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Fabrication of microcapsule arrays on chemically patterned surfaces via covalent linking*

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Abstract: A method for fabricating arrays of microcapsules covalently immobilized onto chemically patterned substrates was developed. The core-shell microparticles with poly(allylamine hydrochloride) (PAH) as the outermost layer were obtained by layer-by-layer (LbL) assembly, which were further treated with glutaraldehyde to endow the particles with abundant aldehyde groups on their surfaces. The particles were then covalently coupled to the chemically patterned regions with amino groups created by microcontact printing (μCP). After dissolution of the core particles, arrays of the hollow microcapsules with unchanged structures were obtained. These arrays could stand rigorous environmental conditions of higher ionic strength, and lower and higher pH values. Thus, the technique could be possibly applied to exploiting chips of microcontainers or microreactors in sensing technology.

Key words: Array, Microcapsules, Microcontact printing (μCP), Covalent interaction
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INTRODUCTION

Microcontact printing (μCP) is one of the soft lithography (Xia and Whitesides, 1998) techniques. Since it was proposed in 1990s (Kumar and Whitesides, 1993; 1994), the microfabrication has been developed rapidly in the fields of biology, chemistry, and material science. The process of μCP is simple, fast and convenient. In brief, after an elastomeric stamp covered with an ink material is brought into contact with a substrate and then peeled off, a pattern of the ink would be left on the surface of the substrate in the contact regions. This method has been diversely used to construct patterns of a variety of chemical compounds, such as thiols (Kumar *et al.*, 1994; Xia and Whitesides, 1995), polyelectrolytes (Jiang *et al.*, 2002; Park and Hammond, 2004), nanoparticles (Hidber *et al.*, 1996), biomolecules (Yang and Chilkoti, 2000; Bernard *et al.*, 2000), and so forth on, various surfaces of solid materials including Au, Ag, SiO_2, polyelectrolyte multilayers, polymer films, etc. Recently, a combination of the μCP with colloid science is attractive due to its ability to obtain micropatterned arrays of colloidal particles, e.g., microspheres (Chen *et al.*, 2000; Zheng *et al.*, 2002; Lee *et al.*, 2002; Karakurt *et al.*, 2006), metal nanoparticles (Jung *et al.*, 2006; Cong *et al.*, 2006), vesicles (Stamou *et al.*, 2003; Shim *et al.*, 2004; Kalyankar *et al.*, 2006), and microcapsules (Nolte and Fery, 2004a; 2004b; Feng *et al.*, 2004; Wang *et al.*, 2006), with various functions such as template materials, protein carriers, chromatically responsive reporters, and reaction vessels. It is of great significance in physics, nanoscience and biotechnology for their promising applications in developing optoelectronic devices (Tessier *et al.*, 2001; Ahn *et al.*, 2005; Li *et al.*, 2007), protein chips (Walter *et al.*, 2000; Kodadek, 2001;

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Fang *et al*., 2002), sensors (Goodey *et al.*, 2001; McCauley *et al.*, 2003), microanalyses (Okumus *et al.*, 2004; Tresset and Takeuchi, 2005), and microreactors (Antipov *et al.*, 2003; Bolinger *et al.*, 2004).

Polymeric microcapsules are a special type of colloids. They have a particular structure that a bigger cavity space is isolated from outside environment by a relatively thin membrane wall, which allows a large amount of substances to be encapsulated. Various techniques have been exploited to fabricate the microcapsules, including the newly developed layer-by-layer (LbL) technique (Sukhorukov *et al.*, 1998; 2005; Peyratout and Dähne, 2004). In this technique, building blocks, typically the oppositely charged polyelectrolytes, are consecutively assembled onto removable cores to form multilayer thin films (usually tens of nanometers in thickness), which give hollow microcapsules after core removal. Besides the numerous features in terms of fabrication and structure control, their permeation is readily adjustable by wall structure and compositions, assembly conditions (salt concentration, pH value, etc.), as well as post treatments (annealing for example). Thus the microcapsules are allowed to selectively encapsulate desired substances. Consequently, integration of such elements into a chip would have potential applications in developing sensing systems for detection, diagnosis and analysis of chemical species.

Significant progress has been made on fabricating microcapsule arrays by interactions between the microcapsules and the substrates, including electrostatic force (Nolte and Fery, 2004a; 2004b; Feng *et al.*, 2004), biological affinity (Wang *et al.*, 2006) and wetting/dewetting behavior (Troitsky *et al.*, 2004). The capsule arrays formed by the hydrophilic/hydrophobic interaction are suffered from the poor stability due to the weak physisorption between the capsules and the substrates. Through electrostatic interaction, the capsules are orientated well to the oppositely charged regions, but the coverage percentage on the pattern regions is lower and the patterned microcapsules can be detached by high ionic strength and extreme pH. Based on the specific recognition of avidin-biotin pair, the capsules can be immobilized firmly on the pattern area. However, the manipulating process is rather complicated, and nonspecific adsorption of the capsules on the undesired area is not easy to avoid. For future utilization of the capsule arrays as containers or reactors, the arrays should not only have ordered structures but also good stability against rigorous conditions. Therefore, the spatial control and stable fixation of the microcapsules are important.

