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Application of Superhydrophobic Surface with High Adhesive Force in No Lost Transport of Superparamagnetic Microdroplet

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Since magnetic nanomaterials conjugating with biomolecules have been widely applied in biochemical separation,[1] targeted drug delivery,[2] immunoassay,[3] biosensor,[4] and other fields,[5] there is an increasing need for controlled transport of their small volumes of liquids. Significant advances have been made over the past few years through microfluidic systems.[6] However, some technological difficulties were also encountered: delivered materials might be adsorbed on the solid walls due to the nature of the contact, leading to contamination or clogging of channels; transport of liquid was confined in permanent microchannels and, hence, limited maneuverability and had poor fault-tolerance capability; abrupt changes in channel direction might cause turbulence and shear. Recent reports have partially overcome these problems through levitation of microdroplets by optical,[7] electrostatic,[8] or electromagnetic[9] techniques, or manipulation of microdroplets freely suspended in fluorocarbon oil by applying an alternating (ac) electric field.[10] However, all have proved to be rather cumbersome and still remain a major technical challenge to directly manipulate droplets on solid surfaces without any leaks.

Superhydrophobic surfaces with high adhesive force offer particular advantages to completely transport water microdroplets.[11] Superhydrophobic surfaces, with water contact angles (CAs) larger than 150°, can avoid the wetting problem.[12] A microdroplet on this surface usually takes a quasi-spherical shape and accordingly dramatically lowers the contact area between droplet and solid surface, which would help to greatly reduce the possible deposition of liquid. Besides, the strong adhesive property of the surface can make the microdroplet accurately hold in place without any sliding or rolling. Here, superhydrophobic surface was used for reversibly oriented transport of superparamagnetic microliter-sized liquid droplets with no lost volume in alternating magnetic fields, which is of great significance for the innovative design of open microfluidic devices.

An aligned polystyrene (PS) nanotube layer was prepared via a simple porous alumina membrane template covering method according to our previous report (for details, see Supporting Information).[11a] The topography is shown in the inset of Figure 1. The nanotube layer showed a strong adhesive effect to a superparamagnetic microdroplet. Figure 1 shows force−distance curves before and after a 4 μL superparamagnetic microdroplet contacted the PS nanotube layer, which was measured by a high-sensitivity microelectromechanical balance system at 83% relative humidity (see Supporting Information). The maximum adhesive force between the microdroplet and the nanotube layer is about 52 μN. Capillary forces and capillarity-induced negative pressure in millions of nanotubes were thought to be the two dominant factors for high adhesion. The final balance force came back to zero again, indicating that the microdroplet had not left the surface even though a strong interfacial adhesive interaction occurred.

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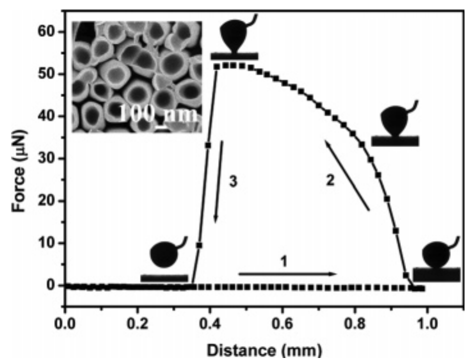

Figure 1. Force−distance curves recorded before and after the superparamagnetic microdroplet contacted the aligned PS nanotube layer. The inset shows a SEM image of the PS nanotube layer and four photographs of the shapes of the superparamagnetic microdroplet taken at the corresponding stages during the measurement process.

The PS nanotube layer with high adhesive force was then used as a "mechanical hand" to transport a 4 μL superparamagnetic microdroplet placed on an ordinary superhydrophobic surface with a water CA of about 160° (Figure 2). The distance between two substrates was kept constant at 2 mm in height. When an external magnetic field was applied along the surface normal with stronger field intensity lying at the top (i.e., magnet A was switched on), the superparamagnetic microdroplet was attracted and flew upward (Figure 2b). Due to the strong adhesive effect of the nanotube layer, the superparamagnetic microdroplet was stuck to the PS nanotube surface (Figure 2c). Once the direction of the magnetic field intensity was switched downward (magnet A was switched off and magnet B was switched on), the superparamagnetic microdroplet fell back to the initial superhydrophobic surface (Figure 2d). If we removed the magnetic field, the superparamagnetic microdroplet's magnetization rapidly decayed (Figures 2e and S3). Such transport processes could be repeated by switching the magnetic fields (Figure 2f). It is especially worth noting that no loss was observed during transport of the superparamagnetic microdroplet. The optimum droplet volume for this system was within 8 μL.

