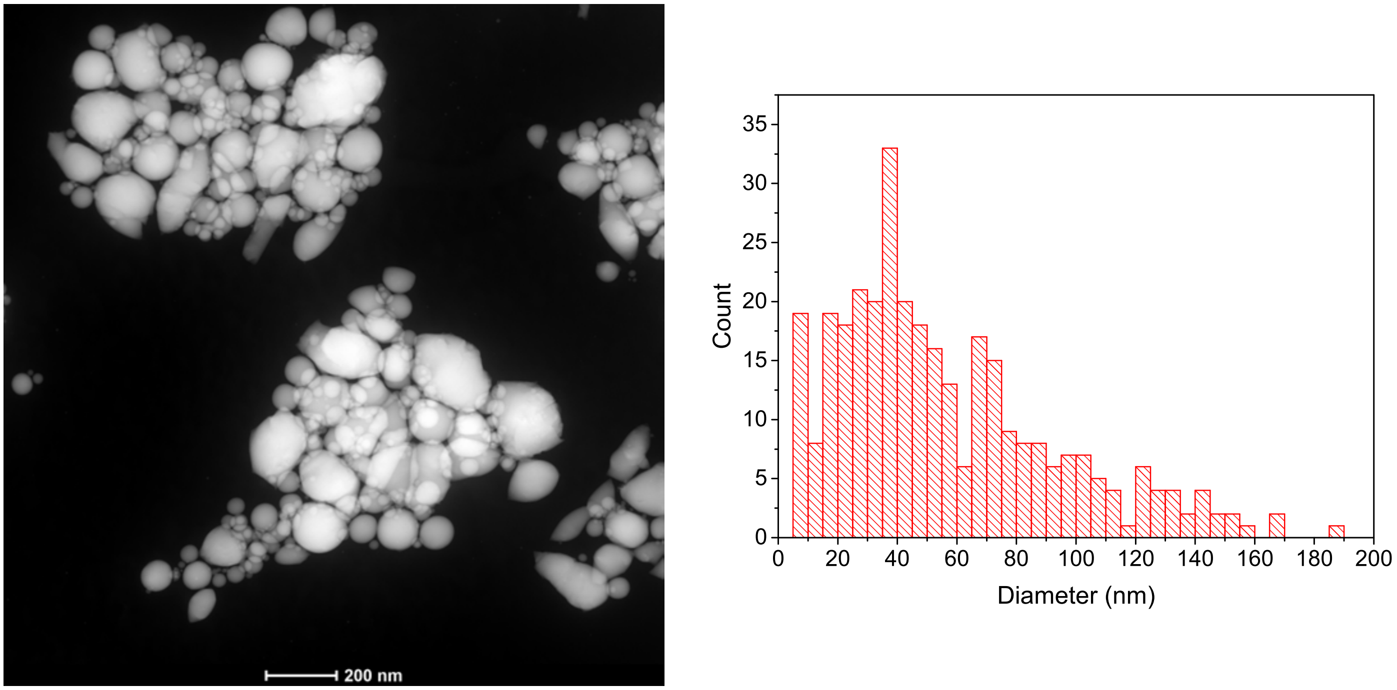

Figure 3 A representative STEM image of dodecylphosphonic acid functionalized EGaIn anoparticles and their corresponding particle size distribution.

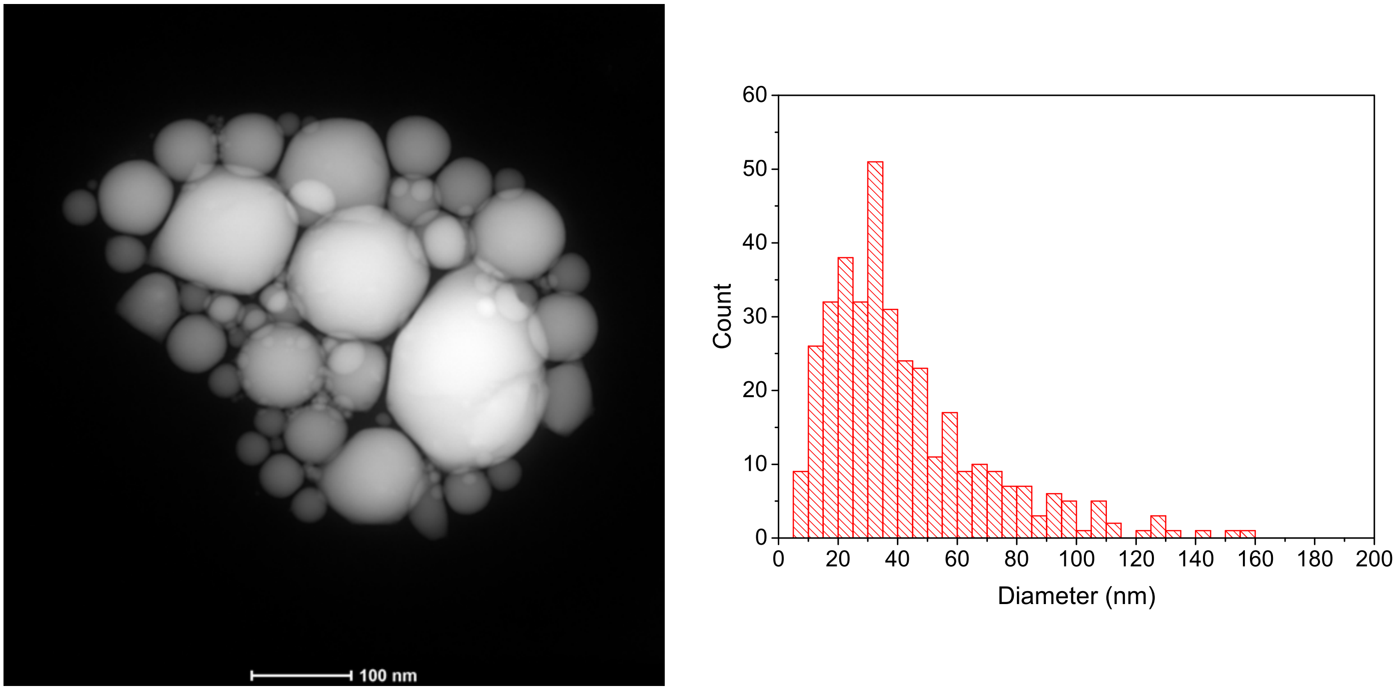

Figure 4 A representative STEM image of dodecanethiol/dodecylphosphonic acid functionalized EGaIn nanoparticles and their corresponding particle size distribution.

