Nanoscale

COMMUNICATION

Check for updates

Cite this: *Nanoscale*, 2017, **9**, 13915 Received 23rd June 2017, Accepted 28th August 2017

DOI: 10.1039/c7nr04554a

rsc.li/nanoscale

Growth and assembly of cobalt oxide nanoparticle rings at liquid nanodroplets with solid junction[†]

Yilong Zhou,^{a,b} Alexander S. Powers,^c Xiaowei Zhang,^{b,d} Tao Xu, ^ba,^b Karen Bustillo, ^b^e Litao Sun ^sa and Haimei Zheng ^b*^{b,f}

Using liquid cell TEM, we imaged the formation of CoO nanoparticle rings. Nanoparticles nucleated and grew tracing the perimeter of droplets sitting on the SiN_x solid substrate, and finally formed necklace-like rings. By tracking single nanoparticle trajectories during the ring formation and an estimation of the forces between droplets and nanoparticles using a simplified model, we found the junction of liquid nanodroplets with a solid substrate is the attractive site for CoO nanoparticles. Coalescing droplets were capable of pushing nanoparticles to the perimeter of the new droplet and nanoparticles on top of the droplets rolled off toward the perimeter. We propose that the curved surface morphology of the droplets created a force gradient that contributed to the assembly of nanoparticles at the droplet perimeter. Revealing the dynamics of nanoparticle movements and the interactions of nanoparticles with the liquid nanodroplet provides insights on developing novel self-assembly strategies for building precisely defined nanostructures on solid substrates.

There has been significant recent interest in the self-assembly of nanoparticles to form thin films or other patterned structures for the application of nanoparticles in functional devices, such as solar cells, batteries, electronics, and information storage. Bottom-up self-assembly is highly promising for building complex nanostructures with well-defined patterns and geometries using nanoparticle building blocks. van der Waals forces,¹ electrostatic or magnetic forces,^{1,2} capil-

^bMaterials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA. E-mail: hmzheng@lbl.gov lary forces,^{3,4} liquid flow,^{5,6} etc., can be exploited to control the motion of individual nanoparticles for self-assembly. In addition, other physical or chemical means, such as Pickering emulsions,⁷ micellization,⁸ etc., may be used for nanoparticle self-assembly. A wide variety of patterns from nanoparticle self-assembly ranging from one-dimensional chains to twodimensional thin films and three-dimensional crystals has been achieved.^{6,9-13} Nanoparticle rings are a two-dimensional structure which could offer plasmonic properties useful for solid-state devices, such as antennae or waveguides.¹⁴ Solution based nanoparticle self-assembly has been demonstrated previously for making nanoparticle rings, for instance, Co nanoparticle ring formation by magnetic dipole-directed selfassembly or evaporation-driven hole formation in viscous wetting layers,² Ag nanoparticle rings by protein templates,¹⁵ and solvent drying mediated nanoparticle coffee rings.5 Many previous studies are on the macro-scale. There are limited studies on nanoparticle self-assembly with liquid nanodroplets.

The nanodroplets of liquids with a circular liquid-gas-solid contact line may be used as a template for nanoparticle selfassembly into rings. The non-uniform curvature of sessile nanodroplets near solids provides unique properties. The contact line front is a transition region, where the liquid/solid/ gas coexist and nanoscale forces exist in very short distances. In this transition region, the droplet surface is not only a simple liquid/gas interface but it is also affected by interactions with the substrate. There is competition between longrange forces from the substrate and capillary forces on the droplet surface.¹⁶ This transition region is typically in the 1-2 nm range.¹⁷ which is negligible for macroscale droplets. However, it may dominate the behavior of nanodroplets and play a critical role for nanoparticle self-assembly. The direct observation of nanoparticle ring formation with nanodroplet templates may provide critical insights on the properties of liquid nanodroplets and future practical applications.

