Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting Information
for

# Growth and Assembly of Cobalt Oxide Nanoparticle Rings at Liquid Nanodroplets with Solid Junction

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**This Supporting file includes:**
Supporting Text
Captions for Movie S1 to S4
Figures S1 to S7

**Image Analysis Algorithm**

Intensity in a TEM image is a result of the scattering of electrons off the sample, which is affected by the local thickness of the scattering medium. Consequently, a perfectly spherical particle should show an approximately Gaussian intensity being thickest at the center and progressively thinner toward the edge.

Gaussian intensity 'blobs' in the image are identified by convolving the image with a Laplacian of the Gaussian filter (LoG), which produces strong signal at the center of a blob matching the size of the filter. This is fast, which is critical for the large size of the images across the hundreds of frames of the movie as seen in Figure S1. The algorithm developed for this study utilizes a 'scale space' approach, which applies successively larger filters to identify different blobs at different scales. The noisy lower resolution videos used filters from 7x7 to 19x19 pixels and the higher resolution used filters from 19x19 to 37x37 pixels. The size of the filter corresponds to 2*ceil(3*sigma)+1 where the radius of a blob is approximated at 1.5*sigma.

At each scale the local maximums of the filtered image were selected and a threshold applied to obtain particle centers, though the threshold applied differed depending on the scale. Because the particles are likely identified at multiple similar scales as in Figure S2, particles with some percent of their area overlapping are filtered by keeping only the particle that gave the largest intensity response to the LoG filter.

Accuracy of the detection method was defined as 1 - (number of particles missed + incorrectly identified noise)/(total number of particles). An example of identification in a difficult image can be seen in Figure S3.

**Analysis of Force Generated from Curvature Gradient**

As most of the interaction generated from the mass is due to a very close range interaction between droplet and NP, a classic two balls condition was employed to estimate the differential in surface forces as shown in the Figure.

The vdW force between two balls is:

$$F(r) = -\frac{AR_1R_2}{(R_1 + R_2)6r^2}$$

Here, we estimate the Hamaker coefficient, $10^{-19}$~$10^{-20}$J, $R_2$=2nm, r=0.1nm,

With $R_1$=20nm，F=0.303~3.03nN;with $R_1$=200nm, F=3.03~30.3nN. The force difference is 2.7~27nN, which is strong enough for NP moving, referring to NP moving by pN order force in previous report[1].

**Analysis of Transition Region**

Three spherical caps (radius 5nm, 10nm, 50nm, respectively; with 1 rad contact angle) are shown for comparison. 0.1nm deviation by $h$ between calculated profile (red line in Fig. S7 C) and corresponding macro spherical profile (blue dashed line in Fig. S7 C) is considered to define the transition boundary, size of the transition region could be ~10 nm(indicated by blue dashed arc in Fig. 4C), which is a considerable part for radius <50 nm droplet. Moreover, because of much smaller $h$ in transition region of these ultrasmall droplets, there is much stronger interaction between substrate and liquid-gas interface, which leads to more deviation from the ideally spherical shape and the transition region would be even wider. Because of the deviation, the aspherical droplet morphology

will lead to a gradient in curvature with a higher curvature at the center and lower on boundary circle.

**Movie captions**

**Movie S1 and S2.** Rapid growth and assembly of CoO nanoparticles around liquid nanodroplets. The original movie was captured at 5 frames per second. Movie plays at 10 times faster than the original speed.

**Movie S3.** Rapid growth and assembly of CoO nanoparticles around liquid nanodroplets. The original movie was captured at 5 frames per second. Movie plays at 20 times faster than the original speed.

**Movie S4.** Self assembly of CoO nanoparticles on a flat SiNx membrane without liquid droplets. The original movie was captured at 5 frames per second. Movie plays at 10 times faster than the original speed.