It is known that the covalent binding is much stable and less sensitive to the environmental stimuli (Berzina *et al.*, 2003). It can be easily applied to creating the microcapsule patterns by proper design of the surface properties of substrates and microcapsules. For this context, glutaraldehyde coupling is adopted in this work to obtain covalently bonded microcapsule arrays. To our best knowledge, covalent patterning of microcapsules onto a substrate has not been reported previously. We shall show further that the as-prepared microcapsule arrays have well-defined structure and good stability against salt, high and low pH treatments.

EXPERIMENT

Materials

Poly(styrene sulfonate) sodium salt (PSS, M_w 70 kDa) and poly(allylamine hydrochloride) (PAH, M_w 70 kDa) were purchased from Sigma-Aldrich. Fluorescein isothiocyanate-labeled PAH (FITC-PAH) was synthesized according to (Ibarz *et al.*, 2001). Poly(dimethylsiloxane) (PDMS) pre-polymer (Sylgard 184) and the curing agent were obtained from Dow Corning. Other reagents (purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai) were of analytical grade and were used as received. Water used in this experiment was triple-distilled.

Fabrication of chemically patterned surfaces

Glass slides were treated with H_2SO_4:H_2O_2 (7:3, v/v) for 10~15 min at 80~100 °C, rinsed thoroughly with water and dried in a stream of nitrogen. PDMS stamp with periodic pillars (50 μm in both diameter and space, 4.5 μm in height) was hydrophilized by air-plasma for 10 min, immersed into 1 mg/ml FITC-PAH aqueous solution (containing 0.5 mol/L NaCl) for 15 min, rinsed slightly with water and blown dried in a gentle stream of nitrogen. The FITC-PAH containing stamp was printed onto a glass slide. 5 min later, the stamp was peeled off. The patterned slide was rinsed with water carefully and blown dried with nitrogen stream.

Preparation of core-shell microparticles

PSS-doped porous $CaCO_3$ microspheres (4~6 μm in diameter, prepared according to (Tong *et al.*, 2005a)) were coated by alternate deposition of PAH and PSS (concentration 2 mg/ml, containing 0.5 mol/L NaCl) with PAH as the outermost layer. One layer of FITC-PAH was assembled instead of PAH for the ease of characterization. The core-shell particles were then treated with extremely excessive 0.1 mol/L glutaraldehyde (GA) for 2 h. After five washings in water and centrifugation, the particles were finally dispersed in water for further use.

Fabrication of microcapsule arrays

A drop of the slurry of core-shell microparticles was put on the patterned slide surface. After sedimentation of the particles for 5 min, the slide (together with the particles) was dried at 50 °C. Then the slide was rinsed with water extensively and then incubated in 0.1 mol/L $NaBH_4$ solution for 2 h. The $CaCO_3$ templates were removed by immersing the slide into 0.1 mol/L ethylenediamine tetraacetic acid disodium salt (EDTA-2Na) solution for 1 h under shaking. To determine the stability of the obtained capsule arrays, the as-prepared chip was sequentially incubated in 2 mol/L NaCl, pH=1 HCl and pH=13 NaOH solutions, each for 10 h under shaking with thorough rinsing with water after each incubation.

Characterization

Fluorescence microscopy, confocal laser scanning microscopy (CLSM), atomic force microscopy (AFM) and scanning electron microscopy (SEM) measurements were conducted on a Zeiss Axiovert 200 microscope (Germany), confocal laser scanning microscope (Zeiss LSM 510, Germany), atomic force microscope (SPI3800N, Seiko Instruments Inc., Japan) and scanning electron microscope (Cambridge Stereoscan 260, UK), respectively.

RESULTS AND DISCUSSION

By employing μCP, a conformal contact of the inked PDMS stamp on a glass slide results in the patterned surface with dot arrays (50 μm in diameter) of FITC-PAH molecules (Fig.1). The FITC-PAH molecules are adsorbed on the glass surface firmly due to the combination of electrostatic force, hydrogen bonding and van der Waals attraction, which could not be removed even at rigorous conditions such as ultrasonication. This feature ensures the good stability of the successive capsule arrays. Note that a few defects in the patterns as indicated by the arrows in Fig.1 could also be observed occasionally, although their sizes are rather small. This is a common phenomenon for the soft lithography techniques, which may be caused by the non-flattened top surface of the stamp or the incomplete contact of the stamp with the substrate during the μCP process.

