Extended Abstracts of the 2020 International Conference on Solid State Devices and Materials, VIRTUAL conference, 2020, pp767-768

Crucial impact of hydrophobicity on the self-assembly of 2D colloidal crystals using Langmuir-Blodgett method

Heping Wu[1], Wei Ren[1], Luyue Jiang[1], Owen Liang[2], Jinyan Zhao[1], Yangyang Liu[1], Ya-Hong Xie[2], Gang Niu[1*]

[1] Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, School of Electronic Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China
Email: gangniu@xjtu.edu.cn
[2] Department of Materials Science and Engineering, University of California, Los Angeles, Los Angeles, CA 90095, United States

Abstract

Langmuir-Blodgett (LB) method is a powerful technique to prepare 2D colloidal crystals. However, the self-assembly and movement of microspheres during the whole LB process are less analyzed. Herein we clarify the crucial impact of hydrophilicity of the microspheres on their self-assembly in Langmuir-Blodgett (LB) process and find that the increase of the surface hydrophobicity of microspheres facilitates their self-assembly on water surface, which further leads to higher coverage and less defects of the 2D colloidal crystals. The 2D colloidal crystal monolayer on the Si substrate scatters the visible light obeying the 2D Bragg scattering formula, showing iridescent colors and opposite contrasts.

1. Introduction

Large-scale close-packed two-dimensional (2D) colloidal crystal with high coverage is indispensable for various promising applications such as photonic crystals, photonic papers and inks, stealth materials, biomimetic coatings and related nanostructures. Various methods to prepare monolayer-thick colloidal crystals have been developed, which can be generally divided into five categories [1]: drop coating, dip coating, spin coating, self-assembly at the gas-liquid interface and electrophoretic deposition. Among these methods, Langmuir-Blodgett (LB) method is a controllable self-assembly technology having advantages like high degree of mechanization and good reproducibility.

Past reports focus mainly on the optimization of the deposition parameters and the experiment conditions, the study of the optical and physical properties of the 2D colloidal crystals, as well as the improvement of the LB equipment. Few study has been reported on the behavior of the microspheres during the whole LB process, including self-assembly on water surface as well as the following transferring process. Furthermore, the traditional method to measure the characteristic surface pressure-area isotherms (π-A curve) [2] is not available for the microspheres for they will sink into water severely during the dispersion period.

2. Experiments

Two types of monodisperse polystyrene (PS) latex microspheres (500 nm) were used, differences between which are whether the surfaces are functionalized by sulphate groups. LB trough was used to fabricate the 2D colloidal crystals on a hydrophilic Si wafer.

