



Liquid–air interface self-assembly: A facile method to fabricate long-range nanoparticle monolayers



K. Chokprasombat^{a,*}, C. Sirisathitkul^a, P. Ratphonsan^b

^a Molecular Technology Research Unit, School of Science, Walailak University, Nakhon Si Thammarat 80161, Thailand

^b Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

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ABSTRACT

A liquid–air interfacial assembly approach is a technique to fabricate long-range well-ordered nanostructures in either two or three dimensions. In this work, magnetic nanoparticles were synthesized by co-reduction of iron acetylacetonate ($\text{Fe}(\text{acac})_3$) and platinum acetylacetonate ($\text{Pt}(\text{acac})_2$) in benzyl ether. A few drops of the as-made nanoparticle suspension with varying concentrations were spread on the surface of diethylene glycol, ethylene glycol, and deionized water. After solvent evaporation, a substrate was placed under the liquid surface and then gently lifted up to collect nanoparticle layers. Although the nanoparticles are irregular in shape, they could well self-assemble on the diethylene glycol surface, forming an extended monolayer with small defects. By contrast, multilayer domains were frequently obtained when deionized water and ethylene glycol were used as the liquid subphases. An appropriate nanoparticle concentration was also a crucial factor in this approach. The lower concentration could not form an extended monolayer while the higher concentration led to multilayer assemblies. The order of the nanoparticle layers also strongly depended on the uniformity of the nanoparticles.

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1. Introduction

Self-assembly of inorganic nanoparticles into a long-range order monolayer is a challenging topic in nanotechnology [1]. Diverse properties in such structures can be implemented in nanodevices [2,3] whose potential applications include catalysis [4], sensors [5], nanoelectronics [6,7], and magnetic bit patterned media [8,9]. However, control of nanoparticle self-assembly into a long-range pattern is not straightforward because a lot of interactions between particles need to be optimized. Self-assembled patterns can be obtained by a slow evaporation of monodisperse nanoparticle suspension on a solid substrate [10]. However, the nanoparticles could only self-assemble in a short-range order by this method [11]. Therefore, a number of techniques have been explored to fabricate long-range nanoparticle monolayers such as spin coating [12], dip coating [13], liquid–liquid interface assembly [14], and Langmuir–Blodgett (LB) technique [15,16]. Among these techniques, the LB technique is an effective method to prepare high density nanoparticle monolayers and multilayer films with controllable layer numbers and thickness [17]. Several monolayers or multilayers of metallic and alloyed nanoparticles have been prepared by the LB technique [15–21]. However, it was known that the small monolayer islands were usually established with significant gaps on the surface of a deionized (DI) water subphase [22–24]. To merge these floating islands to form a large monolayer, a pair of moving barriers was used in the

LB technique to raise a surface pressure. However, nanoparticle monolayers can be wrecked or folded into bilayers due to resulting mechanical forces [25]. Later, Aleksandrovic et al. found a better result by replacing DI water by diethylene glycol (DEG) in the LB deposition [26] and Dong et al. successfully fabricated binary nanocrystal superlattice (BNSL) membranes by allowing nanoparticles to self-assemble at the DEG–air interface [27]. This approach is easier and faster than the LB, and the nanoparticle layers (Langmuir films) could be transferred to arbitrary substrates. Furthermore, structure and thickness of the Langmuir film could be effectively controlled by adjusting particle sizes and concentration [28,29].

In this paper, we report a fabrication of the long-range nanoparticle monolayers by using the liquid–air interfacial assembly approach. In spite of their irregular shapes, Fe–Pt based magnetic nanoparticles could well self-assemble on the liquid surface highlighting the advantages of this approach.

2. Experimental

2.1. Synthesis of nanoparticles

Two samples referred to as samples A and B were chemically synthesized by the co-reduction of $\text{Fe}(\text{acac})_3$ and $\text{Pt}(\text{acac})_2$ in benzyl ether. Oleic acid and oleylamine were employed as surfactants for stabilizing nanoparticles. For sample A, 1.5 mmol of $\text{Fe}(\text{acac})_3$, 0.5 mmol of $\text{Pt}(\text{acac})_2$, and 5.0 mmol each of oleic acid and oleylamine were mixed in 20 mL of benzyl ether, and then the mixture was heated to reflux at 300 °C for 3 h. After refluxing, the black product was cooled down to

* Corresponding author.

E-mail address: komkrich28@gmail.com (K. Chokprasombat).

¹ Tel.: +66 75 673 550; fax: +66 75 672 004.

Table 1
Reaction conditions, average size, and composition of samples A and B.

Sample	Reagents (mmol)				Refluxing		Average size (nm)	Particle composition (at.%)		
	Fe(acac) ₃	Pt(acac) ₂	Oleic acid	Oleylamine	Temp. (°C)	Time (h)		Fe	Pt	O
A	1.5	0.5	5.0	5.0	300	2.0	6.13 ± 1.03	26.52	36.19	37.28
B	1.0	0.5	3.5	3.5	300	3.0	4.92 ± 0.73	17.16	24.63	58.21

room temperature under N₂ blanket, and the nanoparticles were then separated and purified by centrifuging with ethanol for 4 times. Sample B was also synthesized by the same procedure, but the molar ratio of precursors, surfactant concentration, and refluxing time were altered. The synthesis conditions and particle composition measured by energy dispersive X-ray spectroscopy (EDS) are summarized in Table 1. Details of the synthesis and magnetic characterization were described in a previous report [30]. An average size and size distribution of the nanoparticles were determined by transmission electron microscope (TEM) image processing [31].