In the past few years, *in situ* liquid cell TEM has been demonstrated as an effective method for the study of dynamic nanoscale systems in solution, including nanoparticle nuclea-

ROYAL SOCIETY OF CHEMISTRY

View Article Online

^aSEU-FEI Nano-Pico Center, Key Lab of MEMS of Ministry of Education, Southeast University, Nanjing 210096, China. E-mail: slt@seu.edu.cn

^cDepartment of Chemistry, University of California, Berkeley, California 94720, USA ^dNational Laboratory of Solid State Microstructures, School of Electronic Science and Engineering and Collaborative Innovation Centre of Advanced Microstructures, Nanjing University, Nanjing 210093, China

^eMolecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

^fDepartment of Materials Science and Engineering, University of California, Berkeley, California 94720, USA

[†]Electronic supplementary information (ESI) available: Supporting text, figures and analysis; Movies S1–S4. See DOI: 10.1039/c7nr04554a

Communication

tion and growth,¹⁸⁻²⁰ nanoparticle coalescence^{1,21} and the selfassembly of super-lattices.22 Many previous liquid cell studies focused on solid nanocrystals suspended in a liquid and rarely involved the analysis of the interfaces of liquid droplets on a solid. Recently, Lin et al. reported a liquid cell TEM study of the self-assembly of small nanoparticle rings using nanodroplets dispersed in solution. This study described the liquid/liquid interfaces and its interaction with nanoparticles leading to a Pt nanoparticle assembly.²³ The droplets were on the same size order as the nanoparticles and of about 5 nanoparticles. In this work, the sessile liquid droplets on a solid with a triple-phase (solid/liquid/gas) junction provide a new scenario for nanoparticle growth and assembly. We used in situ liquid cell TEM to study CoO nanoparticle ring formation at the solid/liquid/gas interfaces of liquid nanodroplets on a solid silicon nitride substrate. These rings consist of ten or a hundred nanoparticles per ring. We show that these structures are maintained upon drying of the thin liquid droplets. We quantify the growth, dynamics, and forces involved to elucidate the mechanism and parameters of the process.

Window-type liquid cells were fabricated with a micro-fabrication process reported previously.²⁴ 100 µm ultra-thin silicon wafers with a 15 nm SiN_x membrane were used and the viewing windows formed on each chip. The top and bottom chips were assembled face to face, separated by an indium spacer, forming a 100-120 nm thick gap between the windows (refer to the schematic diagram in the table of contents). The reaction solution was prepared by dissolving 1 mmol of Co $(acac)_2$ in oleylamine, oleic acid and benzyl ether (12:4:1) in volume and 10 ml in total). 10 nL of the growth solution was injected into the cavity, forming a liquid layer sandwiched between the viewing windows. The cell was then sealed with epoxy before loading into the TEM as a standard sample. In situ TEM experiments were carried out in a JEOL 2100 TEM (LaB₆ filament) operating at 200 kV. Movies and images were captured by a Gatan CCD camera during the experiments and analyzed with imageJ and Matlab.

When the electron beam illuminated the liquid film (~100 nm thick), a very thin liquid layer was created on the SiN_x membrane by liquid film being pushed away. Subsequently, the liquid layer was ruptured, forming many small droplets (typically <10 nm diameter). These liquid nanodroplets tended to coalesce, as seen in ESI Movie S1 and Fig. S1.† After the liquid nanodroplets formed, we reduced the electron beam intensity for imaging (from ~10³ e⁻ Å⁻² s⁻¹) to ~10 e⁻ Å⁻² s⁻¹). Most nanoparticles nucleated and grew around the droplet perimeters, forming necklace-like nanoparticle rings while the electron beam was maintained. In addition, nanoparticles grew around the droplet, resulting in ring widening locally and nanoparticles being squeezed out of the ring, as shown in ESI Movie S2.†

To obtain detailed information on the nanoparticle ring formation, we tracked and analyzed nanoparticle sizes over time in one typical nanoparticle ring from ESI Movie S2,† as shown in Fig. 1A. As shown in Fig. 1B, the average particle diameter increases approximately linearly from 2 nm to 4 nm over the course of 5 minutes. However, the diameter variance shows a two-stage evolution; the size distribution is sharpening at an early stage and then broadening (Fig. 1B and C). At the early stage, the size focusing is mainly due to smaller nanoparticles growing faster than larger ones. Moreover, as proposed in our previous *in situ* liquid cell study of Pt nanoparticles,²⁵ nanoparticle coalescence is a pathway for nanoparticle size focusing. Small nanoparticles coalesce into larger particles followed by a relaxation period, allowing these particles to catch up to form larger simple growth particles. During the nanoparticle ring growth, the reagent was supplied by the droplet, making the total reagent in one droplet finite and decreasing over time. In the later stage of growth, Ostwald ripening was observed, leading to nanoparticle size broadening.