3. Results and discussion

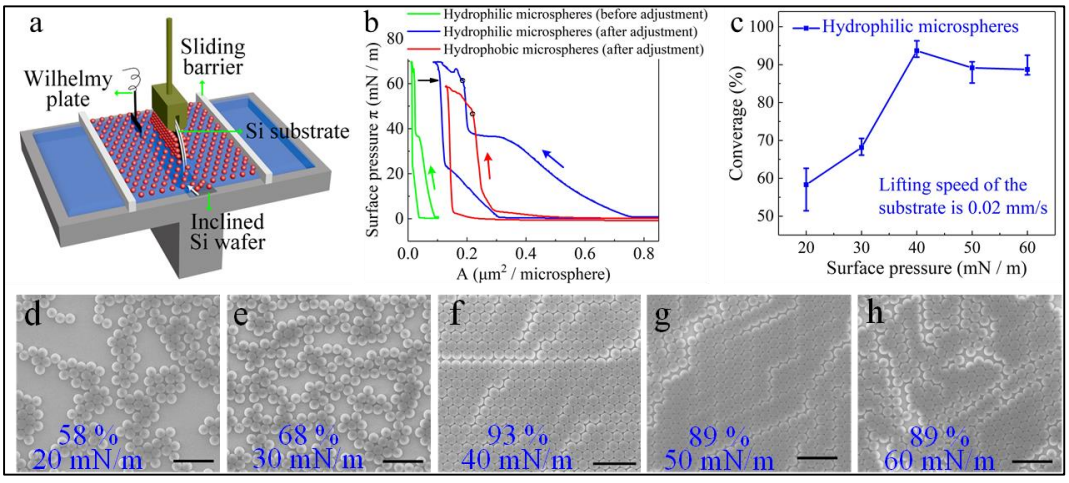

Fig. 1. (a) Schematic illustration of the fabrication process of 2D colloidal crystals using LB method. (b) π-A curves of the 2 types of PS microspheres. (c) The coverage of 2D colloidal crystals on the Si substrate prepared at different surface pressures using hydrophilic PS microspheres. (d-h) SEM figures of the 2D colloidal crystals of hydrophilic microspheres, with surface pressure of 20, 30, 40, 50, and 60 mN/m, respectively. Scale bars in the images are 2 μm.

The experiment parameter, surface pressure during lifting film process, have been optimized using hydrophilic microspheres, as shown in Fig. 1. π-A curves of hydrophilic and hydrophobic microspheres have been corrected (after adjustment) in Fig. 1b

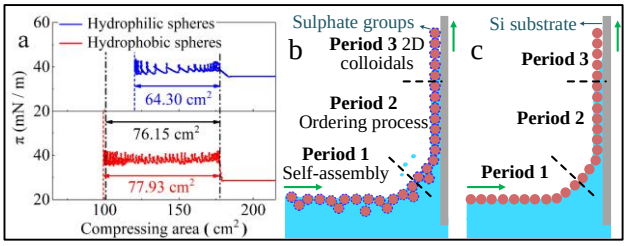

Fig. 2. Self-assembly of PS microspheres on the water surface. (a)The macroscopic relationship between surface pressure and the microspheres area on the water surface during the lifting film process. The compressing area for hydrophilic microspheres during lifting film process is 64.30 cm^2, for hydrophobic microspheres is 77.93 cm^2, and the area for 2D colloidal crystals on the Si substrate is 76.15 cm^2 (black arrow). (b) LB process of the microspheres with sulphate groups (hydrophilic). (c) LB process of the microspheres without any surface functional groups (hydrophobic).

by calculating the quantity of microspheres which are at the air/water interface and have not sank into water. Best coverage for hydrophilic microspheres of 93% has been achieved.

Fig. 2 shows the variation of the surface pressure (π) as a function of the monolayer area of microspheres on the water surface during the lifting film process for hydrophilic (blue curve) and hydrophobic (red curve) microspheres. The compressing area for hydrophilic spheres (64.3 cm^2) is much lower than on Si wafer, indicating bad self-assembly that microspheres overlaps on water surface. An ordering process exists when microspheres transfer to the Si wafer driven by capillary force, as shown in Fig. 2b. While for hydrophobic microspheres, the self-assembly on water surface is good for its compressing area (77.93 cm^2) is a little larger and very close to that on Si wafer (76.15 cm^2).

The defects of two types of 2D colloidal crystals include line defect and point defect, as shown in Fig. 3. 2D colloidal crystals of hydrophobic microspheres have less defects, especially less overlapping spheres, which is in consistent with the self-assembly on water surface. A coverage of 97 % for hydrophobic microspheres has been achieved.

Owing to the periodic structures of the 2D colloidal cyrstals, the iridescent colors in Fig. 4a and opposite contrasts in Fig. 4c origin based on the Bragg diffraction of light due to their complete manipulation of the propagation of light [3].

