

# Aqueous route to prepare large-scale array of highly ordered polystyrene/aluminum hydroxide microspheres

Jiliang Yin,<sup>a</sup> Xuefeng Qian,<sup>a,\*</sup> Jie Yin,<sup>a</sup> Yanbo Zhang,<sup>a</sup> Jianchun Zhang,<sup>b</sup> Meiwu Shi,<sup>b</sup> and Guotai Zhou<sup>b</sup>

<sup>a</sup> *Research Institute of Polymer Materials, School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Number 800, Dongchuan Rd., Shanghai 200240, P.R. China*

<sup>b</sup> *The Quartermaster Research Institute of CPLA, Beijing, P.R. China*

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## Abstract

Monodisperse aluminum hydroxide coated polystyrene (PS) microspheres and their array in large scale was prepared at one step in aqueous solution. The coated PS microsphere arrays are highly ordered and have remarkable structural stability. The arrays can be in plate form and hollow sphere form, depending on the concentration of aluminum sulfate. Hollow aluminum hydroxide shell arrays can be also obtained with calcination.

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**Keywords:** Large-scale array; Polystyrene; Aluminum hydroxide

## 1. Introduction

Ordered porous and core-shell particle solids are of great interest in areas such as catalysis, sensor, size- and shape-selective separation media, adsorbent, and scaffold for composite materials synthesis and also of interest for applications in photonics, optoelectronics, lightweight structural materials, magnetic recording, and thermal insulation [1,2]. Recently, many kinds of core-shell particles such as titania-polymer [3–5], silica-polymer [6], ZnS-polystyrene (PS) [7], copper-polymer [8] and zirconia-PS [9] were prepared through liquid deposited process. How to get highly ordered core-shell arrays is the investigated object due to their potentially application in such as photonic crystals.

Morphosynthesis, the control of the architecture and morphology and the patterning of the inorganic materials with nanoscale to macroscopic dimensions, has rapidly developed into a promising field in materials chemistry. Recently, several methods were disclosed to produce ordered 3D or 2D microsphere arrays and

ordered macroporous. 3D microsphere arrays and ordered macroporous were obtained by filtration [10,11], by centrifugation for microsphere array and soaking the array into metal alkoxide precursors for ordered macroporous [12], at the interface of biphasic [13], and by fluid-solid transformation process [14]. The methods proposed to prepare 2D arrays included capillary forces [15], convective assembling in wetting films [16–18] and magnetic forces [19,20]. Generally, arrays prepared with these methods were based on a solid or liquid substrate [21,22]. Removed from the base, the arrays themselves are not stable. So a major barrier to the practical application of these structures is the lack of simple, easily controlled methods for mounting or shaping the crystals into usable solid objects [23].

2D array of aluminum hydroxide coated PS microspheres was successfully prepared in this paper by a simple and rapid process. The preparation of aluminum hydroxide coated PS microspheres and their arrays can be completed at one step in urea solution at 100°C with aluminum sulfate as precursor. Up to now, few researches were reported to prepare highly ordered arrays directly from solution without using a solid

\*Corresponding author. Fax: +86-21-54741297.

E-mail address: [xfqian@mail.sjtu.edu.cn](mailto:xfqian@mail.sjtu.edu.cn) (X. Qian).

substrate. After calcination, the array of holes in an aluminum hydroxide sheet was obtained.

## 2. Experiment

Styrene (AR, Shanghai Lingfeng Chemical Reagent Co. Ltd.) was purified by reduced pressure distillation. Lauryl sodium sulfate (AR, Shanghai Lingfeng Chemical Reagent Co. Ltd.) and potassium persulphate (AR, Shanghai Qianjin Reagent Factory) were recrystallized twice in water, aluminum sulfate, urea, poly(vinylpyrrolidone) (PVP, weight-average molecular weight 30,000) and azobisisobutyronitrile (AIBN) were all bought from Shanghai Reagent Company and used without further purification.

### 2.1. Preparation of polystyrene spheres

Polystyrene spheres were prepared by dispersion polymerization. In a 250 mL round bottom flask, 2.0 g PVP was dissolved into 7.6 mL distilled water and 60.4 mL ethanol. The system was heated to 70°C and purged with nitrogen for 1 h in order to eliminate the inhibition effect of oxygen, and then 30.0 g styrene and 0.3 g AIBN were added. The polymerization was continued for 12 h with mechanical stirring at 300 rpm. After polymerization, PS beads were collected by filtration and dried in vacuum oven at room temperature for 24 h.