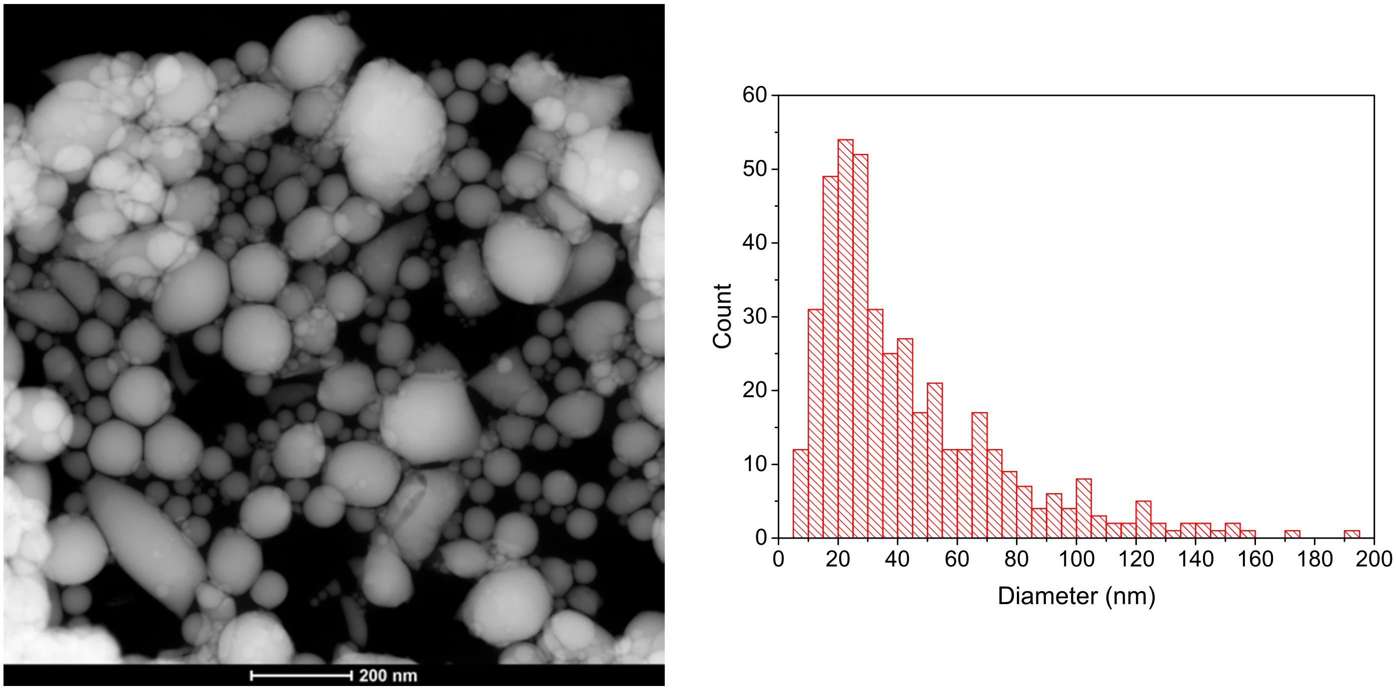

Figure 5 A representative STEM image of the unfunctionalized EGaIn nanoparticles used for 11-phosphonoundecanoic acid functionalization and later EDC-coupling reaction as well as their corresponding particle size distribution.

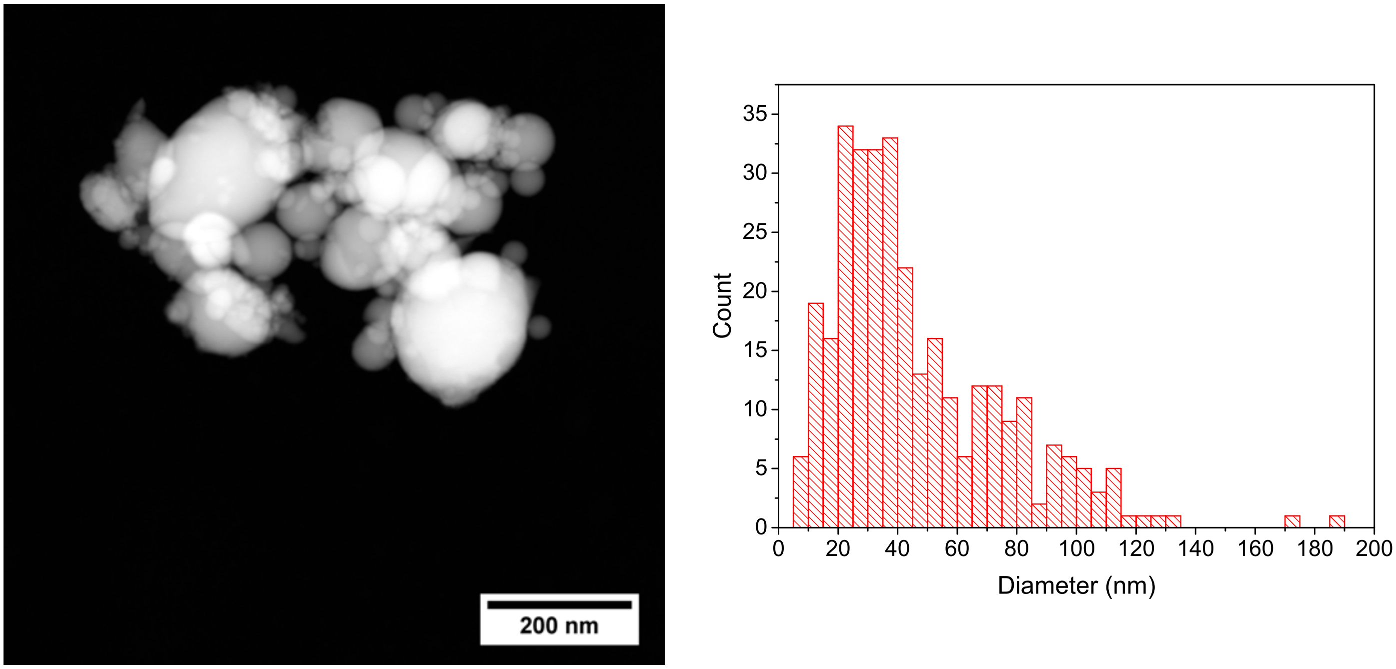

Figure 6 A representative STEM image of H_2O_2/phenol treated EGaIn nanoparticles as well as their corresponding particle size distribution.

XPS Spectra of EGaIn NP Films

From the Ga3d spectra shown in Figure 2, it can be seen that in each sample the Ga3d XPS spectrum is deconvolutable into four major regions; an O2s region (near 24 eV), an In4d region (near 16 eV, further subdivided into 5/2 and 3/2 components in some cases), an elemental Ga3d signal (near 18 eV, subdivisible into 5/2 and 3/2 components), and an oxidized Ga3d signal (attributed generally to Ga_2O_3, also subdivisible into 5/2 and 3/2 components). Following this deconvolution, the area of the Ga3d components (elemental vs. oxidized) are tabulated and used to calculate a fraction of oxidized gallium present. Although calculation of the relative fraction of oxidized gallium in a given sample is useful in a heuristic sense, absolute gallium oxide shell thicknesses are more desirable as they permit better comparison between samples as well as correlation with independent mechanical measurements. To translate from relative measurements to absolute thicknesses, a previously published iterative approach is taken which converges on the absolute thicknesses of shells in core-shell-shell (EGaIn-Ga_2O_3-ligands) particles.[9,10,13] The authors' have previously demonstrated the utility of this technique in examining the impact of thiolation on moderating gallium oxide growth on EGaIn NP systems over time.

