

Colloidal CdSe Quantum Rings

Igor Fedin[†] and Dmitri V. Talapin^{*,†,§}

[†]Department of Chemistry and James Franck Institute, The University of Chicago, Chicago, Illinois 60637, United States

[§]Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439, United States

S Supporting Information

ABSTRACT: Semiconductor quantum rings are of great fundamental interest because their non-trivial topology creates novel physical properties. At the same time, toroidal topology is difficult to achieve for colloidal nanocrystals and epitaxially grown semiconductor nanostructures. In this work, we introduce the synthesis of luminescent colloidal CdSe nanorings and nanostructures with double and triple toroidal topology. The nanorings form during controlled etching and rearrangement of two-dimensional nanoplatelets. We discuss a possible mechanism of the transformation of nanoplatelets into nanorings and potential utility of colloidal nanorings for magneto-optical (e.g., Aharonov–Bohm effect) and other applications.

Colloidal synthesis of inorganic nanostructures has seen impressive development during the past two decades.¹ We are witnessing the emergence of a general synthetic methodology for sculpting inorganic solids into functional nanomaterials with unprecedented physical and chemical properties. Precise engineering of size, shape, and composition of nanoscale crystals is required to fully exploit and utilize optical, electronic, magnetic, and catalytic properties across a broad range of nanomaterials.² In the case of semiconductor nanostructures, the relation between the geometry (i.e., size and shape) and the electronic structure is encoded in quantum confinement: the nanocrystal surface serves as a boundary to confine the electron and hole wave functions. The control over shape and size of quantum-confined semiconductors enables materials with desired optical properties (e.g., the energy and polarization of emitted photons). In addition to the geometry, the topology of the wave function has important implications for materials properties.³ Traditional nanoparticles, nanowires, and two-dimensional nanosheets all belong to the same topological class with the genus (g) equal to zero ($g = 0$) and Euler characteristic $\chi = 2$. In a core–shell nanoparticle, both the core and the shell components are topologically equivalent ($g = 0, \chi = 2$).⁴

In this work we discuss colloidal synthesis of semiconductor nanostructures with a different topology, such as a ring ($g = 1$) and a double ring ($g = 2$). There are only a few examples of semiconductor ringlike nanostructures typically formed by molecular beam epitaxy^{5–7} or oriented attachment of spherical nanocrystals.^{8,9} It is likely due to synthetic difficulties that toroidal topology is currently underrepresented in the field of colloidal quantum-confined semiconductors. CdSe is widely regarded as a model system with well-understood chemistry,

physics, and optical properties utilized in various applications, such as luminescent biotags and flat-panel displays.^{10,11} Generations of synthetic protocols have evolved to afford colloidal CdSe quantum dots (QDs), rods with controlled diameters and aspect ratios, and nanoplatelets (NPLs) with controlled thicknesses and lateral dimensions. We demonstrate that crystalline CdSe nanorings (NRings) can be accessed via a somewhat counterintuitive route involving controlled etching and rearrangement of CdSe NPLs (Figure 1A).

To prepare CdSe NRings, we first synthesized colloidal CdSe NPLs using Ithurria and Dubertret's approach.¹² Nanoplatelet thickness can be varied with true atomic precision, enabling samples where all NPLs contain three, four, or five monolayers (MLs) of CdSe with an additional layer of Cd atoms, so that both sides of the NPLs are Cd-terminated.¹³ In this study, we primarily used 4 ML CdSe NPLs with sharp excitonic emission at 512 nm. These NPLs with lateral dimensions 20 nm × 7 nm (Figure 1B) were dispersed in 1-octadecene and oleylamine (OAm) (3:1 by volume), and Se powder was added to the solution. They were then heated to 140 °C and kept at this temperature for 5–10 min, followed by the addition of tributylphosphine to prevent aggregation, quick heating to 220 °C and cooling. This simple treatment resulted in the formation of CdSe NRings shown in Figure 1C. The reaction is rather sensitive to experimental conditions: the size and concentration of NPLs, amount of Se, duration of heat treatment, and temperature of the treatment as summarized in the Supporting Information (SI, Figures S1 and S2). After Se treatment, CdSe NRings showed only weak photoluminescence (PL), but adding Cd(HCOO)₂ powder to the reaction mixture produced NRings with bright band edge PL (Figure 1D). CdSe NRings showed clear excitonic peaks in the absorption spectra; their PL spectrum peaked at 661 nm with fwhm of 78 meV and a quantum yield (QY) of 25% right after synthesis (Figure 1D). In fact, Peng et al. recently reported that a treatment of CdSe QDs with Se powder in OAm and Cd formate brought the QY of the QDs to unity.¹⁴

