Control of the Geometry of the Adsorbed Thin Layer by the Depletion Interaction

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Addition of nonabsorbing polymer latex into colloid suspension results in a polymer-mediated depletion attraction between the larger colloid pairs.[1] The physical origin of this induced attraction is both simple and general.[2] Each large particle that may be a colloid or a bacteria DNA in a cell is surrounded by a crust that excludes the center of the added polymer latex. Demixing or self-organization of large particles will overlap their crusts and result in extra free volumes for polymer latex to translate and contribute extra translation entropy of the polymer latex, although at the expense of lowering the entropy of mixing. Extensive studies on the depletion interaction have showed its considerable importance in a wide variety of practical materials ranging from frozen desserts to paints and from photonic crystals to biological crowding.[1−6]

Because of the ability to form liquid crystal phases, the phase behavior of the mixtures of rodlike or platelike colloids is found to be even richer after the addition of polymer.[3,4,7−10] When the concentration and size of the polymer coils were mediated, the colloid suspensions may show various liquid crystal phases such as nematic, lamellar, smectic, columnar, and so forth.[4] The isotropic−nematic coexistent region was broadened after the addition of polymer, meaning that we can get the liquid crystal phase at a lower "crowding" by virtue of the polymer-induced depletion interaction.[3,9,10]

The depletion region is present not only at the large particle as crust but also at the hard wall as a layer (with the thickness of about its radius) where the centers of the smaller particle are excluded.[11,12] This makes overlapping of the crust and the layer another driving force for large particle assembly near the hard wall. Poon and Warren predicted that large spheres next to a hard wall crystallized at concentrations well below those corresponding to the bulk crystallization in the presence of smaller spheres.[11] Kaplan et al. found phase separation of binary particle mixtures into ordered surface phase near a hard wall and a disordered bulk liquid phase.[12] Fabricating the ordered colloid liquid crystal or crystal by mediating the depletion interaction does pose significant experimental challenges. Nevertheless, as reported in this Communication, controlling the orientation of platelike molecules in the absorbed monolayer onto the metal substrates is quite straightforward.

Platelike liquid crystal forming compound porphyrin has derivatives which have been arising as longstanding interests due to their great potentials in optical, magnetic, clinical, and catalytic applications[13] and as model compounds for the studies of energy and electron transfer during the electrochemical process.[14] Porphyrin orientation in the absorbed monolayer onto the metal substrates greatly influences the above properties, say, the efficiency in the electrocatalysis of dioxygen reduction.[14] There are several strategies to prepare the self-assembled porphyrin monolayer on the metal substrates: for example, by forming a chemical linkage between the thiol-substituted porphyrin and metal substrates[14,15] or by inserting an intermediate amphiphilic ligand between metallopor-

phyrin and metal substrates.[16] However, as described below, its platedlike shape enables us to control its assembly behavior conveniently by the polymer-induced depletion interaction.

Silver foil, 0.025 mm thick, was immersed into vigorously agitated 3.5 M HNO_3 at ambient temperature for about 2−3 min until the surface of the foil became milky. After etching, the foil was thoroughly rinsed with distilled water and dried in air. Silver foil after such a roughening procedure was reported to exhibit a strong enhanced factor for Raman scattering.[17] The roughened foils were ready for porphyrin absorbing and then for the surface enhanced Raman scattering (SERS) study.

meso-Tetrakis-(4-acetoxyphenyl)porphyrin (*m*-TAPP) was purchased from Strem Chemicals. An *m*-TAPP solution was prepared in ethanol at 0.01 M. Poly(ethyl oxide) (PEO) is the most commonly used polymer to mediate the depletion interaction to produce the self-assembly of colloid particles or the crystallization of proteins.[4,18] As the size of the colloid particles is about a few micrometers, a PEO coil with a radius of gyration of about 20−100 nm is used in those studies. For the study of the much smaller porphyrin molecule, a PEO with a much smaller molecular weight has to be used. Poly-(ethylene oxide) with a molecular weight of 300 (PEO300) was obtained from Aldrich. A certain amount of PEO300 was added to the *m*-TAPP/ethanol solution as the depletant. Two pieces of silver foil were immersed into the *m*-TAPP/ethanol and *m*-TAPP/ethanol/ PEO300 solutions for 10 min, respectively. The foils were then washed with water to clean the PEO300 residue and dried for Raman measurement.

SERS spectra were recorded with a SPEX-1403 Raman spectrometer. The incident excitation wavelength was 647.1 nm from a Kr^+ laser source, with an output power of 20−100 mW. A backscattering geometry in air was used for all samples.