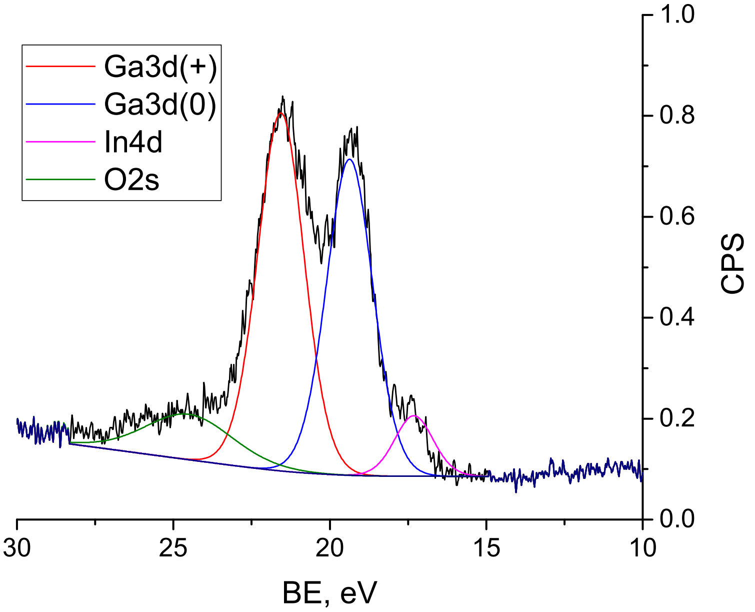

Figure 7 XPS spectrum of the Ga3d transition region for a 30 day old unfunctionalized EGaIn nanoparticle sample with peak deconvolutions for gallium oxide (Ga3d(+)), elemental gallium (Ga3d(0)), indium (In4d), and oxygen (O2s).

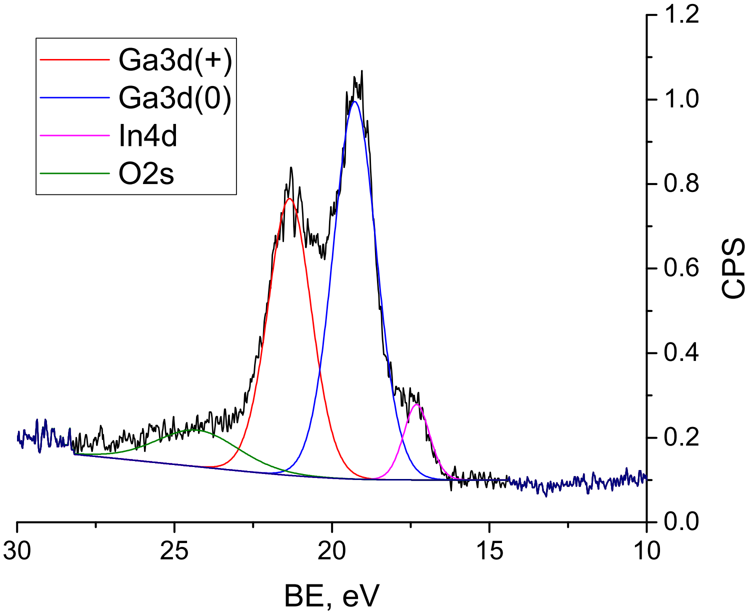

Figure 8 XPS spectrum of the Ga3d transition region for a 1 day old dodecanethiol-functionalized EGaIn nanoparticle sample with peak deconvolutions for gallium oxide (Ga3d(+)), elemental gallium (Ga3d(0)), indium (In4d), and oxygen (O2s).

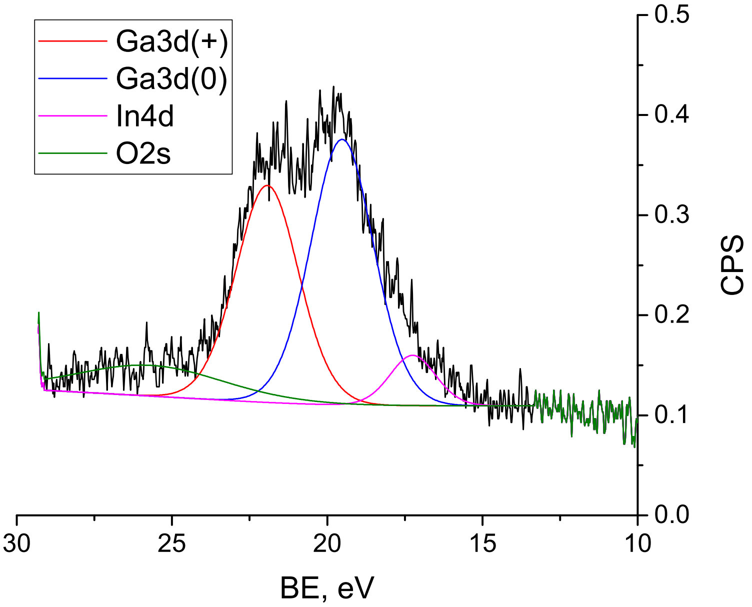

Figure 9 XPS spectrum of the Ga3d transition region for a 30 day old dodecylphosphonic acid-functionalized EGaIn nanoparticle sample with peak deconvolutions for gallium oxide (Ga3d(+)), elemental gallium (Ga3d(0)), indium (In4d), and oxygen (O2s).

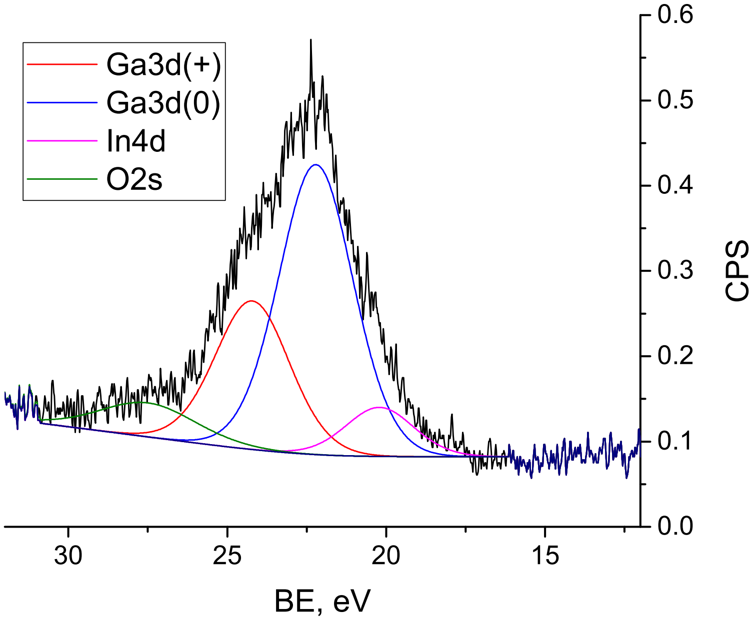

Figure 10 XPS spectrum of the Ga3d transition region for a 1 day old dodecanethiol/dodecylphosphonic acid hybrid-functionalized EGaIn nanoparticle sample with peak deconvolutions for gallium oxide (Ga3d(+)), elemental gallium (Ga3d(0)), indium (In4d), and oxygen (O2s).