It has been reported that elemental Se can oxidize primary amines RCH₂NH₂ into selenoacylamides RC(Se)NH₂, which are the active molecular species when Se powder is used for synthesizing various metal selenide nanocrystals.¹⁵ Our treatment of CdSe NPLs with thioacetamide also resulted in NRings (Figure S3). Such an outcome suggests that the active species is selenoleylamide formed from Se powder and OAm in situ. Similarly, elemental sulfur can be used instead of selenium

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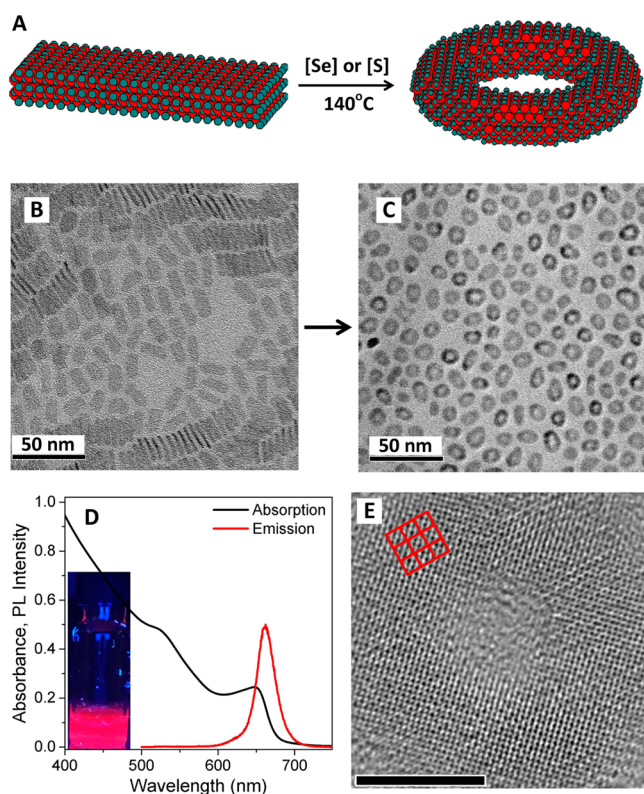


Figure 1. (A) Schematic of the transformation of CdSe nanoplatelet (NPLs) into a NRing. (B) TEM image of 1.2 nm thick CdSe NPLs with 20 nm \times 7 nm lateral dimensions used as precursors for NRings. (C) TEM image of the resulting NRings. (D) Absorption and photoluminescence (PL) spectra of a colloidal solution of CdSe NRings. Inset: A photograph of a colloidal solution of the NRings luminescing under UV light. (E) High-resolution TEM image of a CdSe NRing. The scale bar indicates 5 nm. The red grid shows 3 \times 3 unit cells of zinc blende structure.

(Figure S4), though the transformation of NPLs into NRings was slower. Nanoplatelet perforation does not occur with either Se or thioacetamide in the absence of amines (Figure S5), which serves as indirect evidence of the role of OAm in the reaction.

