

# Self-Organizing Arrays of Size Scalable Nanoparticle Rings

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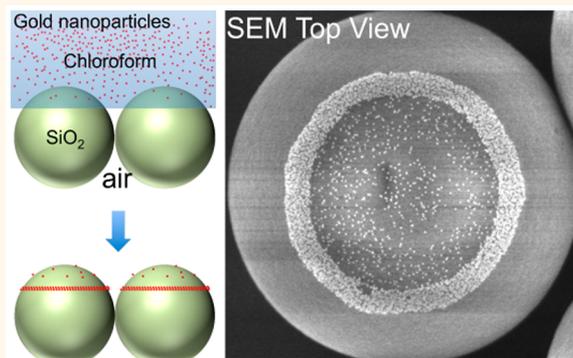
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**S** Supporting Information

**ABSTRACT:** A central challenge in nano- and mesoscale materials research is facile formation of specific structures for catalysis, sensing, and photonics. Self-assembled equilibrium structures, such as three-dimensional crystals or ordered monolayers, form as a result of the interactions of the constituents. Other structures can be achieved by imposing forces (fields) and/or boundary conditions, which Whitesides termed “self-organization”. Here, we demonstrate contact line pinning on locally curved surfaces (*i.e.*, a self-assembled monolayer of SiO<sub>2</sub> colloidal particles) as a boundary condition to create extended arrays of uniform rings of Au nanoparticles (NPs) on the SiO<sub>2</sub> colloids. The mechanism differs from the well-known “coffee-ring” effect; here the functionalized NPs deposit at the contact line and are not driven by evaporative transport.

Thus, NP ring formation depends on the hydrophobicity and wetting of the SiO<sub>2</sub> colloids by the chloroform solution, ligands on the NPs, and temperature. The NP rings exhibit size scaling behavior, maintaining a constant ratio of NP ring-to-colloid diameter (from 300 nm to 2 μm). The resultant high-quality NP ring structures are expected to have interesting photonic properties.

**KEYWORDS:** nanoparticle rings, SiO<sub>2</sub> monolayer, wetting, contact line, scaling behavior



Beyond their aesthetic appeal, ring-like materials have received significant attention over a wide range of real-world cases and technological applications due to their structural symmetry and interesting properties.<sup>1–3</sup> For example, the bacterial light-harvesting assemblies, LH1 and LH2, have ring structures to facilitate excitation transport.<sup>4,5</sup> Ring-like superconductors can sustain “persistent currents”,<sup>6</sup> while metallic rings yield optical resonance properties and special magnetic responses, which make them promising for application in sensing and data storage.<sup>7–9</sup> Recently, micrometer to nanometer scale ordered ring-like structures have received increasing interest for device miniaturization.<sup>3,10–12</sup> For example, ultracompact subwavelength waveguides, including interferometers and ring resonators, were fabricated with ring-like structures for large-angle bending and splitting of radiation.<sup>10</sup> Therefore, robust methods to fabricate large arrays are required to further device development and miniaturization.

Ring-like nanostructures have been prepared using various approaches such as e-beam lithography, microcontact printing, and colloidal templating.<sup>13,14</sup> However, lithography, including evaporating metals on an array of colloidal particles,<sup>15</sup> and microcontact printing can be complex and challenging to obtain nanometer precision over large scales. Alternatively, processes involving direct manipulation of nanomaterials might cause

mechanical damage to the ring-like structures that would alter their physical properties in addition to the difficulty of creating large numbers of repeated structures.<sup>16</sup> Bottom-up self-assembly and self-organization of nanoparticles (NPs) into ordered structures have the potential for parallel fabrication of particular structures with nanoscale precision at relatively low cost.<sup>7,17–26</sup> Self-assembly of NPs into ring-like nanostructures has been accomplished using several approaches. Using water droplet templates<sup>17</sup> resulted in a high yield of ring structures but lacked control of ring size and location over the entire substrate. Therefore, precisely fabricating well-ordered arrays of NP-based ring-like nanostructures with scalable sizes in an efficient and simple manner is still an open challenge.

In the present paper, we report a surprisingly simple method that achieves these goals. Our approach involves NPs in solution attaching to the boundaries defined by the contact line of a solvent that is pinned on locally curved surfaces. The local curvature is provided by nano-to-microscale SiO<sub>2</sub> colloidal spheres that are readily self-assembled into ordered monolayers. These colloids guide the formation of an ordered array of NP

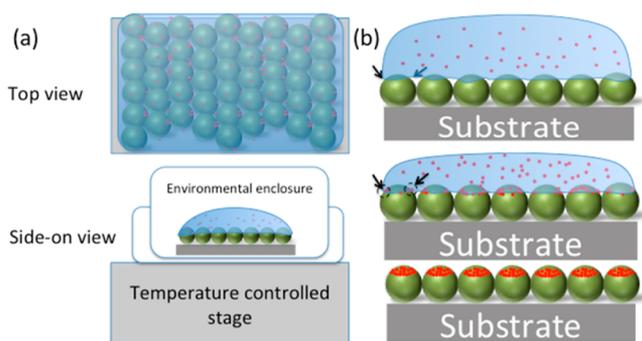
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rings. The driving force for NP transport and self-organization depends mainly on NP segregation at the liquid–air interface and to a lesser degree on the motion of the drying front. Therefore, the morphology (*i.e.*, rings *vs* disordered particle coatings) can be controlled by the experimental parameters such as substrate temperature, NP concentration, packing of the SiO<sub>2</sub> colloid monolayers, and the ligands on the NPs. The sizes of the resulted rings are primarily determined by the size of the SiO<sub>2</sub> colloids and the humidity. The arrays of NP rings can be formed over regions several tens of mm<sup>2</sup> in size. Here, we demonstrate NP ring formation with suitably functionalized Au NPs (~10 nm dia.). However, the process also works for a range of suitably functionalized metal and semiconductor NPs.

## RESULTS AND DISCUSSION

In a typical Au NP self-organization experiment, as shown in Figure 1, a small volume of the Au NP solution is deposited on the SiO<sub>2</sub> colloid monolayer (which is itself formed on a Si substrate), and the chloroform solvent is allowed to evaporate at a selected temperature (details in the Methods Section).