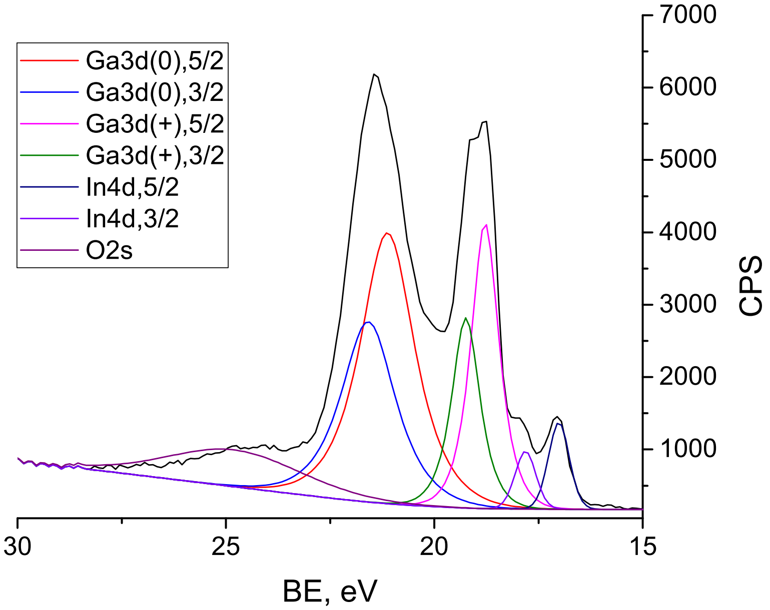

Figure 11 XPS spectrum of the Ga3d transition region for a 100 day old 11-phosphonoundecanoic acid-functionalized EGaIn nanoparticle sample (for EDC coupling) with peak deconvolutions for gallium oxide (Ga3d(+), 5/2 and 3/2), elemental gallium (Ga3d(0), 5/2 and 3/2), indium (In4d, 5/2 and 3/2), and oxygen (O2s).

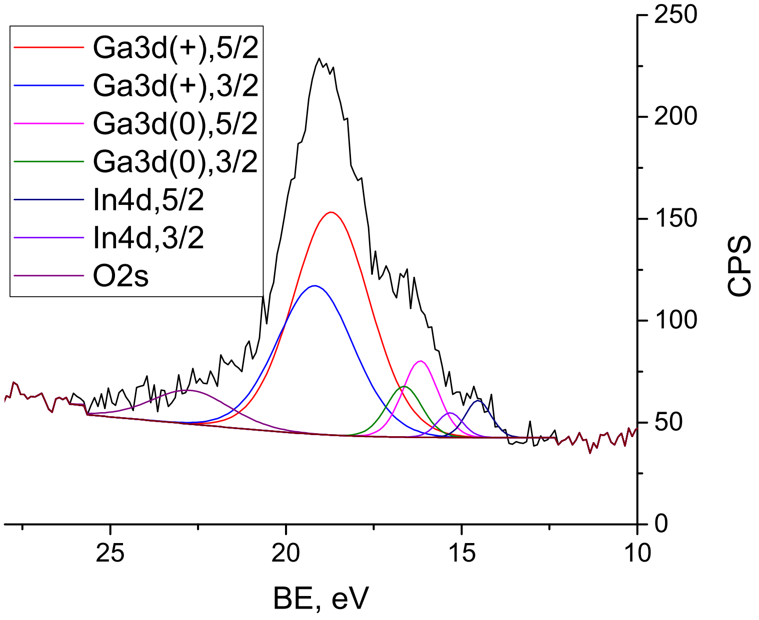

Figure 12 XPS spectrum of the Ga3d transition region for a 28 day old H_2O_2/phenol treated EGaIn nanoparticle sample with peak deconvolutions for gallium oxide (Ga3d(+), 5/2 and 3/2), elemental gallium (Ga3d(0), 5/2 and 3/2), indium (In4d, 5/2 and 3/2), and oxygen (O2s).

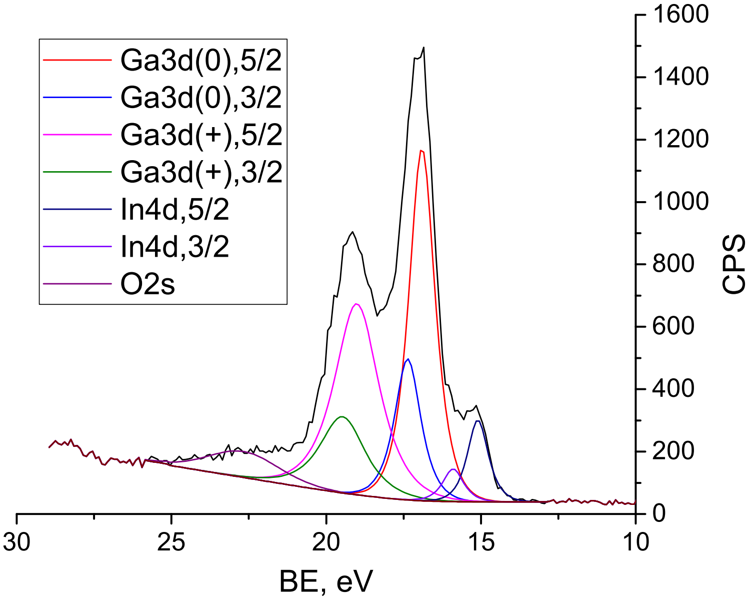

Figure 13 XPS spectrum of the Ga3d transition region for a 28 day old 2,3,4,5,6-pentafluorothiophenol/4-fluorobenzylphosphonic acid functionalized EGaIn nanoparticle sample with peak deconvolutions for gallium oxide (Ga3d(+), 5/2 and 3/2), elemental gallium (Ga3d(0), 5/2 and 3/2), indium (In4d, 5/2 and 3/2), and oxygen (O2s).

Chemical Thickening of Gallium Oxide Shell via H_2O_2/Phenol

As mentioned in the main manuscript body, a chemical treatment protocol was sought and developed to reproduce some of the gallium oxide shell thickening seen in aged samples, without the need to spend months allowing the oxide to naturally progress. To this end, a combination of H_2O_2 and phenol in ethanol was used to treat EGaIn nanoparticle samples after production. As this protocol showed thickened gallium oxide shells in XPS, appropriate controls were set up to determine the effective species/combination in this protocol.

One freshly prepared EGaIn nanoparticle sample (0.8 mL EGaIn) was split into four equal samples and each diluted to 15 mL with absolute ethanol. One sample had no further treatment (control), one sample had 5 mL DI water added, one sample had 5 mL 30% H_2O_2 solution added, and one sample had 5 mL 30% H_2O_2 solution and 50 mg phenol added. These samples were magnetically stirred in sealed vials for 16 hours, centrifuged and washed with fresh absolute ethanol three times, and the final recovered particles redispersed into absolute ethanol. XPS measurements were then taken as described in the main manuscript; the results of these measurements for the Ga3d region are shown in Figure 14.

