Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Self-assembly of nanorods on microspheres at fluid-fluid interfaces

NEETHU THOMAS, SANJANA SHIVKUMAR, ETHAYARAJA MANI*

Polymer Engineering and Colloid Science Laboratory, Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai-600036, India.

Corresponding Author: * Dr. Ethayaraja Mani

ethaya@iitm.ac.in

1. Effect of surface charge of PS particles and AuNR diameter

In-order to investigate the role of electrostatic interaction between the PS particles (details of the PS particles are listed in Table 1 in the main paper) and AuNR in the formation of ring-like structure on PS microspheres, similar experiments are carried out with PS particles of type PS2 (positively charged) and AuNR1 in water side. The ring-like assemblies that are formed on the surface of PS2 particles are shown in Fig. S1 (c) and the average ring diameter calculated from the respective SEM images is 242.38 ± 22.13 nm. The formation of ring-like structure on PS particles of similar surface charge as that of AuNR1, shows that the electrostatic interaction between the particles does not govern the formation of ring. Therefore, it can be concluded that the surface charge of the template particles do not play any key role in ring formation.

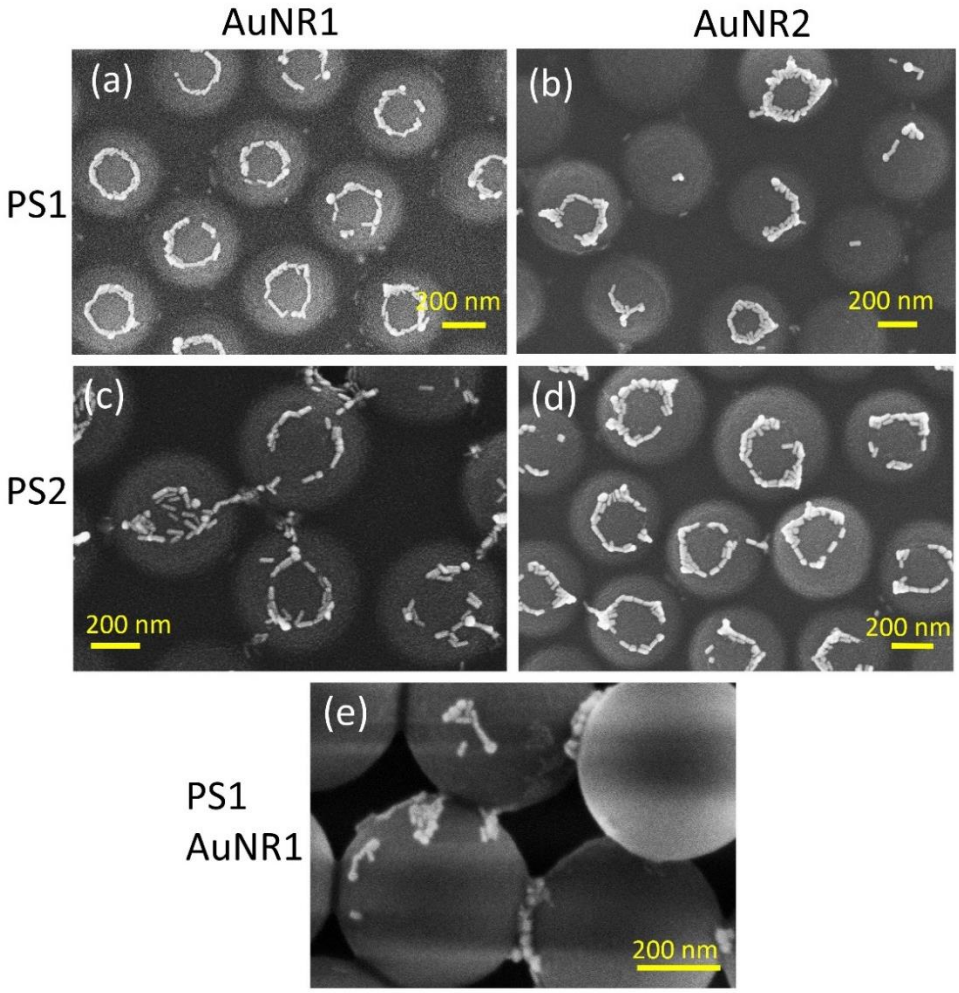

Fig. S1. (a) –(d) Ring formation of AuNR on PS particles in decane-water interface. (e) Interaction in bulk. PS1 are used in (a), (b) & (e) and PS2 are used in (c)-(d). AuNR1 are used in (a), (c) & (e) and AuNR2 are used in (b) and (d) at a number density of 11×10^{13} rods/ml.

