Nano-patterning of solid substrates by adsorbed dendrimers†

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Weakly charged solid substrates can be nano-patterned in liquid-like order with large and well-defined spacing by adsorbing poly(amido amine) (PAMAM) dendrimers; highly charged substrates lead to lower spacing due to electrostatic three-body attractions between the dendrimers and the substrate.

Since their first synthesis by Vögtle and Tomalia, the unique structure and properties of dendrimers continue to attract attention, for example, as chelating agents, light-harvesting antennas, nanoreactors, drug delivery systems, or gene vectors.[1–6] The present communication highlights their potential in the patterning of solid substrates on the nano-scale. Dendrimers are known to adsorb strongly on surfaces, whereby they self-organize into a correlated liquid-like structure with a well-defined nearest neighbour spacing.[7–10] Properties of such nano-patterned surfaces can be tuned by changing the dendrimer generation and the salt level. The structure of these films originates from the long-range electrostatic repulsion between the dendrimers.[5,7] The structuring mechanism resembles the deposition of charged colloidal particles, commonly rationalized within the random sequential adsorption (RSA) model.[11–15] Particle deposition has been successfully used to fabricate surfaces patterned on sub-micrometer length scales, a technique referred to as colloidal lithography.[16,17]

By adsorbing dendrimers, the length scale of these patterns can now be pushed well into the nanometer range. Currently, however, the surface coverage remains high, and it seems impossible to lower it while maintaining the liquid-like order. This communication shows that such structures can indeed be obtained by adsorption of dendrimers to weakly charged substrates. Unexpectedly, the surface charge of the substrate plays a decisive role, and this effect will be explained by attractive three-body interactions acting between a pair of dendrimers and the surface.

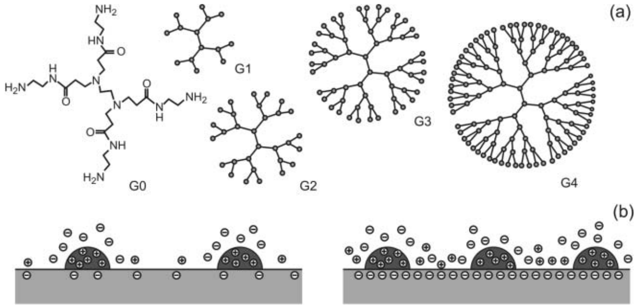

Fig. 1 Adsorption of poly(amido amine) (PAMAM) dendrimers on solid substrates. (a) Schematic representation of the structure of different generations. (b) Proposed mechanism of the decreased repulsion between the adsorbed dendrimers for a highly charged substrate.

Poly(amido amine) (PAMAM) dendrimers of different generations were adsorbed from aqueous KCl solutions with adjusted pH to freshly cleaved mica sheets and to silica substrates (Fig. 1). The latter substrate is either the natural silica layer of about 3 nm in thickness on a silicon wafer, or a silica layer of about 90 nm on such a wafer oxidized at 1000 °C, as characterized by ellipsometry in air. The adsorption was studied at 25 °C from aqueous dendrimers solution at concentrations of 5–10 mg L^{-1} by two techniques. (i) By diffusion under quiescent conditions during 5–12 h, whereby the saturation of the surface was attained. The dried samples were imaged *ex situ* by tapping-mode atomic force microscopy (AFM). (ii) By convection with an impinging-jet cell in an optical reflectometer.[18] A homogeneous slab model was used to determine the adsorbed amount from *in situ* reflectometry, and the measured values agreed well with AFM. With reflectometry one could also demonstrate that the saturated state was attained

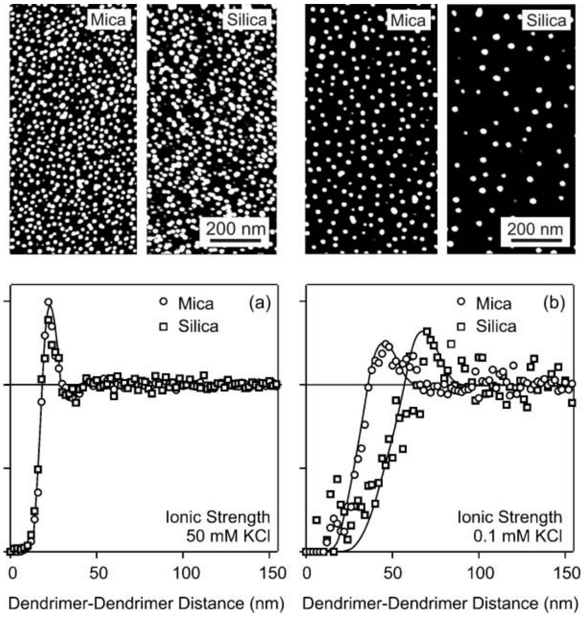

Fig. 2 AFM images and pair distribution functions of the nano-patterned surfaces obtained by adsorption of G10 dendrimers at pH 4, whereby mica is highly charged, while silica weakly. (a) Ionic strength of 50 mM and (b) 0.1 mM. Solid lines serve to guide the eye only.