The observation of enormously enhanced cross sections (up to 10^6) for Raman scattering from molecules adsorbed on metal surface was one of the most important discoveries in the field of surface chemistry in the last two decades of the last century.[19] The development of surface enhanced Raman scattering spectroscopy provides a unique method for measuring the nearest layer of adsorbents to the metal.[20] Figure 1 shows the SERS spectra of a thin layer of *m*-TAPP on silver along with a normal Raman spectrum (Figure 1a) of *m*-TAPP in the solid state. The SERS spectra of Figure 1b and 1c were recorded for specimens of *m*-TAPP on silver adsorbed from a solution in ethanol and ethanol/PEO, respectively. In Figure 1, the SERS spectrum of Figure 1b is similar to the spectrum of solid sample, except for the shifts and relative intensity changes for some bands. There are quite significant differences between Figure 1c and 1a both in vibrational frequencies and in peak intensities. It was reported that the Raman-active ring breathing mode located at 1004 cm^{-1} is sensitive to its environment.[21] In the SERS spectra of Figure 1c, the ring breathing mode was intensified, whereas it remains weak in the spectrum of Figure
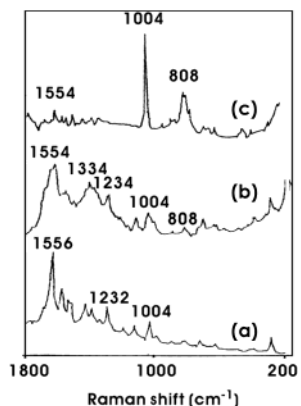
Figure 1. (a) Normal Raman spectrum of *meso*-tetrakis-(4-acetoxyphenyl)-porphyrin (*m*-TAPP) in the solid state, (b) SERS spectrum of *m*-TAPP adsorbed on silver from ethanol solution, and (c) SERS spectrum of *m*-TAPP adsorbed from ethanol/PEO solution.
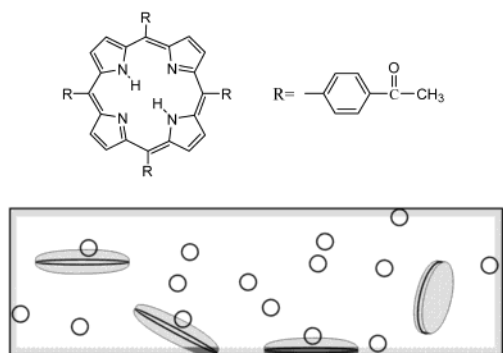

Figure 2. Upper: molecular structure of (*m*-TAPP). Lower: cartoon of *m*-TAPP on the hard wall. The centers of small spheres are excluded from a depletion zone (light shaded regions) outside the large spheres and the hard walls. The heavily shaded region represents the gain of small-sphere excluded volume due to the overlap of the depletion zones. The flat orientation provides the largest dark shaded region which represents the gain of excluded volume (entropy). The cartoon is inspired by Yodh, A. G.; et al. [*Philos. Trans. R. Soc. London, Ser. A* **2001**, *359*, 921].

1b. The normal Raman spectrum of *m*-TAPP and the SERS spectrum (Figure 1b) from ethanol solution have a strong vibrational band at 1544 cm^{-1} which corresponds to the phenyl ring stretching vibration, whereas the spectrum (Figure 1c) from ethanol/PEO shows very weak bands between 1540 and 1600 cm^{-1} but a strong vibration near 808 cm^{-1}, which is due to the phenyl ring out-of-plane vibration mode.[21] We propose that the *m*-TAPP molecules were oriented parallel to the surface when they deposited from ethanol/PEO solution if the SERS selection rule based on electromagnetic theory is applied.[22,23]

Kaplan et al.[12] discovered that the instability arising from binary particle mixtures was phase separation into the ordered surface phase near a hard wall and a disordered bulk liquid phase. Ordered and disordered surface phases can also be understood using simple excluded-volume entropy arguments, in this case, between the large particle and the wall. Figure 2 shows a platelike molecule of *m*-TAPP (left) and a cartoon (right) for the adsorption of *m*-TAPP from an ethanol/PEO solution onto silver, based on the spectroscopic evidence shown in Figure 1c. It can be seen that the flat orientation of the molecule on the surface provides the largest overlapping of the excluded volumes of the wall and the molecules,

indicating that the PEO-mediated depletion interaction induces an "entropic torque"[24] for the adsorption geometry of *m*-TAPP on silver, while *m*-TAPP molecules were oriented randomly on silver when they deposited from an ethanol solution, as shown in SERS spectrum of Figure 1b.

In conclusion, we present a convenient method to deposit a self-assembly monolayer of platelike porphyrin onto the metal substrate by virtue of the depletion effect that has been extensively exploited in the fields of binary hard-core fluids, colloid−polymer mixtures, etc. Although there is much to be optimized if we want to fabricate porphyrin films with three-dimensional assembly, the method present here shows potential in controlling the orientation of other platelike molecules in the absorbed monolayer due to their molecular shape anisotropies.

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