To study the effect of AuNR diameter on ring formation, the experiments are repeated with nanorods of AuNR2 (of average diameter 19 ± 2.3 nm). Both PS1 and PS2 particles are used along with thicker rods and the resulted ring-like structures are shown in Fig. S1 (b) and (d). For AuNR2, the calculated ring diameters are 219.94 ± 20.623 nm (for PS1) and 246.48 ± 27.123 nm (for PS2) respectively. The ring dimensions reported with larger diameter rods (AuNR2) are appear to be closer with the values reported for smaller diameter rods (AuNR1) in decane-water interface. This indicates that the diameter of AuNR is having minimal role in tuning the ring diameter.

For the interaction in bulk, PS1 type particles are mixed with CTAB stabilized, positively charged AuNR1 solution (at a number density = $11x10^{13}$ rods/ml) under sonication and kept without any disturbance overnight. PS particles are separated by centrifugation and the corresponding SEM images are shown in Fig. S1 (e) in which AuNRs are deposited as aggregates. It has been observed that positively charged AuNR deposited as aggregates on oppositely charged PS particles due to the electrostatic interaction between them.

2. Effect of PS microsphere size

The size of PS particle is varied as 0.06 ± 0.01 μm (PS6) and 0.22 ± 0.02 μm (PS7) in the interface experiments. AuNR1 are used at a number density of $11x10^{13}$ rods/ml. Fig. S2 shows the assembly of AuNR on PS microspheres of smaller size.

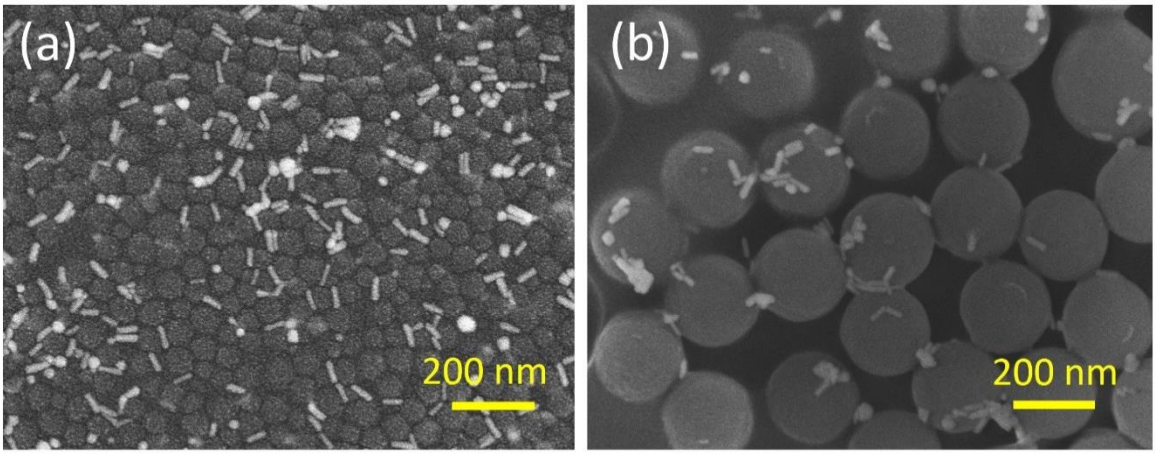

Fig. S2. AuNR ring formation in different size PS microspheres. (a) PS6, (b) PS7. AuNR1 are used at a number density of $11x10^{13}$ rods/ml in (a)-(b).