Emulsion polymerization was adopted to prepare smaller PS microspheres [24].

### 2.2. Preparation of core-shell spheres and their arrays

In order to prepare core-shell composite of PS and aluminum hydroxide, the as-prepared PS microspheres were dispersed into PVP aqueous solution in a 500 mL round bottom flask. Then aluminum sulfate and urea were added consecutively. The mixture was held at 100°C for 12 h with mechanical stirring at 400 rpm.

Upon completion of the heating period, the flask was cooled down to room temperature naturally in the oil bath. The product was collected by filtration and washed with water several times, then dried in air.

### 2.3. Calcination

The dried PS/aluminum hydroxide spheres were calcined in static air at 550°C for 3 h or at 1150°C for 1 h with heating rate of 2°C/min.

### 2.4. Characterization

The morphology of core-shell spheres and their arrays were determined by Hitachi H-8100 transmission

electron microscope (accelerating voltage = 80 kV) and Hitachi S-2150 scan electron microscope. The coated and hollow particles were also examined by infrared (IR) spectroscopy using a Perkin-Elmer Paragon 1000 spectrometer. The thermogravimetric analysis (TGA) was operated on a Perkin-Elmer TGA 7 analyzer at a heating rate of 20°C/min under the stream of nitrogen.

## 3. Results and discussion

PS microspheres prepared with dispersion polymerization were about 2 μm in diameter. PS microspheres prepared with emulsion polymerization were about 265 nm in diameter. Both were monodisperse. With these two kinds of PS microspheres, the aluminum hydroxide coated PS microspheres were prepared.

### 3.1. Arrays of aluminum hydroxide coated PS microsphere

Table 1 lists the relationship between the reaction conditions and the morphologies of core-shell composites. From this we can see that the concentration of aluminum sulfate has great effect on the array of core-shell composites, while the concentration of the protective agent PVP has little effect on the array of core-shell composites.

When the concentration of aluminum sulfate was 0.2 M, larger the core-shell microsphere array sheets were obtained. SEM photographs of the core-shell microsphere array were shown in Fig. 1. It was found that most of the aluminum hydroxide coated PS microspheres were assembled in highly ordered array. Aluminum hydroxide was filled in the inter space of PS microspheres array and formed the matrix. From Fig. 1(a) it was found that the core-shell microspheres are highly ordered and uniform over large scale (~1 mm<sup>2</sup>) (Fig. 1(d)). Besides the matrix, some free aluminum hydroxide particles were formed attached on the surface of the array from the hydrolyzation of

Table 1  
The relationship of the reaction conditions and the morphologies of core-shell composites

Sample	PS (μm)	PVP (mg)	Aluminum sulfate (M)	Urea (mg)	Array
1	2	80	0.2	480	Plate
2	2	80	0.1	240	Sphere
3	2	320	0.2	480	Plate
4	2	320	0.1	480	Sphere
5	2	80	0.05	240	Irregular plate
6	0.265	80	0.2	480	Plate
7	0.265	80	0.1	240	Plate

