

Tunable Infrared Absorption and Visible Transparency of Colloidal Aluminum-Doped Zinc Oxide Nanocrystals

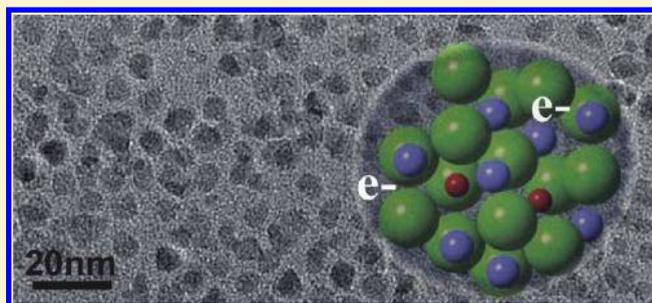
Raffaella Buonsanti, Anna Llordes, Shaul Aloni, Brett A. Helms, and Delia J. Milliron*

The Molecular Foundry, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, MS 67R4110, Berkeley, California 94720, United States

S Supporting Information

ABSTRACT: Plasmonic nanocrystals have been attracting a lot of attention both for fundamental studies and different applications, from sensing to imaging and optoelectronic devices. Transparent conductive oxides represent an interesting class of plasmonic materials in addition to metals and vacancy-doped semiconductor quantum dots. Herein, we report a rational synthetic strategy of high-quality colloidal aluminum-doped zinc oxide nanocrystals. The presence of substitutional aluminum in the zinc oxide lattice accompanied by the generation of free electrons is proved for the first time by tunable surface plasmon absorption in the infrared region both in solution and in thin films.

KEYWORDS: Nanocrystals, metal oxide, doping, synthesis design, plasmon absorption



Aluminum-doped zinc oxide (AZO), with its comparable optical and electronic properties, represents a lower cost, less toxic, Earth-abundant alternative to the widely used transparent conducting oxide (TCO), indium tin oxide (ITO).¹ At the same time, TCO nanocrystals (NCs) have recently gained interest owing to both the low cost of solution processing and the potential to exploit size-dependent properties.^{2–8} Deposition of colloidal TCO NCs as a nanoink is highly appealing for integration into emerging flexible electronics, such as displays, electronic paper, or solar cells.⁹ Moreover, their significantly higher surface area than conventionally deposited TCO thin films could enable improvements in devices like electrochromic windows and dye-sensitized solar cells, as well as biosensors.^{10–16}

While the synthesis of ITO colloidal NCs has recently advanced markedly, it remains still a challenge to control dopant incorporation along with size, shape, and solvent dispersibility in zinc oxide based TCO NCs, i.e., aluminum-doped zinc oxide (AZO), indium-doped zinc oxide (IZO), or gallium-doped zinc oxide (GZO).^{2–8}

Only when the dopants occupy substitutional sites in the interior of the particles are free carriers introduced and the desired electrical and optical properties achieved.^{17–20} Carefully balancing crystal growth and dopant incorporation rates is thus obligatory.

Here, we report the synthesis of AZO nanocrystals with simultaneous control of nanocrystal size and doping level. Reactivity of aluminum (Al) and zinc (Zn) precursors was balanced by rational selection of coordinating ligands to facilitate tuning the Al content from 0 to 8% while achieving size control between 5 and 20 nm by changing the growth temperature.

Effective dopant incorporation is demonstrated by tracking free carrier absorption in the infrared region.

In a typical synthesis, performed under argon, a precursor solution containing zinc stearate (ZnSt_2 , 1 mmol), aluminum acetylacetonate ($\text{Al}(\text{acac})_3$, 0.05–0.5 mmol), and oleic acid (OLAC, 3 mmol) in 4 mL of octadecene (ODE) was injected at high temperature (230–260 °C) into a three-neck flask containing 1,2-hexadecanediol (HDDIOL, 10 mmol) in 11 mL of octadecene (ODE). The temperature dropped ($\Delta T = 20$ °C) following injection, and the reaction mixture was held at this lower temperature for 5 h, resulting in a narrow size dispersion of AZO NCs. By contrast, including all the reagents in the flask and slowly heating this mixture from room temperature resulted in highly polydisperse NCs (Figure S1 in the Supporting Information). The NCs were collected by centrifugation, washed with ethanol, and redispersed in a nonpolar solvent, such as hexane, toluene, or chloroform.

