Ambient Pressure, Low-Temperature Synthesis and Characterization of Colloidal InN Nanocrystals

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Ambient pressure, low-temperature synthesis and characterization of colloidal InN nanocrystals

Jennifer C. Hsieh, Dong Soo Yun, Evelyn Hu and Angela M. Belcher

Highly soluble, non-aggregated colloidal wurtzite InN nanocrystals were obtained through an ambient pressure, low-temperature method followed by post-synthesis treatment with nitric acid.

Group III nitrides have attracted much attention for their optical and electronic properties, such as a wide range of direct band gaps and high electron mobility. Of the three nitrides—AlN, GaN, and InN—InN has been the least studied, but recent results have shown strong potential for a variety of applications: its small effective mass and large intervalley energy separation promise high electron mobility for high-frequency devices, its direct band gap and possibility for alloying with other III-nitride materials hold promise for broad-spectrum solar cell devices. Exploring the possibilities for InN has provided much motivation for understanding its intrinsic materials properties, especially in light of the recently settled debate about its band gap. Amended from the previously accepted value of 1.9 eV, it is now widely accepted that the true band gap lies around 0.65–0.7 eV. InN still remains a material with poor thermal stability and without suitable lattice-matched substrates for epitaxial growth. Therefore, one approach for studying the material is to eliminate the need for a substrate and synthesize InN as free-standing nanowhiskers. The formation of nanocrystalline InN makes possible the heterogeneous integration of InN with other materials and device structures, and allows for integration with the biological regime. In addition, it is of interest to understand how defining characteristics, such as polarization, are manifested at the nanoscale. While several groups have grown InN nanoparticles through solvothermal autoclave methods, ammonolysis, thermal decomposition of indium–urea complexes, or solid-state metathesis reactions, the results were typically large agglomerations of nanocrystalline InN with no reports of high-yield colloidal solubility in organic or aqueous solvents.

Many groups have reported the formation of indium metal as a byproduct of InN nanoparticle synthesis. Wells and Janik were unsuccessful using InBr3 and Li2N as precursors, influencing other researchers, such as Xiao et al. and Wu et al. to specifically avoid InBr3 in solvothermal methods. They cited InBr3’s weaker covalent bond, as compared to In2S3 and InI3, as a low barrier to indium metal formation, despite mild success in solid-state metathesis reactions. In our work, we opted to re-examine the pyrolysis of In(NH2)2 from InBr3 and NaNH2 because these precursors are commercially available, relatively inexpensive, and easily handled. We found that not only could the metal in the resulting mixed metal–nitride product be preferentially removed, but it was also critical in making high-yield colloidal InN nanoparticles.

In the present work, we report a synthesis process for single-phase wurtzite InN nanocrystals using a previously dismissed simple halide salt precursor, InBr3. In addition, our method functions at both low-temperature (250 °C) and ambient pressure, which reduces many of the complications implicit to autoclave, solvothermal-based procedures. Post-reaction processing of the resulting mixed metal–nitride aggregates released the nitride nanoparticles from the large aggregations. Subsequently, when combined with an appropriate surfactant, these individual nanoparticles were easily dispersed in organic solvents, forming brown transparent solution. Our colloidal nanoparticles are substrate independent, amenable to large-area deposition methods, and allow for optical measurements of non-aggregated InN nanoparticles.

In a typical synthesis, 1 mmol of InBr3 was combined with 3 mmol of NaNH2 in 10 mL of hexadecane under a nitrogen atmosphere. For the duration of the reaction, ammonia gas flowed through the flask, creating an oxygen-free atmosphere and allowing the synthesis to remain at ambient pressure. The solution was stirred briskly and heated to 180 °C for 10 min, then ramped to 250 °C over 3 h. The solution was held at 250 °C for 10 h and cooled to room temperature over 5 h. Post-synthesis processing began with separating hexadecane from the resulting black solid by centrifugation followed by a wash with hexane. The black solid was then rinsed with hot methanol to remove NaBr salt. The dried powder was subsequently sonicated with 3.4% nitric acid for 2 min, which oxidized the metal. The sample was then washed with ethanol, and immediately immersed in excess oleylamine. After sonication, the product in oleylamine for 5 min, excess oleylamine was removed by centrifugation with ethanol, and the particles were suspended in toluene. Once in solution, the particles remained stable and did not precipitate over several months.