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rapidly and that no desorption occurred under rinsing. The AFM images show that dendrimers flatten substantially upon adsorption. An adsorbed G10 dendrimer has a height of around 4 nm and a diameter of 18 nm, which should be compared with the diameter of 14 nm in solution.[7,8]

Let us now compare typical AFM images of the adsorbed G10 dendrimers on the mica and silica substrates. The classical RSA situation occurs at a higher ionic strength of 50 mM and pH 4 (Fig. 2(a)). Both substrates behave similarly, whereby the surface coverage remains high, and is situated at 0.33. The pair-distribution function shows a pronounced correlation peak at 22 nm. This value is larger than the dendrimer diameter of 14 nm due to electrostatic repulsion between the dendrimers.

The striking effect of the substrate on the dendrimer adsorption occurs at low ionic strength of 0.1 mM and pH 4 (Fig. 2(b)). The surface coverage is low, but much higher on mica than on silica, whereby the values are 0.11 and 0.018, respectively. In both cases, the adsorption patterns have correlated structures, as evidenced by the peak in the pair-correlation function located at 46 nm for mica and 71 nm for silica.

The ionic strength dependence of the maximum surface coverage $\theta_{\max}$ is illustrated in Fig. 3(a). The abscissa is the dimensionless screening parameter κa, where the Debye length κ^{-1} is defined as $\kappa^2 = 2e^2c/(kT\varepsilon_0\varepsilon_w)$ with a being the dendrimer radius, e the elementary charge, c the ionic strength expressed as a number concentration, ε_0 the vacuum permittivity, ε_w the dielectric constant of water, and kT the thermal energy. Note that in the representation as a function of κa the size dependence of the dendrimers basically disappears. The data points show clearly that the maximum coverage $\theta_{\max}$ increases with increasing κa (*i.e.*, ionic strength), but the coverage is much lower for silica than for mica. Several of the data points were measured by immersing both substrates in the same solution, thus excluding any artefacts due to solution preparation. For silica, reflectometry yields very similar results.

The obvious difference between both substrates is their charge density. While both are negatively charged, the magnitude of the surface charge density σ is much higher for mica than for silica. At pH 4, mica is highly charged with $\sigma \simeq 340$ mC m^{-2} due to isotopic substitution,[19] while $\sigma < 2$ mC m^{-2} for silica.[20] To further confirm that the relevant parameter is indeed the surface charge density, adsorption of dendrimers was studied on silica for different pH. For silica, σ increases with increasing pH, and one has $\sigma \simeq 40$ mC m^{-2} at pH 8 and 10 mM.[20] The results shown in Fig. 2(a) obtained by reflectometry demonstrate that $\theta_{\max}$ increases with increasing pH, particularly at low ionic strength. The important role of the charge density of the substrate on dendrimer adsorption is established.

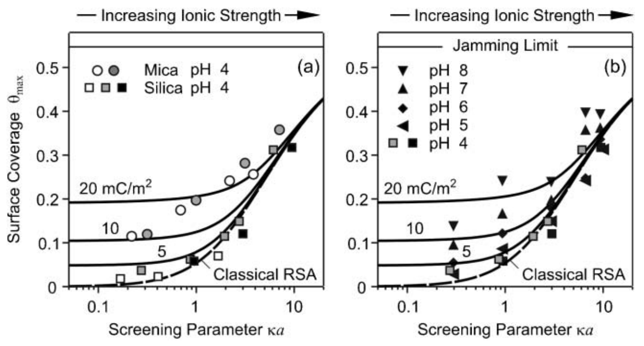

Fig. 3 Maximum dendrimer coverage $\theta_{\max}$ as a function of the dimensionless screening parameter κa. The experimental data (points) are compared with the classical RSA model (dashed line) and the one including the effect of the negatively charged substrate (solid line). (a) Comparison between mica and silica at pH 4. G8 and G10 measured by AFM (white, grey), G10 by reflectometry (black), and (b) G10 on silica at different pH values by reflectometry (black) and by AFM (grey).

