

1 **Layer-by-Layer Assembly of Nanorods on a Microsphere via Electrostatic** 2 **Interactions**

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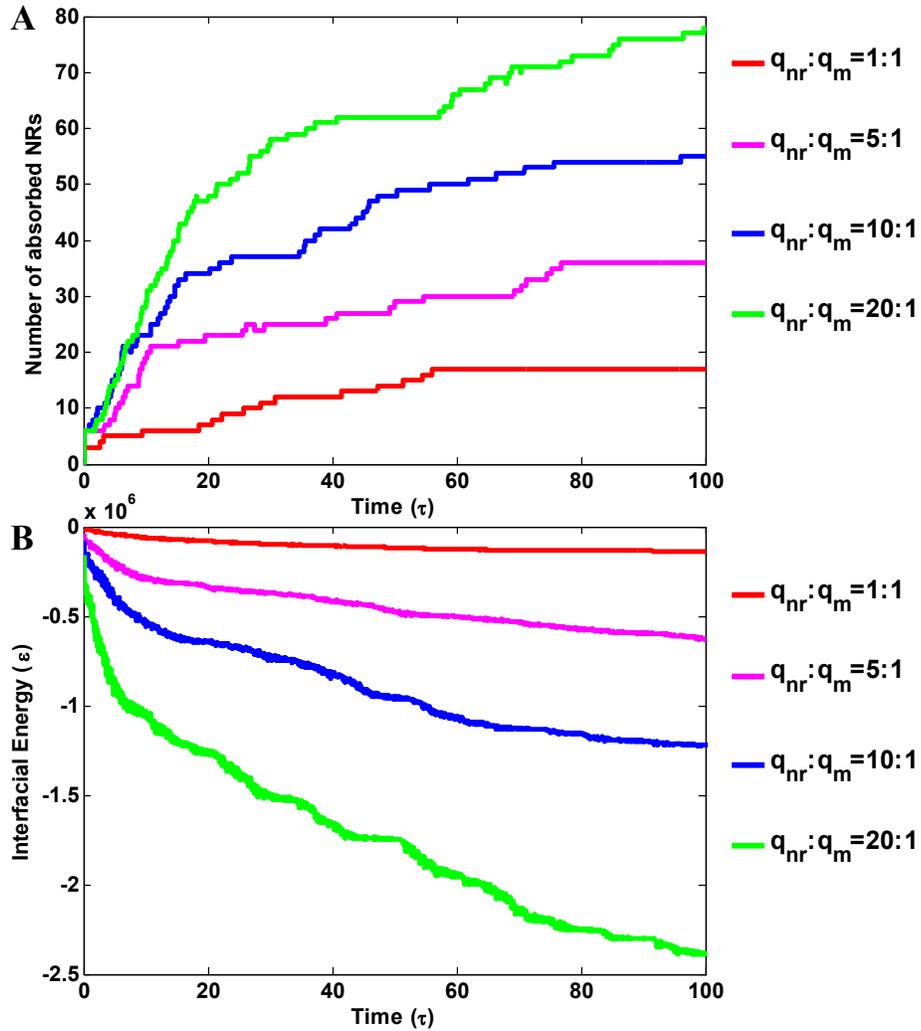
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9 10 **Supplemental Materials**

11 **A. Effect of surface charge density on single and multi-layer NR deposition**

12 The long-range electrostatic interaction is a key factor for the observed LbL assembly process and
13 it demonstrates a nonlocal influence between any charged particles compared with the short range
14 van der Waals interaction. In order to study the effect of charge density of NRs, we set the negative
15 charge on each SRD bead of the MS $q_m = -1e$ and then dip it into a solvent with NR's
16 concentration $c = 0.3$ mg/ml with different positive charges on each SRD bead of the NRs (
17 $q_{nr} = +1e, +5e, +10e, +20e$). The representative $N-t$ plots in Figure S1 clearly show that the
18 charge density of ellipsoidal NRs significantly affect the time evolution of the number of NRs on
19 the MS surface. The time evolution process is similar to the process shown in Figure 4(A). As the
20 charge density of NPs increases, the increased strength of the attractive interactions accounts for
21 the increasing number of ellipsoidal NRs on the MS surface (Figure S1 (A)) and the subsequent
22 increase of the interfacial energy between NPs and the MS (Figure S1 (B)). The time constant to
23 reach equilibrium also becomes smaller when the charge density increases.

