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Ion Exchange Synthesis of III−V Nanocrystals

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Supporting Information

ABSTRACT: III−V nanocrystals displaying high crystallinity and low size dispersity are difficult to access by direct synthesis from molecular precursors. Here, we demonstrate that cation exchange of cadmium pnictide nanocrystals with group 13 ions yields monodisperse, crystalline III−V nanocrystals, including GaAs, InAs, GaP, and InP. This report highlights the versatility of cation exchange for accessing nanocrystals with covalent lattices.

Colloidal synthesis of semiconductor nanocrystals has rapidly developed in the past several decades, expanding beyond the prototypical spherical CdSe[1] to encompass an expanding library of binary and ternary compound semiconductors of various morphologies and complex heterostructures[2−5] for use in biolabeling[6] and electronic devices.[7] However, III−V semiconductors, common materials for epitaxially grown quantum dots, have lagged behind in colloidal synthetic development as the covalency of these materials requires high temperatures for both nucleation and growth, making it difficult to discriminate the two, yielding polydisperse samples.[8,9]

The synthesis of III−V nanocrystals has largely relied upon the dehalosylation reaction of $P(SiMe_3)_3$[10−12] or $As(SiMe_3)_3$[13−15] with group 13 halides in coordinating solvents, though single source precursors[16] and transmetalation reactions[17] have been demonstrated as alternative methods. In these cases, high temperatures (typically at reflux of the solvent) or long annealing times (on the order of days) are needed to achieve crystalline products. More recently, studies have demonstrated that fatty acids in noncoordinating solvents can be used to lower reaction temperatures and significantly reduce growth and annealing times to achieve InP and InAs nanocrystals with dispersities comparable to their II−VI analogues.[18−21] To date, no equivalent synthesis has been developed for the gallium pnictides; thus, state-of-the-art syntheses produce polydisperse samples, many of which are contaminated with molecular impurities.[15,22,23]

Ion exchange has emerged as an alternative to conventional “hot-injection” synthesis for ionic nanocrystals, allowing rapid replacement of the cation between various II−VI, I−VI, and IV−VI semiconductors while preserving particle size and morphology.[24−30] The use of an existing crystal lattice as a template enables the development of syntheses of crystal phases[27] and novel heterostructures[28,31−34] not accessible by conventional synthesis. Though ion exchange has been demonstrated using higher valent ions,[35] these reports have been limited to ionic systems. Here, we demonstrate the extension of ion exchange to synthesize monodisperse, highly crystalline III−V nanocrystals, including GaAs, InAs, GaP, and InP.

Recent synthetic developments in II−V, Cd_3P_2 and Cd_3As_2, semiconductor nanocrystals[36,37] have provided high quality template materials for the ion exchange synthesis of III−V nanocrystals. The thermodynamic driving force for this ion exchange is a balance between the solvation energy of the ions and the lattice binding energy before and after exchange.[24,30,31,35] For the II−V to III−V exchanges of interest, bulk lattice energies favor exchange. Thus, the solvation energies of the ions must be similar to permit facile exchange. Therefore, we selected tri-*n*-octylphosphine (TOP), a soft base, to minimize the binding preference for hard group 13 ions, Ga^{3+} or In^{3+}, relative to Cd^{2+}.

Our approach for the ion exchange synthesis of GaAs from Cd_3As_2 is outlined in Scheme 1. Monodisperse Cd_3As_2 nanocrystals (Figure 1a), synthesized according to prior literature,[37] are dissolved in TOP and injected into a $GaCl_3$:TOP complex (Ga/Cd 100:1) at 300 °C for 15 min. The stronger energy of formation of GaAs compared to Cd_3As_2 ($\Delta G = -25$ kcal/mol, bulk)[38,39] favors the 3:2 replacement of Cd^{2+} with Ga^{3+}. Transmission electron microscopy (TEM) of the GaAs nanocrystals after the ion exchange reaction (Figure 1b) displays a quasi-spherical morphology similar to the initial Cd_3As_2. High-resolution TEM confirms the crystallinity of the GaAs nanocrystals (Figure 1b inset) and X-ray diffraction (XRD) shows the conversion from the lower symmetry tetragonal phase of Cd_3As_2 ($P4_2/nmc$ space group) to the higher symmetry zinc blende phase of GaAs ($F\bar{4}3m$ space group). Likewise, similar reaction conditions can be used to produce InAs nanocrystals from the ion exchange reaction of Cd_3As_2 nanocrystals with an $InCl_3$:TOP complex (Figure 1c,d).