**Figure 1.** Schematic of the self-organization experiment (not to scale). (a) The experimental set up for depositing NPs on a self-assembled monolayer of SiO<sub>2</sub> spheres. (b) An overview of Au NP deposition on a monolayer of SiO<sub>2</sub> spheres as ring-like structures. A drop of Au NP/chloroform solution (blue) covers the surface of the monolayer of SiO<sub>2</sub> spheres (green) and is allowed to evaporate. The evaporation of solvent causes NPs to both deposit and to increase in concentration in the remaining chloroform solution. Under the correct conditions, NPs deposit at the pinned chloroform–SiO<sub>2</sub> contact line. Eventually, the solvent will have completely evaporated leaving the Au NPs deposited on each SiO<sub>2</sub> sphere. Large regions of the SiO<sub>2</sub> colloid array are coated with highly uniform Au NP ring structures.

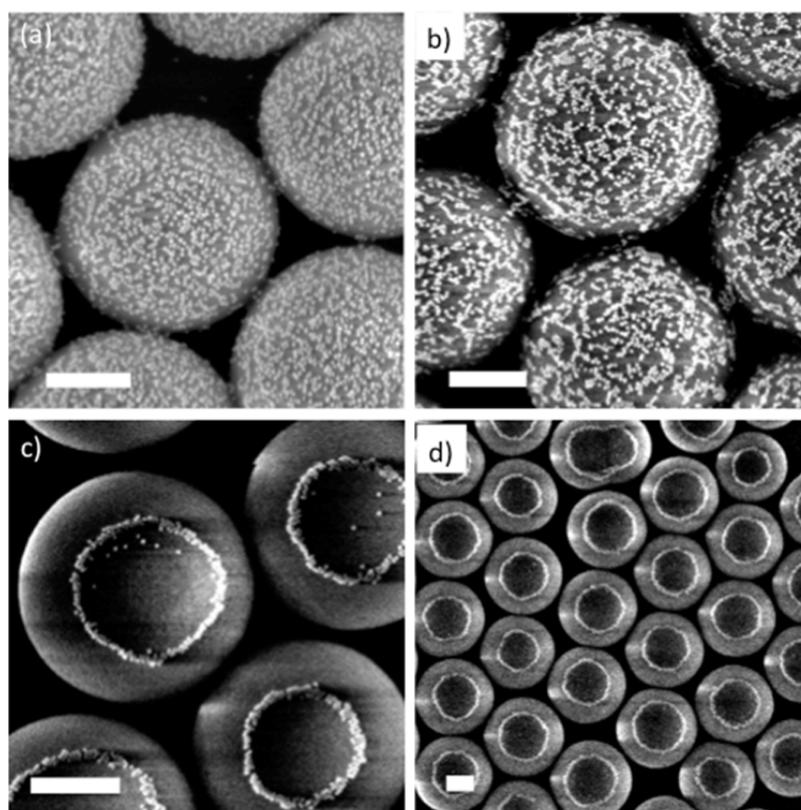
**Temperature Dependence.** The morphologies of the resultant samples were examined by SEM. Figures 2a and S1 reveal that Au@MT(PEG)<sub>4</sub> NPs (diameter ~10 nm, deposition at 21 °C and 50% relative humidity (RH)) are randomly deposited over the entire surface of the SiO<sub>2</sub> colloids (diameter ~600 nm). Such a NP coating reflects significant wetting of the dispersing medium; the contact angle of chloroform to SiO<sub>2</sub> is <10° at room temperature, which means that it can fully wet the SiO<sub>2</sub> spheres.<sup>27</sup> Even the Si wafer substrate supporting the monolayer of SiO<sub>2</sub> spheres was coated with Au NPs (Figure S1). Figure 2b shows the results of another experiment (also performed under ~50% RH), but with the substrate heated to 60 °C while the colloidal solution evaporates. Here, as well as in Figure S2, the Au NPs form string-like structures on the SiO<sub>2</sub> surface. The string-like features are reminiscent of kinetic-driven aggregation, which is more likely at 60 °C than at 21 °C

because the solvent evaporation is much faster; <1 min at 60 °C *vs* ~10 min at 21 °C.<sup>28</sup> Similar types of lateral aggregation of NP formation were also observed in previous reports.<sup>29,30</sup>

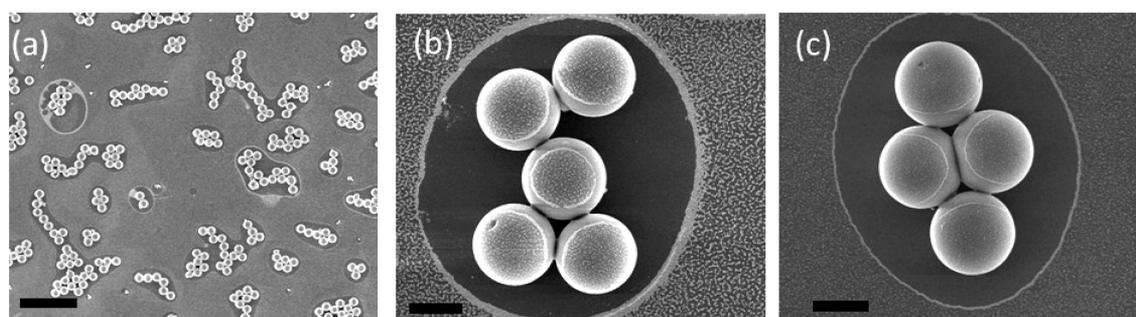
By contrast, Au NP deposition is remarkably different when conducted using a cooled substrate adjusted to near 0 °C with an ice bath. As shown in Figure 2c, the Au NPs self-organize into ring-like structures that are deposited only on the top hemisphere of individual SiO<sub>2</sub> spheres; no NPs are deposited outside of the rings or on the Si substrate. Furthermore, the ring structures form over a major fraction of the SiO<sub>2</sub> colloid monolayer substrate. Figure 2d shows a larger region (~3 × 3 μm<sup>2</sup>) of the sample. The drastically different structures in Figures 2c,d *vs* 2a,b suggest a large change of the wetting behavior of chloroform (*i.e.*, the chloroform solutions) at the lower temperature. It is known that SiO<sub>2</sub> spheres are poorly wetted by chloroform at 0 °C due to their hydrophobicity. In fact, chloroform does not wet the entire surface of the SiO<sub>2</sub> sphere monolayers; the chloroform containing Au NP solution is located only on the top of the SiO<sub>2</sub> spheres at near 0 °C as depicted in Figure 1b. These results clearly demonstrate that the interfacial energy between the chloroform and the SiO<sub>2</sub> surface varies with temperature. We will demonstrate below that the formation of Au NP rings is related to the strong pinning force at the chloroform–SiO<sub>2</sub> contact line.