The NRings retained the zinc blende crystal structure of CdSe NPLs, which was confirmed by X-ray diffraction (Figure S6). High-resolution TEM images show lattice planes of zinc blende lattice viewed along the 001 zone axis when imaged normal to the NRing plane (Figure 1E). The lattice constant agrees with the reported values for zb-CdSe. The transformation of NPLs into NRings occurs with an increase in the thickness and partial relaxation of the quantum confinement as evidenced by structural and spectroscopic studies.

The lateral dimensions of CdSe NPLs can be tuned by adjusting experimental parameters as shown in Figure S7.¹⁶ When longer CdSe NPLs (35 nm \times 8 nm) were treated with Se powder, they transformed into nanostructures with two or three coplanar rings coupled within a single-crystalline unit (Figure 2A,B). These nanostructures showed a strong luminescence peak at 637 nm, fwhm of 91 meV, and a room-temperature PL QY of 50% (Figure 2F). To the best of our knowledge, bi- and tritoroidal topology is unprecedented not only for colloidal but also for MBE-grown nano-semiconductors.

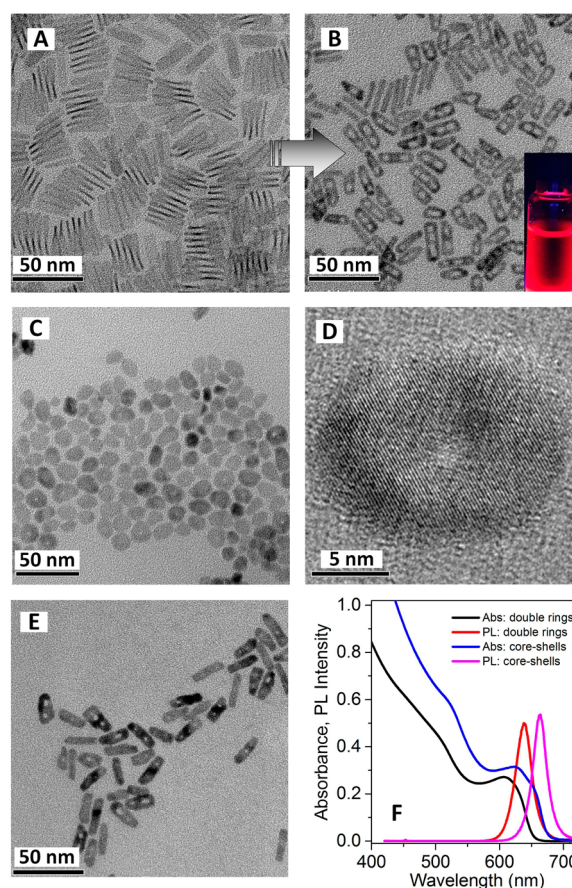


Figure 2. TEM micrographs of (A) 1.2 nm thick CdSe NPLs with 35 nm \times 8 nm lateral dimensions used as precursors; (B) CdSe double rings obtained from long NPLs (inset shows a photograph of the colloidal solution illuminated with UV light); (C,D) CdSe NRings coated with 3 ML of Cd_{1-x}Zn_xS shell; and (E) CdSe double rings coated with 2 ML of Cd_{1-x}Zn_xS shell. (F) Absorption and PL spectra of CdSe double rings shown in panel (B) and Cd_{1-x}Zn_xS core-shell double rings from panel (E).

CdSe NRings represent a convenient platform for building more complex nanostructures with toroidal topology. For example, CdSe/Cd_{1-x}Zn_xS heterostructures can be synthesized from CdSe single and double CdSe NRings using colloidal atomic layer deposition (c-ALD)¹⁷ as described in the SI. The holes in the structures were preserved (Figures 2C–E, S8–S10). The first excitonic peak and the PL peak red-shifted and the core-shell NRings showed bright and stable PL (Figure 2F). Since the chemistry of CdSe nanomaterials is well developed at this point, we believe that many transformations discovered for CdSe QDs (e.g., cation exchange reactions)¹⁸ can be implemented for NRings.