Scheme 1. Ion Exchange Reaction from II−V to III−V Nanocrystals

$$Cd_3As_2 + 2GaCl_3 \xrightarrow{\Delta,\text{TOP}} 2GaAs + 3CdCl_2$$

As no additional source of arsenic was present in the reaction, the formation of GaAs and InAs require either dissolution of the initial Cd_3As_2 nanocrystals and subsequent nucleation and growth of GaAs and InAs or a cation exchange

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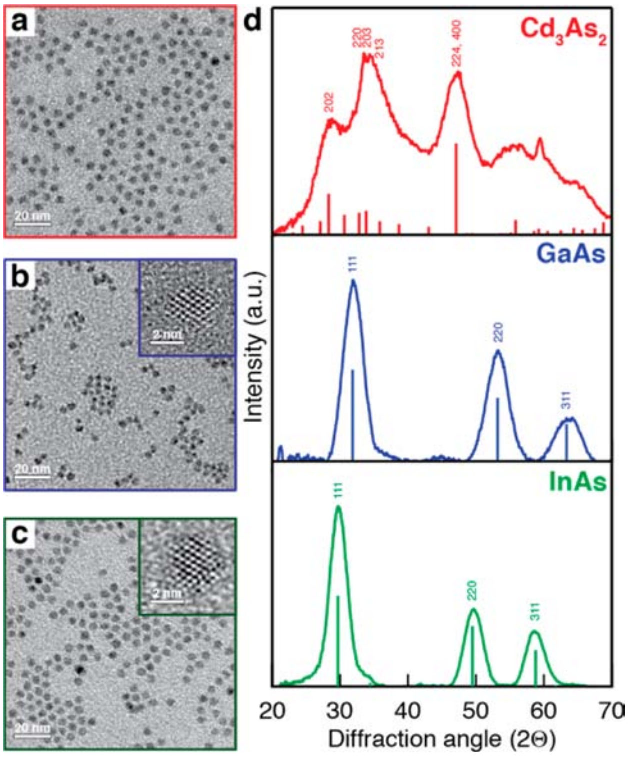

Figure 1. (a) TEM images of the initial Cd_3As_2 nanocrystals and (b) GaAs and (c) InAs nanocrystals obtained from ion exchange. (b, c) Insets show HRTEM images. (d) XRD of the initial Cd_3As_2 nanocrystals (top) and GaAs (middle) and InAs (bottom) nanocrystals after ion exchange. Patterns from the Inorganic Crystal Structure Database (ICSD) for Cd_3As_2 (ICSD no. 23245), GaAs (ICSD no. 107946), and InAs (ICSD no. 24518) are provided for reference.

reaction in which the Cd^{2+} ions are replaced by group 13 ions. Given the precedence for difficulty in synthesizing crystalline GaAs nanocrystals,[15] the 15-min reaction time and monodispersity of the resulting particles argue against a new nucleation process. Furthermore, detailed sizing analysis shown in Figure 2a confirms conservation of the size dispersity during the ion exchange reaction, and that mean diameters are consistent with the predicted trend in volume change associated with the transformation to a denser unit cell. The transformation from the tetragonal unit cell of Cd_3As_2 to the cubic GaAs and InAs should yield a volume contraction of 30% and 15%, respectively. The observed 19% volume decrease for InAs is in line with expectation. For GaAs, an appreciably larger volume decrease of 55% is observed which we attribute to surface etching from phosphines and chlorides.[40] Notwithstanding, the monodispersity of each sample is maintained, as expected for an ion exchange reaction. The initial Cd_3As_2 nanocrystals have a well-controlled, narrow size dispersion of 9%. By using this as a template, we achieve GaAs and InAs particles with dispersities of 12% and 11%, respectively, the lowest dispersity reported for GaAs nanocrystals. Together, we can conclude that the GaAs and InAs nanocrystals were formed from the 3:2 replacement of Cd^{2+} with Ga^{3+} and In^{3+}.