More ex situ TEM characterizations were performed to investigate the nanoparticle ring structure and composition. Liquid cells were disassembled and dried. The reaction areas are reserved for further analysis. With lower magnification TEM images, large numbers of rings were found within the beam illuminated area, as shown in Fig. 2A. The nanoparticle rings in our experiments show a wide range of sizes from tens to hundreds of nanometers in perimeter (histogram inset Fig. 2A) with the nanoparticles traced around the original droplet perimeter. Regardless of ring sizes, the average diameter of the nanoparticles is ~4 nm, reflecting the size distribution of terminated growing nanoparticles. By HRTEM, nanoparticles on the ring are highly crystalline (Fig. 2B). These nanoparticles are possibly Co or Co oxides. By carefully comparing the measured lattice with Co and Co oxides (*i.e.*, CoO, Co_2O_3 or Co_3O_4), a cubic CoO with lattice constant a = 0.43 nm was identified (Fig. 2C). EDS mapping and spectra were further acquired using an FEI titan equipped with super-EDX, and the STEM mode was employed to get the localized elemental distribution. EDS mapping by the Co L-edge (Fig. 2C and Fig. S2[†]) illustrates the Co composition for clarity; while O was found everywhere (not shown) due to the oxygen content in the liquid residue.

In order to understand the evolution of nanoparticle assembly, the dynamics of the nanoparticles and droplets were tracked and the forces that the droplets exerted on the nanoparticles were estimated. Fig. 3A and B show the sequential images of nanoparticle motion between two coalescing droplets from ESI Movie S3.[†] Nanoparticles were pinned on the droplet perimeter and pushed forward by the contact bridge between the droplets. Nanoparticles were finally extruded out to the newly-formed droplet perimeter. Fig. 3C gives the trajectory of the nanoparticles and droplets, which reveals that the motions of the nanoparticles were perpendicular to the droplet coalescing direction. This clearly shows that nanoparticles were squeezed in the gap between a newly formed droplet and another droplet. It is likely that the compressive force exerted by the droplets on both sides aligned and vertically stacked the nanoparticles (see nanoparticles 1 + 4 and 2 + 3 in Fig. 3A) in the gap. This chain of double stacked nanoparticles was fixed in the gap, which probably prevented



Fig. 1 In situ TEM observation and analysis of the CoO nanoparticle ring evolution in a liquid cell. (A) Selected image sequence of one nanoparticle ring (colored) from Mov. S2.† (B) Statistics on data of nanoparticle size as a function of time; black solid dot refers to nanoparticle average diameter (left side scale), blue open square dot refers to diameter variance (right side scale). (C) Histograms reflecting nanoparticle size distribution evolution by time. Colored rings in (A), dots in (B) and histogram in (C) correspond to each of the four time points that have the same color.



Fig. 2 Characterization of the CoO nanoparticle rings. (A) TEM image shows a mass of as-grown rings within the beam irradiated area. The histogram gives statistics on the ring size. (B) HRTEM image of the highly crystalline nanoparticles, nanoparticles are colored. (C) HRTEM and corresponding FFT (inset) indicate a zone axis along CoO [0 0 1]. (D) STEM-EDX elemental mapping (right) reveals Co in the ring within the yellow squared area (left).



Fig. 3 Dynamic behaviors of nanoparticles and nanodroplets. (A) TEM image sequence from Mov. $S3^{\dagger}$ and (B) its schematic illustration; four typical nanoparticles are labeled with numbers and different colors to indicate their motions, with 1 and 2 stacked onto 3 and 4 by droplet squeezing, respectively; all nanoparticles are aligned in the inter-droplet gap. (C) The trajectory of all the nanoparticles and coalescing droplets in (A) and (B) reflects their motions. (D) Time-series TEM images show nanoparticle motions on a coalesced nanodroplet surface, with off-perimeter nanoparticles finally trapped on the nanoparticle ring; inset, schematic illustration gives a cross-section view. (E and F) Nanodroplet coalescence. (E) Coalescence of two droplets shown with time-series TEM images; the contact bridge width W_b is indicated. (F) W_b by time. Blue boxes correspond to (E).