The wetting behavior of chloroform at 0 °C and ~50% RH was further studied on sparsely deposited SiO<sub>2</sub> spheres of ~2 μm diameter. Figure 3a–c shows that the Au NPs were deposited either on the Si substrate, but only starting a significant distance away from the isolated SiO<sub>2</sub> spheres, or on the surface of SiO<sub>2</sub> spheres as ring-like structures. On the Si substrate, Au NPs were densely packed at the “edge of a bubble” and sparsely deposited at larger distances. The location and size of the Au NP ring structures on the SiO<sub>2</sub> spheres vary depending on the local packing condition of the SiO<sub>2</sub> spheres and the proximity of each SiO<sub>2</sub> colloid to the perimeter of the cluster (see Figure 3b,c). Specifically, the SiO<sub>2</sub> spheres that are packed with neighboring spheres have Au NP ring structures that are similar to what we observe on monolayer samples (Figure 2c,d). However, the SiO<sub>2</sub> spheres located at the periphery of a group have larger ring structures that might also be skewed off center of the sphere. These results demonstrate that chloroform poorly wets the SiO<sub>2</sub> spheres at 0 °C and in fact only contacts the top hemisphere of the spheres. From Figure 3b,c, it is readily apparent that the chloroform solution smoothly extends as a dome of small curvature to the Si substrate enclosing a vapor bubble. Therefore, a contact line was formed on each SiO<sub>2</sub> sphere. It is important to note that an ordered monolayer of SiO<sub>2</sub> spheres is not necessary for the formation of Au NP ring structures.

**Scaling of Au NP Ring Size.** The effect of SiO<sub>2</sub> sphere size on the Au NP ring structure was investigated using SiO<sub>2</sub> spheres from 300 nm to 2 μm diameter (all values are summarized in Table 1). Three sizes of SiO<sub>2</sub> spheres with mean diameters of 306 ± 23, 556 ± 22, and 693 ± 21 nm at ~50% RH and three sizes of SiO<sub>2</sub> spheres with mean diameters of 378 ± 24, 554 ± 20, and 1775 ± 54 nm at ~35% RH were used to fabricate high-quality SiO<sub>2</sub> monolayers for the preparation of Au NP coatings and ring structures. SEM images (Figure 4a–f) show that Au NP ring structures formed on all samples at 0 °C. We define the relative size, *r*, as the ratio of ring radius (*R*) to SiO<sub>2</sub> sphere radius (*L*); *i.e.*,  $r_i = R_i/L_i$  for each colloid of type *i*, as illustrated in Figure 4g. Scatter plots of the scaled ring radius  $r_i$  to scaled SiO<sub>2</sub> colloid radius  $L_i/\langle L_i \rangle$ , are shown in Figure



**Figure 2.** SEM images of various Au@MT(PEG)<sub>4</sub> NP structures formed as a function of substrate temperature. (a) SEM image of Au NPs on SiO<sub>2</sub> spheres under ~50% RH and the substrate maintained at 21 °C during evaporation. (b) SEM image of the formation of Au NPs on SiO<sub>2</sub> spheres at ~50% RH and the substrate maintained at 60 °C during evaporation. (c) SEM image of the formation of Au NPs on SiO<sub>2</sub> spheres at ~50% RH and substrate at 0 °C during evaporation. (d) A zoomed-out SEM image of (c). The Au NPs are the bright dots, strings or rings in the images. All scale bars are 200 nm.