We attempted to understand the mechanism behind the transformation of NPLs into NRings. This process may look unusual from the point of view of traditional crystal etching, where chemically active surfaces typically get etched away first.¹⁹ Indeed, the synthesis of NPLs implies that acetate-capped (001) zinc blende faces of NPLs are the most passivated facets of NPLs.¹³ Why do these stable facets get selectively perforated during treatment with Se powder in the presence of OAm?

The top and bottom NPL faces are Cd-terminated (001) facets of zb-CdSe lattice as shown in Figure 3A.²⁰ For the NPL family emitting at 512 nm, each NPL has five Cd layers and

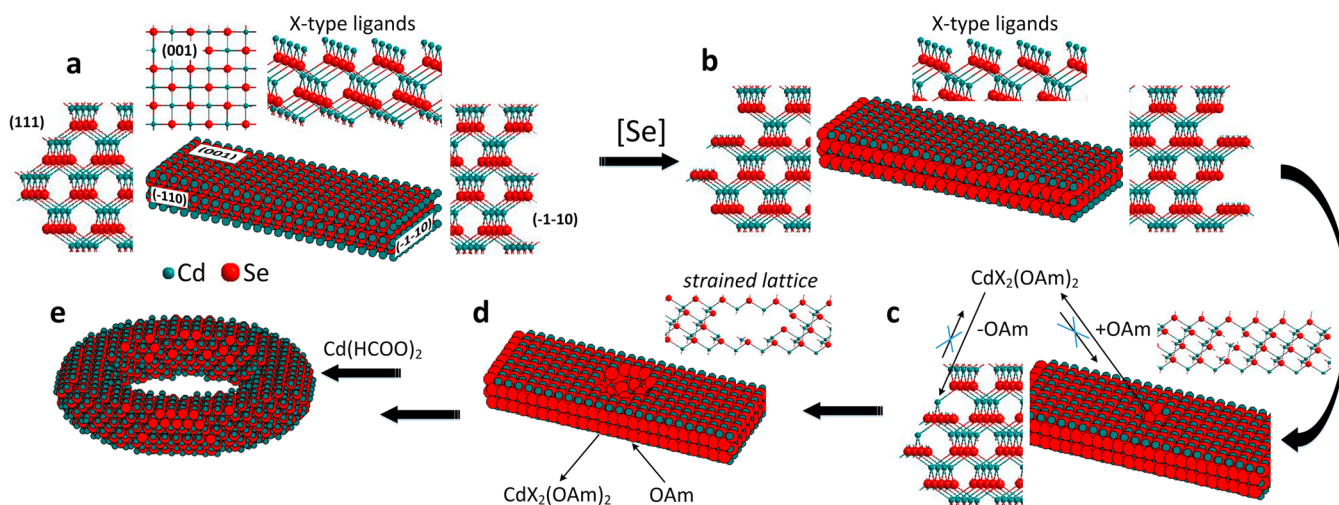
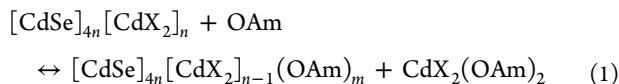


Figure 3. Proposed reactions sequence for the transformation of CdSe nanoplatelets (NPLs) into nanorings. (A) Initial CdSe NPL is a thin slab of zb-CdSe lattice terminated by (001) top and bottom facets and side facets represented by either [110]- or [111]-type facets. The atomic structure of corresponding surfaces are shown. (B) When treated with a Se precursor, the side facets get Se-terminated while the top and bottom facets remain Cd-terminated and ligated by X-type ligands. (C) Cd atoms can leave (001) facet via the Z-type ligand displacement reaction promoted by L-type oleylamine (OAm) ligands. The removed Cd atoms can deposit at the side facets. (D) The etch-pit developed in CdSe NPL generates strain that distorts crystal lattice and may activate the etching of the bottom facet. (E) Final CdSe nanoring.