further droplet coalescence. During the coalescence process, there appeared to be strong repulsive forces between the nanoparticle and the droplet surface such that nanoparticles did not merge into the droplet. This clear interface between the nanoparticles and droplet can be seen in the images of Fig. 3A. We consider two important factors that may contribute to the maintaining of a distinct liquid droplet. Firstly, a repulsive nanoparticle surface may have formed from the oleylamine surfactant molecules covering the nanoparticles.^{18,26} Secondly, a very small droplet radius leads to a high capillary pressure difference Δp across the interface, as described by the Young–Laplace equation $\Delta p = 2\gamma/R$, in which γ is the surface tension and *R* is the radius of curvature.

We also investigate the overall droplet kinetics in order to elucidate the unique behaviors of liquid nanodroplets compared with macro scale droplets. Nanoparticle rings made low contrast droplet perimeters more visible when observing droplet behavior. Two typical values were tracked during the droplet coalescence, a contact bridge width W_b (Fig. 3E and F) and the combined length L_{a+b} (Fig. S4†). As shown in Fig. 3E, with an initial size ratio of ~1:1 for the two coalescing droplets, W_b shows an expanding rate of ~0.5 nm s⁻¹. This coalescence rate is size ratio dependent. With a large ratio of 2:1, coalescence slows down dramatically (Fig. 3F). With an initial size ratio of ~1:1, L_{a+b} gives a shrinking rate by ~0.05 nm s⁻¹. Comparing with macro scale counterparts,²⁷ these nanodroplets show a several orders of magnitude slower evolution speed (nm *vs.* µm), which is comparable with nanoscale solid evolution, such as nanoparticle coalescence in a liquid.²⁸ It is likely that the high surface to volume ratio of the nanodroplet leads to dominant surface effects, meaning interactions with the substrate and nanoparticles slow down the droplet coalescence and movement.

As the TEM images only give a projection of the assemblies and droplets, the 3D profile could not be revealed directly. However, the 3D morphology of a liquid nanodroplet can be inferred from the nanoparticle configuration and movements. During the nanoparticle ring formation, nanoparticle motion was strongly biased towards the droplet perimeter. We studied this process by tracking the motion of nanoparticles in Movies

Nanoscale

S1 and S3[†] and comparing them to a control video of the motion and assembly with no liquid droplets. In the control video (ESI Movie S4[†]), nanoparticles were assembled into a 2-D lattice on the flat substrate. To illustrate the relevant distances of these interparticle forces, we measured the distance over time of pairs of particles. The results in Fig. 4A demonstrate that nanoparticles are strongly attracted only when the surface to surface distance is <4 nm, which is on the order of the particle diameter. By investigating the motion of several particle trajectories, it is clear that the motion of nanoparticles is uncorrelated for pairs of particles when separated by more than 7 nm. These results are consistent with previous studies and nanoparticles are attracted by weak magnetic and van der Waals forces.²² On the contrary, nanoparticle trajectories when influenced by droplets revealed a different behavior. Due to the rapid droplet coalescence, it appears that some nanoparticles were lifted onto the droplet top surface (Fig. 4B). These nanoparticles were found moving rapidly on the liquid surface straight towards the droplet boundary (~0.5 nm s⁻¹, accelerating slightly faster upon approaching the triple line). The distance to the edge of the droplet is up to 15-20 nm, such that nanoparticle force interactions alone would be too weak to explain this behavior. These nanoparticles finally stopped on the droplet perimeter and became part of the nanoparticle ring. The average velocity profile in Fig. 4C reflects that there is a clear directional force directing the nanoparticle toward the droplet perimeter. This demonstrates the 3D elevation of the droplet which drives the particles to

roll off toward the droplet perimeter as well as the attractive forces from the particles in the ring.

To study nanodroplet morphology more quantitatively, we analyzed stacked nanoparticles which lean on the droplet surface to calculate a rough value of the contact angle for the nanodroplet. The nanoparticle projection reveals the stacking relationship as well as nanoparticle size, which can be used to calculate the contact angle; detailed calculations are illustrated in ESI.[†] According to our measurements, the average contact angle of the droplet shown in Fig. 4D is ~60°. Because of the relatively large size of the nanoparticle (average 4 nm by diameter), we cannot directly analyze the detailed profile of the contact line.