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2 **Figure S1.** Effect of charge density ratio on the deposition of NRs on a MS. A: Time evolution of
 3 the number of NRs adsorbed onto MS surface. B: Time evolution of the interfacial energy between
 4 NRs and MS.

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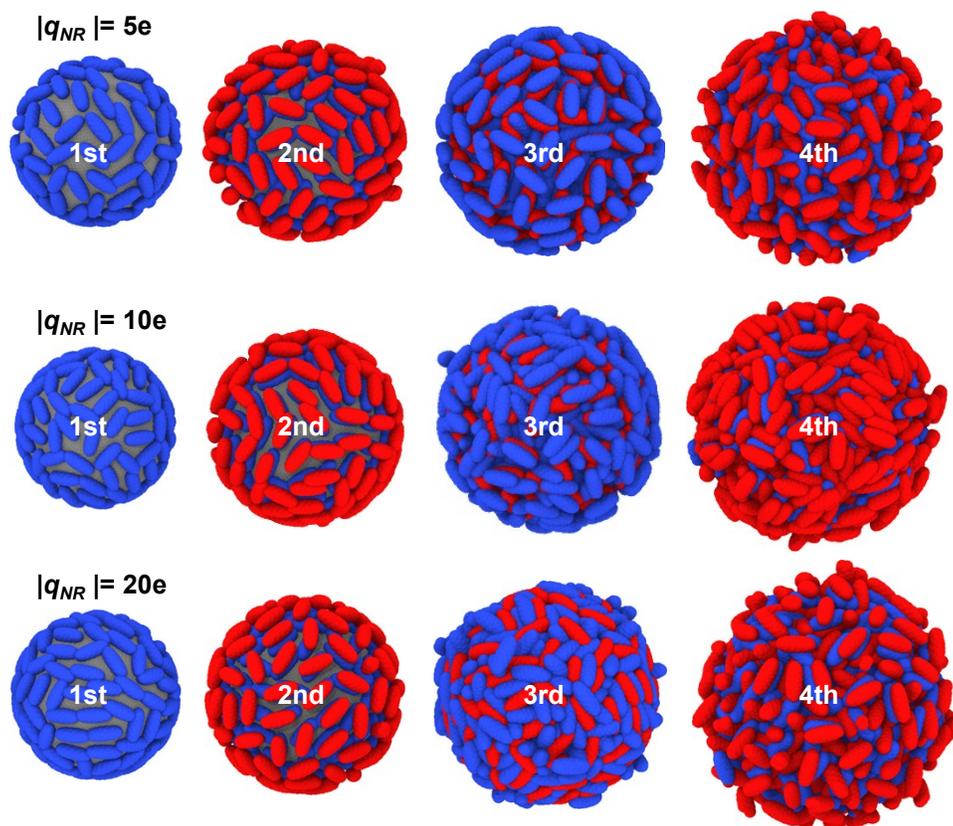
6 In order to prove the q_{NR} effect on the multilayer LbL assembly process, we have computationally
 7 explored the morphology of LbL assembly as well as the attached NRs by varying q_{NR} on the NRs.
 8 We keep q_{NR} constant but alternative signs, three cases are tested as shown in Figure S2. When
 9 q_{NR} increases to $|q_{nr}|=20e$, the number of NRs attaching on the MS do not necessarily increase as
 10 the increment of q_{NR} brings with large repulsion force between the NRs (Table S1). The NRs
 11 assembly process for high q_{NR} is similar to that with low q_{NR} . The details of assembly process for

1 each dip was detailed in the main text. In the current work, we aim to study the effect of c_{NR} on
 2 the LbL process and demonstrate the effectiveness of Langmuir adsorption model on the single
 3 dip and multi LbL adsorption process.

