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Assembly of Fullerene Nanoparticles Using a Liquid–Liquid Interface

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Fullerene (C_{60}) nanoparticles were assembled in two-dimension using a liquid–liquid interface. C_{60} nanoparticles dispersed in ethyl lactate/water solution were added to a glass vessel. Then, hexane was added to the dispersion solution to create the liquid–liquid interface. C_{60} nanocrystals were assembled at the interface, when ethanol was added to the water dispersion–hexane solution. The assembled film was transferred onto a solid substrate and the film morphology was observed by a scanning electron microscope (SEM) and atomic force microscope (AFM).

Keywords Liquid–liquid interface; orientation; single-walled carbon nanotubes

Introduction

Nanometer-sized particles of fullerene (C_{60}) have received much attention, because they are considered to be inter-mediate states between molecules and bulk materials. Hierarchical assembly of C_{60} nanoparticles is the key issue for applying those unique properties to real devices. Several processes, such as layer-by-layer assembly and electrophoretic deposition have been applied to assemble fullerene nanoparticles in a tailor-made manner [1,2]. We and other groups have applied a liquid–liquid interface to assemble nanomaterials in a two-dimensional manner [3–8]. Recently, we have succeeded to assemble a pristine single-walled carbon nanotube, which is another class of carbon cluster, using a liquid–liquid interface [9–11]. The assembling

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technique is a versatile technique because it requires no counter charged polymers or electric fields.

In this paper, fullerene nanoparticles were assembled at a hexane-water interface by controlling their surface energy. The assembled nanoparticle film were transferred onto a solid substrate and characterized by a scanning electron microscope (SEM) and atomic force microscope (AFM).

Experimental Section

C_{60} nanoparticles (diameter = ~60 nm) were fabricated by a reprecipitation method using ethyl lactate as a poor solvent as reported previously [12]. The nanoparticles was diluted with water to the concentration of 0.001 wt%. The ζ–potential analysis of the nanocrystal was performed at 20°C with an electrophoretic light scattering spectrometer (ELS-8000; Otsuka Electronics). The surface morphology of the nanocrystal films was observed by an environmental scanning electron microscope (S-4800; Hitachi Ltd., accelerating voltage = 5 kV) and AFM (SPI400; Seiko Instruments).

Results and Discussion

We have reported that the control of the surface wettability of water-dispersed nanoparticles is the key factor to assemble the nanoparticles at a liquid–liquid interface. It was reported that ethanol could control the surface wettability of the nanoparticles which were dispersed in water [3,5,6]. The ζ–potential of C_{60} nanoparticles was measured with changing the amount of ethanol added. The ζ–potential of C_{60} nanoparticles initially showed a high negative value. With addition of ethanol, the negative ζ–potential of the C_{60} nanoparticles gradually decreased (Fig. 1). The smaller dielectric constant of ethanol compared to that of water would decrease the amount of static charge at the C_{60} nanoparticle's surface.

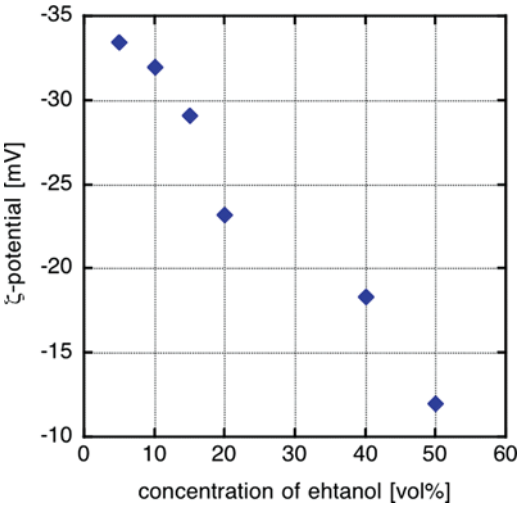

Figure 1. Values of ζ–potential for the aqueous dispersion of C_{60} nanocrystal at the different ethanol concentration.

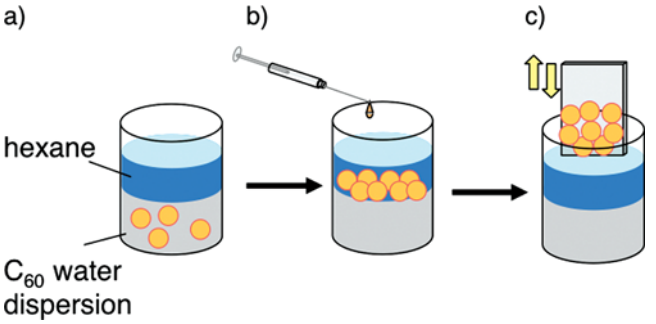

Figure 2. Fabrication process of C_{60} nanocrystal assembly. a) Preparation of water-hexane interface, b) Addition of ethanol (10–20 vol%) to the interface, and c) Transfer the assembled film onto a solid substrate.

