Influence of the substrate zeta potential on the electrostatic deposition kinetics and its simulations by Monte Carlo method

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Introduction

Immobilization of oriented plasmonic silver nanoplates (AgNPls) gained much interest in the last decades due to numerous sensing and biomedical applications, e. g., surface-enhanced Raman scattering[1]. Recently, we have developed a novel technique for deposition of AgNPls onto transparent polycationic film bearing tertiary amino groups (TAGs). Such substrates, transparent to e-beam and visible light, allow its simultaneous examination by TEM and UV-vis spectroscopy[2].

Objectives and Aims

In this work, we studied how surface zeta potential (SZP) of the film governs the process of deposition of AgNPls. We also aimed to developed an *ab initio* mechanistic model that would allow simulation of the kinetics of deposition.

Methods

Colloidal AgNPls were synthesized by a wet-chemical two-step route[2]. They were stabilized by 11-mercaptoundecanoic acid. Copolymers of ethyl methacrylate and (2-diethylamino)ethyl methacrylate with 10, 25, 35 and 50 mol.% TAGs were synthesized by bulk radical copolymerization. Then, a droplet of 2 wt.% copolymer solution was placed onto the surface of distilled water, let it dry to form a film, transferred the film onto quartz glass slide and immersed into AgNPls' colloid for 24 h. AgNPls concentration was 4.4×10^{-10} nM, pH 6.6 (0.02 phosphate buffer). Periodically we extracted films to perform UV-vis spectroscopy.

Fig. 3. Appearance of the as-deposited AgNPls' monolayer in the transmitted and reflected light.

Results

We studied the deposition kinetics by of UV-vis spectroscopy. Measured optical densities were recalculated using AgNPls molar extinction coefficient, calculated from TEM images. It reveals (Fig. 1) that the initial stage of growth of surface AgNPls concentration C_S is linear and similar for all the copolymers. On the contrary, the transition to the adsorption-limited regime (slowed by already deposited AgNPls) occurs at different times and C_S regarding to the TAGa percentage:

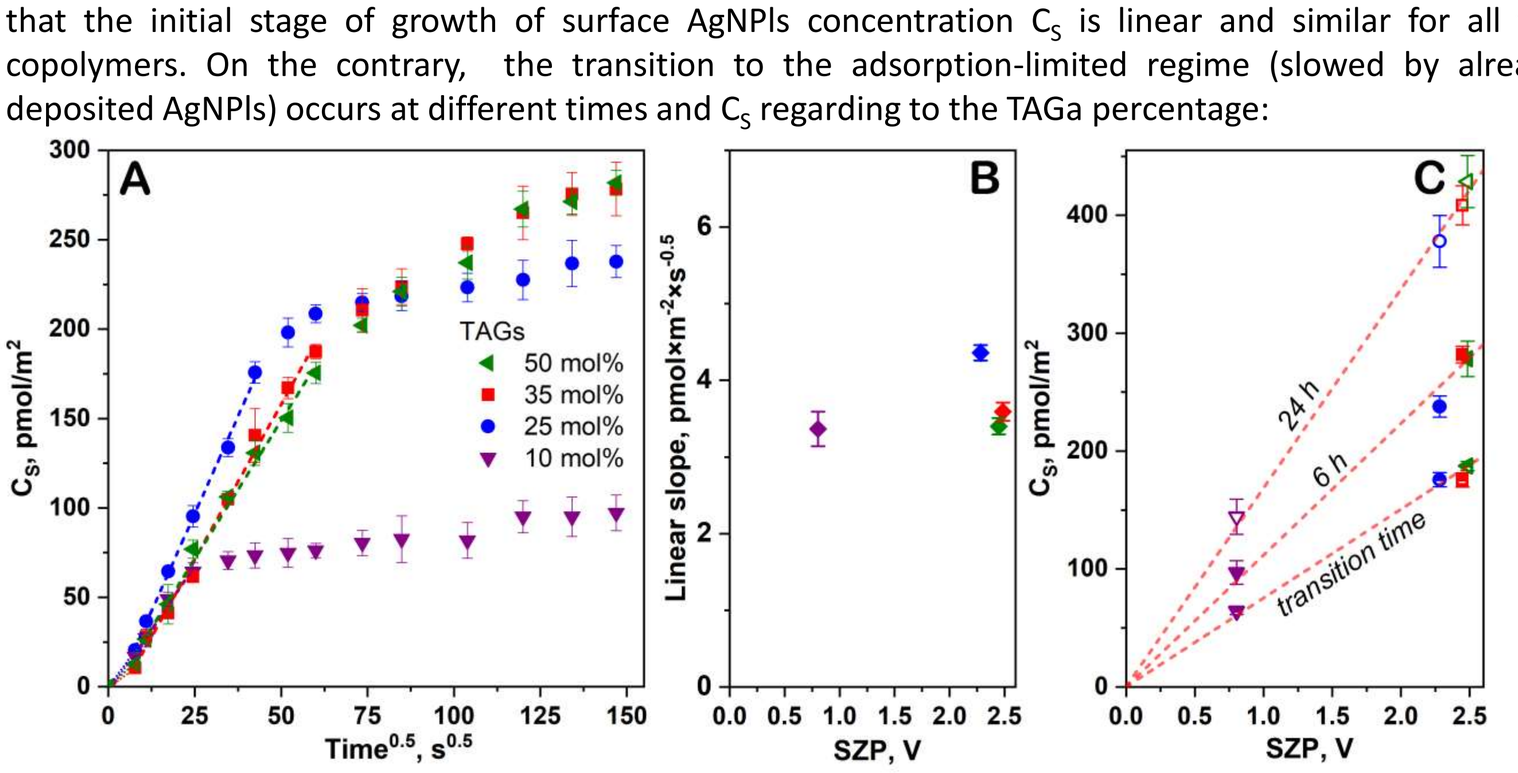

Fig. 1. a) Experimental kinetic curves of AgNPls deposition on films with different TAG percentage. (b) Impact of film SZP on surface concentration. (c) Experimental and (d) simulated slopes of the linear regime.