As has been shown above, nanoparticle ring formation appears to be related to the region near the triple-phase contact circle. Nucleation was preferential in this region and nanoparticles were fixed on the ring. We propose that the nanoparticle interacts with droplet surface in this perimeter region due to a gradient in curvature. As illustrated in Fig. 4D, there is a transition region between the assumed spherical profile and the contact line. A microscopic interpretation shows that, at this front, the liquid–gas interface directly interacts with the solid substrate. A transition region near the contact front is formed to compensate for this surface deformation and thus the profile of this region is no longer ideally spherical. When the droplet size is nanoscale, a notable deviation from the ideal spherical cap is expected. We calculated a transition region profile using a model accounting for



Fig. 4 (A) The surface-to-surface distance of pairs of nanoparticles were tracked over time. The control trajectories were measured on a flat surface without droplets with both interacting particles (red) and non-interacting particles (blue). The particle velocities at each distance from multiple trajectories were averaged. (B) A sample TEM image showing particle motion (blue) toward the edge of droplet with a reference particle (black). (C) Nanoparticle motion based on trajectory measurements between the blue particle and the red reference particle. Droplet height not to scale. (D) Nanoparticle leaning and stacking on the droplet surface near the droplet perimeter; the stacking relationship is illustrated by red (1st), blue (2nd) and yellow (3rd) labeled nanoparticles as illustrated in the lower diagram. Schematic illustration (bottom) of the sessile droplet transition region near the contact line with the estimated contact angle.

attractive Van der Waal forces²⁹ and parameters from our experimental results. The equation is given by

$$h = \tan \theta_{\rm e} \left(x - \frac{\delta_0}{\sqrt{1 - \cos \theta_{\rm e}}} \arctan\left(\frac{\sqrt{1 - \cos \theta_{\rm e}}}{\delta_0} \cdot x \right) \right) \quad (1)$$

where *h* and *x* are droplet height and horizontal position from droplet edge, respectively. δ_0 is a distance given by

$$\delta_0 = \sqrt{\frac{A}{12\pi\gamma(1-\cos\,\theta_{\rm e})}}\tag{2}$$

where θ_{e} is the equilibrium contact angle (1 rad is adopted in calculation), A is the attractive Hamaker constant (e.g. SiN_r water-air is on the order of 10^{-20} J (ref. 30)), 1×10^{-19} J is adopted in the calculation, γ is the surface tension (*e.g.* oleylamine (31.4 mJ m⁻²), oleic acid (32.79 mJ m⁻²), benzyl ether (40 mJ m⁻²)), 30 mJ m⁻² is adopted in the calculation. In Fig. S7[†] we calculate a possible profile for droplets of different sizes demonstrating that the transition region dominates an area of about 2-3 nm on the edge of the droplets and may introduce some effect on the curvature up to 10 nm from the droplet edge. Surface curvature is an important factor in nucleation and may explain the preference for particle nucleation near the contact line. Previous reports demonstrated that crystals nucleate more readily on lower curvature surfaces.³¹ This is consistent with our results, in which the lowest curvature part of the droplet occurs near the perimeter due to deviation from the spherical cap. Interaction between nanoparticle and droplet surfaces is driven by van der Waals forces. As the nanoparticles grow on the droplet surface, the lower curvature part should give a stronger attractive force while a higher curvature corresponds to a weaker interaction (for more details, see ESI[†]). This local curvature difference near the droplet perimeter may further explain why nanoparticles grow and assemble around the liquid nanodroplet edge. All the free offperimeter nanoparticles on the droplet are collected by the nanoparticle ring as they roll off the top or are squeezed toward the perimeter by coalescing droplets.

In summary, we observed CoO nanoparticle ring formation in a TEM liquid cell. CoO nanoparticles tracing a sessile nanodroplet perimeter resulted in necklace-like rings. The ring size varied depending on the size of the droplet template, but the ring width reflects the nanoparticle average diameter of ~4 nm. The rings were ideally circular in most cases with nanoparticles fixed in a 2D circle. We propose that the nanodroplet morphology contributes to the nanoparticle ring formation: firstly, nanoparticle nucleation and growth prefer the region near the perimeter; secondly, the curvature of the nanodroplet creates a gradient force that drives nanoparticles to the perimeter forming a ring. The nanoparticles retained their geometry on the substrate after liquid removal, demonstrating that this approach is viable for applications. Our study suggests a novel bottom-up nanostructure fabrication strategy, which could be applied to other materials systems in the future.

