Vol 18 No 3, March 2009
1674-1056/2009/18(03)/0997-05

Chinese Physics B

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Fabrication of grating-like polystyrene latex monolayer structure as three-dimensional calibration standards for scanning probe microscope*

Zhu Guo-Dong(朱国栋)[a)†], Zeng Zhi-Gang(曾志刚)[a)], Guo Zhang(国 璋)[b)], Du Qiang-Guo(杜强国)[b)], and Yan Xue-Jian(严学俭)[a)]

[a)] *Department of Materials Science, Fudan University, Shanghai* 200433, *China*

[b)] *Department of Macromolecular Science, Fudan University, Shanghai* 200433, *China*

(Received 23 June 2008; revised manuscript received 5 August 2008)

This paper illuminates the preparation of grating-like polystyrene latex monolayer structure, which can minimize the effects of the size deviation of spheres and the defect transfer on the accuracy as calibration samples for microscopes. The latex films are grown on freshly cleaved mica substrates by vertical deposition method. The concentration dependence of the structure and the topography of latex films is characterized by optical microscope, ultraviolet–visible transmission spectrum and scanning probe microscope. The origination of such a grating-like structure is also discussed.

Keywords: polystyrene spheres, scanning probe microscope, grating-like structure, calibration sample

PACC: 0779, 8270D, 6865, 8116

1. Introduction

In recent years monodispersed colloidal spheres and colloidal crystals have received more and more attention due to their potential applications as templates to prepare photonic crystals,[1] nanodot arrays[2] and macro- and meso-porous structures[3,4] and also as calibration standards[5] for scanning electron microscope (SEM), tunnelling electron microscope (TEM) and scanning probe microscope (SPM), and so on. Up to now, several techniques, based on self-assembly principle, have been successfully demonstrated to fabricate colloidal crystals, such as vertical deposition,[6] water–air interface selfassembly,[7] confinement cell technique,[8] Langmuir–Blodgett method[9] and so on. However, the production of three-dimensional periodic structures with large ordered area remains a challenge. Though colloidal crystals with multilayer (from several layers up to several hundred layers) still possess relatively ordered two-dimensional surface structure, any defects (such as point and line defects, dislocation) underneath the surface can be transferred onto the surface and the size deviation of sphere diameters can also be magnified by the propagation of errors layer by layer,[10] it seems that colloidal crystals can hardly be used as accurate calibration samples for microscopes.

This paper illuminates the preparation of grating-like polystyrene (PS) latex monolayer structure, which can minimize the effects of the size deviation of spheres and the defect transfer on the accuracy as calibration samples for microscopes.

2. Experimental details

PS aqueous suspension was prepared by microemulsion method[11] with an original concentration of about 0.6 wt.%. The diameter of PS spheres was about 206 nm, which was measured by SEM in Shanghai Institute of Measurement and Testing, China, and the coefficient of variance of these spheres was ∼4%, measured by light scattering (Autosizer 4700, Malvern, UK). The original suspension was diluted by deionized water with various volume fractions.

About 8 ml diluted suspensions were used to prepare the latex films on freshly cleaved mica substrates (∼1.5 cm×3 cm) by vertical deposition method.[6] The growth temperature was set at 55°C, which was validated by several authors.[12,13] A relative humidity

*Project supported by Science and Technology Commission of Shanghai Municipality (Grant No 0652NM028), Shanghai Leading Academic Discipline Project of China (B113) and the International Research Training Group (IRTG).

†Corresponding author. E-mail: gdzhu@fudan.edu.cn.

of $\sim 40-50\%$ was kept during the film growth and drying process.

The structure and the topography of latex films were characterized by optical microscope, ultraviolet–visible (UV–vis) transmission spectrum (UV-2450, Shimadzu, Japan) and SPM (UltraObjective, SIS, Germany).