2.2. Liquid–air interfacial self-assembly

To prepare nanoparticles for the liquid–air interface assembly, the colloid of the as-synthesized nanoparticles was mixed with excess ethanol and then centrifuged at 5000 rpm for 15 min. The supernatant was discarded and the precipitate was allowed to dry at room temperature before further drying with N₂ flow. The dried nanoparticles were redispersed in hexane to obtain the concentration of 0.5 mg/mL, and then the nanoparticle suspension was further diluted with hexane for 0.1, 0.2, 0.3, and 0.4 mg/mL. The self-assembling process at the liquid–air interface could be carried out with a setup illustrated in Fig. 1. For each concentration, the glass cylinder (2 cm in diameter and 1.5 cm in height) was cleaned by chloroform and placed on a flat table. DEG of 2 mL was added in the glass cylinder. Then, 20 μL of the nanoparticle suspension was carefully dropped on the surface of the liquid subphase by a micropipette. The glass slide was placed on the top of the cylinder with a small gap left to allow evaporation of the hexane within 15 min. After that, the glass slide was taken off. A carbon coated copper grid was carefully placed under the floating film which could be seen by the naked eyes and then slowly lifted up to collect the nanoparticle layers. Finally, the collected nanoparticle layers were completely dried. To investigate the effect of liquid subphases, DEG was successively replaced by DI water and ethylene glycol (EG). The TEM (FEI, Tecnai G² 20) with an accelerating voltage of 200 kV was used to examine particle morphology and self-assembled patterns.

3. Results and discussion

Fig. 2 shows TEM images of as-synthesized nanoparticles. Histograms with lognormal distributions are illustrated as insets. The nanoparticles in samples A and B have average sizes of 6.13 ± 1.03 and 4.92 ± 0.73 nm, respectively. According to the particle composition in Table 1, atomic percentage of Fe was lower than that of Pt and a substantial amount of O was also found. It follows that the nanoparticles may consist of Pt-rich nanoparticles and iron oxide phases. Iron oxides may be in the form of shell around the Pt-rich nanoparticles and heterodimer structures [32].

To investigate the effect of liquid subphases, the FePt-based nanoparticles (sample A with a concentration of 0.2 mg/mL) were allowed to separately self-assemble on the surface of DEG, DI water, and EG. TEM images of nanoparticle assemblies are compared in Fig. 3. Directly dropped on a substrate, the nanoparticles dispersed in all directions and no long-range order was observed (Fig. 3(a)). By contrast, some short-range self-assembled patterns could at least be obtained with an assistance of the liquid–air interface technique. Above all, a long-range (more than 3 μm²) self-assembled pattern without any significant gaps or holes can be obtained when DEG was used as the liquid subphase (Fig. 3(b)). However, the regular arrays were not acquired because nanoparticles were not uniform in size and shape. When DI water was used as a subphase, nanoparticles tended to self-assemble into multilayers instead of monolayers as shown in Fig. 3(c). Fig. 3(d) shows a self-assembled pattern of the nanoparticles when EG was used as a subphase. The nanoparticles preferred to self-assemble into islands which multilayers were densely formed in the center according to a previous report on the self-assembly of binary nanocrystal superlattice [27]. These results indicated that DEG is suitable for use in the liquid–air interface technique. The advantages of DEG compared to DI water and EG may originate from several appropriate physical properties, including a lower evaporation rate [27], higher viscosity, and lower polarity [33]. Liquid subphase with low evaporation rate and high viscosity might behave as a stable substrate during the self-assembly. However, the evaporation rate and viscosity of the liquid might also affect the interfacial forces such as a capillary interaction.

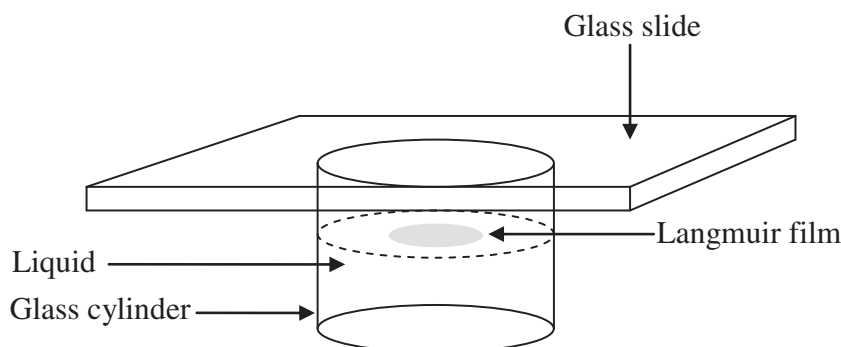


Fig. 1. Schematic diagram for self-assembly of nanoparticles by liquid–air interface technique.

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