Large-Scale Fabrication of Ordered Monolayer Self-assembly of Polystyrene Submicron Spheres

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Abstract Fabrication of ordered array and its applications have emerged as a critical tool for micro-structure, with which generally apply in sensing, wastewater detecting, and field emission. This review focuses on the fabrication of ordered patterned array polystyrene (PS) submicron particles monolayer as well as its effect factors. Substantial progress in the two dimensional (2D) regular patterned array has made by developing variety of method. One effective method of fabricating PS submicron spheres with full regular patterned, aligned monolayer ordered array is discussed in this paper and SEM was used to characterize the performance of the monolayer. This approach opens the simplicity and convenience of creating patterned two-dimensional nanostructure. Its greatest advantage is that suitable for large particle size spheres, Finally, the development tendency and prospect of in theses research areas are outlined.

Keywords Polystyrenes microspheres · Micro-structure · Ordered pattern Self-assembly

1 Introduction

Recently, as an assembled micro-structure, the ordered microsphere array is of great importance in biosensor [1], wastewater detecting [2], solar cell [3] and other microstructure device [4]. Polystyrenes (PS) microspheres are a generally organic material of two dimensional (2D) regular patterned array, which is applied as previous substrate of single-layer microsphere film preparing microstructure [1–5].

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Besides its spatiality of the ball cavity structure, it is of utmost importance to deposit this material as thin film in a way that represents a general applicability for 2D materials. There are many methods to grow the thin film of PS spheres such as gravity deposition [1], langmuir-blodgett assembled methods [4, 5], micro-propulsive injection methods [6]. Due to the large diameter spheres have over big quality and over fast deposition velocity, the currently methods unable to realize orderly arrangement in the large diameter spheres [7].

This paper will briefly describe an effective method that used for self-assemble of regular patterned, aligned monolayer film of PS microspheres [5]. This method opens the simpleness of fabricating patterned 2D microstructures which have many advantages. For example, it can satisfy the large diameter spheres arrangement and realize large-area array, save time and materials and raise the efficiency. The scanning electron microscope was used to characterize the performance of the monolayer.

2 Experiment

2.1 Raw Materials and Preparation

Monodispersed polystyrenes (PS) spheres (2, 6 μm, 2.5%) were purchased from J&K Chemical. First, a centrifuge separated the polystyrenes spheres from the suspension liquid, concentrating them in order to suitable proportion (10%). For this, PS solutions dissolved in ethyl alcohol (the proportion of PS spheres and ethyl alcohol was 1:2). Then the diluted solution was for 5 min strong ultrasonic oscillated in order to make sure its dispersion. For substrate, we used the ITO glasses, which were separated into 1 cm × 1.5 cm. In order to increasing the hydrophobicity of ITO glasses surface, surface modification was needed. The glasses substrates were cleaned and immersed in sodium dodecyl sulfate (SDS) for 24 h.

2.2 Fabrication of Ordered PS Spheres Film

Our fabrication approach firstly used 200 μL the PS spheres suspension being slowly dropped into the surface of the substrate and gently shaked the substrate so that it was spread evenly on the surface. Secondly, the substrate with the PS sphere suspension was slowing immersed into the deionized water with a certain angle of 15°. Then, to form a better thin monolayer of PS spheres, waiting for the PS sphere spreaded out the surface of water when after one or two drops of 1% peregal was dropwise added to the water. This moment, we would found that the PS spheres was pushed aside because peregal change the tension of the surface and it obtained the full regular patterned, aligned monolayer thin film. Next, we need to make the thin

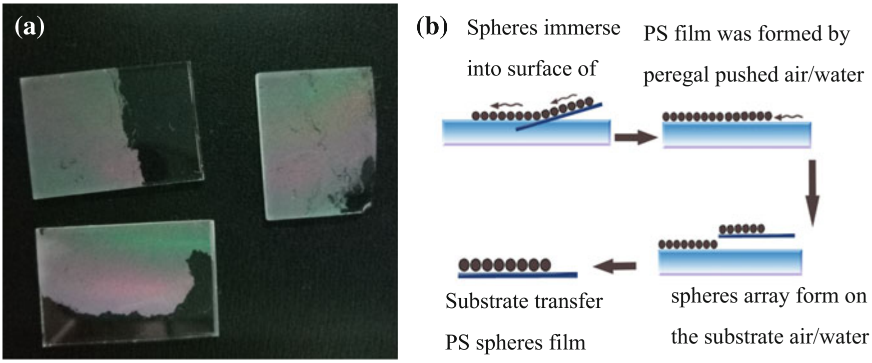

Fig. 1 **a** An optical image of the self-assembled monolayer structure on the ITO substrate. **b** The processing of fabrication of PS spheres array

film transfer from surface to substrate. The substrate slowly immerse into water where without PS spheres and then horizontally lifted substrate where PS spheres arrayed of monolayer [8]. Waiting for dry of PS spheres film, We can see that the substrate appear white PS film. This is because the diameter of PS spheres is at micron level, which produce diffracting light outside the wide of visible light [9]. Figure 1a presents an optical image of the monolayer structure formed by this method. Figure 1b presents the processing of fabrication of PS spheres array.