four Se layers in between.²¹ To satisfy charge neutrality in a nonpolar solvent, (001) facets require passivation with X-type ligands,²² such as carboxylate RCOO^- , leading to $[\text{CdSe}]_{4n}[\text{CdX}_2]_n$ stoichiometry where n reflects the lateral dimensions. This stoichiometry implies one X-type ligand per Cd atom on the top and bottom facets containing $5.4 \text{ Cd atoms/nm}^2$ ($0.185 \text{ nm}^2/\text{atom}$). The typical footprint of a COO^- headgroup ($\sim 0.3 \text{ nm}^2$)^{22,23} is larger than the available area per surface atom and some fraction of X-type ligands can be represented by small ions, e.g., hydroxyl (OH^-).^{22,23} We hypothesize the existence of some particularly favorable arrangement of surface ligands that greatly stabilizes (001) CdSe facets with respect to other NPL facets during synthesis. The side facets of as-synthesized CdSe NPL are normal to the [110] direction.²⁰ These can be true $(-1-10)$ facets with 90° angle to the (001) NPL faces (Figure 3A, right) or a combination of Cd-rich (111) faces and Se-rich (-111) faces (Figure 3A, left). In either case, every surface Cd or Se atom forms three bonds with other lattice atoms and has one dangling bond.

Similar to phosphine selenides, selenoacylamide can transfer the chalcogen to an electrophilic metal ion.¹⁵ We therefore expect that during the treatment of colloidal CdSe NPLs with Se-OAm complex, Se atoms deposit on side facets forming a rim around the NPL. It has been shown that NPL side facets show much higher reactivity toward further growth, consistent with the synthesis of CdSe/CdS,²⁴ CdSe/CdTe,²⁵ and CdS/CdSe²⁶ core-crown NPLs under somewhat similar experimental conditions. Figure 3B outlines the formation of Se-terminated side facets while preserving Cd-termination for (001) facets due to strong X-type ligation.

The CdX_2 units can bind to and desorb from the NPL surface in the presence of OAm (Figure 3C), establishing the equilibrium:



where X are negatively charged ligands (e.g., CH_3COO^- , OH^-). During NPL lateral growth or synthesis of core-crown NPLs,^{20,24–26} the excess of $\text{Cd}(\text{RCOO})_2$ in solution shifts the equilibrium left. In contrast, during the formation of NRings, the excess Se precursors facilitated the desorption reaction, known as L-promoted Z-type ligand displacement.²⁷ This process is facilitated by L-type ligands (OAm) which stabilize CdX_2L_2 molecular species in solution and bind to the NPL surface after removal of CdX_2 units. Stripping one Cd from a (001) facet requires breaking two Cd–Se bonds. In comparison, stripping a Cd atom from a side (110) or (111) facet would require breaking three Cd–Se bonds. Therefore, side NPL facets are more susceptible to growth but less susceptible to dissolution than (001) faces of CdSe NPLs. Released CdX_2L_2 molecules can diffuse out or react with side facets, forming three Cd–Se bonds as shown in Figure 3C.

The removal of CdX_2L_2 leaves neighboring Cd and Se atoms unsaturated, destabilizing the structure locally and making it susceptible to further etching and developing an etch pit. Amines can facilitate the dissolution of undercoordinated chalcogen atoms from the etch pit.²⁸ As the etching progresses, Cd and Se atoms depart from the middle of the NPL and settle at the rim. The development of the pit disrupts tetrahedral coordination of Cd and Se atoms, developing strain in the NPL lattice. Such strain may destabilize surface atoms on the opposite (bottom) NPL facet and make them more susceptible to reaction 1 compared to other atoms in the bottom face of the NPL as shown in Figure 3D. Such coordinated etching of the top and bottom faces, combined with re-deposition of Cd and Se atoms at the rim around the NPL, should proceed until the NPL develops a hole and transforms into a toroidal particle (Figure 3E). Further studies will be necessary to fully test this proposed mechanism.