The size, shape, and crystallinity of the AZO NCs were assessed by both low- and high-resolution transmission electron microscopy (TEM) (Figure 1).

Depending on the injection temperature, for a fixed $\text{Al}(\text{acac})_3$: ZnSt_2 molar ratio, different sizes can be obtained (Figure 1A–C and Figures S2 and S3 in the Supporting Information). AZO NCs with diameters of 5, 10, and 15 nm with a standard deviation within 15% and an isotropic shape were obtained at 230, 240, and 260 °C, respectively, for $\text{Al}(\text{acac})_3$: ZnSt_2 1:5 (Figure 1A–C and Figure S2 in the Supporting Information). High-resolution TEM

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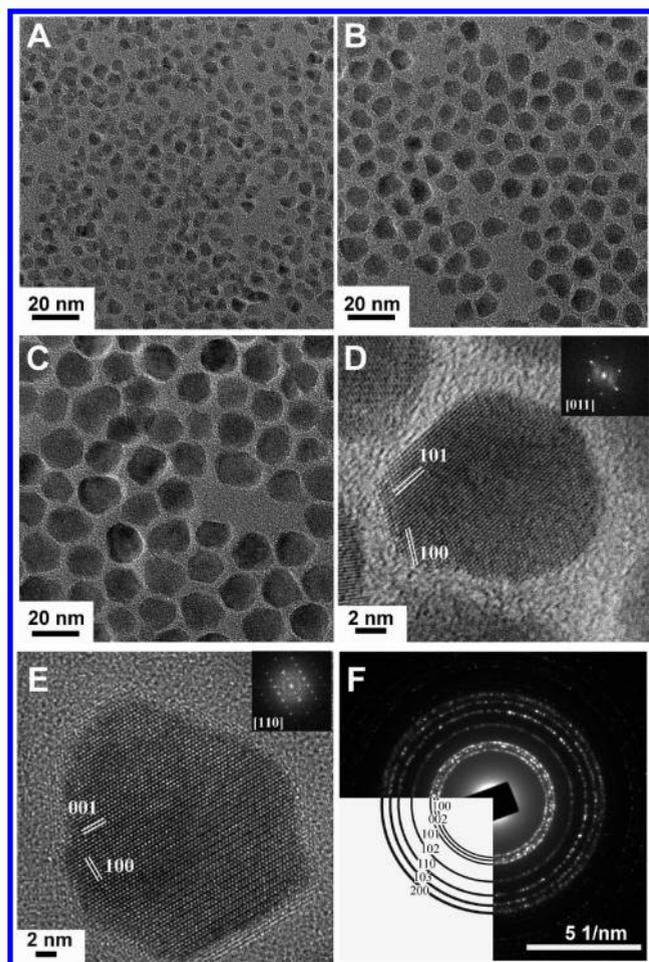


Figure 1. Low- and high-resolution TEM images of AZO NCs. (A–C) AZO NCs of different sizes were obtained by injecting precursor solutions containing 0.2 mmol of $\text{Al}(\text{acac})_3$ at 230, 240, and 260 °C, respectively. (D) HRTEM image of a pseudospherical AZO NC oriented along the [011] zone axis and the corresponding fast Fourier transform (FFT) in the inset indicating the hexagonal structure of the wurtzite. The lattice fringes correspond to spacings of 2.42 and 2.79 Å derived from FFT which match well the d spacing of the (101) ($d_{\text{ZnO}}^{101} = 2.47$ Å) and (100) planes ($d_{\text{ZnO}}^{100} = 2.81$ Å) of wurtzite ZnO. (E) HRTEM image of a bullet-shaped AZO NC oriented along the [110] zone axis and the corresponding FFT in the inset. The lattice fringes correspond to 2.79 and 2.58 Å, derived from FFT, consistent with the (100) and the (001) ($d_{\text{ZnO}}^{001} = 2.60$ Å) planes, respectively, of wurtzite ZnO. (F) Electron diffraction of AZO NCs with the expected wurtzite pattern indicated in the lower left.

analysis of typical NCs revealed that they were single crystalline with pseudospherical or bullet-like shapes (Figure 1D,E). The lattice fringes matched well the hexagonal wurtzite phase of ZnO, which was confirmed by electron diffraction (Figure 1F). No structural defects were apparent as a consequence of doping.