Author contributions

Y. Z. performed the *in situ* TEM experiments. Y. Z., A. P. and H. Z. analyzed the results. X. Z. prepared the liquid cells and samples. Y. Z., X. T. and K. B. performed the *ex situ* experiments. H. Z. designed the experiments and supervised the project. Y. Z. wrote the paper with discussion with L. S. and H. Z. All the authors participated in finalizing the paper.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

We used the facility at NCEM/Molecular Foundry in Lawrence Berkeley National Lab, which is funded by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, under contract no. DE-AC02-05CH11231. Y. Z. acknowledges funding support from the China Scholarship Council (201406090067). X. Z. acknowledges funding support from the China Scholarship Council (201406190080). L. S. acknowledges support from the National Natural Science Foundation of China (No. 51420105003, 11525415 and 113279028). H. Z. thanks the support of the DOE Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-05-CH11231 within the KC22ZH program.

References

- 1 H. G. Liao, L. Cui, S. Whitelam and H. Zheng, Real-Time Imaging of Pt3Fe Nanorod Growth in Solution, *Science*, 2012, **336**(6084), 1011–1014.
- 2 S. L. Tripp, S. V. Pusztay, A. E. Ribbe and A. Wei, Selfassembly of cobalt nanoparticle rings, *J. Am. Chem. Soc.*, 2002, **124**(27), 7914–7915.
- 3 P. A. Kralchevsky and K. Nagayama, Capillary forces between colloidal particles, *Langmuir*, 1994, **10**(1), 23–36.
- 4 P. A. Kralchevsky and K. Nagayama, Capillary interactions between particles bound to interfaces, liquid films and biomembranes, *Adv. Colloid Interface Sci.*, 2000, 85(2–3), 145– 192.
- 5 R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel and T. A. Witten, Capillary flow as the cause of ring stains from dried liquid drops, *Nature*, 1997, 389, 827– 829.
- 6 T. P. Bigioni, X. M. Lin, T. T. Nguyen, E. I. Corwin, T. A. Witten and H. M. Jaeger, Kinetically driven self assembly of highly ordered nanoparticle monolayers, *Nat. Mater.*, 2006, 5(4), 265–270.
- 7 E. Vignati, R. Piazza and T. P. Lockhart, Pickering emulsions: Interfacial tension, colloidal layer morphology, and

trapped-particle motion, *Langmuir*, 2003, **19**(17), 6650–6656.

- 8 J. X. Wang, O. Morales-Collazo and A. Wei, Micellization and Single-Particle Encapsulation with Dimethyl ammoniopropyl Sulfobetaines, *ACS Omega*, 2017, 2(4), 1287– 1294.
- 9 K. J. M. Bishop, C. E. Wilmer, S. Soh and B. A. Grzybowski, Nanoscale Forces and Their Uses in Self-Assembly, *Small*, 2009, 5(14), 1600–1630.
- 10 S. H. Sun, C. B. Murray, D. Weller, L. Folks and A. Moser, Monodisperse FePt nanoparticles and ferromagnetic FePt nanocrystal superlattices, *Science*, 2000, 287(5460), 1989– 1992.
- E. V. Shevchenko, D. V. Talapin, N. A. Kotov, S. O'Brien and C. B. Murray, Structural diversity in binary nanoparticle superlattices, *Nature*, 2006, 439(7072), 55–59.
- 12 C. B. Murray, C. R. Kagan and M. G. Bawendi, Synthesis and characterization of monodisperse nanocrystals and close-packed nanocrystal assemblies, *Annu. Rev. Mater. Sci.*, 2000, **30**, 545–610.
- 13 S. A. Claridge, A. W. Castleman, S. N. Khanna, C. B. Murray, A. Sen and P. S. Weiss, Cluster-Assembled Materials, ACS Nano, 2009, 3(2), 244–255.
- 14 W.-S. Chang, L. S. Slaughter, B. P. Khanal, P. Manna, E. R. Zubarev and S. Link, One-Dimensional Coupling of Gold Nanoparticle Plasmons in Self-Assembled Ring Superstructures, *Nano Lett.*, 2009, 9(3), 1152–1157.
- 15 S. Behrens, W. Habicht, K. Wagner and E. Unger, Assembly of Nanoparticle Ring Structures Based on Protein Templates, *Adv. Mater.*, 2006, **18**(3), 284–289.
- 16 I. V. Kuchin, O. K. Matar, R. V. Craster and V. M. Starov, Influence of the Disjoining Pressure on the Equilibrium Interfacial Profile in Transition Zone Between a Thin Film and a Capillary Meniscus, *Colloids Interf. Sci. Commun.*, 2014, 1, 18–22.
- 17 A. Méndez-Vilas, A. B. Jódar-Reyes and M. L. González-Martín, Ultrasmall Liquid Droplets on Solid Surfaces: Production, Imaging, and Relevance for Current Wetting Research, *Small*, 2009, 5(12), 1366–1390.
- 18 H.-G. Liao, D. Zherebetskyy, H. Xin, C. Czarnik, P. Ercius, H. Elmlund, M. Pan, L.-W. Wang and H. Zheng, Facet development during platinum nanocube growth, *Science*, 2014, 345(6199), 916–919.