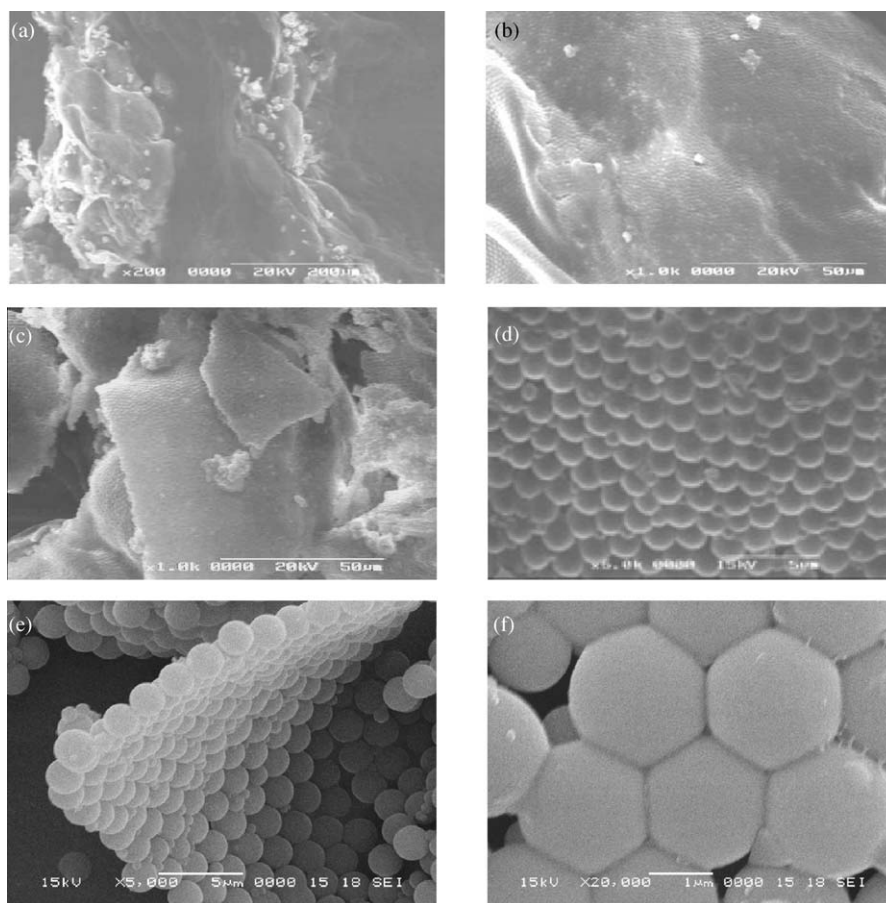


Fig. 1. SEM photograph of aluminum hydroxide coated PS microspheres (2  $\mu\text{m}$ ) array obtained in 0.2 M aluminum sulfate aqueous solution, (a)–(c) panorama, (d) face side, (e) side face, (f) the connection among PS microspheres.

aluminum sulfate (Fig. 1(d)). It is interesting to find that the obtained core–shell microspheres were arrayed monolayer (Fig. 1(e)). 2D arrays were already obtained by other methods [15–20], but most of them are on the solid substrate. And the arrays themselves were not free-stand if the substrate was removed. In this study, highly ordered 2D arrays were successfully prepared without using any substrate in one-step process. The formation of the arrays may be due to the interfacial effect of aluminum hydroxide among the PS spheres. To some extent, this aluminum hydroxide may serve as matrix, which can be further confirmed after calcination. The highly ordered array can be kept intact after ultrasonic process for 20 min or calcination at 550°C for 3 h.

When the concentration of aluminum sulfate was reduced to 0.1 M while maintaining other condition unchanged, it was interesting to find that most of the plates of the final PS/aluminum hydroxide arrays were turned to large hollow spheres with different sizes. The diameter of the spheres was from 30 to 100  $\mu\text{m}$  (Fig. 2(a)). A detailed observation found that the large hollow spheres were self-assembled from a single layer of PS/aluminum hydroxide core–shell spheres (Fig. 2(b)).

The hollow spheres were slightly deformed due to the extrusion stress (Fig. 2(c)), while the self-assembled coated PS microspheres were highly ordered (Fig. 2(d)).

If the concentration of aluminum sulfate was 0.05 M, the obtained plate of aluminum hydroxide coated PS microspheres was irregular (Fig. 3) due to the weak linkage of the aluminum hydroxide matrix.

In addition to the concentration of aluminum sulfate, the size of PS microspheres also has much effect on the morphology of the aluminum hydroxide/PS composite arrays. When the smaller PS spheres (265 nm) prepared by emulsion polymerization were adopted as cores, a highly ordered array was also formed. From the SEM photographs of core–shell microsphere arrays in Fig. 4, it can be found that most of the microsphere assembly was in plate form regardless the concentration of aluminum sulfate (0.1 and 0.2 M). We also found that some hexagonal holes randomly embedded on the array due to the contact friction between the microspheres when the dispersed microspheres assembled into highly ordered array, which was explained and simulated in Ref. [25].