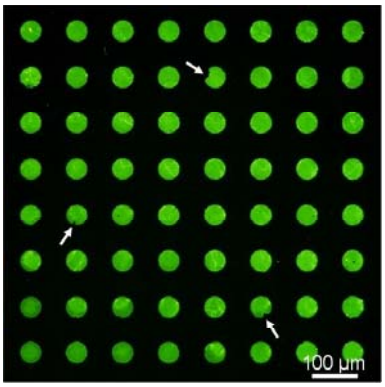


Fig.1 Fluorescence microscopy image of the FITC-PAH patterns on a glass slide (which were created by μCP). The arrows indicate a few defects of the pattern

The PSS/PAH coated $CaCO_3$ particles with the outermost layer of PAH were treated with GA, yielding aldehyde groups on the particle surface in parallel with crosslinking of the PAH component (Tong *et al*., 2005b). Removal of the $CaCO_3$ particles by EDTA-2Na produced hollow microcapsules with good shell completeness as shown in Fig.2. Since the hollow microcapsules have a wall thickness of around 90 nm (This relatively "thick" wall comparing with the traditional capsules is attributed to the entrapped PSS and the crosslinked capsules. For details, see (Tong *et al.*, 2005a; 2005b)) and a relatively large size in the order of micrometers, they easily collapsed in a dry state or deformed under a rigorous disturbance. The collapsed or deformed microcapsules cannot be restored to their original round shape anymore. Therefore, to obtain the capsule arrays, instead of the pre-formed microcapsules, the GA treated core-shell particles were brought into contact with the patterned slide directly. During this process, the existing

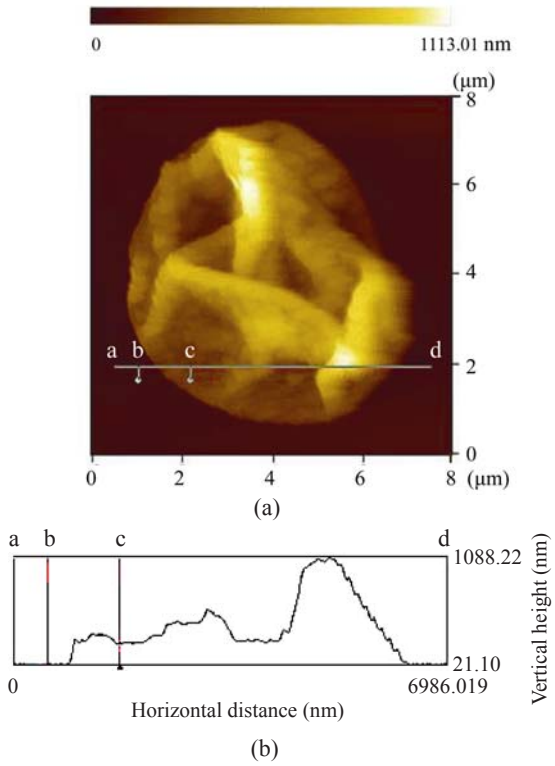


Fig.2 (a) AFM image of a dried $(PAH/PSS)_5PAH$ hollow microcapsule which was initially assembled on a PSS-doped $CaCO_3$ particle and treated with GA. The scales represent the real size in horizontal direction. The color bar above the image indicates the total height in vertical direction; (b) The line profile recorded from the position shown in (a). The height difference between the two arrow-marked places (b and c) is 192.65 nm, indicating that the wall thickness is about 96 nm

aldehyde groups on the particles reacted with the PAH patterns having amino groups to form Schiff base linkages. Since the contacting area between the rigid spherical particles and the rigid flat substrate is very small, a heating at 50 °C was performed to accelerate the conjugation of the adsorbing molecules on both surfaces. Due to the limited contacting area and the lack of strong interaction between the aldehyde enriched particles and the glass slide, the particles resided on the PAH uncovered regions were washed off easily. Further treatment of the particle arrays with $NaBH_4$ then reduced the Schiff bases into stable covalent linkages of $-CH_2-NH-$ between the microcapsules and the PAH patterns, finally yielding the covalently linked particle arrays (Fig.3a).