A similar mechanism may be also applicable to other compound semiconductors. Indeed, the treatment of CdTe NPLs with Se powder resulted in perforations similar to those observed in the case of CdSe, though large lateral dimensions of initial NPLs prevented us from obtaining uniform NRings (Figure S11).

What are colloidal semiconductor NRings good for? We envision two broad directions for future explorations of toroidal semiconductor nanostructures. First is the study of properties of quantum-confined semiconductor NRings themselves. Because of synthetic inaccessibility, relatively little theoretical and experimental work has been devoted to this interesting class of low-dimensional electronic systems. It has been shown that epitaxially grown toroidal InAs/GaAs nanostructures exhibit oscillations of the lowest-energy electron and hole states, and a stepwise transition of the angular momentum quantum number, l , from zero to higher values with an increasing magnetic field penetrating the ring.^{5,29,30} The latter results in transitions between bright ($l_e = 0$ and $l_h = 0$, $l_e = -1$ and $l_h = +1$, etc.) and dark ($l_e = 0$ and $l_h = +1$, $l_e = -1$ and $l_h = 2$, etc.) excitons⁶—an optical manifestation of the Aharonov–Bohm effect.³¹ There are theoretical studies predicting formation of magnetoexcitonic states in quantum rings,^{32,33} terahertz absorption,³⁴ and other effects that require semiconductor nanostructures with nontrivial topology.

In addition, our colloidal CdSe NRings represent the first example of luminescent topological nanocolloids. Recent work by Senyuk et al. introduced the concept of topological colloids, such as colloidal rings and double rings shown in Figures 1C and 2B, and described nontrivial behavior of such particles introduced in a nematic liquid crystal, leading to topological defects and new memory effects in the liquid crystals³⁵ calling for new explorations of topology-dictated colloidal phenomena.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05862.

Experimental details and Figures S1–S11 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*dvtalapin@uchicago.edu

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Park, J.; Joo, J.; Kwon, S. G.; Jang, Y.; Hyeon, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 4630.
- (2) Peng, X. G.; Manna, L.; Yang, W. D.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59.
- (3) Zhang, Y.; Tan, Y.-W.; Stormer, H. L.; Kim, P. *Nature* **2005**, *438*, 201.
- (4) Massey, W. S. *Algebraic Topology: An Introduction*; Harcourt, Brace & World, Inc.: New York, 1967.
- (5) Lorke, A.; Luyken, R. J.; Govorov, A. O.; Kotthaus, J. P.; Garcia, J. M.; Petroff, P. M. *Phys. Rev. Lett.* **2000**, *84*, 2223.
- (6) Govorov, A. O.; Ulloa, S. E.; Karrai, K.; Warburton, R. J. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2002**, *66*, 66.
- (7) Kim, H. D.; Okuyama, R.; Kyhm, K.; Eto, M.; Taylor, R. A.; Nicolet, A. L.; Potemski, M.; Noguees, G.; Dang, L. S.; Je, K.-C.; Kim,

J.; Kyhm, J.-H.; Yoen, K. H.; Lee, E. H.; Kim, J. Y.; Han, I. K.; Choi, W.; Song, J. *Nano Lett.* **2016**, *16*, 27.

(8) Cho, K. S.; Talapin, D. V.; Gaschler, W.; Murray, C. B. *J. Am. Chem. Soc.* **2005**, *127*, 7140.

(9) Jia, G.; Sitt, A.; Hitin, G. B.; Hadar, I.; Bekenstein, Y.; Amit, Y.; Popov, I.; Banin, U. *Nat. Mater.* **2014**, *13*, 301.

(10) Medintz, I. L.; Uyeda, H. T.; Goldman, E. R.; Mattoussi, H. *Nat. Mater.* **2005**, *4*, 435.

(11) Shirasaki, Y.; Supran, G. J.; Bawendi, M. G.; Bulovic, V. *Nat. Photonics* **2013**, *7*, 13.