To evaluate dopant incorporation, the aluminum content of the AZO NCs was assessed by elemental analysis, performed with an inductively coupled plasma atomic emission spectrometer (ICP-AES, Table 1). The composition determined by elemental analysis was in close agreement with that obtained by energy-dispersive X-ray spectroscopy (EDX) performed on individual NCs (Figure S4 in the Supporting Information). Thus, the Al detected by ICP-AES analysis was indeed that

Table 1. ICP-AES Analysis of AZO NCs Synthesized at Different Temperatures and Metal Precursor Ratios^a

| $T_{\text{inj}}/T_{\text{growth}}$ (°C) | $\text{Al}(\text{acac})_3$ (mmol) ^b | Al atomic % |
|---|--|-------------|
| 260/240 | 0.2 | 7.3 |
| 240/220 | 0.2 | 5.5 |
| 230/210 | 0.2 | 4.4 |
| 230/210 | 0.05 | 1.4 |
| 230/210 | 0.1 | 3.5 |
| 230/210 | 0.3 | 5.2 |
| 230/210 | 0.5 | 6.2 |
| 230/210 | 1 | 20 |

^a TEM images corresponding to the listed sample are shown in Figures S3 and S12 in the Supporting Information. ^b The amount of ZnSt_2 is constant at 1 mmol.

incorporated into the NCs and not due to excess aluminum precursor or other species in solution.

Increasing the aluminum precursor concentration in the growth medium, for a fixed injection temperature, resulted in greater Al incorporation into the NCs, while contributing to increase the NC size (even if with less extent than temperature) and the shape anisotropy (Figure S3 in the Supporting Information). The aluminum incorporation itself and/or the higher concentration of acetylacetonate in the reaction mixture could both contribute to this effect.^{21,22}

Growth temperature also played a critical role in terms of doping content. In particular, for a fixed $\text{Al}(\text{acac})_3:\text{ZnSt}_2$ molar ratio, more Al was incorporated into the NC lattice at higher reaction temperatures. This trend is contrary to that expected on the basis of self-purification since diffusion of dopants to the surface would be enhanced at higher temperatures corroborating the main role played by kinetics versus thermodynamics also in these doped metal oxide nanocrystals.^{23–27} It highlights the importance of reaction kinetics for controlling dopant incorporation although, owing to the complexity of the reaction system, it is difficult to propose a complete explanation of the effect of temperature. Nonetheless, further insight into the interplay between growth kinetics and doping was found by investigating the growth mechanism and by making systematic variations in the coordinating ligands of the metal precursors.

By Fourier transform infrared spectroscopy (FTIR), we found that esters were a byproduct of the NC growth reaction (Figure S5 in the Supporting Information), indicating that an alcoholysis reaction took place. Specifically, the carbonyl groups of the ZnSt_2 can undergo nucleophilic attack by HDDIOL to form esters. Polycondensation reaction of the resulting hydroxylated zinc precursors subsequently produces a nanocrystalline $[\text{Zn}-\text{O}]_n$ network. The predominant role of HDDIOL in the growth mechanism was confirmed by the lack of any recoverable product when HDDIOL was omitted from the reaction mixture. Also, when less sterically hindered shorter-chain diols were substituted, highly anisotropic shapes were obtained (Figure S6 in the Supporting Information), consistent with a more rapid crystal growth.²⁸

Considering that alcoholysis dominates the reaction pathway, the rate of monomer addition to the growing NCs can be tuned by varying the coordinating ligands to the metals. Since Al^{3+} is a harder Lewis acid than Zn^{2+} , an aluminum precursor with the same carboxylate ligands as Zn^{2+} should be much less reactive. Indeed, we observed far less Al incorporation when a