Fig.3a shows that all the particles located exactly in the circular patterns of PAH. That no particles were found outside the PAH patterns illustrates the good selection of the particles and the success of the present protocol. A brief estimation gives that the coverage ratio of the particles on the PAH pattern (with a diameter of 50 μm) reaches around 70%. This is a quite high value considering the very large PAH patterns, the large particle size (with a diameter of 4~6 μm) and the rigid nature of the particles and the substrate. However, unlike those particle arrays obtained with smaller particles and pattern size, the arrangement of our core-shell particles in each circular region was not hexagonal close-packed. Several reasons may cause this result. First, due to the difficulty to obtain homogeneously distributed $CaCO_3$ particles, the particles used here have a rather wide range of size (4~6 μm), which is not favorable of the ordered arrangement in geometry; Second, the chemically inhomogeneous surface, with relatively hydrophobic circle regions surrounded by extremely hydrophilic area, might cause the flowing tendency of the colloidal suspension from the center of each circle to the boundary (Troitsky *et al.*, 2004), resulting in the incompact aggregations of the core-shell particles; Third, the electrostatic repulsion of the particles with the same charge leads to the formation of gaps among

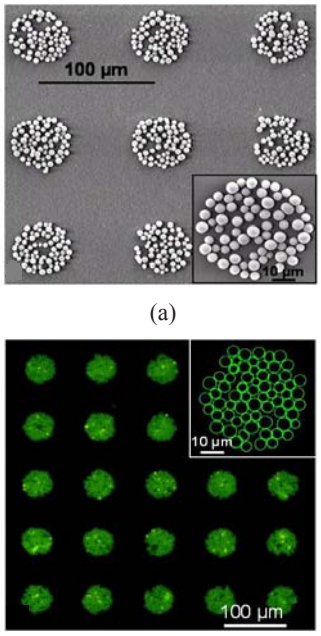


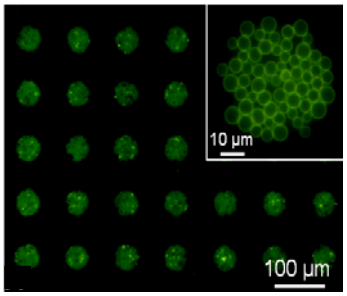
Fig.3 (a) SEM image of the core-shell microparticle array (the inset shows a magnified SEM image of individual circle area); (b) Fluorescence microscopy image of the hollow microcapsule array (the inset shows a magnified CLSM image of individual circle area)

them. Of course some of the larger gaps may also be caused by the initially existing defects in the PAH patterns.

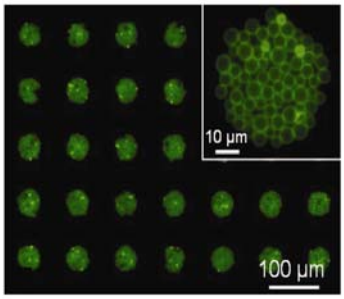
To exclude the suspicion that it is other interactions such as hydrogen bonding and hydrophobic force dominating the formation of the particle arrays, PSS/PAH coated particles (PAH as the outmost layer) without GA treatment were put onto the PAH patterned glass slide and treated following the same procedures as mentioned above. Very occasionally few particles could be observed in the PAH regions. It is obvious that the charge repulsion between the particles and the PAH patterned area rejects the adhesion of the particles. Thus, the particle arrays obtained here are surely driven by the covalent linking, and other contributions are rather minor and can be neglected.

After dissolving the $CaCO_3$ cores, an array of hollow microcapsules was obtained as displayed in Fig.3b. It reveals clearly that neither colloid detached from the substrate in the process of core removal, nor capsules were found on the bare glass slide. This fact confirmed to some extent the good stability of the capsule array. Further investigation showed that the microcapsule array could survive from rigorous environmental conditions such as high ionic strength and extreme pH value. As shown in Fig.4, after successive treatments with salt, acid and alkali of high concentration, no microscopically detectable change of the array was found. This confirms the conclusion that the microcapsules are linked to the substrate by covalent bonding. It is known that the hydrogen bonding and the electrostatic interaction are easily destroyed by pH variation, for example at pH 12 for the PSS/PAH combination (Tong *et al.*, 2005b). The survival of the microcapsules at high pH is apparently attributed to the GA treatment, resulting in a crosslinked shell structure.

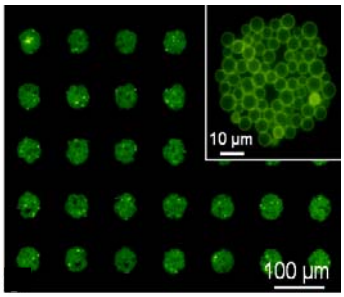
The good stability of the microcapsule arrays fabricated by the present strategy is beneficial to their future applications as chips of microcontainers and microreactors. The architecture of the array including the array shape, the approximate number of the microcapsules in one cluster and the space between two clusters can be facilely mediated by changing the stamp with surface features of different circle area and distance. Also other types of capsule arrays can be obtained similarly. Functionalization of the microcapsule array is under way.



(a)



(b)



(c)

Fig.4 Fluorescence microscopy images of the arrays of hollow microcapsules (a) After treated with 2 mol/L NaCl solution for 10 h; (b) After further treated with pH=1 HCl solution for 10 h; (c) After further treated with pH=13 NaOH solution for 10 h. Each inset is the magnification of one arbitrary cluster in the corresponding image

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