The formation of aluminum hydroxide coated PS microsphere (265 nm) array obtained in 0.1 and 0.2 M

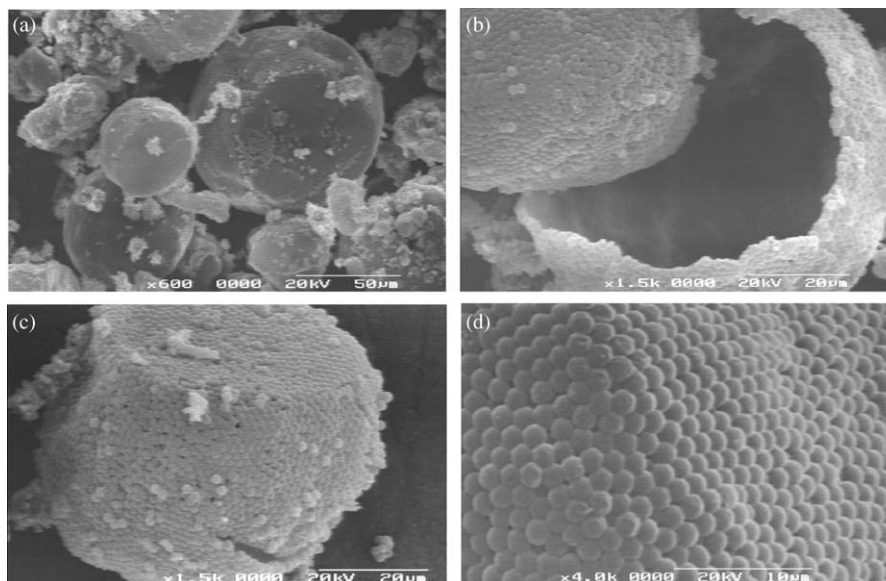


Fig. 2. (a–d) SEM photographs of aluminum hydroxide coated PS microspheres (2 μm) array obtained in 0.1 M aluminum sulfate aqueous solution.

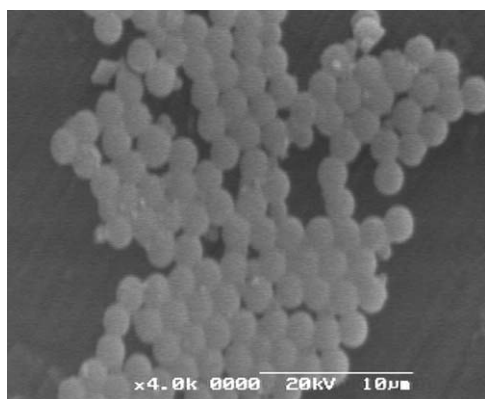


Fig. 3. SEM photographs of aluminum hydroxide coated PS microspheres (2 μm) array obtained in 0.05 M aluminum sulfate aqueous solution.

aluminum sulfate aqueous solution through one-step process was further confirmed by the TEM photographs (Fig. 5(a)). From these photographs we can see that core-shell microspheres assembled into highly ordered monolayer array and some regular hexagonal holes were found in the array (Fig. 5(b)). These results are consistent with those of SEM.

It is usually hard to obtain regular arrays of microspheres in solution. However, plates and hollow spheres of the monolayer core-shell sphere arrays were formed here. Fig. 6 is the schematic illustration of self-assembly of PS microspheres into the highly ordered array. Firstly, PS microspheres were fully dispersed. The aluminum hydroxide was coated on them, and the coated spheres joined together with the shear process of the stirring [26,27]. If the weight percentage of aluminum hydroxide is high enough, the layer of core-shell spheres array can be kept in plate in the solution

with the shear process, otherwise the layer of core-shell sphere arrays turned into hollow spheres with the shear process.

### 3.2. Arrays of holes in aluminum hydroxide sheet

When the obtained PS (2 μm)/aluminum hydroxide core-shell spheres calcined from room temperature to 550°C at the rate of 2°C/min and maintained at 550°C for 3 h, the plate of core-shell microsphere array was burned into hollow hole structure and aluminum hydroxide hole array was obtained (Fig. 7). From Fig. 7(a), it was found that the plate of core-shell microsphere array was burned into smaller ones. However, most of the holes array was kept intact (Fig. 7(c)). By comparing Fig. 7(b) with (c), it was found that when the “matrix” of aluminum hydroxide was thick enough the holes can be kept intact without deformation after calcination. It further indicated that the aluminum hydroxide among the PS spheres served as the “matrix”.