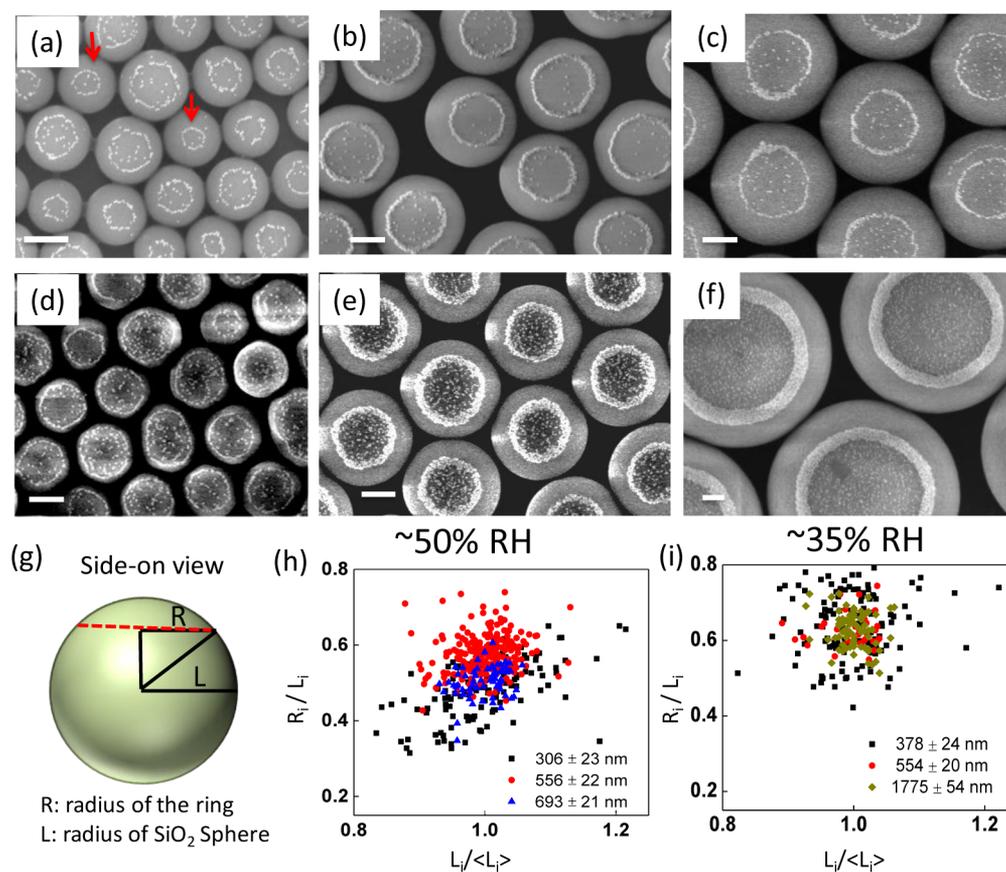


**Figure 3.** SEM images of formations of Au@MT(PEG)<sub>4</sub> NPs on a sparsely deposited SiO<sub>2</sub> sphere (with diameter ~2 μm) sample, which was prepared under 35% RH and the substrate temperature was kept at 0 °C. (a) Low- and (b, c) high-magnification SEM images. Scale bars: (a) 10 and (b, c) 1 μm. (Analogous results are obtained for other size SiO<sub>2</sub> colloids.)

4h,i. The relative sizes of the Au NP rings are  $r_i = 0.47, 0.57,$  and  $0.51$  for the 306, 556, 693 nm SiO<sub>2</sub> sphere samples at ~50% RH and  $r_i = 0.64, 0.63,$  and  $0.64$  for the 378, 554, 1775 nm sphere samples at ~35% RH, respectively. Note, the evaporation rate of chloroform under these relative humidity conditions should be the same by Dalton's law. The close agreement of the measured values of  $r_i$  for each humidity condition shows that the formation of Au@MT(PEG)<sub>4</sub> NP rings occurs for a wide range SiO<sub>2</sub> sphere sizes. Moreover, Figure 4h,i which shows that the ratio of Au NP ring radius to SiO<sub>2</sub> sphere radius is constant under same relative humidity condition, regardless of SiO<sub>2</sub> sphere radius. This demonstrates size scaling (with the mean as the scaling parameter). That is,

the self-organization of Au NP rings is a scale-free phenomenon.

Furthermore, the size of the Au NP ring on a given SiO<sub>2</sub> sphere also depends on the packing of the nearby SiO<sub>2</sub> spheres and thus varies in certain ranges associated with the polydispersity and packing quality of the SiO<sub>2</sub> spheres. For example, for 306 nm diameter SiO<sub>2</sub> spheres, the Au NP rings indicated by red arrows in Figure 4a have significantly smaller radii than the surrounding rings. Therefore, since the 306 nm SiO<sub>2</sub> spheres have a greater polydispersity than the other ones (Figure 4h), there is greater scatter in  $R/L$ . Conversely, the monolayers of the larger size SiO<sub>2</sub> spheres are more uniform and better packed, and thus the distributions of Au NP ring diameters are narrower. This conclusion is further confirmed by



**Figure 4.** SiO<sub>2</sub> size impacts the properties of the Au NP ring structures. (a–f) SEM images of Au NP rings on the monolayers prepared, separately, with SiO<sub>2</sub> spheres of three sizes. Their mean diameters: (a) 306 ± 23, (b) 556 ± 22, (c) 693 ± 21, (d) 378 ± 24, (e) 554 ± 20, and (f) 1775 ± 54 nm. Scale bar: 200 nm. (g) a schematic side view of a SiO<sub>2</sub> sphere, defining  $r = R/L$ ; (h,i)  $R_i/L_i$  plotted against  $L_i/\langle L_i \rangle$ , for SiO<sub>2</sub> monolayer substrates with  $\langle L_i \rangle = 306, 556, 693$  nm at ~50% RH and  $\langle L_i \rangle = 378, 554, 1775$  nm on the ~35% RH, respectively.

**Table 1. Parameters for Au NP Ring Formation**

relative humidity	SiO <sub>2</sub> diameter (nm)	ratio ( $R/L$ )	relative standard deviation ( $L, R/L$ )
~50%	306 ± 23	0.47 ± 0.08	(7.5%, 17.9%)
~50%	556 ± 22	0.57 ± 0.06	(4.0%, 10.0%)
~50%	693 ± 21	0.51 ± 0.05	(3.0%, 10.4%)
~35%	378 ± 24	0.64 ± 0.09	(6.4%, 13.6%)
~35%	554 ± 20	0.63 ± 0.05	(3.7%, 7.3%)
~35%	1775 ± 54	0.64 ± 0.05	(3.0%, 8.3%)

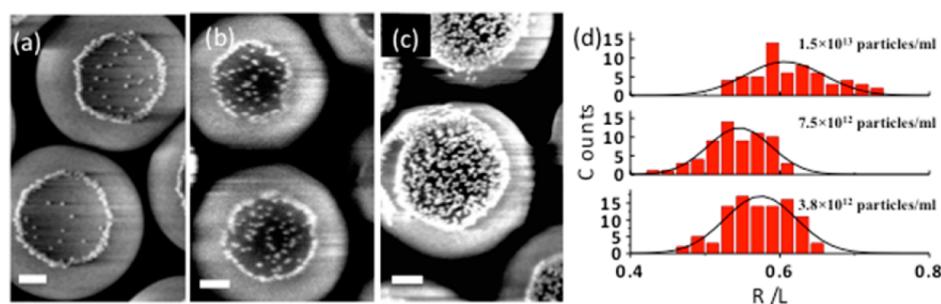
the relative standard deviation (RSD) of relative ring sizes ( $R/L$ ) vs RSD of SiO<sub>2</sub> sphere diameters ( $L$ ) shown in Figure S3. The yellow shaded region of Figure S3 highlights the larger RSDs of  $L$  (7.5%, 6.4%) associated with the smaller SiO<sub>2</sub> spheres (306 nm, 378 nm dia.) that exhibit larger RSDs of  $R/L$  (17.9%, 13.6%), while the blue shaded region highlights the more uniform samples (554 nm, 556 nm, 693 nm, 1775 nm dia.) with smaller RSDs of  $L$  that exhibit smaller RSDs of  $R/L$ ; the ( $L, R/L$ ) are (4.0%, 10.0%); (3.0%, 10.4%), (3.7%, 7.3%); (3.0%, 8.3%), respectively.