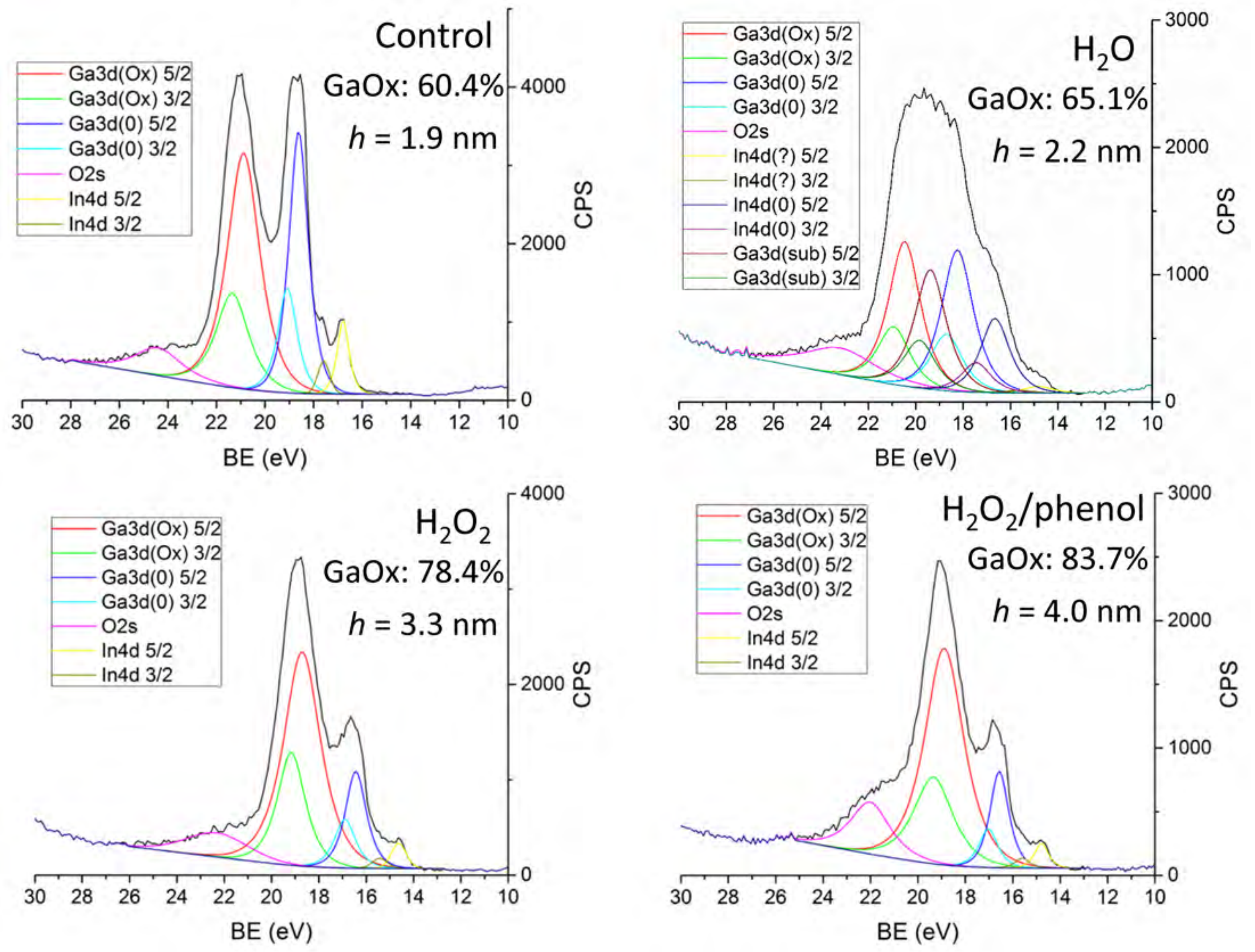

Figure 14 A comparison of the XPS spectra for EGaIn samples treated with a variation of the H_2O_2/phenol chemical thickening protocol to determine the necessity of H_2O_2 and phenol to the process. It is clear that the H_2O_2 is essential for rapid gallium oxide shell thickening and the phenol, while not essential, does significantly increase the shell thickness from 3.3 nm to 4.0 nm. Interestingly, the H_2O-only-treated sample shows a unique Ga3d peak structure, as there appear to be at least three Ga chemical species present. Presently, the intermediate peak is attributed to a defect-rich gallium suboxide.

As the H_2O_2/phenol sample showed the thickest gallium oxide shell of the set, this treatment protocol was adopted as the standard approach for making EGaIn nanoparticles with very thick oxide shells without a need for sample aging.

Nanoindentation Film Images

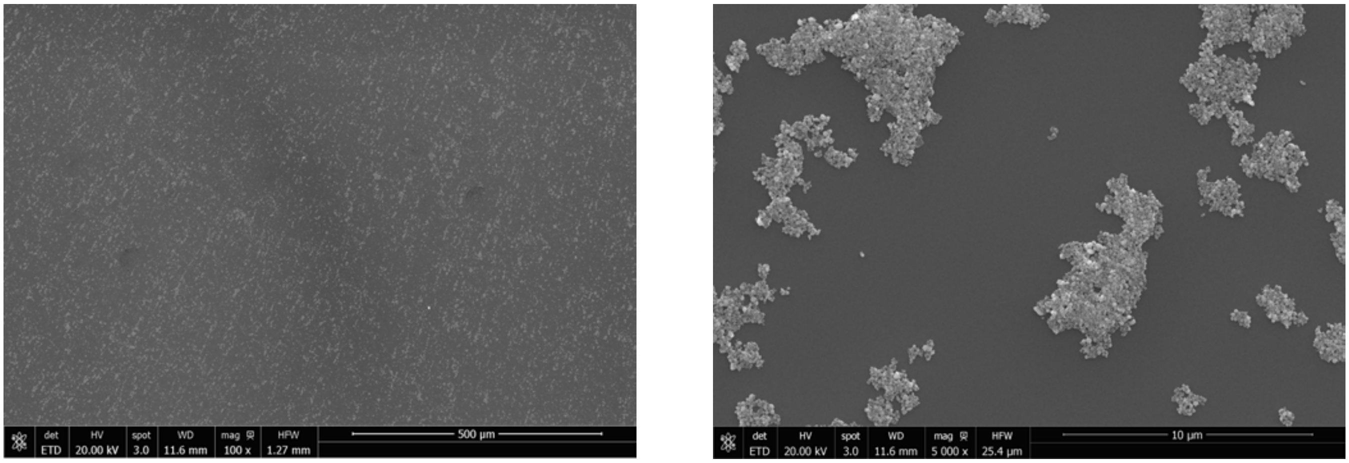

Figure 15 SEM images of unfunctionalized EGaIn particle film produced by spin-coating onto a silicon substrate.

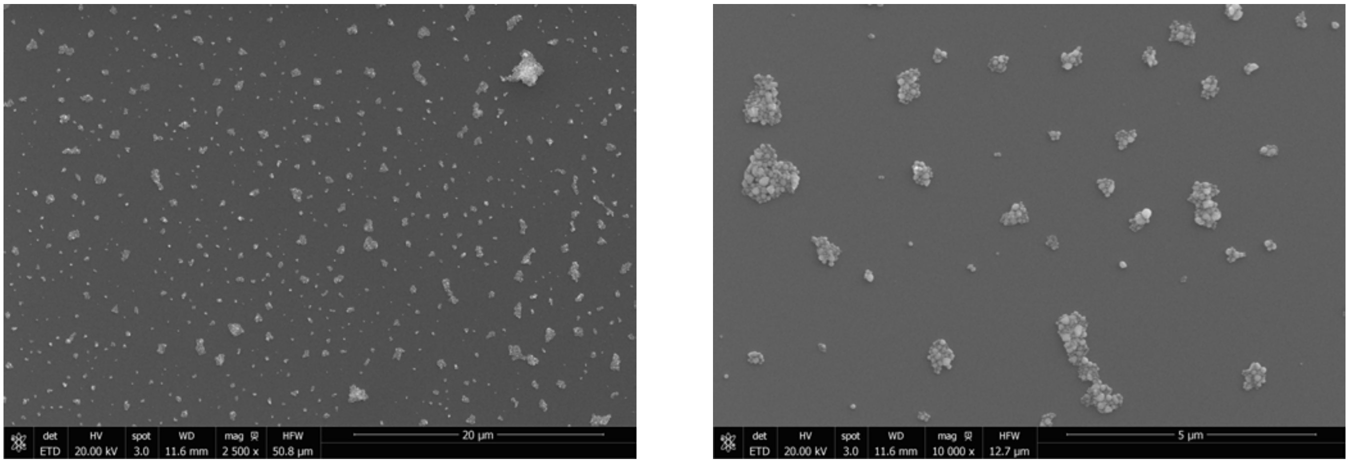

Figure 16 SEM images of dodecylphosphonic acid-grafted EGaIn particle film produced by spin-coating onto a silicon substrate.