Absorption spectroscopy shows the expected blue shift of the optical gap from the near-infrared bandgap of Cd_3As_2 to InAs and GaAs (Figure 2b); however, in line with literature precedent for III−V nanoparticles with no shell, negligible photoluminescence was observed.[9] The expected quantum confinement blue shift of the bandgap when the exchange reaction is performed on smaller Cd_3As_2 nanocrystals is added substantiation of a cation exchange reaction as opposed to a dissolution and subsequent nucleation process (Figure 2c). The monodispersity of the nanocrystals synthesized by ion exchange is evident by the excitonic absorption in the InAs nanocrystals. However, the GaAs nanocrystals show a featureless absorption spectrum, although the size dispersity is similar to the InAs. This may be due to Cd atoms residual from the ion exchange (see below) potentially broadening the spectrum; however, the same is true of the InAs nanocrystals. The lack of excitonic absorption is also in line with theoretical predictions of an indirect bandgap for strongly confined spherical GaAs quantum dots.[41] The ability to synthesize monodisperse GaAs nanocrystals through ion exchange provides a method for future work to more systematically investigate the evolution of the electronic structure and optical properties of GaAs as a function of size.

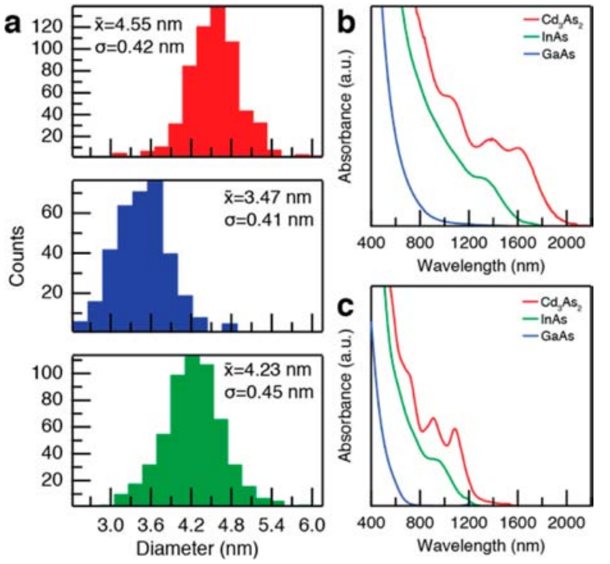

Figure 2. (a) Particle size histograms of the initial Cd_3As_2 nanocrystals (top) and GaAs (middle) and InAs (bottom) nanocrystals after ion exchange showing preservation of size dispersity. (b) Absorption spectra of initial 4.5 nm Cd_3As_2 nanocrystals and those that have been exchanged to InAs and GaAs. (c) Absorption spectra of initial 3 nm Cd_3As_2 nanocrystals and those that have been exchanged to InAs and GaAs.

Further highlighting the versatility of ion exchange for the synthesis of III−V semiconductors, GaP and InP can also be synthesized by ion exchange of Cd_3P_2 nanocrystals (Figure 3). In each instance, similar size dispersities and morphologies are obtained after the cation exchange process and the absorption spectra blue shift from Cd_3P_2 to InP to GaP as expected from their bulk bandgaps (Figure S1). XRD, shown in Figure 3d, confirms the conversion from the tetragonal Cd_3P_2 to the cubic crystal phase of GaP and InP, consistent with the results achieved for the arsenide materials.