- 19 T. Xu and L. Sun, Investigation on material behavior in liquid by in situ TEM, *Superlattices Microstruct.*, 2016, **99**, 24–34.
- 20 H.-G. Liao, K. Niu and H. Zheng, Observation of growth of metal nanoparticles, *Chem. Commun.*, 2013, **49**(100), 11720.
- 21 K.-Y. Niu, H.-G. Liao and H. Zheng, Visualization of the Coalescence of Bismuth Nanoparticles, *Microsc. Microanal.*, 2014, 20(02), 416–424.
- 22 J. Park, H. Zheng, W. C. Lee, P. L. Geissler, E. Rabani and A. P. Alivisatos, Direct Observation of Nanoparticle Superlattice Formation by Using Liquid Cell Transmission Electron Microscopy, *ACS Nano*, 2012, **6**, 2078–2085.
- 23 G. Lin, X. Zhu, U. Anand, Q. Liu, J. Lu, Z. Aabdin, H. Su and U. Mirsaidov, Nanodroplet-Mediated Assembly of Platinum Nanoparticle Rings in Solution, *Nano Lett.*, 2016, **16**(2), 1092–1096.
- 24 W.-I. Liang, X. Zhang, K. Bustillo, C.-H. Chiu, W.-W. Wu, J. Xu, Y.-H. Chu and H. Zheng, In Situ Study of Spinel Ferrite Nanocrystal Growth Using Liquid Cell Transmission Electron Microscopy, *Chem. Mater.*, 2015, 27(23), 8146– 8152.
- 25 H. Zheng, R. K. Smith, Y.-w. Jun, C. Kisielowski, U. Dahmen and A. P. Alivisatos, Observation of Single Colloidal Platinum Nanocrystal Growth Trajectories, *Science*, 2009, **324**, 1309–1312.
- 26 S. Mourdikoudis and L. M. Liz-Marzan, Oleylamine in Nanoparticle Synthesis, *Chem. Mater.*, 2013, **25**(9), 1465– 1476.
- 27 D. G. A. L. Aarts, H. N. W. Lekkerkerker, H. Guo,G. H. Wegdam and D. Bonn, Hydrodynamics of Droplet Coalescence, *Phys. Rev. Lett.*, 2005, 95, 164503.
- 28 J. M. Yuk, J. Park, P. Ercius, K. Kim, D. J. Hellebusch, M. F. Crommie, J. Y. Lee, A. Zettl and A. P. Alivisatos, High-Resolution EM of Colloidal Nanocrystal Growth Using Graphene Liquid Cells, *Science*, 2012, 336, 61–64.
- 29 A. Stocco and H. Möhwald, The Influence of Long-Range Surface Forces on the Contact Angle of Nanometric Droplets and Bubbles, *Langmuir*, 2015, **31**(43), 11835–11841.
- 30 L. Bergstrom, Hamaker constants of inorganic materials, *Adv. Colloid Interface Sci.*, 1997, **70**, 125–169.
- 31 A. Cacciuto, S. Auer and D. Frenkel, Onset of heterogeneous crystal nucleation in colloidal suspensions, *Nature*, 2004, **428**, 404–406.