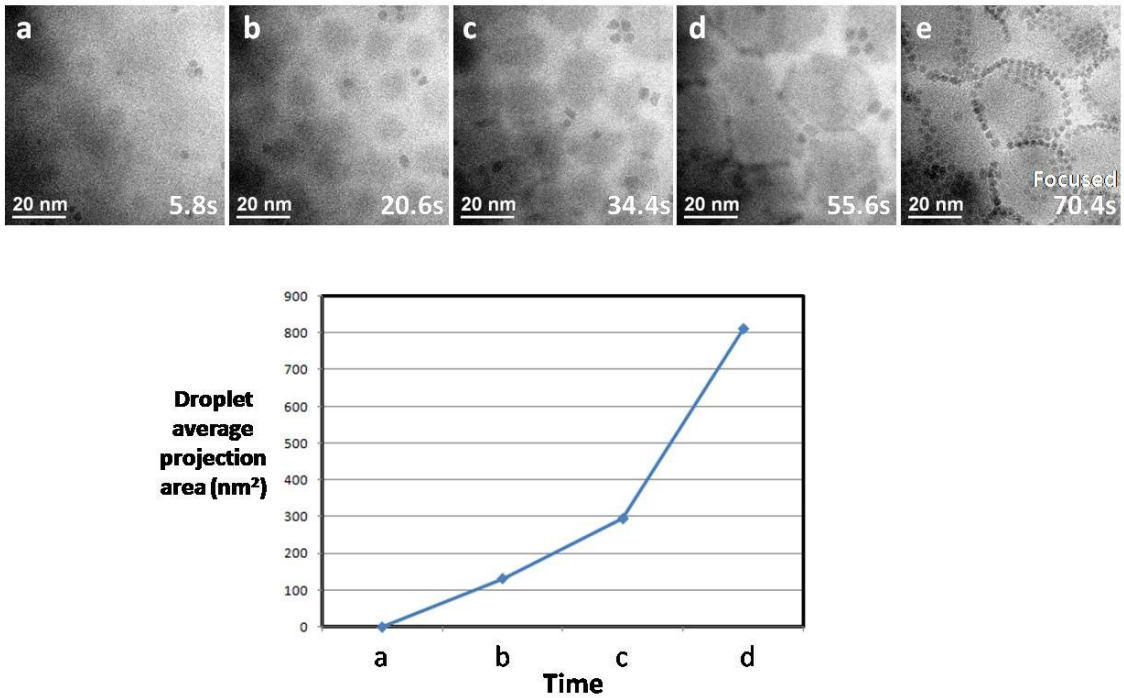


**Figure S1.** Sequential images from Mov. S1. Formation of the nanodroplets occurs near the beginning of the video in parallel with NP growth. In Fig. a to d, images are defocused to enhance liquid contrast. Nanodroplet grow quickly by coalescence, doubling in area each 10-20 seconds.