3. Results

Latex films grown from suspensions with different concentrations were firstly imaged by optical microscope, as was shown in Fig.1. Optical image (Fig.1(a)) of the latex films grown from the original PS suspension showed blue colour, which originated from the Bragg diffraction of the three-dimensional periodic structure in colloidal crystals,[14] and the dark cracks along the direction of film growth were due to drying process. The surface of such a film was not an ideal plane and could not be regarded as an accurate calibration standard, due to the effects of defects inside the crystal body and of the size deviation of spheres, both of which cause a rough surface. When the original suspension was diluted by 30 times, its optical image (Fig.1(b)) showed various colours, which were caused by the light interference due to different film thickness.[15] Interestingly, we obtained a grating-like monolayer structure (Fig.1(c), imaged at the area about 1.5 cm below the beginning of film growth, the light yellow strips correspond to the monolayers, while the relatively dark areas correspond to mica substrate) when the suspension was diluted by 60 times. The direction of strips is vertical to the film growth direction. The width of latex monolayers is about $50\,\mu$m and the width of bared substrate stripes is about $30\,\mu$m, so the period of this grating-like structure is about $80\,\mu$m. The area of such a grating-like structure is about $1.5\times2.5\,\mathrm{cm}^2$. When the suspension is overdiluted, no continuous films can be observed from the optical image (Fig.1(d)).

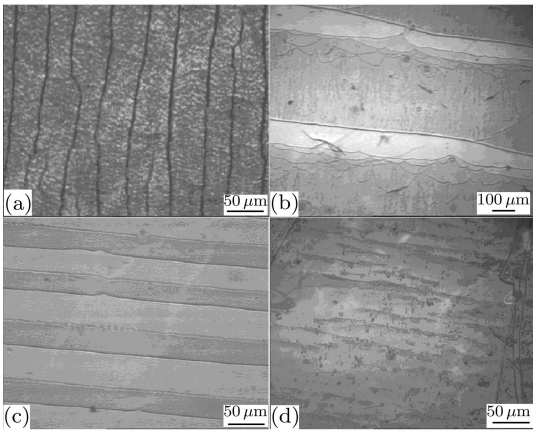


Fig.1. Optical microscope images of latex films grown from original suspension (a) and suspensions diluted by 30 (b), 60 (c) and 90 (d) times.

UV–vis transmission spectra (Fig.2) show that with the decrease of suspension's concentration, the characteristic peak, due to the Bragg diffraction, gradually weakens and finally vanishes when the suspension is diluted by 60 times. From the Bragg equation,[14] we can also approximately obtain the average diameter of our PS spheres, 195.6 nm, taking 1.59 as the refractive index of PS spheres.[16] The average transmissivity increases with the decrease of suspension's concentration, due to the decrease of film thickness.

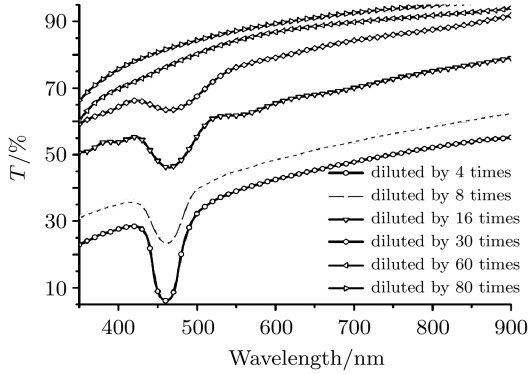


Fig.2. UV–vis transmission spectra of latex films grown from suspensions with different concentrations.

The typical SPM topographies of these latex films are displayed in Fig.3. SPM image of films grown from

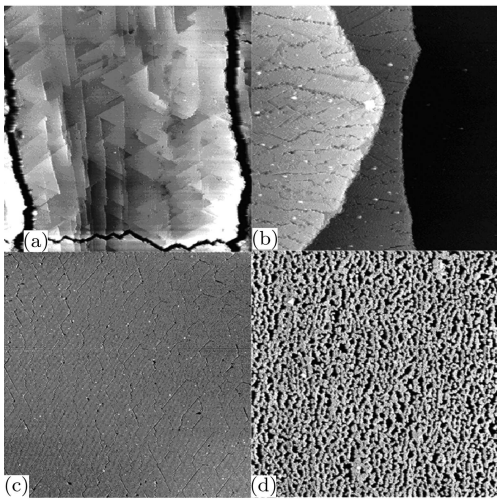


Fig.3. SPM images scanned on the surface of the latex films grown from the original suspension (a) and the suspension diluted by 30(b), 60(c) and 90(d) times. Scan size: $40\,\mu\mathrm{m}\times40\,\mu\mathrm{m}$.