These dependences of ring size and ring position on the SiO<sub>2</sub> colloid correspond well to the expected shifts in the chloroform solution contact lines on the SiO<sub>2</sub> spheres. For example, we show in the geometrical model in the Supporting Information that when a large sphere is adjacent to a smaller one, its contact line should be displaced toward its neighbor. Likewise, the contact line on the smaller sphere is displaced away from its

larger neighbor. Thus, the contact line for a smaller sphere surrounded by larger ones is displaced away from its neighbors in all directions and thus contracts, as shown in Figure 4a.

**Au NP Concentration Dependence.** The concentration of the Au NP colloidal solution also plays a role in Au NP ring formation on SiO<sub>2</sub> spheres. Figure 5a–c shows SEM images of Au NP rings obtained for three different Au NP colloid concentrations (number densities) in chloroform. It is clear that Au NP rings are not affected by the Au NP concentration. All ring-like structures formed at various Au NP concentrations exhibit the same relative size,  $r$ . The distributions of the relative size,  $r$ , at different Au NP concentrations are shown in Figure 5d. From Gaussian fitting, the distributions for the three cases are centered at  $0.61 \pm 0.05$ ,  $0.55 \pm 0.04$ , and  $0.57 \pm 0.05$ , respectively, indicating that the relative size of the rings is not affected by the Au NP concentration in solution. On the other hand, the concentration of Au NPs does impact their deposition and density within the boundary of the Au NP ring. There are few or no NPs observed inside the rings (Figure 5a), when a low concentration Au NP solution is used. The number of interior NPs increases with concentration, as does the width of the ring annulus.

The location and motion of the chloroform drop on the SiO<sub>2</sub> spheres can affect the details of the density of Au NPs deposited and presumably also their transport in the droplet. We monitored the progression of the chloroform drop shape and volume during evaporation at 21 °C and ~50% RH. The motion of a chloroform drop (Movie S1) clearly shows that it



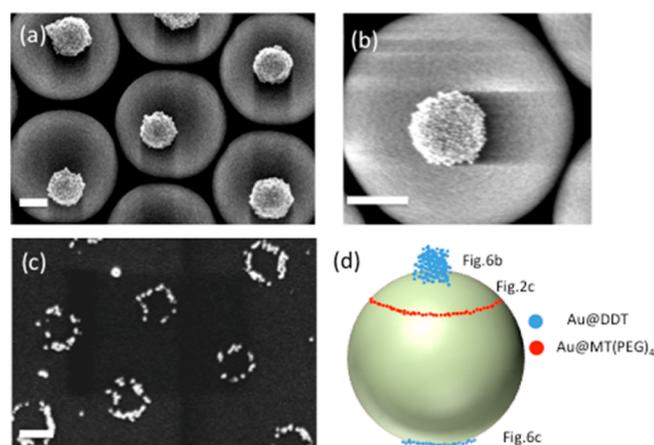
**Figure 5.** Impact of concentration on the properties of the Au NP ring structures. Samples were  $556 \pm 22$  nm SiO<sub>2</sub> spheres with 10 nm Au NP, prepared under 50% RH and 0 °C substrate temperature. (a–c) SEM images of Au NP rings assembled with various concentrations of Au NPs in solution. Number densities: (a)  $3.8 \times 10^{12}$ , (b)  $7.5 \times 10^{12}$ , and (c)  $1.5 \times 10^{13}$  particles/mL. Scale bar: 100 nm. (d) Relative sizes,  $r = R/L$  plotted for different concentrations of Au NP colloids in solution.

shrinks to smaller size, and the contact angle on the SiO<sub>2</sub> colloid monolayer remains unchanged throughout. Thus, the chloroform drop shrinks to maintain the contact angle and does not spread (Movie S1).

Therefore, the density of Au NPs on the surface varies across the entire substrate due to more rapid reduction of the solution volume *vs* the rate of Au NP deposition. That is, the Au NP solution becomes more concentrated as the evaporation of the chloroform solution proceeds. Figure S4 shows SEM images from various locations on the SiO<sub>2</sub> monolayer. It is obvious that the density of Au@MT(PEG)<sub>4</sub> NPs is increasing from the edge to the center as the solvent evaporates. We confirmed this by taking SEM images on the edge and near the center of the samples (Figure S4). Depending on the initial Au NP concentration, regions a–d will have different relative areas on the substrate as expected.