(12) Ithurria, S.; Tessier, M. D.; Mahler, B.; Lobo, R.; Dubertret, B.; Efros, A. *Nat. Mater.* **2011**, *10*, 936.

(13) Jana, S.; Phan, T. N. T.; Bouet, C.; Tessier, M. D.; Davidson, P.; Dubertret, B.; Abécassis, B. *Langmuir* **2015**, *31*, 10532.

(14) Gao, Y.; Peng, X. *J. Am. Chem. Soc.* **2015**, *137*, 4230.

(15) García-Rodríguez, R.; Hendricks, M. P.; Cossairt, B. M.; Liu, H.; Owen, J. S. *Chem. Mater.* **2013**, *25*, 1233.

(16) She, C.; Fedin, I.; Dolzhenkov, D. S.; Dahlberg, P. D.; Engel, G. S.; Schaller, R. D.; Talapin, D. V. *ACS Nano* **2015**, *9*, 9475.

(17) Ithurria, S.; Talapin, D. V. *J. Am. Chem. Soc.* **2012**, *134*, 18585.

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

(19) Sangwal, K. *Etching of Crystals: Theory, Experiment, and Application*; North-Holland Physics Publishing: Amsterdam, 1987.

(20) Bouet, C.; Mahler, B.; Nadal, B.; Abecassis, B.; Tessier, M. D.; Ithurria, S.; Xu, X.; Dubertret, B. *Chem. Mater.* **2013**, *25*, 639.

(21) She, C.; Fedin, I.; Dolzhenkov, D. S.; Demortière, A.; Schaller, R. D.; Pelton, M.; Talapin, D. V. *Nano Lett.* **2014**, *14*, 2772.

(22) Boles, M. A.; Ling, D.; Hyeon, T.; Talapin, D. V. *Nat. Mater.* **2016**, *15*, 141.

(23) Zherebetsky, D.; Scheele, M.; Zhang, Y.; Bronstein, N.; Thompson, C.; Britt, D.; Salmeron, M.; Alivisatos, P.; Wang, L.-W. *Science* **2014**, *344*, 1380.

(24) Tessier, M. D.; Spinicelli, P.; Dupont, D.; Patriarche, G.; Ithurria, S.; Dubertret, B. *Nano Lett.* **2014**, *14*, 207.

(25) Pedetti, S.; Ithurria, S.; Heuclin, H.; Patriarche, G.; Dubertret, B. *J. Am. Chem. Soc.* **2014**, *136*, 16430.

(26) Delikanli, S.; Guzelurk, B.; Hernandez-Martinez, P. L.; Erdem, T.; Kelestemur, Y.; Olutas, M.; Akgul, M. Z.; Demir, H. V. *Adv. Funct. Mater.* **2015**, *25*, 4282.

(27) Anderson, N. C.; Hendricks, M. P.; Choi, J. J.; Owen, J. S. *J. Am. Chem. Soc.* **2013**, *135*, 18536.

(28) Li, R.; Lee, J.; Yang, B.; Horspool, D. N.; Aindow, M.; Papadimitrakopoulos, F. *J. Am. Chem. Soc.* **2005**, *127*, 2524.

(29) Grochol, M.; Grosse, F.; Zimmermann, R. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2006**, *74*, 115416.

(30) Grochol, M.; Zimmermann, R. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *76*, 195326.

(31) Aharonov, Y.; Bohm, D. *Phys. Rev.* **1959**, *115*, 485.

(32) Li, X. *Phys. E* **2009**, *41*, 1814.

(33) Ulloa, S. E.; et al. *Phys. E* **2002**, *12*, 790.

(34) Zhang, T. Y.; Cao, J. C. *J. Appl. Phys.* **2005**, *97*, 024307.

(35) Senyuk, B.; Liu, Q.; He, S.; Kamien, R. D.; Kusner, R. B.; Lubensky, T. C.; Smalyukh, I. I. *Nature* **2013**, *493*, 200.