original suspension (Fig.3(a)) shows many triangular planes, which seems to imply the separate growth of these triangles at different growth sites, due to plentiful supply of spheres from the suspension during the growth process. These triangles increase the roughness of film surface. The boundaries of three layers grown from 30-time diluted suspension are imaged and shown in Fig.3(b). The topography of the grating-like monolayers is shown in Fig.3(c). A few point and line defects can be observed. The films show a monolayer structure and no triangular planes are superposed onto the monolayer. Such a monolayer structure can be used as a standard samples for three-dimensional calibration of SPM piezoelectric tubes, as is shown in Fig.4. When the suspension is overdiluted, a discontinuous monolayer is observed (Fig.3(d)) and the two-dimensional periodicity is destroyed.

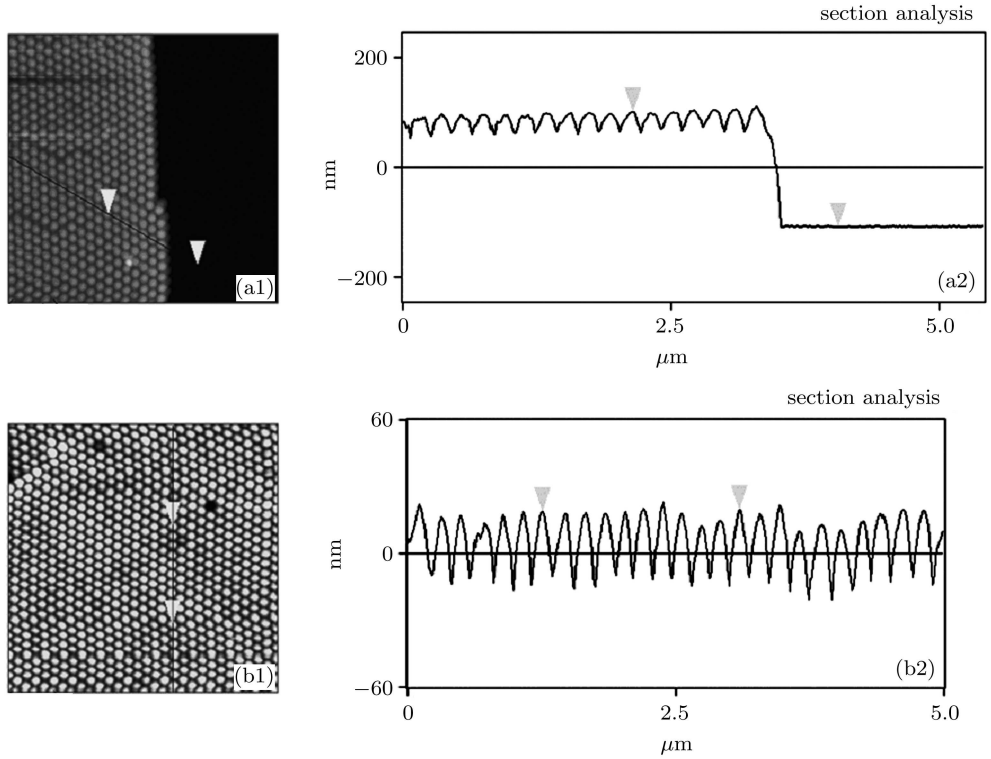


Fig.4. Grating-like monolayer structure as a standard sample for the calibration of Z-axis (a) and X- and Y-axis (b) piezoelectric tubes of SPM. Scan size: $5\,\mu m \times 5\,\mu m$, scan rate: 0.8 Hz.

The grating-like samples should be pre-calibrated by metrology-SPM before they could be used as calibration standards, the averaged height and diameter of these closely packed spheres and their deviations should be determined. Based on the pre-calibrated grating-like monolayer structure, the three-dimensional calibration for SPM piezoelectric tubes could be performed, as was simply described in Fig.4. Further calibration procedure would be developed to minimize the errors from scan parameters, monolayer defects, plane fit processing and so on.