However, the large hollow spheres of the monolayer core-shell sphere array obtained with 0.1 M aluminum sulfate (sample 2) were burned into smaller particles (Fig. 8). And the holes were found to embed in the particles. This indicates that the “matrix” of aluminum hydroxide was too weak to keep the holes array intact after the PS microspheres were removed from the matrix with calcination. This also demonstrates that the formation of large hollow spheres was partly because the weight percentage of aluminum hydroxide in the PS/aluminum hydroxide composite was low.

When the obtained PS/aluminum hydroxide core-shell spheres calcined from room temperature to 1150°C at the rate of 2°C/min and maintained at 1150°C for 3 h,

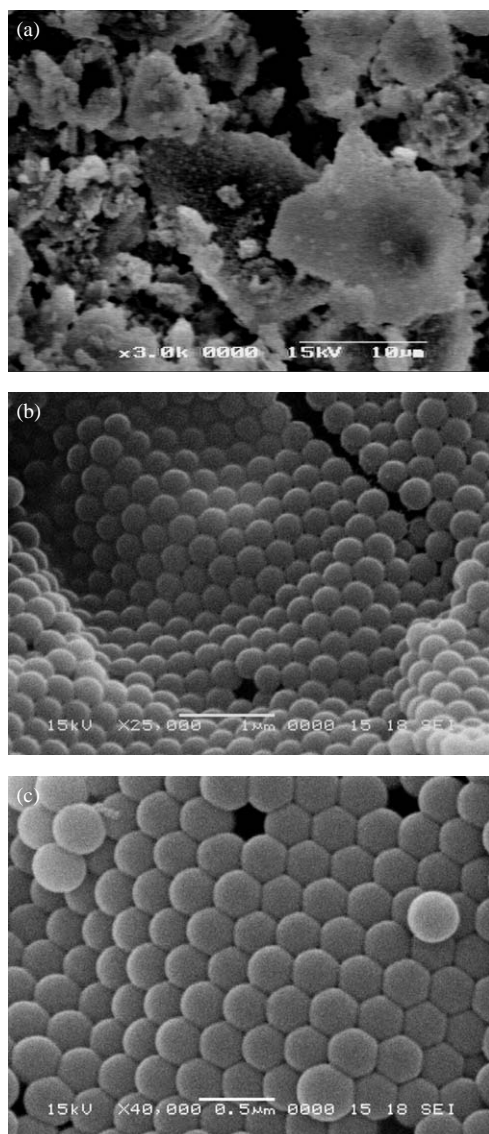


Fig. 4. (a–c) SEM photographs of aluminum hydroxide coated PS microspheres (265 nm) array obtained in aluminum sulfate aqueous solution.

the plate and lager hollow spheres of monolayer core-shell microsphere array were burned into powder.

### 3.3. Infrared (IR) spectra

Fig. 9 shows the infrared (IR) spectra of PS microspheres, PS/aluminum hydroxide core-shell spheres, aluminum hydroxide spheres obtained by calcining PS/aluminum hydroxide at 550°C and alumina obtained by calcining PS/aluminum hydroxide at 1150°C, respectively. The IR spectrum of PS (Fig. 9(a)) reveals C–H stretch at around 3000  $\text{cm}^{-1}$ , aromatic C–C stretch at around 1470  $\text{cm}^{-1}$ , C–H out-of plane bend at 765  $\text{cm}^{-1}$ , and aromatic C–C out-of-plane bend at 700  $\text{cm}^{-1}$ . Aromatic overtones are visible at 1700–2000  $\text{cm}^{-1}$ . Fig. 9(c) shows the band due to OH stretching

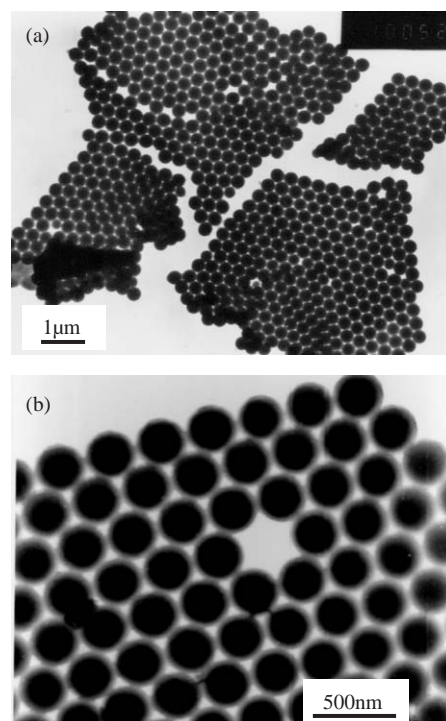


Fig. 5. (a–b) TEM photograph of aluminum hydroxide coated PS microspheres (265 nm) array obtained in aluminum sulfate aqueous solution.