Forces acting on the superparamagnetic microdroplet dominated its behaviors of levitation and falling. Typical forces include magnetic force, gravitational force, and adhesive force. When magnetic force was stronger than the sum of the other two, the superparamagnetic microdroplet could not maintain its equilibrium but was driven to extricate from the surface. As the changes of the gravitational force of the microdroplet and the adhesive force between the microdroplet and the PS nanotubes were ignored, the magnitude and the direction of magnetic force could control the transport of the superparamagnetic microdroplet.

Magnetic force results from magnetic field gradients (grad B) acting on magnetic dipole moments, which can be described as[13]

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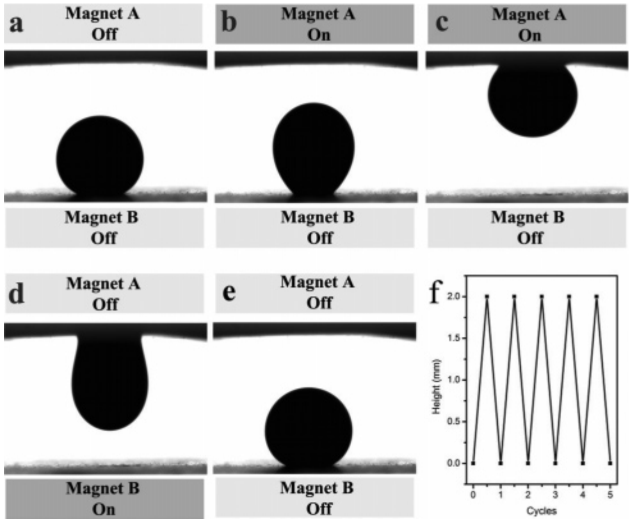

Figure 2. No lost transport processes of a superparamagnetic microdroplet in alternating magnetic fields (for movie, see Supporting Information). (a) A magnetic microdroplet was placed on an ordinary superhydrophobic surface, above which was positioned the PS nanotube layer with the distance of 2 mm in height. Magnets A and B were assembled outside. (b) When magnet A was switched on, the microdroplet was magnetized and attracted to fly upward. (c) Microdroplet was stuck to the surface of PS nanotubes due to strong adhesion between them. (d) When magnet A was switched off and magnet B was switched on, the direction of magnetic force was reversed and the microdroplet fell down the initial surface. (e) When both magnets were switched off, transport was stopped. (f) The superparamagnetic microdroplet was reversibly transported upward and downward by alternating magnetic fields.

$$F = NS\mu_B \text{ grad } B$$

where S and N are the number of Bohr magnetons (μ_B) and superparamagnetic nanoparticles per microdroplet, respectively. Therefore, intensity and direction of external magnetic field (H) are mainly dependent on N and when N increased, minimum H gradually decreased (Figure 3).

In the system, the microdroplet must be superparamagnetic, meaning that it is only magnetic under a very strong applied magnetic field, but retains no permanent magnetism once the magnetic field is removed (see Supporting Information). It is crucial to its success for rapidly reversible transport of the magnetic microdroplet between two superhydrophobic solid surfaces. If the microdroplet possessed a remnant magnetic field, such as ferromagnetic microdroplet, it would act as a small magnet to counteract the external magnetic field, resulting in an unavailing transport of the microdroplet.

In conclusion, the superhydrophobic PS nanotube layer was applied to perform no lost reversible transport of microliter-sized superparamagnetic liquid droplets by alternating magnetic fields. It is very important for the design of novel microfluidic devices and useful in a wide range of applications, such as many localized chemical or biological reactions, traced analysis, and in situ detection.

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Supporting Information Available: Preparation and characterization of PS nanotube layer, adhesive force of an ordinary superhydrophobic surface, preparation and magnetic property of the microdroplet, transport process between hydrophobic surfaces (PDF), and movie of

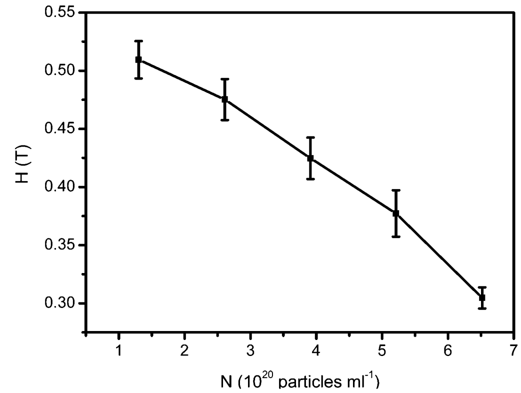

Figure 3. Dependence of intensity of external magnetic fields on the number of superparamagnetic nanoparticles per microdroplet.

reversibly no lost transport (AVI). This material is available free of charge via the Internet at http://pubs.acs.org.

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