The diffusivity of ions can be orders of magnitude lower in covalent semiconductors compared to ionic systems.[42] Prior work has demonstrated that residual amounts of impurity ions may remain after cation exchange reactions in ionic nanocrystals;[43] thus, it might be expected that residual Cd may be present in the ion exchanged III−V nanocrystals given the increased activation energy for diffusion. Indeed, inductively coupled plasma atomic emission spectroscopy (ICP-AES) confirms residual Cd concentration of a few atomic percent

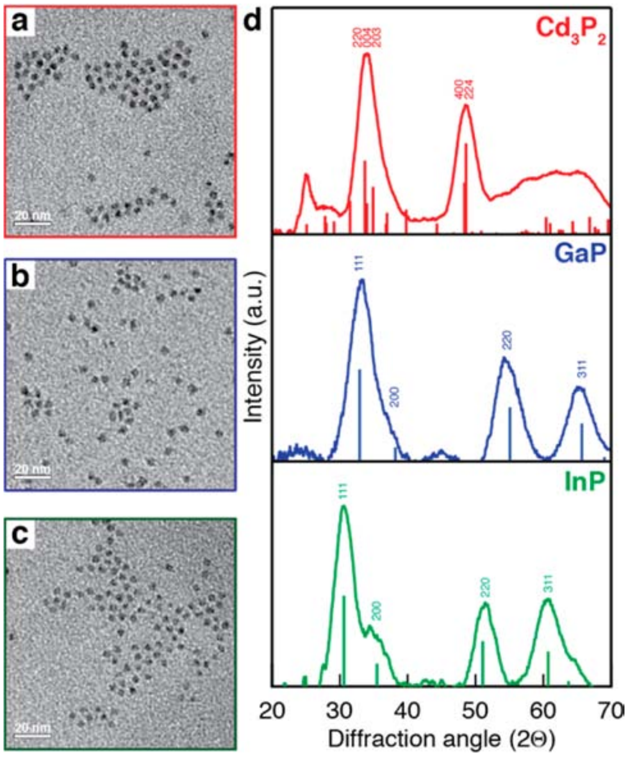

Figure 3. (a) TEM images of the initial Cd_3P_2 nanocrystals and (b) GaP and (c) InP nanocrystals obtained from ion exchange. (d) XRD of the initial Cd_3P_2 (top) and GaP (middle) and InP (bottom) nanocrystals after ion exchange. Patterns from the ICSD for Cd_3P_2 (ICSD no. 158864), GaP (ICSD no. 77088), and InP (ICSD no. 24517) are provided for reference.

remain in all samples post-exchange (Table S1). While the Ga^{3+} ion exchange of Cd_3As_2 successfully yielded crystalline zinc blende GaAs in only 5 min at 200 °C, the amount of residual Cd is dependent on the reaction temperature, time, and particle size as expected for a thermally activated, diffusion limited process (Figure S2, Table S2), warranting the ion exchange to be performed at higher temperatures for longer times. For initial exchanges, the residual Cd concentration reaches a steady state at longer times; however, the residual Cd content can be further reduced by sequential exchanges (Table S1). XRD and optical spectroscopy show no signs of the cadmium pnictide phases or signs of alloying, analogous to InAs nanocrystals intentionally doped with high Cd concentrations (2:1 In/Cd).[44] Preliminary etching experiments[45] imply the cadmium is distributed throughout the nanocrystals as opposed to being localized to the surface (Table S1). Similar to this prior study,[44] the remnant Cd may be useful as a means to control the carrier concentration in nanocrystal solids, in line with previous examples of using cation exchange as a means of controlled doping.[46,47]

Ion exchange reactions for III−V nanocrystals differ from those in ionic II−VI nanocrystals in several key aspects. The majority of the II−VI ion exchange reactions can be performed reversibly at room temperature due to the high lability of metal M^{1+} and M^{2+} ions and by modulating the ion energy in solution to drive species in and out.[24−26,30,32,33] In contrast, the III−V ion exchange reactions demonstrated here are highly irreversible, largely driven by the difference in lattice energies of the reactant and product phases, and require higher temperatures to enhance diffusion of the exchanging ions, a process which is inhibited at room temperature in these materials.

In summary, we have demonstrated the extension of cation exchange to form nanocrystals with covalent lattices, enabling the synthesis of highly crystalline, monodisperse III−V nanocrystals. In particular, the availability of monodisperse semiconductor nanocrystals such as GaAs presents new opportunities for comparison studies of epitaxially grown and colloidally synthesized quantum dots.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials and methods, ICP-AES results, absorbance of phosphides. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.

(2) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545.

(3) Yin, Y.; Alivisatos, A. P. *Nature* **2005**, *437*, 664.