We supposed that the difference in the kinetics stems from the difference in SZP of the copolymer films. We measured streaming potentials of the copolymer films by spinning disk method and recalculated them to SZPs of the copolymers. Linear slopes of graphs in the diffusion-limited regime appear to be SZP-independent (Fig. 1b), but the C_S in the adsorption-limited regime linearly depend on the film SZP (Fig. 1c). To give an explanation, we developed a simple *ab initio* deposition model, based on the random sequential adsorption model[3]. To simulate substrate SZP, we improved the model with alternating effective exclusion radius of the disk $\boldsymbol{r_{ex}}$. Intuitively, each Ag NPl compensates a larger area of the substrate with lower SZP. We assumed simply $\boldsymbol{r_{ex}^2}$ =1/SZP. To imitate stochastic deposition process, we applied Monte Carlo program code which simulates attaching of uniform disks on the surface. The result of the simulation is in Fig. 2.

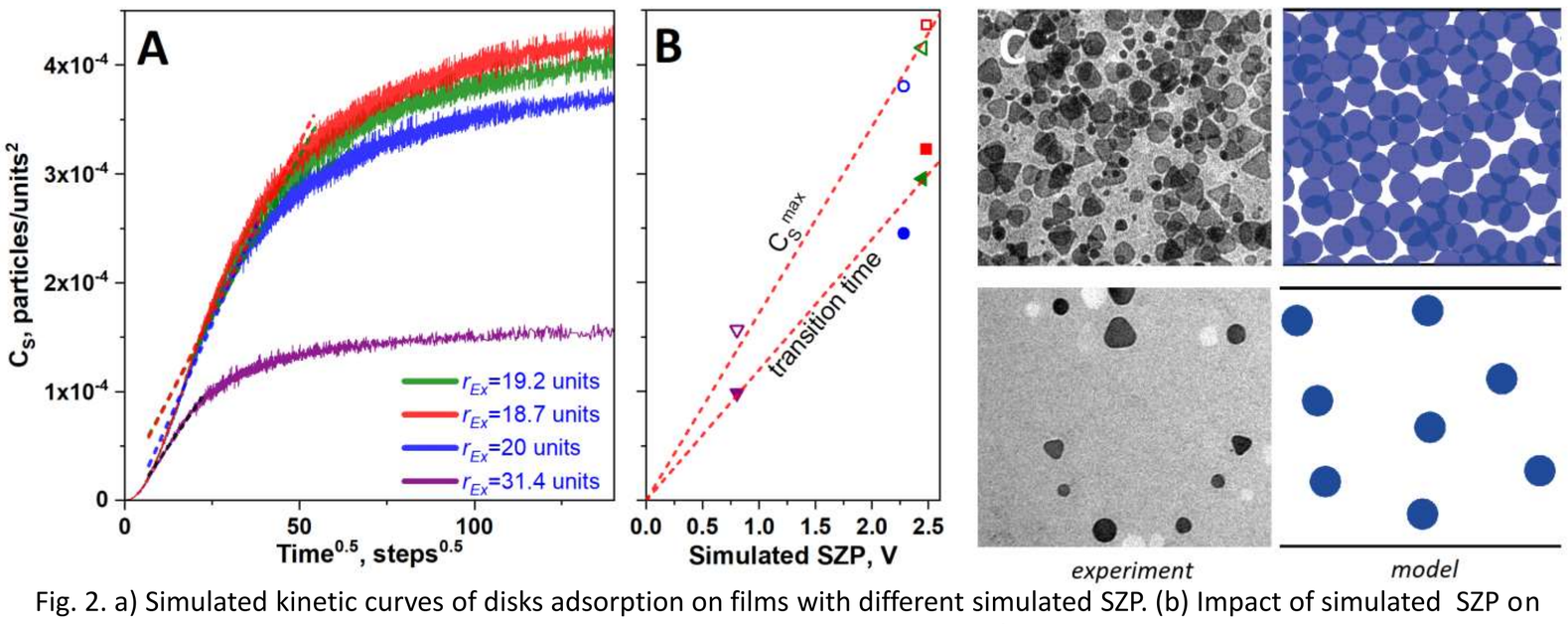

Fig. 2. a) Simulated kinetic curves of disks adsorption on films with different simulated SZP. (b) Impact of simulated SZP on surface concentration. (c) Experimental and simulated arrangement of AgNPls/disks.

Our model correctly simulates the kinetics of AgNPls deposition (Fig. 2a). It also reveals why C_S linearly depends on substrate SZP (Fig. 2b). Moreover, the introduction of the exclusion radius principle allowed to simulate the arrangement of the AgNPls on the surface (Fig. 2c).

Conclusion

We developed a novel method for electrostatic deposition of AgNPls onto thin copolymer films that allow their simultaneous examination by TEM and UV-vis spectroscopy. By optical spectroscopy, we were able to study the kinetics of AgNPls deposition. We demonstrated that SZP affects the saturation C_S. To simulate this linear dependence, we constructed a simple model and applied Monte Carlo method. Our approach not only correctly predicted the saturation C_S, but also quite smoothly simulated real kinetic curves and confirmed linear dependence between SZP and C_S in the adsorption-limited regime. Our deposition technique can be easily extended to other types of nanoparticles, and the model can be improved for better simulations and prognoses.

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References

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