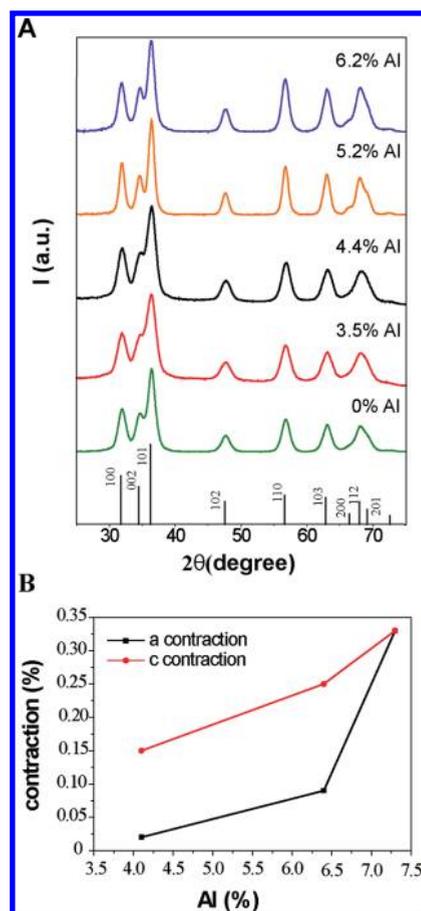


Figure 2. (A) X-ray diffraction patterns and (B) variation of lattice parameters derived from Rietveld analysis for AZO NCs with different Al content. The reference diffraction pattern of bulk wurtzite is shown at the bottom of (A) (JPCD 5-0664).

more reactive Zn precursor, such as zinc acetate or zinc acetylacetonate, was substituted for ZnSt_2 . Likewise, when AlSt_3 was used in place of $\text{Al}(\text{acac})_3$, no doping was achieved. While FTIR suggests that OLAC partially substitutes the acac ligands of Al (Figure S7 in the Supporting Information), in addition to acting as a passivating ligand at the AZO surface (Figure S8 in the Supporting Information), the Al precursor remained sufficiently reactive to introduce appreciable doping at the slow growth rates enforced by employing a ZnSt_2 precursor.

The structural implications of dopant incorporation in the AZO NCs were probed by X-ray diffraction (XRD) (Figure 2A). At all doping levels, the patterns were readily assigned to the wurtzite phase, with no other crystalline phases, such as aluminum oxide (Al_2O_3) or gahnite (ZnAl_2O_4) which are common secondary phases in AZO thin films, emerging.^{17,19} In each case, the line broadening in the Bragg peaks was consistent with coherent domain sizes at the nanoscale. In addition, there were no significant alterations in the relative intensity compared to the standard wurtzite pattern, in agreement with the isotropic shape observed by TEM.

Refining structural and microstructural parameters by Rietveld analysis, we obtained the lattice parameters, domain sizes, and inhomogeneous lattice strain of our AZO NCs and, for reference, undoped ZnO NCs (Figure S9 in the Supporting Information). As generally observed for metal oxide NCs, the ZnO lattice expands slightly as size decreases.²⁹ Furthermore,

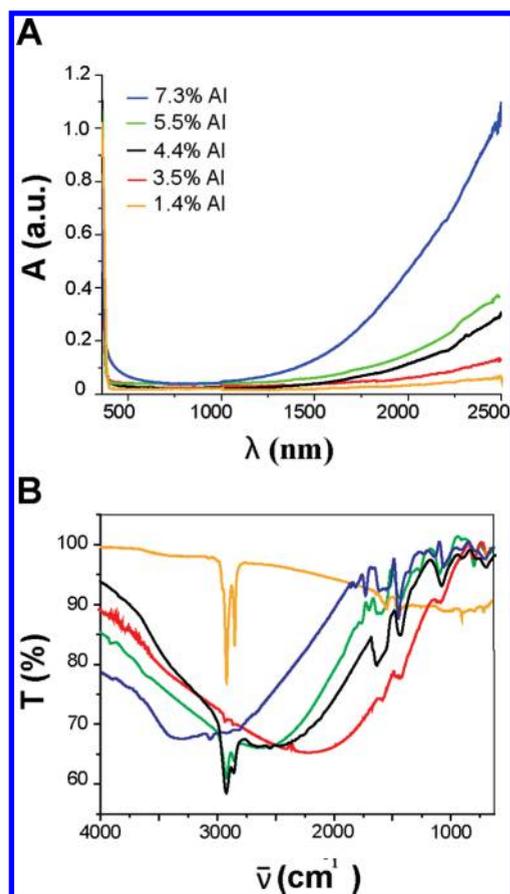


Figure 3. Optical properties of AZO NCs: (A) vis-NIR absorbance of equimolar dispersions and (B) FTIR spectra of AZO NCs containing varying degrees of Al doping. The additional sharper peaks in the FTIR spectra come from the organic ligands present on the surface of the nanoparticles. (TEM images of the samples corresponding to the spectra are shown in Figure S3 in the Supporting Information.)