(4) *Nanocrystal Quantum Dots*, 2nd ed.; Klimov, V. I., Ed.; CRC Press: Boca Raton, FL, 2010.

(5) Park, J.; Joo, J.; Kwon, S. G.; Jang, Y.; Hyeon, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 4630.

(6) Michalet, X.; Pinaud, F. F.; Bentolila, L. A.; Tsay, J. M.; Doose, S.; Li, J. J.; Sundaresan, G.; Wu, A. M.; Gambhir, S. S.; Weiss, S. *Science* **2005**, *307*, 538.

(7) Talapin, D. V.; Lee, J.-S.; Kovalenko, M. V.; Shevchenko, E. V. *Chem. Rev.* **2010**, *110*, 389.

(8) Nozik, A. J.; Mićić, O. I. *MRS Bull.* **1998**, *23*, 24.

(9) Heath, J. R.; Shiang, J. J. *Chem. Soc. Rev.* **1998**, *27*, 65.

(10) Wells, R. L.; Aubuchon, S. R.; Kher, S. S.; Lube, M. S.; White, P. S. *Chem. Mater.* **1995**, *7*, 793.

(11) Guzelian, A. A.; Katari, J. E. B.; Kadavanich, A. V.; Banin, U.; Hamad, K.; Juban, E.; Alivisatos, A. P.; Wolters, R. H; Arnold, C. C.; Heath, J. R. *J. Phys. Chem.* **1996**, *100*, 7212.

(12) Mićić, O. I.; Sprague, J. R.; Curtis, C. J.; Jones, K. M.; Machol, J. L.; Nozik, A. J.; Giessen, H.; Fluegel, B.; Mohs, G.; Peyghambarian, N. *J. Phys. Chem.* **1995**, *99*, 7754.

(13) Wells, R. L.; Pitt, C. G.; McPhail, A. T.; Purdy, A. P.; Shafieezad, S.; Hallock, R. B. *Chem. Mater.* **1989**, *1*, 4.

(14) Guzelian, A. A.; Banin, U.; Kadavanich, A. V.; Peng, X.; Alivisatos, A. P. *Appl. Phys. Lett.* **1996**, *69*, 1432.

(15) Olshavsky, M. A.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1990**, *112*, 9438.

(16) Kim, Y.-H.; Jun, Y.-W.; Jun, B.-H.; Lee, S.-M.; Cheon, J. *J. Am. Chem. Soc.* **2002**, *124*, 13656.

(17) Lauth, J.; Strupeit, T.; Kornowski, A.; Weller, H. *Chem. Mater.* **2012**, DOI: 10.1021/cm3019617.

(18) Battaglia, D.; Peng, X. *Nano Lett.* **2002**, *2*, 1027.

(19) Xie, R.; Battaglia, D.; Peng, X. *J. Am. Chem. Soc.* **2007**, *129*, 15432.

(20) Lucey, D. W.; MacRae, D. J.; Furis, M.; Sahoo, Y.; Cartwright, A. N.; Prasad, P. N. *Chem. Mater.* **2005**, *17*, 3754.

(21) Xu, S.; Kumar, S.; Naan, T. *J. Am. Chem. Soc.* **2006**, *128*, 1054.

(22) Uchida, H.; Curtis, C. J.; Nozik, A. J. *J. Phys. Chem.* **1991**, *95*, 5382.

(23) Uchida, H.; Curtis, C. J.; Kamat, P. V.; Jones, K. M.; Nozik, A. J. *J. Phys. Chem.* **1992**, *96*, 1156.

(24) Son, D. H.; Hughes, S. M.; Yin, Y.; Alivisatos, A. P. *Science* **2004**, *306*, 1009.

(25) Sadtler, B.; Demchenko, D. O.; Zheng, H.; Hughes, S. M.; Merkle, M. G.; Dahmen, U.; Wang, L.-W.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2009**, *131*, 5285.

(26) Luther, J. M.; Zheng, H.; Sadtler, B.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2009**, *131*, 16851.

(27) Li, H. B.; Zanella, M.; Genovese, A.; Povia, M.; Falqui, A.; Giannini, C.; Manna, L. *Nano Lett.* **2011**, *11*, 4964.