3. Formation of ring-like structure of Au nanorods on different size PS microspheres (extra images)

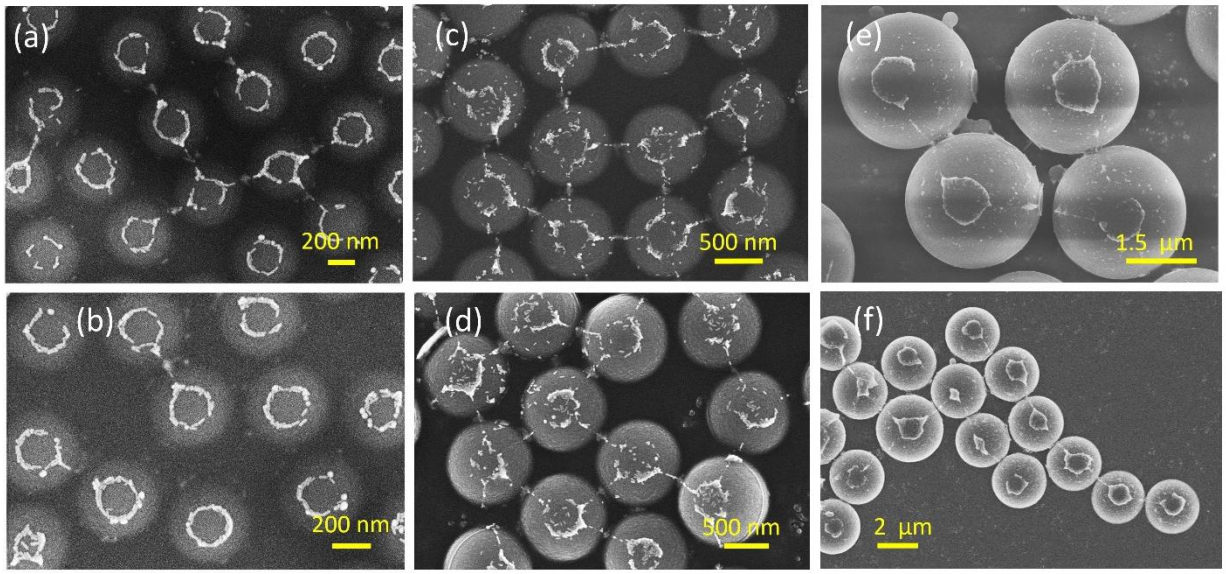

Fig. S3. (a) - (b) PS1, (c) - (d) PS3 and (e) - (f) PS5 type PS particles are used in decane-water (D-W) interface. AuNR1 are used at a number density =$11x10^{13}$ rods/ml in (a)-(d) and at a number density = 3.08 $x10^{14}$ rods/ml in (e) - (f).

4. Effect of surface charge and diameter of AuNR on 1 μm PS microsphere

PS3 and PS4 type PS particles are used in interfacial experiments in oil-water interfaces. Both AuNR1 and AuNR2 are used in the experiments. The ring dimensions are calculated from SEM images (as shown in Fig. S4) and the observed values are listed in Table S1. The ring dimension that are reported for both PS3 and PS4 type PS microspheres in decane-water interface are identical.

