Journal of Industrial and Engineering Chemistry 16 (2010) 879–883

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Short communication

Highly ordered monolayer formation of silica beads assisted by ultra-sound and microscopic barrier at air/water interface

Young-Soo Seo [a,*], Kyunghwan Yoon [b], M. Rafailovich [c]

[a] Department of Nano Science & Technology, Sejong University, Republic of Korea
[b] Department of Chemistry, SUNY at Stony Brook, USA
[c] Department of Materials Science and Engineering, SUNY at Stony Brook, USA

ARTICLE INFO

Article history:
Received 24 March 2010
Accepted 10 June 2010

Keywords:
Silica monolayer
Self-assembly
Ultra-sound assisted ordering
Diblock copolymer

ABSTRACT

We fabricated closely packed monolayer of hydrophobically modified non-porous silica (NPS) beads at air/water interface. Hydrophilic silica beads were modified by hydrocarbon that render hydrophobic on their surface. Ultra-sound applied to the water subphase, inducing large scaled two-dimensional ordering of the beads by reducing three-dimensional irregular cluster formations while spreading solvent evaporated. Furthermore, surface pressure generated by polymeric surface micelle effectively pushes the silica beads and reduces voids between the 2D silica clusters.

1. Introduction

The fabrication of close-packed monolayers of spherical colloids has been developed and will be potentially used for electronic devices [1–3]. Mainly two methods have been proposed for two-dimensional crystal fabrications, e.g. stacking by capillary force during water evaporation [4] and self-assembly at air/liquid or liquid/liquid surfaces [5,6]. Former case, a lot of efforts has been devoted to control water evaporation rate to get large-sized and close-packed monolayer. Among them 'confined convective assembly' has successfully been developed for accurate control of water evaporation [7]. Latter case, in order to trap colloids at the interfaces and induce self-assembly, as one of the key issues, various surface modifications has been tried [8]. In a special case, charged colloidal particles were trapped at hexane/water interface and formed fairly ordered structure obtained by a balance between van der Waals and electrostatic interactions even without surface modification [9]. For further processing, however, it is difficult to transfer the layer to the solid substrate from hexane/water interface. Therefore recently air/water interface has been more attracted in research groups. For example, carboxylate-modified polystyrene nanospheres formed centimeter-sized ordered domains on the water and transferred to solid substrates [9].

Here we focus a self-assembly of colloidal particles at air/water interface where non-porous silica (NPS) bead was chosen for 2D crystal formation. Major commercial application of NPS is so far separation media for chromatographic column in the form of surface modifications by hydrocarbon or metal coating because there is no pore on its surface that reduces signal broadening. It is also interesting to apply NPS monolayer for lithography and separation media of microfluidic devices. Recently two and three-dimensional stacking structure of NPS has been used for DNA separation media as an artificial gel with controlled pore sizes [10,11].

Hydrophilic NPS beads should be hydrophobically modified in order to spread them on the water. Even though hydrocarbon attached NPS beads are commercially available, they are so hydrophobic that they form large aggregates on the water. Moreover, NPS beads with low surface coverage of hydrocarbons that can still be floating on the water cannot form 2D crystal but disordered array because repulsive interactions between them are strong enough. Therefore surface coverage needs to be controlled to render intermediate hydrophobicity on the silica beads for 2D crystal formation on the water. "Intermediate" hydrophobicity means that repulsive and attractive interactions on the water are somewhat balanced.

In this paper we provide a novel method to fabricate large scaled and highly ordered monolayer of NPS beads with intermediate hydrophobicity at air/water interface where NPS was modified with octadecyl trichlorosilane (OTS) on its surface. The hydrophobically modified NPS beads spread on the water so as to form 2D crystal assisted by ultra-sound and polymeric surface micelles.

---

* Corresponding author.
E-mail address: ysseo@sejong.ac.kr (Y.-S. Seo).

1226-086X/$ – see front matter © 2010 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.jiec.2010.09.009

2. Experimental

2.1. Materials

Monodisperse and micrometer-sized non-porous silica (NPS) beads (1 and 3 μm in diameter) and hydrophobic NPS were purchased from Eichrom Technologies Inc. Micrometer-sized silica beads were chosen to easily monitor monolayer formation by optical microscopy. Monodisperse polymers purchased from Polymer Source Inc. were Polystyrene (PS, molecular weight, Mw = 65,000) and Poly (methyl methacrylate) (PMMA, Mw = 62,000) and diblock copolymers were PS-b-PMMA (Mw = 196,300–201,000), Poly vinyl-2-pyridine (PS-b-P2VP, Mw = 104,000–105,000) and Polystyrene-b-Poly ethyleneoxide (PS-b-PEO, Mw = 69,000–420,000). HPLC grade anhydrous DMF and chloroform were used as purchased.

2.2. Surface modification

NPS beads purchased were hydrophilic and easily dispersed in water. In order to spread them at the air/water interface they were first functionalized with hydrocarbon molecules that render them hydrophobic. NPS beads were cleaned by H_2SO_4:H_2O_2:H_2O (3:1:1) solution in order to introduce hydroxyl groups (OH) on the surface [12]. After separation by centrifugation, in order to remove water, the NPS beads were rinsed with anhydrous DMF (N,N,-dimethyl formamide) at least three times.