(28) Mews, A.; Eychmüller, A.; Giersig, M.; Schooss, D.; Weller, H. *J. Phys. Chem.* **1994**, *98*, 934.

(29) Camargo, P. H. C.; Lee, Y. H.; Jeong, U.; Zou, Z.; Xia, Y. *Langmuir* **2007**, *23*, 2985.

(30) Wark, S. E.; Hsia, C.; Son, D. H. *J. Am. Chem. Soc.* **2008**, *130*, 9550.

(31) Pietryga, J. M.; Werder, D. J.; Williams, D. J.; Casson, J. L.; Schaller, R. D.; Klimov, V. I.; Hollingsworth, J. A. *J. Am. Chem. Soc.* **2008**, *130*, 4879.

(32) Robinson, R. D.; Sadtler, B.; Demchenko, D. O.; Erdonmez, C. K.; Wang, L.-W.; Alivisatos, A. P. *Science* **2007**, *317*, 355.

(33) Jain, P. K.; Amirav, L.; Aloni, S.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2010**, *132*, 9997.

(34) Li, H.; Brescia, R.; Krahne, R.; Bertoni, G.; Alcocer, M. J. P.; D'Andrea, C.; Scotognella, F.; Tassone, F.; Zanella, M.; De Giorgi, M.; Manna, L. *ACS Nano* **2012**, *6*, 1637.

(35) Dong, C.; van Veggel, F. C. J. M. *ACS Nano* **2009**, *3*, 123.

(36) Xie, R.; Zhang, J.; Zhao, F.; Yang, W.; Peng, X. *Chem. Mater.* **2010**, *22*, 3820.

(37) Harris, D. K.; Allen, P. M.; Han, H.-S.; Walker, B. J.; Lee, J.; Bawendi, M. G. *J. Am. Chem. Soc.* **2011**, *133*, 4676.

(38) Collaboration: Scientific Group Thermodata Europe (SGTE). *Thermodynamic Properties of Compounds, Al2O3-SrO to GeAs*; SpringerMaterials—The Landolt-Börnstein Database (http://www.springermaterials.com). DOI: 10.1007/10652891_13.

(39) Collaboration: Authors and editors of the volumes III/17E-17F-41C. *Cadmium Arsenide* (Cd_3As_2) *Entropies, Enthalpies, Free Energy*; Madelung, O., Rössler, U., Schulz, M., Eds.; SpringerMaterials—The Landolt-Börnstein Database (http://www.springermaterials.com). DOI: 10.1007/10681727_249.

(40) Traub, M. C.; Biteen, J. S.; Michalak, D. J.; Webb, L. J.; Brunschwig, B. S.; Lewis, N. S. *J. Phys. Chem. C* **2008**, *112*, 18467.

(41) Luo, J.-W.; Franceschetti, A.; Zunger, A. *Phys. Rev. B* **2008**, *78*, 035306.

(42) Dutt, M. B.; Sharma, B. L. *3 Diffusion in Compound Semiconductors*; Beke, D. L., Ed.; SpringerMaterials—The Landolt-Börnstein Database (http://www.springermaterials.com). DOI: 10.1007/10426818_10.

(43) Jain, P. K.; Beberwyck, B. J.; Fong, L.-K.; Polking, M. J.; Alivisatos, A. P. *Angew. Chem., Int. Ed.* **2012**, *51*, 2387.

(44) Geyer, S. M.; Allen, P. M.; Chang, L.-Y.; Wong, C. R.; Osedach, T. P.; Zhao, N.; Bulovic, V.; Bawendi, M. G. *ACS Nano* **2010**, *4*, 7373.

(45) Battaglia, D.; Blackman, B.; Peng, X. *J. Am. Chem. Soc.* **2005**, *127*, 10889.

(46) Mocatta, D.; Cohen, G.; Schattner, J.; Millo, O.; Rabani, E.; Banin, U. *Science* **2011**, *332*, 77.

(47) Sahu, A.; Kang, M. S.; Kompch, A.; Notthoff, C.; Wills, A. W.; Deng, D.; Winterer, M.; Frisbie, C. D.; Norris, D. J. *Nano Lett.* **2012**, *12*, 2587.