To assemble C_{60} nanoparticles using a liquid–liquid interface, the C_{60} nanoparticle water dispersion was placed in a glass vessel. Then hexane was added slowly to the vessel to create the liquid–liquid interface. Ethanol (10∼20 vol% against water phase) was added to the vessel dropwise (Fig. 2). We observed that some of the nanoparticles were assembled after the addition of ethanol. The assembled nanoparticle film was transferred onto a solid substrate by dipping the substrate into the vessel. Figure 3 shows the SEM images of the transferred nanoparticle assembly prepared from different concentration of ethanol. The density of nanoparticle in the assembled film increased with increasing the addition amount of ethanol. The absolute value of the ζ–potential of the C_{60} nanoparticles decreased with adding ethanol, which indicates that the dispersibility of the nanoparticles in water was decreased. The destabilized nanoparticles were assembled at the interface to stabilize the interfacial energy. Therefore, addition of 20 vol% of ethanol formed a denser film than the film prepared with adding 10 vol% of ethanol. The heights of the assembled film

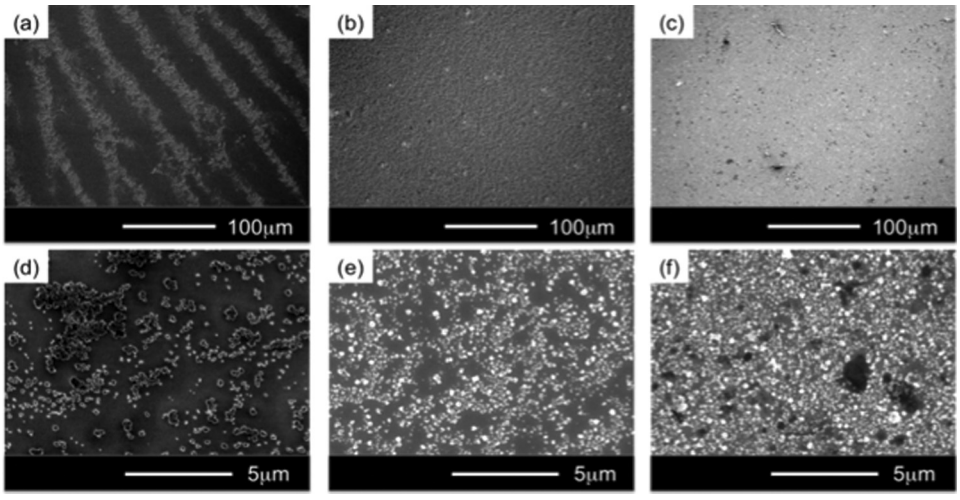

Figure 3. SEM images of C_{60} nanocrystal films fabricated with addition of different amount of ethanol (top: ×400, bottom: ×10000). The concentrations of ethanol are (a, d) 10 vol%, (b, e) 15 vol%, (c, f) 20 vol%.

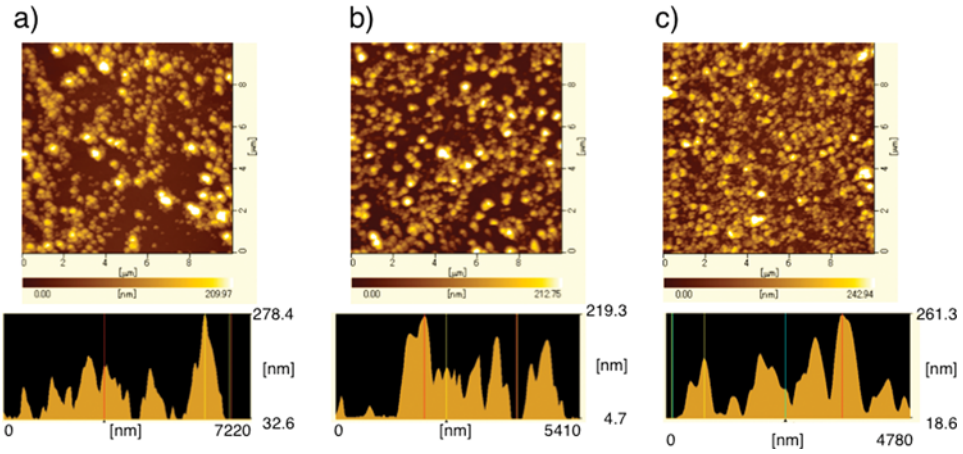

Figure 4. AFM images of C_{60} nanocrystal films fabricated with addition of different amount of ethanol. The concentrations of ethanol are a) 10 vol%, b) 15 vol%, and c) 20 vol%.

were about 100–200 nm and were irrespective of the film density (Fig. 4). Large aggregated domains were not observed in the present condition. Interestingly, the film prepared with adding of 10 vol% of ethanol formed a striped pattern. The direction of the stripes was parallel to a withdrawal direction of the substrate, which indicates the liquid flow generated during the deposition process induced the pattern formation.

Conclusion

C_{60} nanoparticles were assembled using the liquid–liquid interface. Addition of ethanol reduced the surface charge of the nanoparticles and induced the nanoparticles to assemble at the interface. The density of the assembly was increased with increasing the amount of ethanol added. A striped pattern of the assembled film was formed in the case of 10 vol% of ethanol added.

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