Even though effective silanation on hydrophilic Si-wafer has been accomplished using non-polar solvent mixture of $CHCl_3$/CCl_4/Hexadecane [13–15], this solvent mixture cannot be applied to this study because it causes coagulation of hydrophilic NPS beads. We have chosen a solvent mixture of anhydrous DMF and Chloroform (4:1 in volume) for suspending hydrophilic NPS. DMF may increase the reaction activity of silanols on silica bead surface or hydrolyzed organosilane via hydrogen bonding between hydroxyl group in silanols and carbonyl group in DMF [16]. Occasionally water contamination in DMF may induce a polymerization of the trichlorosilane in the silanation solution [17,18]. However, it is noted that trace amount of water in the mixture, especially in DMF, may enhance chemical reactivity of OTS on NPS beads by catalytic action of thin water layer adsorbed on the silica surface [19].

Modification of NPS beads with OTS in a DMF-chloroform mixture was performed in N_2 purged glove box for 2 h at room temperature. After the reaction, OTS functionalized NPS beads (C_{18}-NPS) were washed with methanol and chloroform for more than 3 times to remove any organic residues. C_{18}-NPS were finally dispersed in chloroform.

Surface coverage of C_{18} on NPS beads can be controlled by molar concentration of OTS in the reaction solution. C_{18}-NPS bead with intermediate hydrophobicity was chosen by contact angle measurement of water droplet. The contact measurement has been performed on C_{18}-NPS beads layers that were prepared by spreading them on the water and then transferring on a glass slide. In this study C_{18}-NPS bead having contact angle of 50° has been chosen as an intermediately hydrophobic sample while less hydrophobic one had a range of 20–30° and hydrophobic NPS purchased had 90–100°.

2.3. 2D crystal formation

Finally the intermediately hydrophobic C_{18}-NPS was dispersed in chloroform and then spread on the water. Ultra-sound was applied under the water while spreading. The C_{18}-NPS layer was then squeezed by Teflon barrier. Alternatively diblock copolymer solution in chloroform was spread on the corner of the C_{18}-NPS layer in order to squeeze the layer. These processes were monitored by an optical microscope. After the squeeze, the layer was transferred on to Si-wafer by Langmuir–Blodgett technique and the morphology of the layer was measured by Atomic Force Microscope.

3. Results and discussions

3.1. Ultra-sound effects

Once we spread 3 μm C_{18}-NPS beads with intermediate hydrophobicity dispersed in chloroform on the water, white layers are readily formed while the solvent evaporates. After the white layer was transferred on to Si-wafer, it was monitored by an optical microscope, where 2D crystals were mainly found and occasionally 3D clusters shown as dark spots in Fig. 1(a). For less hydrophobic C_{18}-NPS beads, individual silica bead was floating around on the water and neither 2D nor 3D clusters were formed because repulsive interaction between the silica mediated by water is dominant. On the other hand hydrophobic NPS purchased forms mostly 3D clusters.

In the Figure large voids are also found mainly in the vicinity of the 3D clusters. Even though the layer was squeezed with Teflon barrier until it was physically deformed on the water, the voids

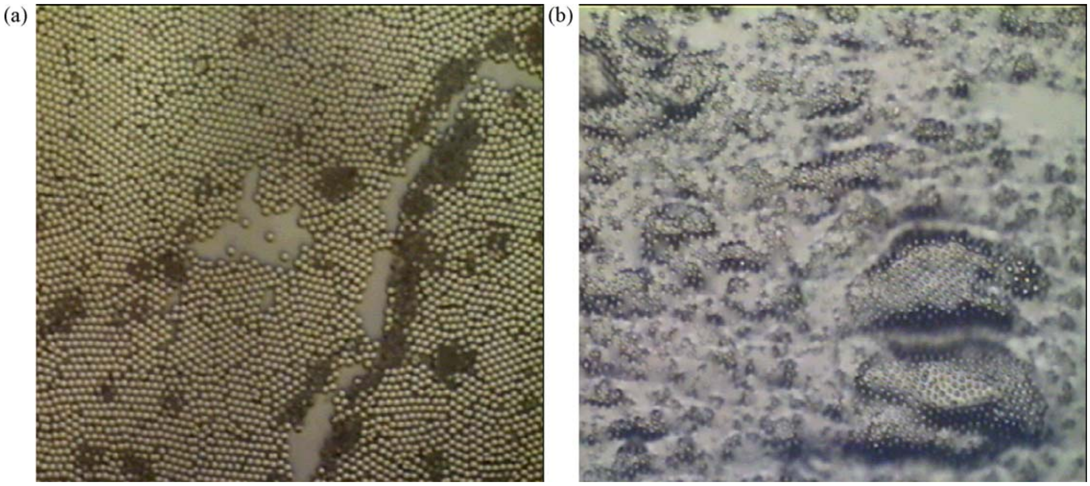

Fig. 1. (a) A microscopic image of 3 μm C_{18}-NPS layer on Si-wafer transferred from the water surface. (b) *In situ* microscopic image of C_{18}-NPS layer on the water after physical deformation occurs in the layer. Bead diameter of 3 μm indicates itself as a scale bar in the image.