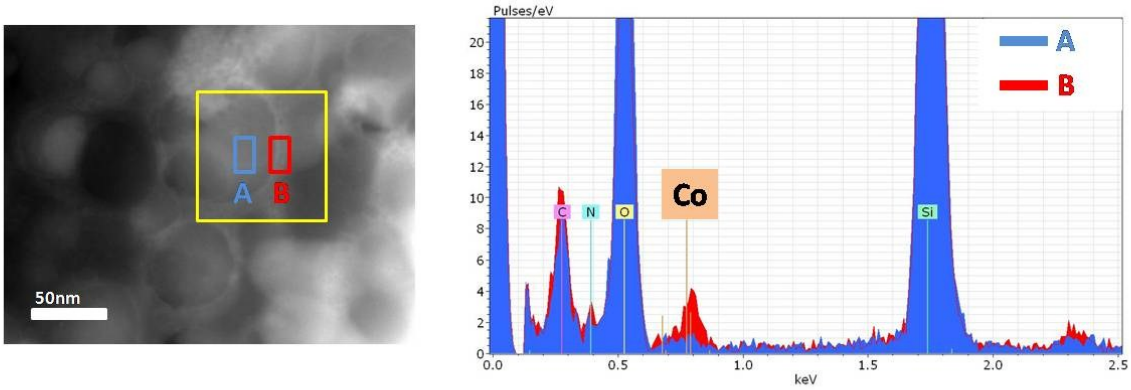


**Figure S2.** EDS spectrums of two positions show that Co concentrates on ring. For Fig. 2D.

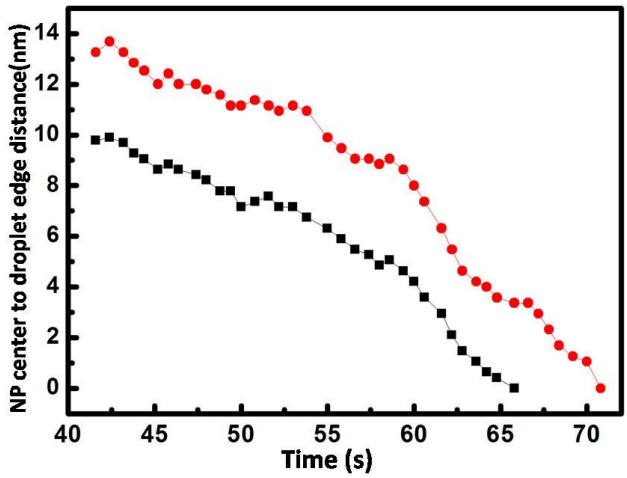


**Figure S3.** Measurement of the distance between NP to droplet border by time.

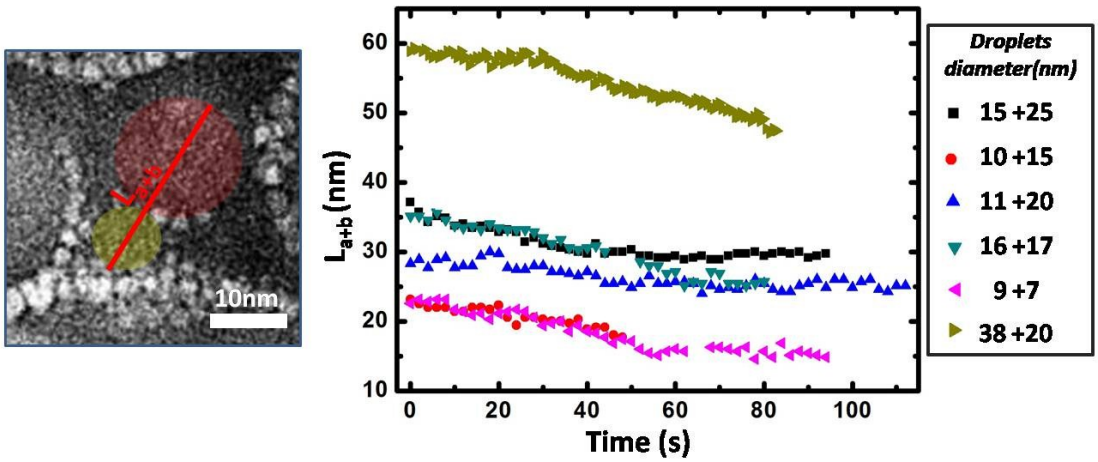


**Figure S4.** Combined length $L_{a+b}$ of coalescing droplets for droplets of different size ratios. The length shows a decreasing trend as the droplet assumes the new spherical shape of the coalesced droplet.