The step between the monolayer and the substrate (i.e. the height of spheres) could be used to calibrate the Z-axis piezoelectric tube (Fig.4(a)). Before calibration, the SPM tip should be positioned just upon the edge between the substrate and the monolayer and an image with proper scan size was obtained. A simple plane fit was performed to make the bared mica substrate, shown in atonic force microscope (AFM) images, as an ideal plane, as could be seen in Fig.4(a): the dark area in the right of Fig.4(a1) corresponds to the flattened mica substrate, the section analysis shown in Fig.4(a2) indicates that the flattened mica substrate is an ideal level and can be used for the further calibration of Z-axis piezoelectric tube. A lateral line profile is taken along the points of contact between nearest neighbours as illustrated in Fig.4(a1). In every line profile, the vertical distances between the summit of a single sphere and the flatten mica substrate were read and recorded. About 100 data of vertical distances from 10−20 line profiles were statistically averaged. The averaged height value was compared with the one obtained by metrology-SPM and then the Z-axis tube could be calibrated.

The two-dimensional periodicity of ordered closely-packed latex monolayers ensured their application to the calibration of X- and Y-axis piezoelectric tubes (Fig.4(b)). At this time, AFM images should be obtained at the centre of the monolayer structure. Similar to the calibration of Z-axis tube, a lateral line profile was taken along the points of contact between nearest neighbours. Most importantly, the line profile drawn in AFM image for the calibration of X- or Y-axis tubes should be parallel to one of the scan axes, that is to say, when X-(Y-) tube is calibrated, the line profile should be parallel to the X-(Y-) axis. So, before AFM scanned an image for the calibration of X- or Y-axis tubes, the sample should be accurately pre-positioned to ensure that the line profile could be parallel to the corresponding axis. A sample for the calibration of Y-axis tube was given in Fig.4(b). The image in Fig.4(b1) was simply flattened by X- and Y- plane fit before the vertical line was drawn. The horizontal distances between every 10 neighbouring spheres were recorded. About 10 data of horizontal distances from ∼10 line profiles were statistically averaged. The average diameter of the spheres was compared with the one obtained by metrology-SPM and then the X-(Y-)axis tube could be calibrated.

4. Discussions

The principle of vertical deposition has been well understood and is attributed to the faster water evaporation near the concave meniscus and consequently the convective transport of latex spheres towards the substrate–suspension–air contact line.[17] The substrate–suspension–air contact line should be a straight line if the hydrophilicity of substrate surface is homogeneous and the horizontal dimension of the substrates is large enough. The parallel grating-like stripes in Fig.1(c) prove the homogeneity of hydrophilicity of the mica substrate.

The formation of the stripe structure is well expatiated by Teh *et al*[18] as can be demonstrated according to the scheme in Fig.5. At the beginning of the self-assembly of latex spheres onto the substrate (Fig.5(a)), the suspension rides up the substrate, forming a concave meniscus at the substrate–suspension–air contact line (the contact line is indicated by the horizontal dash line in Fig.5). At the contact line, the cosine component ($T_{\rm s}'$) of the suspension's surface tension ($T_{\rm s}$), $T_{\rm s}' = T_{\rm s}\cos\theta$, is in competition with the wetting-film's surface tension, $T_{\rm f}$,[18] where θ is the angle between the substrate and the meniscus. At the initial stage of growth, $T_{\rm s}'$ is smaller than $T_{\rm f}$. If the suspension is diluted enough, a monolayer begins to self-assemble onto the substrate, due to convective mass transport at the meniscus.[17] With water evaporation, the bulk liquid surface falls and $T_{\rm s}'$ increases due to the decrease of θ (Fig.5(a)). Just when θ is small enough to cause $T_{\rm s}' > T_{\rm f}$, the contact line suddenly descends, stabilizes at a new position and forms the new contact line, a little far below the initial position of the contact line (see Figs.5(b) and 5(c)). This process is also called stick-slip motion, the repetition of which induces the formation of grating-like structure. The distance (h) of this slip determines whether a grating-like monolayer or bilayer structure will occur. If the slip distance is larger than the vertical dimension (H) of the monolayer which has grown