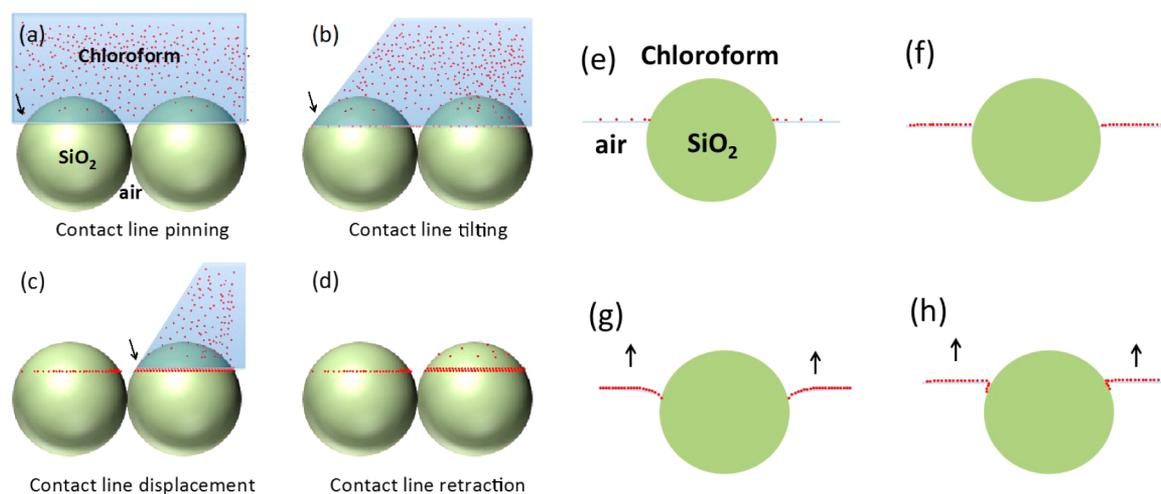
**Surface Wetting and Hydrophobicity.** The way that chloroform wets the SiO<sub>2</sub> spheres is related to the interfacial energy between the chloroform and the SiO<sub>2</sub> surface. In our experiments, condensation of water on the surface of the SiO<sub>2</sub> spheres at near 0 °C would affect the interfacial energy, wetting behavior, and contact angles.<sup>31</sup> To demonstrate the importance of water condensation, a control experiment was conducted under continuous nitrogen purge while the substrate was cooled to 0 °C so that the particle deposition occurs in the absence of humidity. As shown in Figure S5, no Au NP ring structures form on the SiO<sub>2</sub> spheres! This result indicates that a condensed layer of water forms on the surface of SiO<sub>2</sub> spheres as the freezing point of water is approached (*i.e.*, below the dew point) and that this plays a key role in Au NP ring formation. It should be emphasized that the morphology is due to the relative humidity instead of the evaporation rate; while the evaporation rate is faster under the nitrogen purge condition than other relative humidity conditions ( $\sim 35\%$  RH,  $\sim 50\%$  RH), the evaporation is also faster at elevated temperatures where NP rings do not form.

To further confirm the role of surface hydrophilicity on the formation of Au NP ring structures, we altered the ligand coating on the Au NPs. Figure 6a,b shows that dodecanethiol-coated Au NPs (Au@DDT NPs) organize into “compact mound” structures under the same experimental conditions (the substrate cooled to 0 °C,  $\sim 50\%$  RH at 21 °C in the lab). This result is in striking contrast to the rings formed for PEG-coated Au NPs and confirms that the different affinity of Au NPs, with hydrophilic or hydrophobic ligands, to SiO<sub>2</sub> (and the water layer coating SiO<sub>2</sub>) determine the type of Au NP structures formed.



**Figure 6.** Impact of humidity and ligands on Au NP-SiO<sub>2</sub> interactions. (a, b) Low- and high-magnification SEM images of Au@DDT NPs forming compact Au NP mounds under  $\sim 50\%$  RH, substrate at 0 °C. (c) SEM image of Au@DDT NPs forming rings beneath the SiO<sub>2</sub> colloids under  $\sim 50\%$  RH, substrate at 21 °C. Scale bar: 200 nm. (d) Schematic of Au NP structures formed: Au NP ring-like structures as in Figure 2c, compact mound structure as in (b) and ring formation as (c) are depicted relative to where they form on or near an SiO<sub>2</sub> colloid.

Given the hydrophobic nature of the Au@DDT NPs, there should only be a weak interaction between them and the water coated SiO<sub>2</sub> surface. Since we did not find any Au@DDT NPs on SiO<sub>2</sub> spheres at the outer edge of the chloroform drop, we deduce that in the early stage of chloroform evaporation, the Au@DDT NPs remain in the solvent rather than attach to the contact line. In the later stage of evaporation, when the Au@DDT NPs become over saturated in the chloroform solvent, nucleation events will occur, and Au@DDT NPs will precipitate from the solvent. The nucleated Au@DDT NPs self-assemble into a close packed structure in order to minimize their overall energy, analogous to the colloidal microscopic “soccer balls” formed when evaporating a hydrophilic colloidal solution on a superhydrophobic surface.<sup>32</sup> Thus, we observe small compact mounds of Au NPs, as shown in Figure 6a,b. Ultimately, at the completion of chloroform evaporation, there are large accumulations of Au@DDT NPs. Figure S6 is an SEM image taken at the center of the sample showing a region that has both the compact mounds on selected SiO<sub>2</sub> spheres and continuous Au@DDT NPs aggregations at the end of evaporation. The compact mounds are not correlated to



**Figure 7.** A schematic representation of our proposed mechanism for the evaporation of Au NP (red dots) solution on the boundary of the sample (arrows indicate the change of the contact line) (a–d) and mechanism of contact line pinning (and rising) and for the deposition of Au NP (red dots) to form Au NP rings (e–g) (not to scale): (a) initial fluid shape; (b) evaporation occurs, and the deposited NPs at contact line pin the meniscus and allows the contact angle to decrease; (c) when the contact angle reaches zero, the meniscus shifts to the adjacent sphere; and (d) any NPs bound to the sphere at the contact line would be left behind without solvent as the contact line rises, resulting in a dense ring deposit. Note that multiple concentric rings can form for sufficient NP concentration. (e) Initial fluid shape, Au NP adsorb to the solvent–air interface; (f) over time, adsorption increases and creating a dense NP layer on the interface; (g) adsorbed layer decreases the air–solvent interfacial energy causing the contact line to rise on the spheres; and (h) with the air–solvent interfacial energy decrease, the contact line rises on the SiO<sub>2</sub> spheres, and the particles at the contact line are pushed onto the sphere at progressively higher latitudes.

individual SiO<sub>2</sub> spheres and also reside in the gaps between SiO<sub>2</sub> spheres, as indicated by the arrows in Figure S6.

We also conducted an experiment with Au@DDT NPs at 21 °C and found that the hydrophobic Au NPs rarely deposit on the surface of the SiO<sub>2</sub> spheres. By removing the monolayer of SiO<sub>2</sub> spheres (*i.e.*, lift off using Scotch tape, see Methods) after evaporation of the chloroform solution, we find that the Au NPs prefer to form rings beneath the SiO<sub>2</sub> spheres on the Si substrate (Figure 6c), as has been observed by others.<sup>33</sup> This result is not surprising considering the hydrophobicity of the colloidal solution and the Si substrate. Therefore, it is clear that the ligand on the Au NPs strongly affects the interaction of NPs with the SiO<sub>2</sub> spheres, and these interactions are extremely important in the formation of the Au NP ring structures. Figure 6d schematically summarizes these observations.