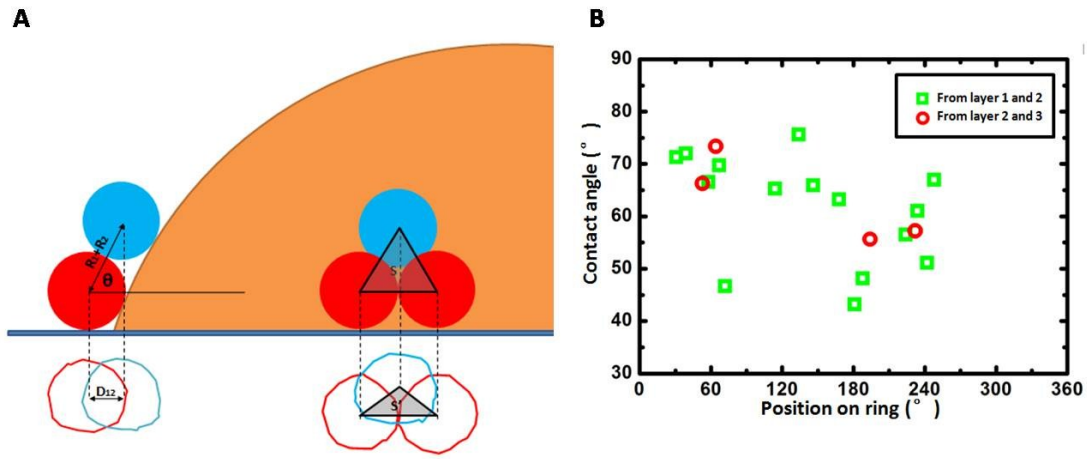


**Figure S5.** (A) Schematic diagram of contact angle calculation by NP projection. Contact angles were calculated as following: vertical stacking (left): $cos\theta = \frac{D_{12}}{(R_1 + R_2)}$; triangle stacking(right): $cos\theta = \frac{S'}{S}$. (B) Measured contact angle from Fig. 4A. Green squares calculated from 1st and 2nd NP layers, and red dots calculated from 2nd and 3rd layers.

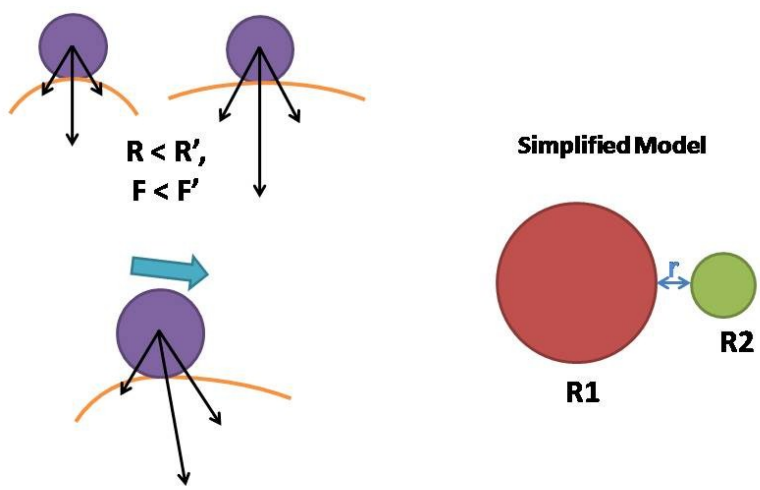


**Figure S6.** Illustration of the vdW force between NP and droplet. A non-uniform surface curvature may generate a directional force on the nanoparticle resting on the droplet surface.

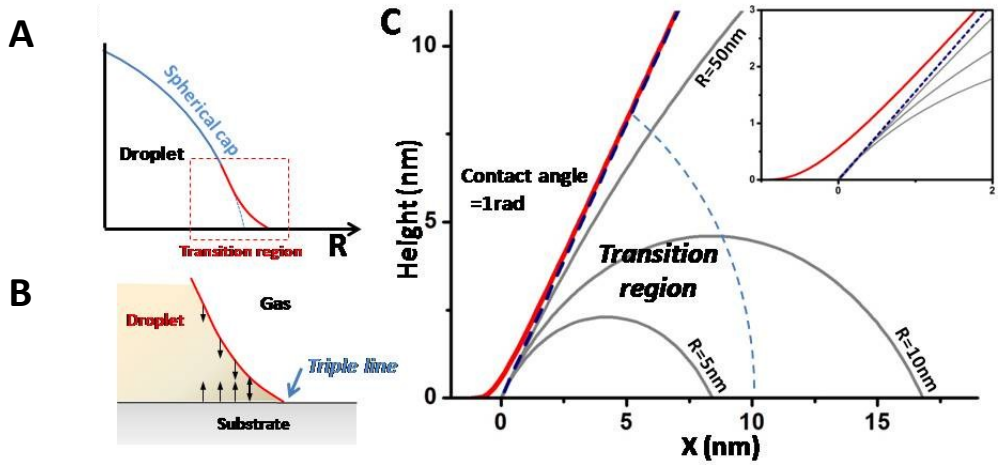


**Figure S7.** (A) Proposed droplet profile and (B) interpretation of its generation by attractive vdW forces between liquid-gas interface and substrate. (C) Comparison of calculated transition region profile (red), macro scale spherical cap profile (dashed blue) and three nano-scale spherical profiles (radius 5nm, 10nm, 50nm) with 1rad contact angle. 10nm transition region is illustrated. (Inset) magnified contact front showing the aspherical transition region.