comparing AZO NCs to ZnO NCs of similar size, the lattice contracts with increasing Al incorporation (Figure 2B). This is consistent with the substitution of smaller Al^{3+} ions (radius 0.53 Å) on Zn^{2+} (radius 0.74 Å) lattice sites. By contrast, interstitial Al^{3+} should induce lattice expansion.^{18,19} While the lattice contracts along both the a and c axes of the hexagonal wurtzite unit cell, the c axes varied to a greater extent, particularly at lower doping levels, perhaps due to some preferential site occupation of the Al. Moreover, the incorporation of Al in the lattice induced a substantial increase of the inhomogeneous strain in doped samples (Figure S9 in the Supporting Information).

The efficacy of doping toward the generation of free carriers can be directly assessed from the optical properties of the NCs. The appearance of absorption in the infrared region (IR) is a clear signature of n-doping and can be attributed to surface plasmon absorption in the case of AZO.^{30–32,6,7} To the best of our knowledge, this is the first report of the optical properties of AZO NC dispersions, which was facilitated by the excellent solvent dispersibility and uniformity of our NCs. As the Al doping concentration was increased from 1.4 to 7.3%, the IR absorption increased monotonically (Figure 3A). The absorption peak (Figure 3B) shifted systematically to higher energy with increasing Al content. The extinction at the low energy edge of the absorption peaks diminishes at higher doping levels,

contrary to the spectral characteristics expected for filling of localized trap states.^{30–32} These optical properties provide strong evidence that the IR absorption is, in fact, surface plasmon absorption and that the Al occupies substitutional sites, effectively creating free electrons in the NCs.^{17–20}

Free electrons introduced by doping accumulate in the conduction band, which should cause an increase of the optical band gap, known as the Burstein–Moss effect, besides the surface plasmon absorption in the IR.^{33–35} The optical band gaps ($E_{g,opt}$) of AZO NCs with different aluminum content were determined from linear fits to plots of $(\alpha h\nu)^2$ versus the photon energy ($h\nu$) extrapolating to $\alpha = 0$, since ZnO is a direct band gap semiconductor (Figure S10 in the Supporting Information).³⁶ The resulting values were compared to undoped ZnO NCs of similar size in order to exclude any contribution of quantum confinement (Table 2).

The progressive blue shift of the band gap is another clear indication of effective Al doping.^{33–35} Again, this effect was clearly observable owing to the high quality and uniformity of our AZO NCs.

Even at the higher doping levels, the NCs remained highly transparent across the visible region (Figure S11 in the Supporting Information). However, attempting to further increase the

doping level beyond 8% resulted in scattering in the visible region with no further increase in IR absorption (Figure S12 in the Supporting Information). These nanoparticles appeared larger by TEM, yet the crystallite size determined by XRD was not substantially increased (Figures S9 and S12 in the Supporting Information). Rather than increasing the substitutional dopant concentration, it may be that domains of an amorphous material, such as Al_2O_3 , are forming when the concentration of aluminum precursor is very high.

Finally, for many applications it is necessary to deposit the NCs as a film while preserving the optical and electronic properties. By drop casting AZO NCs from a dispersion in 85:15 hexane/octane, very uniform films were obtained (Figure 4A–C). There was no scattering, the films were completely transparent in the visible region (Figure S11 in the Supporting Information), and a prominent surface plasmon peak in the IR region indicates that effective doping is preserved (Figure 4D).