#### Au NP Deposition and Mechanism of Ring Formation.

Figure 1 summarizes the mechanism of ring formation. The NP rings form at the contact line where the fluid meniscus meets the spheres. However, it leaves an open question of how the Au NPs in the fluid drop travel to the contact line and then form the rings. One possible mechanism is that the solvent will leave individual micro- or nanodroplets on each SiO<sub>2</sub> sphere during evaporation, and transport occurs within these to the contact line forming the Au NP ring-like structures. However, the creation of individual microdroplets from the initial chloroform drop, which extends over macroscopic scales, requires kinetic detachment events. There is also the issue of the large energy cost associated with forming (sub)micro-scale chloroform droplets with high curvature on each SiO<sub>2</sub> colloid. Therefore, we view this mechanism as unlikely. Another possible mechanism considers the ring formation as analogous to the “coffee-ring effect”<sup>16</sup> seen in macroscopic sessile drops on a solid surface. In the coffee-ring effect, solute particles are transported to the contact line by an outward capillary flow throughout the drop. This results in a strongly concentrated deposit at the contact line. The contact lines in our system

resemble these coffee stains. However, in the present case, most of the evaporation occurs at the outer perimeter of the drop and perhaps some from beneath for the spheres near the edge of the droplet. However, for the spheres in the inner region, little to no evaporation can occur from below. Therefore, we favor the view that *mainly nonevaporative effects create the NP rings*. As Figure 3 shows, the rings form even when the spheres are confined in a small air bubble. Here, no (or very slow) evaporation in the bubble is expected, yet the rings form.

The retraction of the drop of chloroform solution involves evaporation, retraction, and Au NP deposition on each SiO<sub>2</sub> colloid. Initially, the fluid drop has a large equilibrium contact angle on each SiO<sub>2</sub> colloid due to poor wetting. A layer of air (vapor) exists beneath the chloroform and in the interstices of the SiO<sub>2</sub> monolayer (*i.e.*, air in the gaps). If a macroscopic drop spans many closely sized spheres, the top has to be flat since the mean curvature has to be the same everywhere and thus, the fluid–air interface must be almost flat as shown in the initial fluid shape Figure 7a. The changes of the contact line position at the drying front are indicated by arrows in Figure 7a–c. During drying, the contact line on a SiO<sub>2</sub> colloid tilts. Thus, any NPs bound to the sphere at the contact line would be left without solvent on each SiO<sub>2</sub> sphere resulting in ring formation by NP deposition (Figure 7d). Based on the motion of droplet shrinkage (Movie S1), when evaporation occurs, the contact line at the outer perimeter of the drop can no longer be horizontal (Figure 7b); the meniscus must curve inward. This inward curvature tends to displace the contact line inward until it is no longer stable. The unstable contact line then retracts inward to the neighboring spheres until it reaches a stable geometry, as shown in Figure 7c.<sup>34</sup> This retraction process continues until the entire macroscopic drop has fully retreated and evaporated leaving SiO<sub>2</sub> colloids decorated with Au NP rings (Figure 7d).

In the region where no evaporation occurs, we interpret ring formation at the contact line as follows. Due to the attractive

particle–interface interaction, the NPs adsorb strongly to the liquid–air interface, forming a dense monolayer extending to the SiO<sub>2</sub> sphere (shown in Figure 7b,e).<sup>35,36</sup> The adsorbed layer decreases the air–solvent interfacial energy. Over time, the adsorption increases (Figure 7f), thus causing the contact line to rise on the spheres (indicated as black arrows in Figure 7c,g), and NPs at the contact line are pushed onto the sphere (Figure 7h). If the sphere is sufficiently hydrophilic, the particles may remain where they were deposited and if there are enough Au NPs the contact line will rise causing multiple concentric rings to form (Figures 4f and 7h). The differences seen with Au@DDT NPs result from the fact that these particles do not adsorb on the air–solvent interface and are not pushed to and pinned at the chloroform–SiO<sub>2</sub> contact line.

In addition, this model also suggests that the spheres that get dewetted early in the process should look different from those that get dewetted late due to the change of Au NP concentration. NP adsorption at the liquid–air interface is not only at the bottom but also on the top of the droplet.<sup>35</sup> As shown in Figure S4a, instead of ring formation, dense monolayers of NPs were observed in the center of the sample. SEM images taken from the inner region to the edge of the sample are shown in Figure S4. Figure S4e indicates the locations on the sample for the corresponding SEM images. These results also agree with our model. The innermost area (a in Figure S4e) should contain the highest density of Au NPs (Figure S4a). The outermost region (Figure S 4d) not only has the lowest density of Au NPs but also indicates the shrinkage direction of the droplet. As indicated in Figure S4d, spheres to the right side of the red curve have incomplete Au NP ring formation, while spheres to the left of the curve have complete ring formation, which indicates that the spheres on the right get dewetted earlier than spheres on the left side.

## CONCLUSIONS

We presented a simple drop evaporation method to assemble chemically functionalized Au NPs into large arrays of ring structures on locally curved surfaces, in this case SiO<sub>2</sub> colloids. The large wettability change of chloroform is caused by both the temperature and relative humidity in the system. Controlled condensation of water on SiO<sub>2</sub> spheres is crucial for changing the contact angle of the hydrophobic chloroform solvent. The formation of Au NP ring structures on top of individual SiO<sub>2</sub> spheres is influenced by the distance between SiO<sub>2</sub> spheres and local heterogeneity in sphere size and ordering. The facile deposition of Au NP rings is a scale-free approach that can be utilized on monolayers of SiO<sub>2</sub> spheres with various diameters. Moreover, the ligands on these Au NPs determine whether one obtains the Au NP ring morphology or compact multiparticle mounds on the SiO<sub>2</sub> colloids. That the SiO<sub>2</sub> colloids are readily removed from the Si substrate, but the Au NP structures remain intact on each SiO<sub>2</sub> colloid, would facilitate experiments with Janus-like particles. This self-organization method is applicable to other NPs, *i.e.*, silver, CdSe NPs, *etc.* The large arrays of NP rings formed can be used in a variety of fields. We expect these ring structures to have interesting photonic properties that we will report elsewhere.