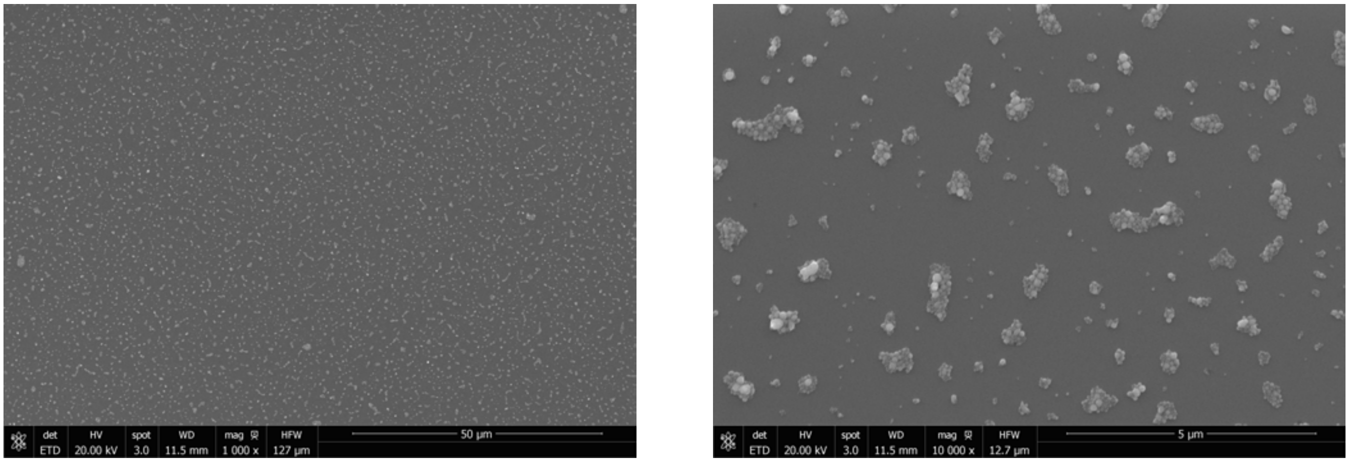

Figure 17 SEM images of dodecanethiol-functionalized EGaIn particle film produced by spin-coating onto a silicon substrate.

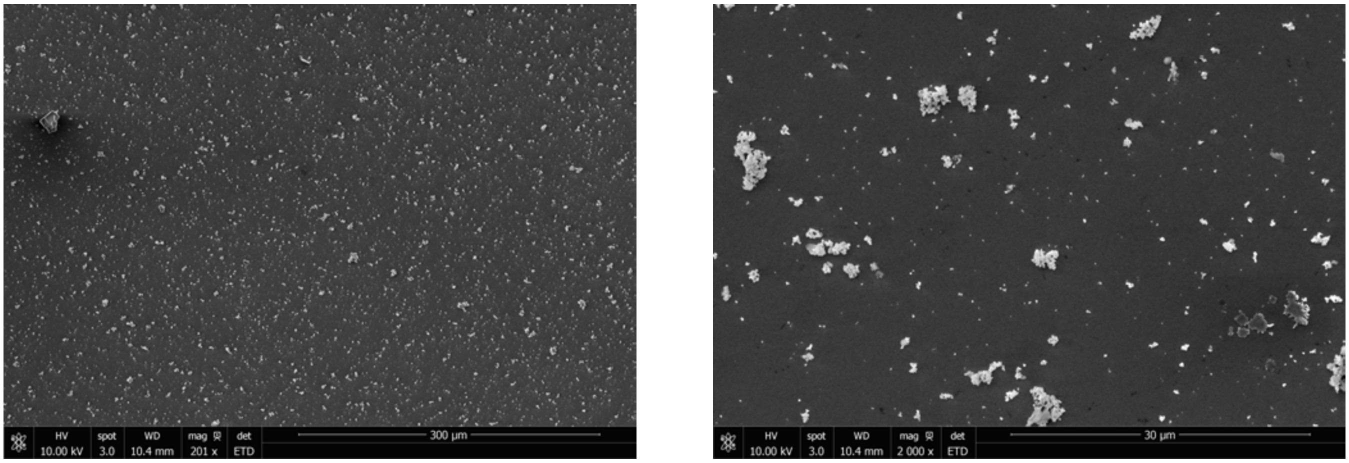

Figure 18 SEM images of H_2O_2-treated EGaIn particles spin-coated onto on ITO-coated glass substrate.

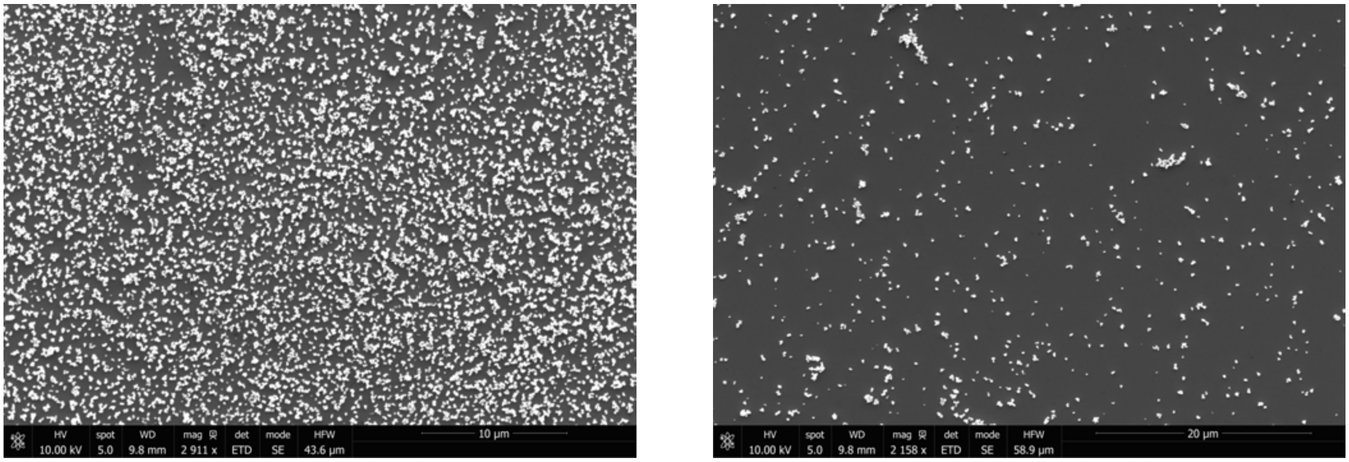

Figure 19 SEM images of 11-phosphonoundecanoic acid functionalized EGaIn particles linked via EDC-coupling to an APTES-functionalized silicon substrate.