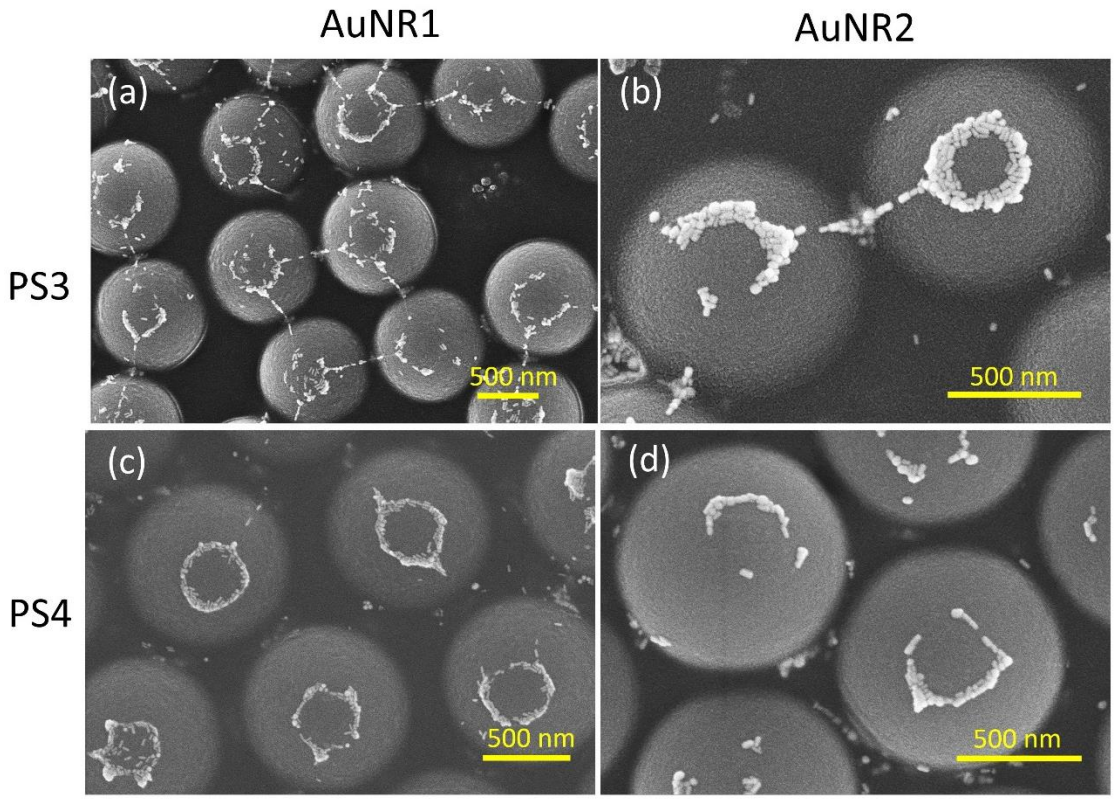

Fig. S4. AuNR ring formation on 1 μm PS microspheres. (a) - (b) PS3, (c) - (d) PS4 in decane-water interface. AuNR1 in (a) & (c) and AuNR2 in (b) & (d) at a number density of 11×10^{13} rods/ml.

Table S1:- Ring dimensions on 1μm PS microspheres

AuNR	Decane-water interface Ring diameters (nm)	
	PS3	PS4
AuNR1	380.33 ± 48.13	378.15 ± 33.45
AuNR2	392.91 ± 56.90	372.11± 5.11

5. Deposition of Au NRs on the surface of PS particles other than ring-like structure during drying

During the drying of samples, the deposition of AuNR on the surface of template PS particles other than ring-like is also found along with the ring-like structure at some random places of the sample. At the initial stages, the evaporative drying of liquid bridges between the neighboring PS particles deposit AuNR on the lateral contact point of two neighboring PS particles as shown in Fig. S5 (indicated by red arrows). When the evaporation area exposed to air became a smaller triangular opening between three neighboring PS particles, the solvent carries AuNR to the centroid of this triangular opening and deposit at this region as shown in Fig. S5 (indicated by blue arrows) [1]. Because of the small size of AuNR and the transfer of particles to the carbon tape, these deposits may not be clearly seen in the SEM images. Such deposits are not observed on the surface of all PS particles. However the liquid film between two adjacent PS particles and at the triangular openings are very thin due to close proximity of the template particles. The depositions of AuNR at this thinner region can be explained by the 2D crystallization mechanism proposed by Denkov et al [2], where the upper surface of the liquid film presses the nanoparticles against substrate/water interface. If any nanorods becomes trapped in this thinnest region, it leads to the accumulation of more nanorods and further forms a nucleus of the particle array in this region. Once the nucleus forms, the nanorods direct towards the nucleus and deposit there.

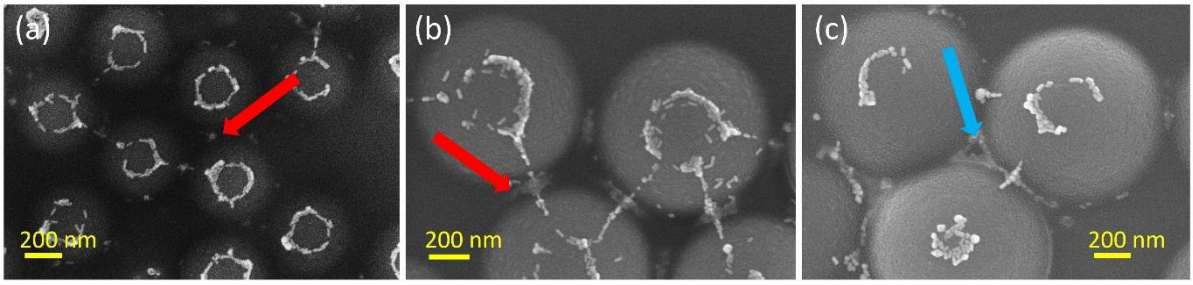

Fig. S5:- Deposition of AuNRs on PS particles (a) PS1, (b) & (c) PS3. Deposition of AuNRs between two neighboring PS spheres are indicated by red arrow. Blue arrows point to the deposition at the small triangular region between three neighboring PS spheres. AuNR1 at a number density of $11x10^{13}$ rods/ml is used.