4 Table S1. Number of NRs N on MS versus the number of dipoles M .

$c_{NR}=1\text{mg/ml}$	M1	M2	M3	M4
$ q_{NR} =5e$	115 (± 6)	211 (± 10)	405 (± 20)	747 (± 38)
$ q_{NR} =10e$	110 (± 5)	227 (± 11)	556 (± 27)	895 (± 45)
$ q_{NR} =20e$	120 (± 6)	207 (± 10)	545 (± 22)	890 (± 42)

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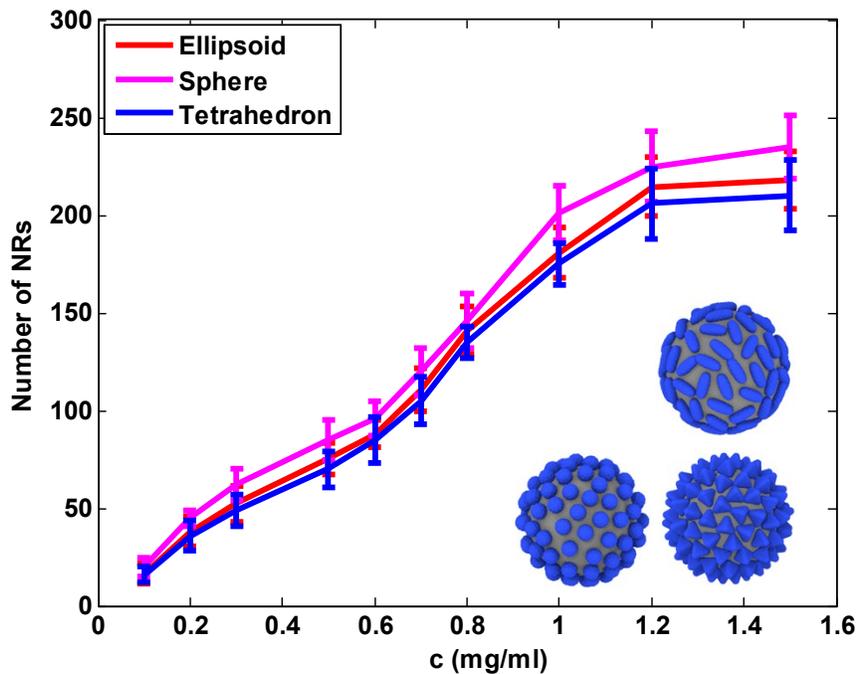
7 **Figure S2.** Snapshots of multilayer NRs deposited on MS for $|q_{NR}| = 5e, 10e,$ and $20e,$
 8 respectively. c_{NR} is fixed as 1 mg/mol for each dip. The blue NRs are positively charged while the

1 red NRs are negatively charged.

2 **B. Effect of NRs geometry**

3 As the shape of the NR is important to the NR-MS interfacial interaction, we have also investigated
4 the deposition process of spherical and tetrahedral nanoparticles (NPs) on the MS surface (only
5 for 1 dip). In the simulation, these two types of NPs have the same volume as that of ellipsoidal
6 NRs. As shown in Figure S3, regardless of NP's shape, the number of NPs adsorbed on the MS
7 surface follows a similar incremental trend as the ellipsoidal NRs does, and shows trivial
8 differences. The number of adsorbed NPs on the MS surface is almost independent of NPs' shape.

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11 **Figure S3.** Number of NRs with different morphology with respect to c ; inset snapshots are of c
12 = 0.5 mg/ml samples with different NP types attached.