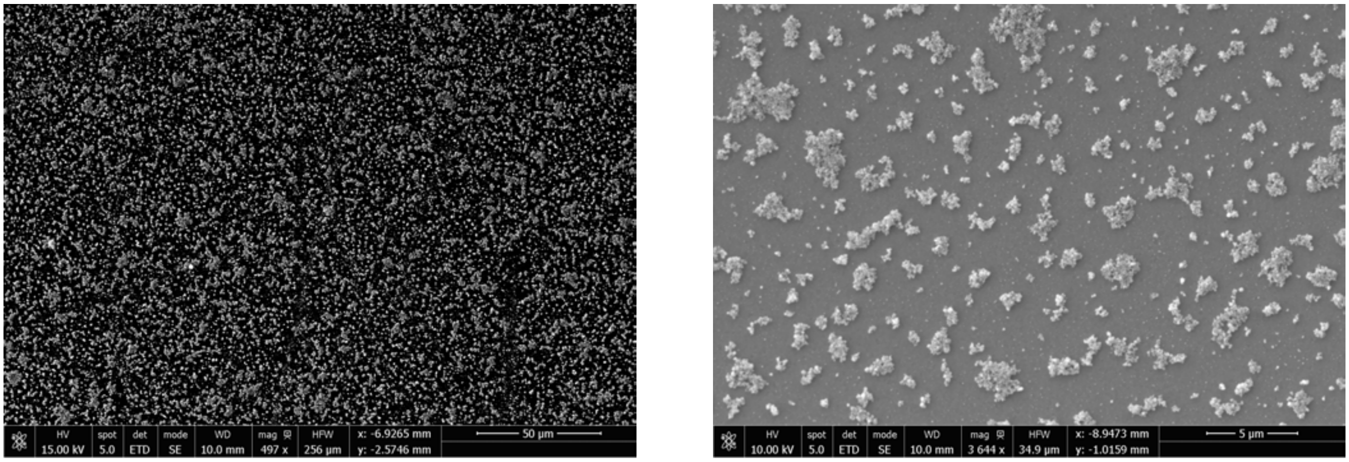

Figure 20 SEM images of 2,3,4,5,6-pentafluorothiophenol/4-fluorobenzylphosphonic acid functionalized EGaIn nanoparticles adsorbed onto an MTES-functionalized ITO-coated glass substrate.

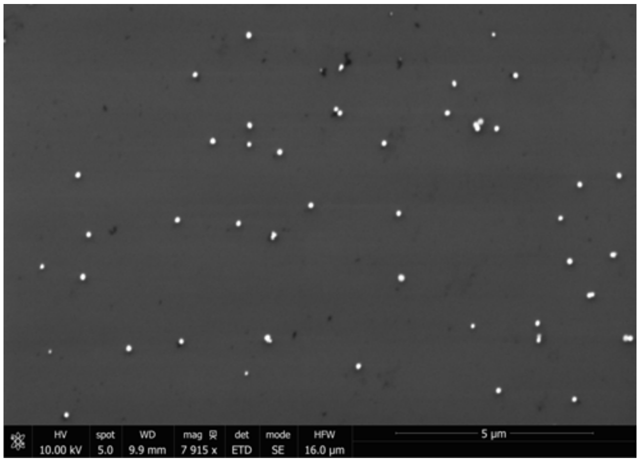

Figure 21 SEM images of citrate-protected silver nanoparticles adsorbed onto an APTES-functionalized silicon substrate.

Particle Coverage Calculations

The number of particles under compression during flat-punch nanoindentation experiments were estimated using SEM analysis of particle coverage in areas directly adjacent to indentation sites. Image analysis was performed on SEM micrographs using the particle counting package of ImageJ. At least three images of each sample were averaged for analysis and care was taken to measure particle coverage near indentation sites.

The estimated average number of particle under the flat-punch indenter tip was estimated using Equation 1

$$N_p = \frac{D_i^2}{D_n^2} p A_{cover} \tag{1}$$

where N_p is the average number of particles underneath the indenter tip, D_i is the diameter of the cylindrical indenter, D_n is the measured average particle diameter, p is the areal packing factor of 0.82 for random packing, and A_{cover} is the average area fraction of particle coverage for each sub-monolayer film, determined though SEM image analysis.[14]

Nanoindentation of Silver Nanoparticles

Silver nanoparticles were used as a calibration standard for nanoindentaton experiments. Ag nanoparticles of comparable size were prepared (Figure 22).

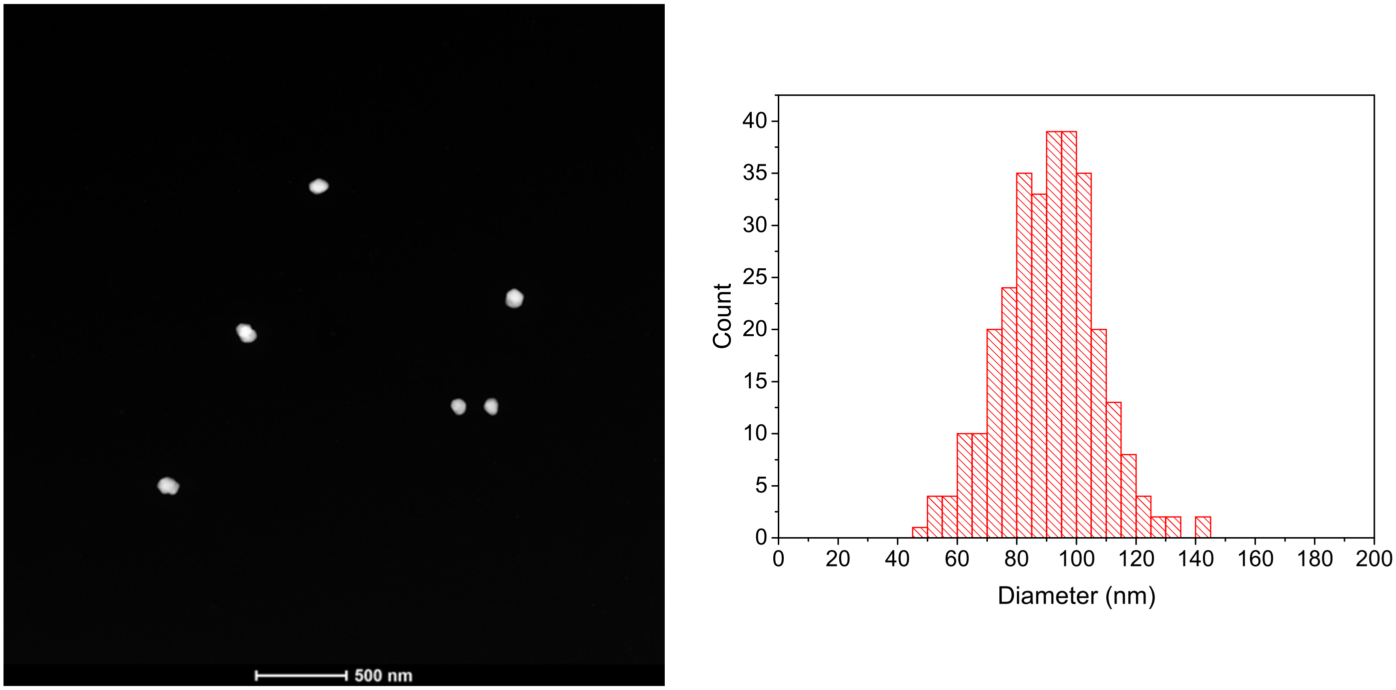

Figure 22 A representative STEM image of the silver nanoparticles used in benchmarking the nanoindentation methods and their corresponding particle size distribution.

Nanoindentation experiments were performed on cast sub-monolayer films on bare silicon, matching the procedure for EGaIn core-shell particle systems. The stiffness was measured and the indentation modulus was calculated using Equation 2.