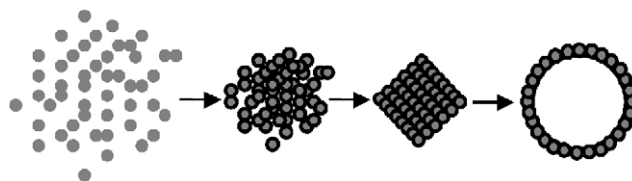


Fig. 6. Schematic illustration of PS microspheres self-assembly into highly ordered array.

vibrations (3000–3500  $\text{cm}^{-1}$ ), as well as bands resulting from water of hydration (1650  $\text{cm}^{-1}$ ). Absorption bands in 950–1400  $\text{cm}^{-1}$  region correspond to the stretching modes of  $\text{AlO}_4$  as well as of Al–OH–Al groups. Absorption bands at 600–800  $\text{cm}^{-1}$  arise from the stretching modes of  $\text{AlO}_6$  as well as the liberation mode of OH groups. The spectrum of PS/aluminum hydroxide (Fig. 9(b)) shows bands characteristic of polystyrene in addition to aluminum hydroxide. Fig. 9(d) shows a band due to Al–O. Absorption bands below 600  $\text{cm}^{-1}$  are attributed to the bending modes of vibration. The IR spectra indicate that the aluminum compound in PS microspheres array was aluminum hydroxide. The hole array obtained at 550°C was still aluminum hydroxide. After calcining at 1150°C, it was turned into alumina.

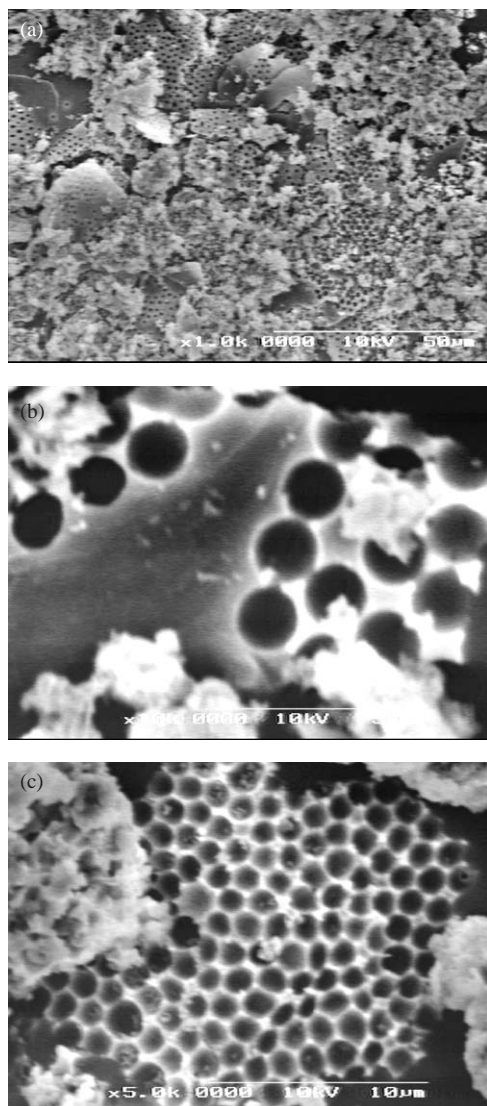


Fig. 7. (a–c) SEM photographs of aluminum hydroxide hole array obtained by calcining aluminum hydroxide coated PS microspheres (2 μm) array of sample 1.

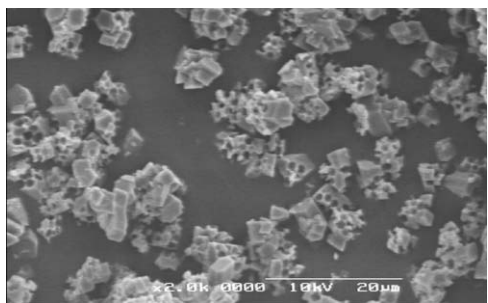


Fig. 8. SEM photograph of aluminum hydroxide particles obtained by calcining aluminum hydroxide coated PS microspheres (2 μm) array of sample 2.