## METHODS

**Materials and Methods.** The silica (SiO<sub>2</sub>) spheres, citrate-stabilized gold NPs and methyl-PEG-thiol compounds were purchased from Fisher Scientific. Silicon wafers were obtained from Ted Pella, Inc. Nanopure water with a resistivity of 18 M $\Omega$  was used in all

experiments. The preparation of methyl-PEG4-thiol-modified Au NPs, the characterization of the chemical modification of the Au NPs and the Langmuir–Blodgett self-assembly of colloidal SiO<sub>2</sub> monolayer films on Si substrates are described in detail in the Supporting Information (SI). The Scotch tape used to remove the monolayer of SiO<sub>2</sub> sphere is 3 M 600 transparent Scotch tape (model no. S-9782).

**Preparation of Methyl-PEG4-Thiol-Modified Gold NPs (Au@MT(PEG)<sub>4</sub> NPs).** The colloids used for these studies are methyl terminated (PEG)<sub>4</sub>-thiol-modified 10 nm Au NPs (Au@MT(PEG)<sub>4</sub> NPs) dispersed in chloroform solvent. The purchased Au NPs were initially stabilized by citrate buffer. Surface modification of citrate coated Au NPs was conducted as follows. Approximately 10 mL Au@citrate solution (concentration  $6.0 \times 10^{12}$  particles/mL) and 10 mL of MT(PEG)<sub>4</sub> (w/v:1%) aqueous solution were added to a 20 mL vial. The solution was vigorously stirred for a minimum of 5 h, but typically overnight. The Au NPs were then collected *via* a high-speed centrifugation and redispersed in methanol and well suspended by mild sonication. The Au NPs were collected again *via* high-speed centrifugation and then well redispersed in chloroform solvent by mild sonication. Unlike citrate ligand, which undergoes dynamic exchange with free molecules in solution to stabilize Au NPs, methyl terminated (PEG)<sub>4</sub> thiol is covalently bonded to the surface of a Au NP and can stabilize Au NPs even when no free surfactant is present. The highest number density used in the experiment is  $31.5 \times 10^{13}$  particles/mL. The chloroform solution droplet is about 50  $\mu$ L.

**Experimental Set up and Procedure.** The set up for fabricating Au NP coatings and rings on the SiO<sub>2</sub> spheres is illustrated schematically in Figure 1a. In the experiment, the SiO<sub>2</sub> monolayer fabricated on the Si substrate was placed in a Petri dish with its temperature (hence that of the substrate) controlled. A drop of Au NPs in chloroform solution was placed on the SiO<sub>2</sub> monolayer and allowed to evaporate under controlled conditions. Various Au NP films and ring structures remained after the solvent has completely evaporated and adhere to the SiO<sub>2</sub> colloidal particles (Figure 1b).

**Characterization of Au NP Surface Modification.** The  $\zeta$  potential of the Au NPs was characterized using a Zeta analyzer (Malvern Instrument Ltd.). Changes in the  $\zeta$  potential were taken as evidence for the modification of the Au NP surfaces. As shown in Table S1, Au@MT(PEG)<sub>4</sub> NPs exhibit a positive  $\zeta$  potential (+43.6 mV) which is dramatically different from the pristine Au NPs that have a negative charge (−23.9 mV) due to the citrate coating. The change of  $\zeta$  potential for Au NPs clearly reveals the replacement of MT(PEG)<sub>4</sub> ligands on the surface of Au NPs during the ligand exchange process. Au@MT(PEG)<sub>4</sub> NPs have an average diameter ( $\pm$ SD) of  $17.0 \pm 6.7$  nm as determined by dynamic light scattering. This value is slightly smaller than that of the original NPs, which could be due to the large change of the dielectric constant of the solvents (from water (80.1) to chloroform (4.81) at 20 °C) and compression of the electrical double layer.<sup>37</sup>

**Langmuir–Blodgett (LB) Assembled SiO<sub>2</sub> Sphere Monolayer.** Silicon-wafer substrates, typical size of  $10 \times 10$  mm, were first treated with piranha solution [3:1 (v/v) H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>] for 30 min. Attention: Piranha solution is extremely dangerous and should be handled very carefully. After cleaning, the substrates were rinsed with Nanopure water at least three times and then stored in Nanopure water until use. The SiO<sub>2</sub> sphere monolayer films were prepared in a LB trough (Nima technologies).<sup>38</sup> First, 1 mL, 10 wt % SiO<sub>2</sub> solution was collected by centrifugation and well redispersed in methanol by sonication. This process was repeated two times, and finally the SiO<sub>2</sub> spheres were dispersed in 2 mL of methanol after few minutes of sonication. Then, 3 mL chloroform solvent was added to the SiO<sub>2</sub> sphere solution, and the final solution was sonicated and well mixed for 10 min. In order to prepare the SiO<sub>2</sub> sphere monolayer, a 1 mL CHCl<sub>3</sub>/Methanol (v/v:3/2) solution of SiO<sub>2</sub> spheres was dropwise deposited on the water subphase surface of a LB trough and allowed to spread. The solvent was allowed to fully evaporate for 30 min. Then, the SiO<sub>2</sub> nano- to microparticles on the water–air interface were compressed by barriers until achieving a target pressure of about 12 mN/m. To fabricate the monolayer films of SiO<sub>2</sub> spheres on Si substrates, the Langmuir layer was transferred to the pre-cleaned silicon

substrate while holding the surface pressure constant. We could continuously transfer the SiO<sub>2</sub> particle films onto at least 10 separate substrates from the LB trough in a single deposition operation.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.6b04965.

Experimental details and data (PDF)

Motion of a chloroform drop shape and volume during evaporation at 21 °C and ~50% RH (AVI)

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### Author Contributions

Y. B. and N.F.S. designed the research. Y.B. performed all the experiments. T.A.W. provides the geometrical theory. Y.B., T.A.W. and N.F.S. discussed results and wrote the manuscript.

### Notes

The authors declare no competing financial interest.

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