In conclusion, we have shown how a rational selection of precursors and reaction conditions makes possible the manipulation of the ZnO NC growth rate in order to obtain monodisperse particles with different sizes simultaneously with effective Al doping. The NC size and IR absorption, related to the number of Al atoms incorporated in the nanocrystals, both increase over the course of the reaction time (Figure S13 in the Supporting Information), which suggests that dopants may be excluded from the initial nuclei and only incorporated as growth progresses.^{24–26} The radial inhomogeneous distribution of the dopants emerges also from energy-dependent XPS data (Figure S14 in the Supporting Information) and could account for the large inhomogeneous strain found by Rietveld analysis (Figure S9 in the Supporting Information). The uniformity and dispersibility of our AZO NCs allowed observation of a distinct surface plasmon feature, tunable by varying the

Table 2. Extrapolated Optical Band Gaps for AZO NCs with Different Aluminum Content

| Al (%) | $E_{g,opt}$ (eV) |
|--------|------------------|
| 0 | 3.32 |
| 1.4 | 3.37 |
| 3.5 | 3.38 |
| 4.4 | 3.39 |
| 6.2 | 3.50 |
| 7.3 | 3.54 |

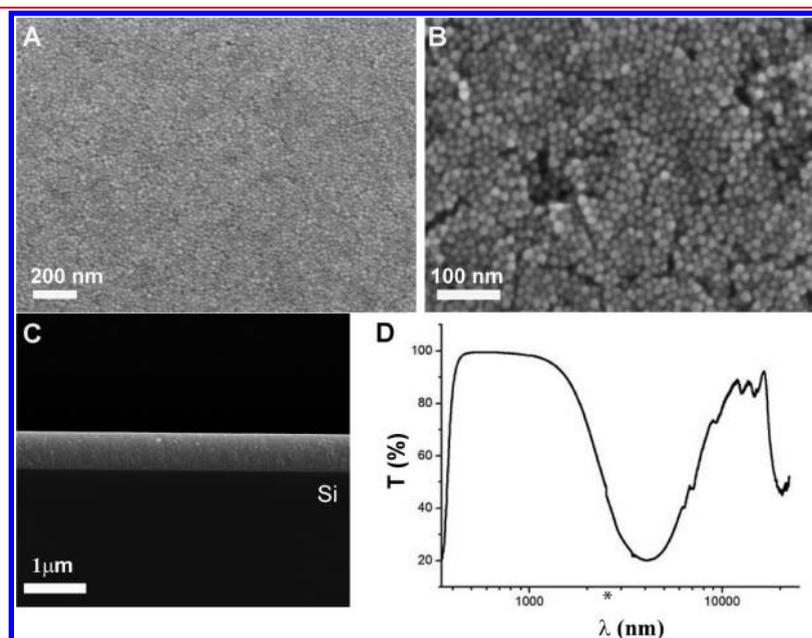


Figure 4. Morphological and optical characterization of a thin film of 15 nm AZO NCs with a 7.3% Al content. (A) Low- and (B) high-magnification top-view scanning electron microscopy (SEM) images and (C) cross-sectional-view SEM image of the AZO film deposited on silicon. (D) Transmittance of the AZO film. This wide range spectrum has been obtained by combining a spectrum from 350 to 2500 nm of a film deposited on quartz, recorded by a visible/NIR spectrophotometer, with a spectrum from 2500 to 25000 nm of a film deposited on silicon, acquired by FTIR. The peak at long wavelength (20235 nm) corresponds to the Zn–O vibration. The symbol (*) on the x axis indicates the junction point between the two spectra.

doping level. This result opens up the way both to fundamental studies toward a deeper understanding of the influence of the free electrons on the properties of metal oxide nanocrystals and to promising practical applications for AZO NCs.^{30–32} In particular, AZO NCs could be used as a lower cost and more environmental friendly alternative to ITO NCs in a wide range of applications, from displays and smart windows to even bioelectronic devices.^{10–16} Moreover, having shown for the first time the tunability of surface plasmon absorption in the NIR for AZO NCs enables their use even in more specific optical-based application, such as waveguide modulators and switches at telecommunication wavelengths.^{37–40}

■ ASSOCIATED CONTENT

S Supporting Information. Experimental details, additional TEM images, size distribution histograms, EDX analysis, FTIR and NMR measurements on purified nanocrystals, Rietveld refinement details, band gap extrapolation plots, evolution over time of the optical spectrum and XRD pattern along with aluminum content, and energy-dependent XPS. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dmilliron@lbl.gov.

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