3 The Results and Discussion

3.1 Effect of the Substrate of Hydrophilic Treatment

Before the experiment started, the ITO glasses were washed according to the standard cleaning method. For this, the substrates were respectively ultrasonic cleaned about 30 min by acetone, ethyl alcohol and deionized water to remove grease stains and small particles. Due to the surface of pure ITO glasses substrates possess low surface free energy, it shows hydrophobicity [10] which is adverse to preparation the ordered monolayer of PS nanospheres. In order to increase the hydrophilia and surface energy of ITO glasses surface, the ITO glasses were immersed in SDS about 24 h [11] to increase the hydrophilia of the surface.

3.2 Influencing Factors of Film Forming Properties

In order to self-assembly grow regular patterned, aligned monolayer film of PS spheres, we need to control various kinds of influencing factors of film forming

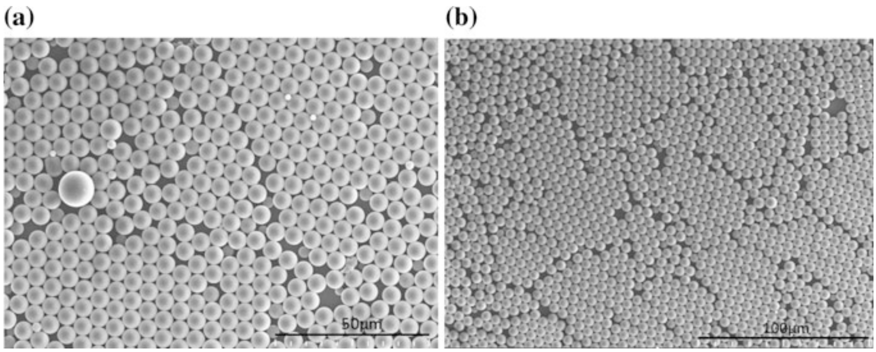

Fig. 2 The SEM images of different types of PS array defects. **a**, **b** The diameter of PS spheres is 6 μm

stability. The first one, the cleanliness and the hydrophobic of substrates and uniformity of diameter of PS spheres would influence the completeness of film and the adhesive force of PS spheres such as point defect (Fig. 2a). And with the increase of diameter of spheres, the homogeneity of diameter gradually change terrible, which could be demonstrate by Fig. 2. Secondly, for experimentation, monolayer film is very weakness and any physical vibration, especially, in the process of transferring the spheres to substrate and drying the spheres film on substrate, that would affect the completeness of film such as line imperfection (Fig. 2b).

3.3 Ratio of Ethanol and Deionized Water

In order to make PS spheres at the air/water surfaces immersed into liquid of a small number, we choose the mixture of ethanol and water as the diffusant [12]. The ratio of ethanol and deionized water of PS spheres suspension was an important element of fabrication the PS spheres array. With the increase of ethanol concentration, the order of PS spheres array presented more perfect. Some of PS spheres sedimentate into solution and film-forming performance was poor (Fig. 3a). This reason was surface density of PS spheres suspension greater than deionized water [12–15]. For another, when ethanol concentration was excessive, PS spheres array would appear some lacuna with the volatilization of ethanol [15]. Thus, for all above reasons, we choice difference ratio of ethanol and deionized water with difference diameters. Figure 3a shows the SEM images of the a full ordered structure of 2 μm with the ratio of ethanol and deionized water is 1:2, Fig. 3b shows the SEM images of the a full ordered structure of 6 μm with the ratio of ethanol and deionized water is 3:5.

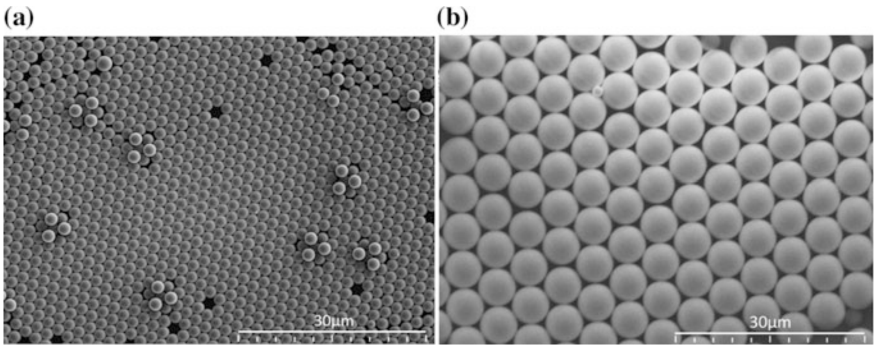

Fig. 3 **a** The SEM images of suspensions with 1:2 of 2 μm PS spheres. **b** The SEM images of suspensions with 3:5 of 6 μm PS spheres

4 Conclusions

The strategy of fabrication of fairly ordered PS spheres film appears to be quite general and applicable to many microstructure. It is based on readily available precursors and simply operation. Although there are many influence factors to obtain large-area arrangements, the fairly ordered structures meet requirements of preparative microstructure [16]. This method uses a simple fabrication technique to control the alignment, size, shape, and periodic of self-organized PS spheres monolayer patterns with feature sizes down to several micrometer and over surface area of square centimeters. Due to the various property of PS spheres, they can be template to direct the self-assembly of functional monolayer and microstructures, which can be used as biosensors, wastewater detecting and other biofunctionalized structures and systems [16–20].

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