For the case of a flat punch indenter:

$$E_{ind} = \frac{\pi}{2} \frac{s}{\sqrt{A_p}} \tag{2}$$

where E_{ind} is the indentation modulus, s is the stiffness measured from the intial portion of the load-displacement curves, and A_p is the projected contact area between the nanoparticles and the flat diamond surface of the indenter tip.

Based on Hertzian contact theory, the reduced modulus was calculated using Equation 3.

$$\frac{1}{E_r} = \frac{1-\nu_p^2}{E_p} + \frac{1-\nu_i^2}{E_i} \tag{3}$$

where E_r is the reduced modulus of the indenter and the sample, ν_p and E_p are the Poisson's Ratio and elastic modulus of the particle film, and ν_i and E_i are the Poisson's Ratio and elastic modulus of the indenter.[15] Because the diamond indenter is considered nondeformable in comparison to the silver nanoparticles, its component of the reduced modulus was considered negligible in this study.

Single particle stiffnesses and calculated particle indentation modulus values are shown in Figure S23 and matched well with the expected bulk values for silver (76.0 GPa).[16]

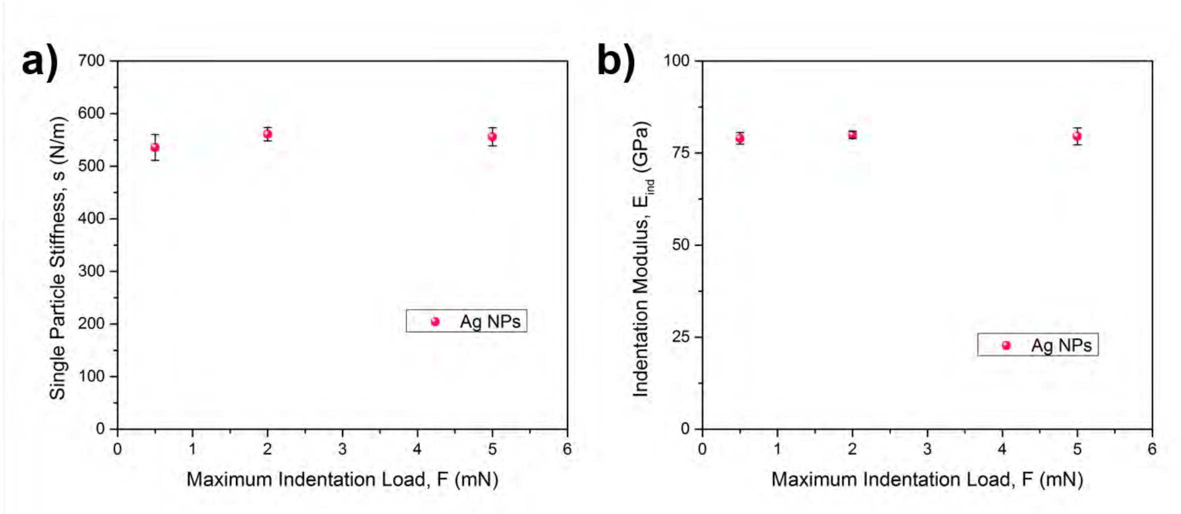

Figure 23 a) Single particle stiffness for Ag nanoparticles used as a calibration standard and method verification b) Calculated indentation modulus as a function of maximum applied load for Ag nanoparticles.

Conductive Tip Nanoindentation

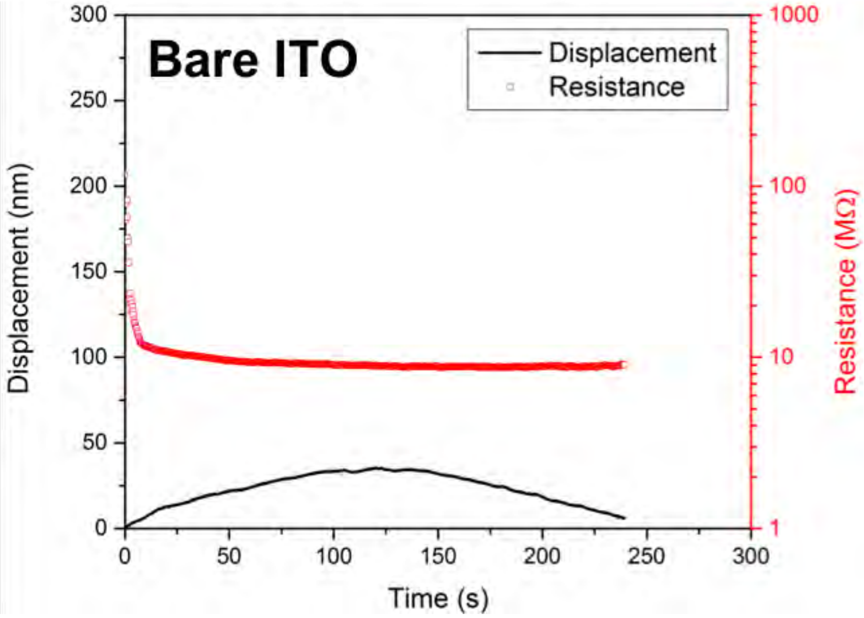

Figure 24 Conductive tip nanoindentation graph with no particles between the tip and virgin ITO surface.

References

[1] T. R. Lear, S. H. Hyun, J. W. Boley, E. L. White, D. H. Thompson and R. K. Kramer, *Extreme Mech. Lett.*, 2017, **13**, 126–134.

[2] X. Y. Yin and G. S. Collins, in *The Solubility of Indium in Liquid Gallium Supercooled to 12 K*, Trans Tech Publications, 2012, vol. 323, pp. 503–508.

[3] P. Patnaik, *Handbook of Inorganic Chemicals*, McGraw-Hill, 2003.

[4] P. J. Hotchkiss, S. C. Jones, S. A. Paniagua, A. Sharma, B. Kippelen, N. R. Armstrong and S. R. Marder, *Accounts Chem. Res.*, 2012, **45**, 337–346.

[5] Z. J. Farrell, N. Reger, I. Anderson, E. Gawalt and C. Tabor, *J. Phys. Chem. C*, 2018, **122**, 26393–26400.

[6] N. G. Bastus, F. Merkoci, J. Piella and V. Puntes, *Chem. Mater.*, 2014, **26**, 2836–2846.

[7] J. C. Rife, R. N. Dexter, P. M. Bridenbaugh and B. W. Veal, *Phys. Rev. B*, 1977, **16**, 4491–4500.

[8] R. I. Blyth, F. P. Netzer and M. G. Ramsey, *Surf. Sci.*, 2000, **465**, 120–126.

[9] Z. J. Farrell and C. Tabor, *Langmuir*, 2018, **34**, 234–240.

[10] D. J. H. Cant, Y. C. Wang, D. G. Castner and A. G. Shard, *Surf. Interface Anal.*, 2016, **48**, 274–282.

[11] M. Seah, *Surf. Interface Anal.*, 2012, **44**, 497–503.

[12] Interchim, *Carbodiimides (EDAC) - Heterobifunctionnal Cross-Linkers*.

[13] A. G. Shard, *Journal of Physical Chemistry C*, 2012, **116**, 16806–16813.

[14] H. Kausch, D. Fesko and N. Tschoegl, *Journal of Colloid and Interface Science*, 1971, **37**, 603–611.

[15] A. C. Fischer-Cripps, in *Analysis of Nanoindentation Test Data*, Springer New York, New York, NY, 2011, pp. 39–75.

[16] R. B. Ross, in *Silver Ag*, Springer US, Boston, MA, 1992, pp. 286–292.