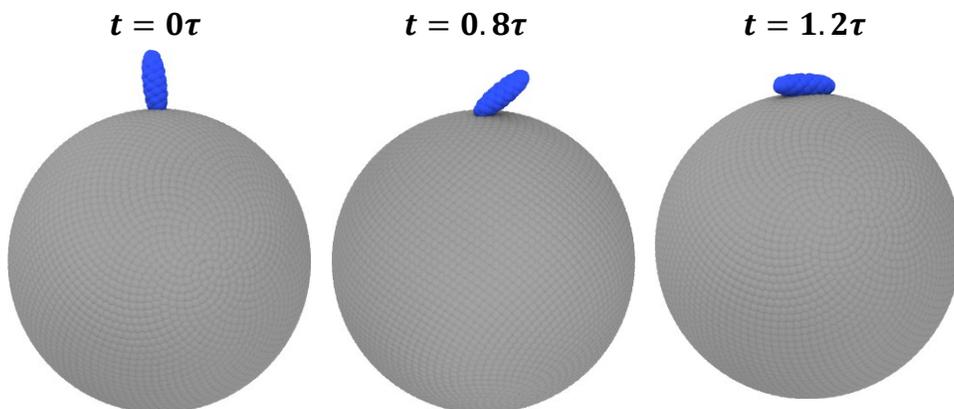
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14 **C. NR movement on MS surface**

15 With respect to the mobility of NRs on the MS surface, an intriguing phenomenon is observed
16 during the adsorption process of a single NR. As shown in Figure S4, the ellipsoidal NR prefers to
17 have a tip contact with the MS first and then lie down onto the MS surface. The rotation of the NR
18 toward the MS surface can be attributed to the increased electrostatic interactions between the NP

1 and the MS. The rotation of the NR on the MS surface allows for a maximization of the contact
 2 area and interfacial energy between them. On the MS surface, asymmetrical ellipsoidal NRs prefer
 3 to orient its major axis parallel to the tangential direction of the MS surface in order to maximize
 4 the electrostatic interactions, while the symmetrical spheres and tetrahedrons show no initial
 5 orientation preference.

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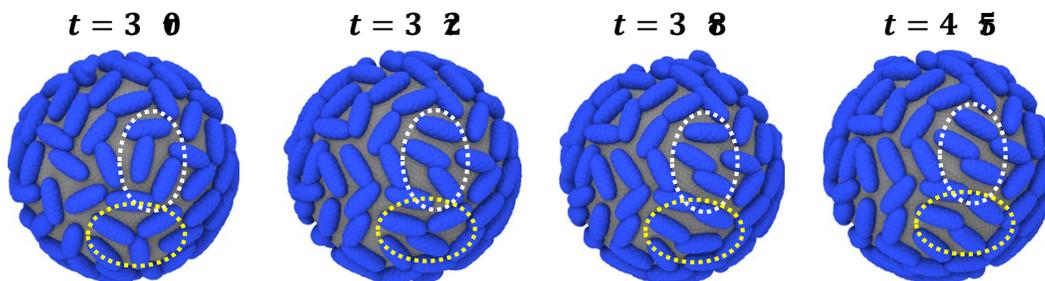


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8 **Figure S4.** Snapshots of the rotation process of a single ellipsoidal NR on the MS surface. $t = 0\tau$:
 9 the initial configuration of ellipsoidal NR with tip contact; $t = 0.8\tau$: the rotating configuration;
 10 $t = 1.2\tau$: the final stable configuration.

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12 In addition to the tip rotation of single NR on the MS surface, we also observe in Figure S5 that
 13 certain NRs rearrange their positions (highlighted in white and yellow dash lines) on the MS
 14 surface plane due to the electrostatic repulsion between adjacent NRs. This adjustment or
 15 movement may be attributed to the energy minimization of the system, which may help absorb
 16 more NRs on the MS surface. We think that the mobility of NRs on the MS surface is an interesting
 17 topic for future research. We will further explore its fundamental mechanism in our future studies.



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- 1 **Figure S5.** Snapshots of movement of NRs on the MS surface during the equilibrium stage
- 2 ($c_{NR}=1\text{mg/ml}$).