### 3.4. Thermogravimetric analysis

Fig. 10 shows the weight loss curves of coated particles on heating to 600°C in nitrogen. The first

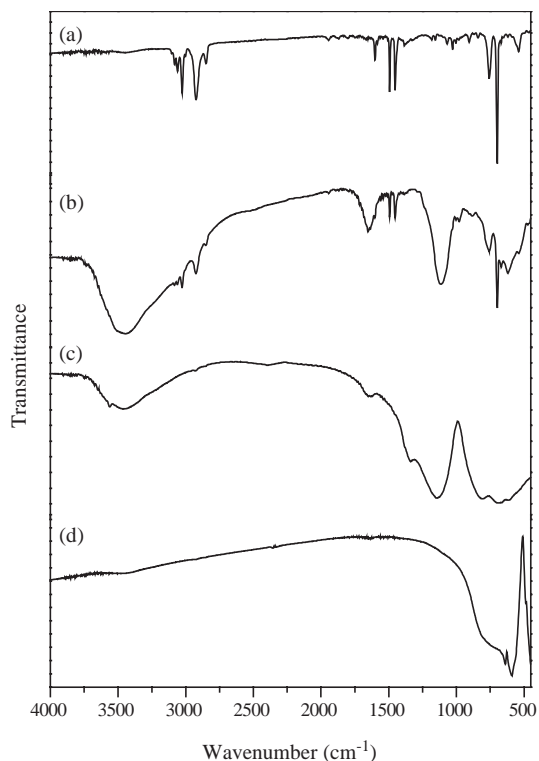


Fig. 9. IR spectra of (a) PS microspheres, (b) PS/aluminum hydroxide, (c) alumina obtained by calcination at 550°C, (d) alumina obtained by calcination at 1150°C.

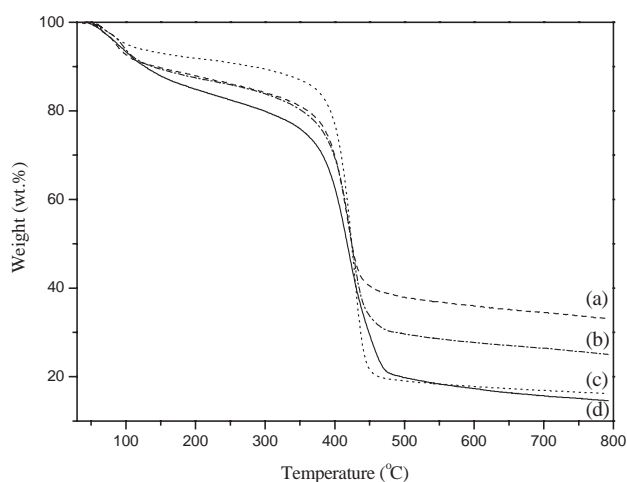


Fig. 10. Thermogravimetric trace of the PS/aluminum hydroxide spheres array of (a) sample 6, (b) sample 1, (c) sample 7 and (d) sample 2.

weight loss was the release of water between 50°C and 200°C. The second weight loss was at 350–500°C, which is associated with the weight losses due to the decomposition of polystyrene. If the weight of water was taken into account, the final weight loss at 350–500°C of coated particles is (a) 57%, (b) 66%, (c) 78% and (d)

77%, respectively. The thermogravimetric traces show the absence of the transformation of aluminum hydroxide to alumina below 800°C.

#### 4. Conclusions

Aluminum hydroxide coated PS microspheres and their arrays in large scale were prepared at one step in aluminum sulfate aqueous solution. The concentration of aluminum sulfate poses great effect on morphology of the arrays. Irregular plate, large hollow spheres and intact plate of PS/aluminum hydroxide microsphere arrays were obtained in 0.05, 0.1 and 0.2 M aluminum sulfate aqueous solution, respectively. The formation of the monolayer PS/aluminum hydroxide microsphere arrays may be contributed to the bonding of aluminum hydroxide and shear process of the stirring. PS microspheres were removed by calcination and hollow alumina hole arrays were successfully obtained.

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