4. Conclusions

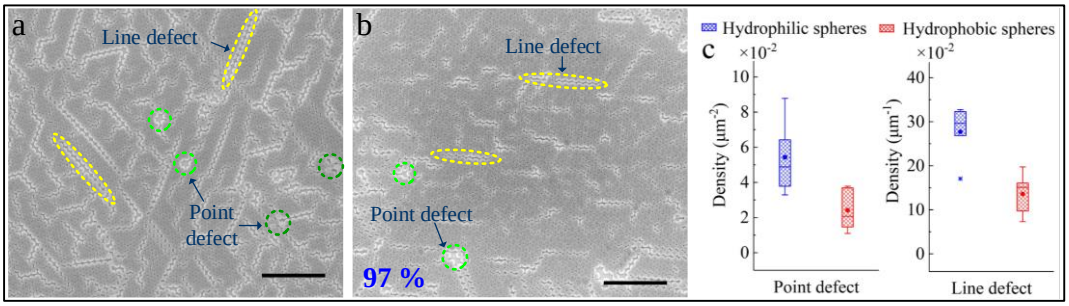

Fig. 3. SEM figures of the prepared 2D colloidal crystals with defects. (a) Hydrophilic microsphere crystal. Point defects include vacancies (light circle) and overlapping spheres (dark circle). (b) Hydrophobic microsphere crystal. (c) Statistics of the defects of the 2 types of colloidal crystals. Scale bars are 5 μm.

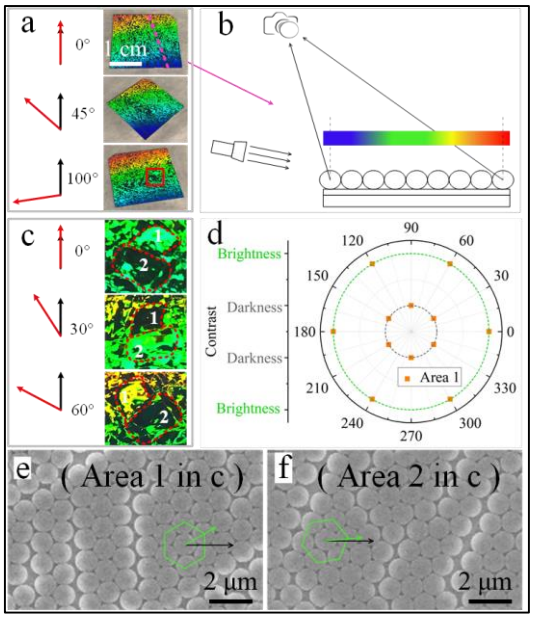

Fig. 4. (a) Visible light diffraction phenomenon of the monolayer on Si substrate. (b) Schematic illustration of the iridescent colors caused by the diffraction. (c) Opposite contrasts at local adjacent regions (box in Fig. 4a) and multiple directions. (d) Polar plot of the brightness variation of area 1in Fig. 4c. (e, f) SEM figures of the adjacent regions (region1 and region 2 in Fig. 4c, respectively). The black and green arrows in Fig. 4e and Fig. 4f are the horizontal direction and crystal orientation.

High coverage (97 %) and high quality 2D colloidal crystals have been successfully fabricated on Si wafers and the significant impact of the hydrophilicity of microspheres on their self-assembly and subsequently on 2D colloidal crystals quality have been studied. The 2D colloidal crystal diffracts visible light, causing iridescent colors and opposite contrasts at local adjacent regions, which is in accordance with the hcp lattice.

Acknowledgements

We acknowledge the funding support from Key R&D Program of Shaanxi Province of China (2020GY-271), The Fundamental Research Funds for the Central Universities (xjj2018016), the "111 Project" of China (B14040) and Natural Science Foundation of China (Grant No. 51602247).

References

[1] X. Ye, L. Qi, *Nano Today 6 (2011) 608-631.*

[2] A. Tanaka, Y. Tsuchiya, K. Usami, S.-i. Saito, T. Arai, H. Mizuta, S. Oda, *Jpn. J. Appl. Phys. 47 (2008) 3731.*

[3] J.-T. Zhang, L. Wang, J. Luo, A. Tikhonov, N. Kornienko, S.A. Asher, *J. Am. Chem. Soc. 133 (2011) 9152-9155.*