A linear chain-like assembly of AuNR with an end-to-end orientation (as shown in Fig. S5 (b)) is observed on the surface of few of the PS template particles along with ring structure. This is more pronounced in the cases of larger PS particles. If the neighboring PS template particles are far apart, at the final stages of evaporative drying, AuNR that remain in the liquid capillary bridge

between the neighboring PS particles can arrange as a linear chain with a preferential tail-to-tail orientation interconnecting the ring-like assembly. A similar observation was reported in the drying experiments presented in [3-4], where the suspension of Au nanoparticles deposited on a 2D lattice of 50 μm latex particles deposited on the glass substrate. Slow evaporation of gold nanoparticles suspension formed regular wire networks which connected the pendular rings at the base of latex particles on the glass substrate. A stable nanoparticle liquid bridge network connected between the neighboring latex particles was attributed to this wire network on substrate after the removal of PS particles.

6. AuNR deposition by drop casting method on PS monolayers.

A monolayer of PS particles (PS1) (as shown in Fig. S6 (a)) is prepared on a glass substrate via dip coating. Further, 50 μL of concentrated AuNR1 solution (number density is 11×10^{13} rods/ml) is drop casted on the PS monolayer that is deposited on a glass slide and the solution dries under the same conditions as that of ring formation. This is similar to the case of drying a sessile liquid drop on a flat hydrophilic substrate. After the complete drying of the drop, a colored ring like structure is noticed at the edges of the glass slide. When AuNR dispersion droplet is dried over a PS monolayer on the glass substrate, AuNR are transported to the pinned contact line of the

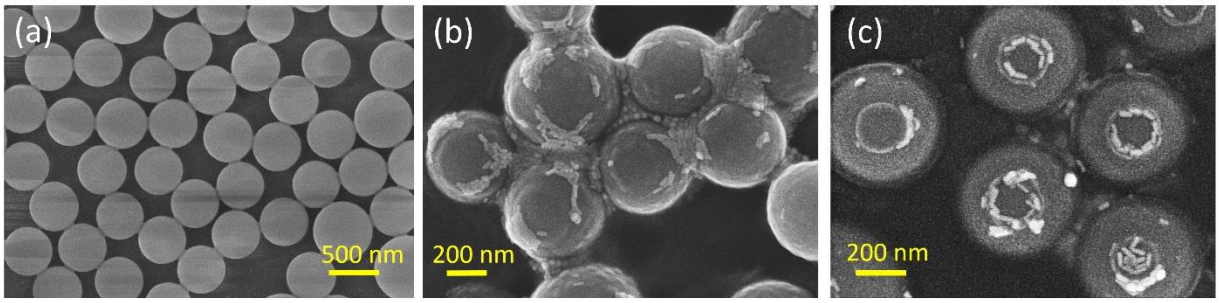

Fig. S6:- Drop casting of AuNR solution on PS monolayer deposited on a glass slide. (a) PS monolayer (b) Top view of PS particles nearby the edges of the glass substrate. (c) Ring-like assembly of AuNRs on the PS particles at the edges of glass substrate.

liquid on the substrate (nearby the edges of the substrate) by an outward capillary flow and forms coffee-ring with a concentrated deposit at the contact line. It has been observed that AuNR form non-uniform depositions on the surface of a larger fraction of PS particles that deposited on the substrate as shown in Fig. S6 (b). At this region, the surface of the PS particles and their interstices are occupied by nanorods. However, less coverage of AuNR is observed at the central regions of the PS monolayer (at the center of glass slide). On reversing the PS particle monolayer, it has been

noticed that few PS particles nearby the substrate edge carries a signature of ring-like assembly of AuNR as shown in Fig. S6 (c). The PS particles at the center of the monolayer do not have any ring-like assembly. In the present case, as the drying process is similar to a sessile drop drying over the PS monolayer, most of AuNR deposit on the top and lateral surface of the PS particles. Very few of them are deposited via evaporative drying of liquid capillary bridge between the PS particles. Therefore, ring formation is not uniform on the surface of PS particles compared to that in the newly proposed interface method.

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