The ionic strength dependence of the maximum coverage by dendrimers has been previously modelled with the classical RSA model including mutual electrostatic repulsion.[7] This effective hard-sphere model has been successfully used to model the deposition of colloidal particles.[11,12,14] However, the influence of the substrate comes as a surprise, since the RSA model assumes that the surface behaves as an ideal collector. The RSA model replaces the actual radius a of the dendrimer by an effective radius a_{eff}, which is determined such that the interaction potential $u(r)$ evaluated at this distance is comparable to the thermal energy kT. If one sets $u(2a_{\text{eff}}) = \lambda kT$ with $\lambda = 2.8$, the result coincides with the definition of a_{eff} based on the low density of the pair correlation function.[11,12] The interaction energy of two dendrimers at distance r is given by the screened Coulomb interaction:

$$u(r) = \frac{Z^2 L_B kT}{r(1+\kappa a)^2} \exp[-\kappa(r-2a)] \tag{1}$$

where $L_B = e^2/(4\pi\varepsilon_0\varepsilon_w kT) \simeq 0.72$ nm is the Bjerrum length and the effective charge of the dendrimer is given by the saturation value $Z = (4\kappa a + 6)a/L_B$. For pH $\leqslant 8$, this approximation is fully justified, as the charge of the dendrimers remains high.[7,21]

Based on the RSA model, no influence of the substrate is expected, as the surface is assumed to represent an ideal collector. While the screened Coulomb potential is certainly appropriate in the bulk, it is surmised to remain valid near a charged wall.[11,14] This conclusion is indeed correct on the Debye–Hückel level, as the pair-interactions are additive. On the Poisson–Boltzmann (PB) level, however, the interaction potential between two dendrimers will be influenced by the presence of the wall. The validity of this conjecture has been recently demonstrated by showing the existence of attractive three-body interactions between charged colloidal particles with elegant optical-tweezer experiments and numerical solutions of the PB equation.[22] Here, we present a perturbation solution of the PB equation around the exact solution for a flat plate, where point charges near the wall are treated on a linear level. Adapting the expressions proposed earlier for a periodic lattice[23] to the continuous case, we write the interaction potential between two point charges situated at the water/solid boundary as a two-dimensional Fourier transform:

$$u(r) = \frac{e^2 Z^2}{8\pi^2 \varepsilon_0} \int \frac{e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}}{\varepsilon_w p + \varepsilon_s k} d^2k \tag{2}$$

where $\boldsymbol{k}$ is the wave vector, ε_s the dielectric constant of the solid, and $p = u + \kappa^2 s^2/[u + \kappa(1 + s^2)^{1/2}]$ where $u^2 = k^2 + \kappa^2$ and the dimensionless surface charge density $s = \sigma L_B/(e\kappa)$. Eqn (2) can be approximated analytically by realizing that one has $p^2 \simeq k^2 + \kappa_{\text{eff}}^2$ where $\kappa_{\text{eff}}^2 = \kappa^2(1 + s^2)$. In the case of $\varepsilon_w \gg \varepsilon_s$, this approximation yields an interaction potential again of the screened Coulomb form, but the substitution $\kappa \rightarrow \kappa_{\text{eff}}$ in the argument of the exponential function in eqn (1) must be made. Thereby, the value of the potential at contact is assumed to remain the same.

The presence of the charged wall diminishes the range of the interaction potential, and the present RSA model predicts a much higher surface coverage at low salt (Fig. 3). Given all the inherent approximations, the semi-quantitative agreement between the model and the data is gratifying. The model further rationalizes that the classical RSA model is valid only for a substrate with small charge densities, typically <1 mC m^{-2}. For the highly charged substrates, the charge densities needed to explain the data lie below the bare charge densities, which can be understood by the presence of specifically adsorbed ions at the surface. In spite of additional repulsions due to image charge effects, we suspect that the suggested approximation still overestimates the effect of the wall. The higher correlation peak for the less charged substrate further indicates that the interaction potential is modified by the nature of the substrate (Fig. 2(b)).

The mechanism of weakening the repulsive forces through the presence of a charged wall is illustrated in Fig. 1(b). A weakly charged surface accumulates few additional ions in its diffuse layer, and thus the interaction between the dendrimers is well approximated by the screened Coulomb potential even in the proximity of the surface. On the other hand, a strongly charged surface attracts a substantial amount of counter-ions in its diffuse layer, and these ions screen the dendrimer charges in its vicinity, thus reducing the range of this potential and the magnitude of the repulsion. This mechanism is most pronounced for small objects at low ionic strength and fully equivalent to the attractive three-body interaction between charged colloidal particles.[22]

In conclusion, surfaces can be patterned on the nanometer scale with adsorbed dendrimers in liquid-like order with large and well-defined spacing at low ionic strengths, provided the surface charge is sufficiently small. Highly charged substrates lead to substantially lower spacing, since coulombic repulsions between the dendrimers are additionally screened by the counter-ions bound in the diffuse layer of the substrate.

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