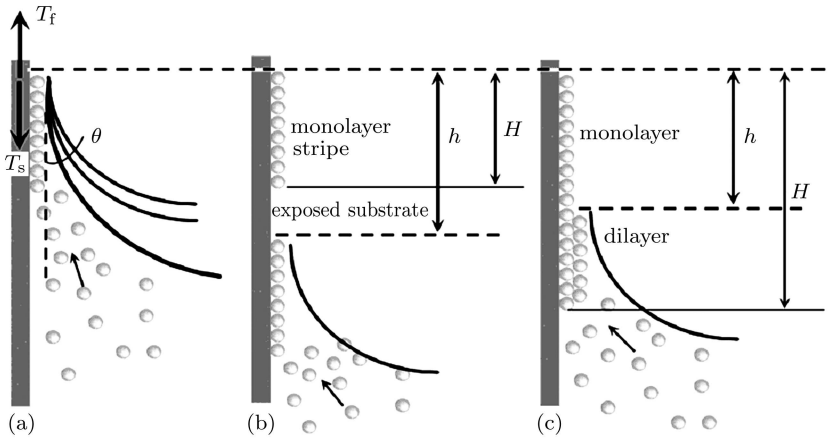


Fig.5. Scheme of the growth of grating-like mono- or bi-layers

on the substrate before the slip, i.e. $h > H$, a new monolayer begins to grow onto the bared substrate and the separation of both monolayers is $h - H$ (Fig.5(b)); however, if $h < H$, the existing monolayer continues its growth and at the same time a second layer grows onto the existing monolayer, and forms the bilayer structure.

The competition between H and h is concentration dependent, though it can also be influenced by temperature and the addition of surfactant. A lower concentration should correspond to a slower growth rate of the monolayer and consequently a smaller H, and a lower concentration also induces the increase of suspension's surface tension[18] and the increase of critical angle θ_c at which the contact line jumps below, and consequently a smaller h can be expected. All these deductions can be validated from Fig.1(c) and Fig.6. The optical image of Fig.6(a) is imaged at the area about 0.5 cm below the beginning of film growth from the same sample as Fig.1(c). Figure 6(b) is imaged on the surface of the film grown from 40-time diluted suspension. Check the difference between Fig.1(c) and Fig.6(a): the width (H) and the periodicity (h) of the monolayers shown in Fig.1(c) are about 50 μm and 80 μm, respectively, while both values are 25 μm (H) and 60 μm (h) in Fig.6(a). These differences can be attributed to the increase of the suspension's concentration with water evaporation during vertical deposition process. The area shown in Fig.1(c) is about 1.0 cm below that shown in Fig.6(a), the concentration, corresponding to the film growth in Fig.1(c), should be higher than that corresponding to the film growth in Fig.6(a), while a higher concentration should result in a larger h and H, as has been discussed above. Figure 6(b) gives us a more obvious evidence for the increase of h with the increase of concentration. The 40-time diluted concentration is high enough to form a bilayer structure, and the periodicity (h) of bilayers is about 200 μm, much larger than the periodicity obtained from Figs.1(c) and 6(a).

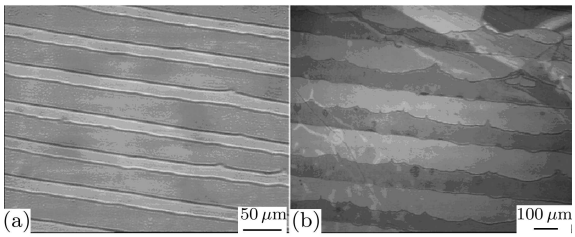


Fig.6. Monolayer (a) and bilayer (b) stripes grown at 55°C on mica substrates. Figure 6(a) was imaged at the area about 0.5 cm below the beginning of film growth from the same sample as Fig.1(c). Figure 6(b) was imaged on the surface of the film grown from 40-time diluted suspension.

5. Conclusion

In this paper we reported the preparation of a grating-like monolayer structure on mica substrates by vertical deposition method and the concentration dependence of colloidal films was characterized by optical microscope, UV–vis transmission spectrum and SPM. Such grating-like monolayer structure could be used as an ideal standard samples for the three-dimensional calibration of SPM's piezoelectric tubes. The formation of such a grating-like structure was also discussed based on the dynamic balance of surface tension forces and the convective transport of latex spheres.

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