Powder X-ray diffraction (XRD) was conducted on a Rigaku X-Ray Diffractometer with Cu-Kα radiation operating at 300 mA and 50 kV to determine both the resulting crystal structure of the InN and to verify the removal of indium metal. Fig. 1 depicts the diffraction spectrum of a typical sample before nitric acid treatment (a) and the diffraction spectrum of an aliquot of the same sample after nitric acid treatment (b). The two sets of three peaks at 2θ = 28–34° and 50–64° correspond to wurtzite phase InN with lattice parameters $a = 3.547 \pm 0.002 \text{Å}$, $c = 5.759 \pm 0.016 \text{Å}$ and grain sizes of 6.6 ± 2.0 nm. The lattice values are close to previously published values for InN nanopowders, $a = 3.552 \text{Å}$, $c = 5.716 \text{Å}$. Removal of the metal was confirmed by the disappearance...
of peaks at $2\theta = 36^\circ$ and $39^\circ$ and a change in the intensity ratios of peaks $2\theta = 29^\circ : 33^\circ$ from 1 : 3.2 to 1 : 2.1. Rietveld analysis showed no evidence of preferred orientation.

The chemical states of the nanoparticles before and after nitric acid treatment were further examined by X-ray photoelectron spectroscopy (XPS). XPS data were collected with a Kratos Axis 165 using monochromatic Al-K$_{\alpha}$ of photon energy 1486.6 eV over a 400 $\mu$m$^2$ area and a maximum depth of 10 nm. The data were calibrated to the C 1s peak (284.8 eV). Examination of the In 3d$_{5}/2$ and In 3d$_{3}/2$ peaks of the powder before nitric acid treatment shows two separate chemical species. In Fig. 2, the peaks at 444.8 eV and 452.2 eV correspond to In–N bonds$^{15-17}$ while the peaks at 443.8 eV and 451.3 eV correspond to indium metal.$^{18}$ As shown in Fig. 2a, the deconvoluted peaks are a very good fit with the observed data. The calculated peaks for Fig. 2b reveal a slight asymmetry in the observed data, but no additional peak could be reasonably extracted from the data. Calculating the chemical state ratios from the peak areas gives an average nitride : metal atomic ratio of 79.7 : 20.2. Atomic ratios of In : N were measured to be 1.2 : 1 after acid treatment, using commercially available InN powder (Aldrich, 99.9% metals basis) as a reference standard. Our relative peak areas are similar to two previous reports, though it is unknown whether those reports used a standard to calibrate their quantitative results.$^{7,8}$

High resolution transmission electron microscope (HRTEM) images were taken on a JEOL 2010F TEM at 200 kV. Fig. 3 shows the distribution and crystallinity of the resulting InN nanoparticles. Before the nitric acid treatment, the large agglomerations were similar to the morphologies of previously reported nanopowders.$^{8,13}$ The morphology after the acid treatment is shown in Fig. 3a; the agglomerations separated into many smaller, individual, irregularly shaped InN nanocrystals, which were easily solubilized in toluene with the addition of oleylamine. Although the particles were irregularly shaped, the average particle “diameter” was approximated by averaging the particle areas as seen under HRTEM. From the highly polydisperse particles seen in Fig. 3a, our average particle size was 6.2 ± 2.0 nm, in close agreement with the XRD FWHM estimations. Diffraction patterns obtained from fast Fourier transformation (FFT) of high resolution images (Fig. 3b and c), confirmed that these InN single crystals have the $\{0001\}$ zone axis for wurtzite InN with $P6_{3}mc$ space group. The nearest three spots in the diffraction patterns with $[0001]$ zone axis can be indexed to the $(10 \overline{1} 0)$, $(01 10)$ and $(11 \overline{2} 0)$ planes. According to the lattice fringes of the InN nanocrystals, the lattice spacing between two planes is $\approx 0.307$ nm, corresponding to the distance of two $\{100\}$ planes (JCPDS01-088-2362). Theoretically, the angle between the nearest spots should be $60^\circ$ and the distance between origin point and spots should be the same in the single crystal.
with [0001] zone axis. As seen in the diffraction pattern, both inter-planar angles measured among three spots are ~60° and the ratio of B to A is ~1, consistent with theoretical values of [0001] zone axis.

Absorption measurements on sample powders were taken on a Cary 5E spectrophotometer with a praying mantis diffuse reflection accessory and referenced to KBr. IR photoluminescence measurements were conducted in toluene at room temperature and at 77 K on a Fluorolog equipped with argon laser (488 nm) excitation. Absorption data indicate an extrapolated band gap value of 1.29 eV (Fig. 4). This value is larger than 0.7–0.9 eV but lower than the earlier quoted value of 1.9 eV.

Absorption data indicate the InN nanopowder synthesized herein has a band gap value of ~0.8 eV, which may be related to the nitrogen deficient nature of the material, and further studies are under way to better understand the optical and electronic structure of this material.

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**Notes and references**