Manipulation of Low-Dimensional Nanomaterials Using Water Meniscus

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This paper reports on a colloidal manipulation of low-dimensional nanomaterials such as nanoparticles and nanowires. This colloidal manipulation enables the arrangement of nanoparticles and nanowires on a substrate with controlled location and orientation. The conducted research includes the study of conditions such as the water contact angle by surface treatment and the nanowire length for the optimized colloidal manipulation of nanomaterials. The measured minimum water contact angle, required to drive gold nanoparticles, is 50° on top of a Teflon-coated surface. Further, the required maximum length of the nanowires to be driven by the meniscus overcoming friction between the nanowires and the surface is on the order of 1 micron.

Keywords: Colloidal Assembly, Nanowire, Nanoparticle, Pulsed Laser Deposition, Water Contact Angle.

1. INTRODUCTION

The assembly of individual nano-objects is critical for developing high-throughput nanofabrication techniques. There have been a number of reports on the assembly of individual or many nanoparticles,1–5 and on nanowires6–14 on a substrate in desired patterns. Among the assembly methods reported, the colloidal assembly of nanoparticles provides high assembly yields (∼90%) and controllability of individual objects.1,2,4 A water meniscus surface can drive nanoparticles without losing them along its movement direction. Kraus1 used this technique to assemble nanoparticles onto the pre-patterned, dimpled network of silicon or polymer substrates. In this technique, the water contact against the substrate is the critical factor in determining the success of the colloidal assembly. If the water contact angle is relatively small below a threshold value, the meniscus does not have enough driving force on the nanoparticles. As a result, the nanoparticles are left behind the meniscus in the convective assembly. However, if the angle is larger than the threshold, the nanoparticles follow the meniscus until they are trapped at the geometrical depressions, i.e., colloidal assembly. The natural questions following such an achievement are then: Can the same technique be used for the assembly of nanowires? What would the determining factors be for successful colloidal assembly? This paper presents our preliminary study on the optimized conditions for driving of nanoparticles and nanowires using a water meniscus, which can potentially be used to assemble nanowires in a desired pattern (Fig. 1). It outlines the driving conditions of nanowires with water meniscus that are affected by the change in water contact angle after surface treatment, as well as the effect of nanowire friction.

2. COLLOIDAL ASSEMBLY OF NANOPARTICLES AND NANOWIRES

2.1. Nanoparticle Trapping Using Nano-Dimples

If an object is immersed in a water drop on a surface, the object is trapped inside, and it cannot escape from the water–air interface. Even if the water–air interface moves due to evaporation, the object will follow the water movement to stay within the interface. This phenomenon is due to the water induced surface tension applied on the object. When a portion of the object is out of a water meniscus, the water surface tension induces a force along the water–object edge. Here, the circumferential length of a portion of the nanoparticle or a nanowire in the air is given by $2\pi R$ for a particle where $R$ is the radius and $2(L + \pi R)$ for a wire where $L$ is length and $R$ is cross-sectional radius. For high aspect ratio nanowires, this can be simply approximated as $2L$. The meniscus driving force acting on a nanoparticle or a nanowire is given as (Fig. 2(a)):

$$F_{\text{in}} = \text{(Exposure length)} \times \sigma \times \sin\varphi$$

(1)

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Manipulation of Low-Dimensional Nanomaterials Using Water Meniscus

Sul et al.

Fig. 1. Conceptual schematics on the colloidal assembly technique. Functionalized nanoparticles are self-assembled into a nanodimple network, creating nanoparticle-nodes for further guided assembly of nanowires. Assembly sequence: (a) Nanodimple fabrication by electron beam lithography (EBL) on a polymer layer. (b) and (c) Assembly of nanoparticles and nanowires using colloidal assembly. (d) Completed structures. The nanoparticles and the tips of nanowires are functionalized by linker molecules, such as complementary single strand DNAs.

Here $\sigma$ is surface tension between water and air, 72 mN/m, and $\varphi$ is water contact angle on the gold surface, 76°, and $\psi$ is the water contact angle against the substrate. The direction of this force is downward if the water contact angle, $\psi$, is below 90° (non-superhydrophobic). If there is a geometrical depression (like a dimple in Fig. 2(b)), the meniscus force will trap a nanoparticle into the dimple. In this situation, three forces; meniscus force, reaction from dimple, and adhesion from the substrate are acting on the nanoparticle. From simple geometrical consideration, the height of the dimple step determines the tapping result.

The successful colloidal driving condition for the gold nanoparticles (Ted Pella, 250 nm gold colloid) was investigated using a translational moving stage under an optical microscope. (Fig. 3(a)) A nanoparticle suspension was dropped on a substrate, which is on a translation stage. The substrate moving speed was set at 1 $\mu$m/sec. A thin glass coverslip was touching the water drop and thereby holding the water drop by surface tension. The height of the coverslip was 500 $\mu$m, which was kept constant.

Fig. 2. (a) Water edge applies surface tension at the protruding portion of a nanoparticle. (b) A depression on a polymethyl methacrylate (PMMA) layer can trap a nanoparticle by the reactive force from the dimple step. There is a critical height of the dimple for successful trapping.

Fig. 3. (a) Experimental setup for nanoparticle colloidal assembly. The glass coverslip was holding the water drop while the substrate was moved at a constant speed. (b) Scanning electron microscope (SEM) image of a network of assembled nanoparticles inside the nanodimples (blue circles). The scale bar is 5 micron. Inset: Magnified view of a nanodimple. Scale bar is 200 nm.
using a translation stage. Before colloidal driving, distilled water contact angle was measured first on various substrates. On the bare silicon oxide surface, the water contact angle, $\psi$ was measured by side view pictures to be $30 \pm 5^\circ$ against a substrate (Fig. 4(a)). nanoparticles cannot be driven by water and were scattered randomly through diffusion. Then, the oxide was spin coated with polymethyl methacrylate (PMMA) for 40 seconds at 4000 rpm and 980 K (C4 grade). $\psi$ was increased to $45 \pm 5^\circ$, but the convective diffusion was still observed, indicating that the contact angle is not large enough to drive particles. $\psi$ was further increased to $70 \pm 5^\circ$ by a hydrophobic coating with Teflon deposited on top of the PMMA. To deposit a thin (30 nm) Teflon film, a target of Teflon piece was put inside a vacuum chamber, and a high power laser (Quanta-Ray, DC10A) was focused on it through a glass window of the chamber with 150 mJ pulses at 355 nm wavelength at 10 Hz for 30 minutes. At the angle of $70 \pm 5^\circ$, 90% of the gold nanoparticles followed the water meniscus.

A network of nanodimples was prepared by electron beam lithography (EBL) on top of the PMMA layer. With a spin coating condition of 4000 rpm for 40 seconds, the PMMA dimples were 750 nm wide and 500 nm deep. Gold nanoparticles are trapped onto the nanodimples on the PMMA layer after the water meniscus was driven over the substrate (Fig. 3(b)). The nanoparticle assembly yield was roughly ~80%. If $\psi$ was above 90° due to the self-assembled super hydrophobic monolayer molecules like ODP (octadecylphosphate) coating, the gold nanoparticles would initially be trapped at the nanodimples, but would be released from the dimples by the water surface tension, leaving no particle assembly behind. Therefore, the optimized range for $\psi$ was found to be from 50° to 70° by the PLD technique. Even when $\psi$ was optimized, a minimum dimple depth was required for the particle trapping. The critical dimple depth was 80 nm by calculation and we observed successful trapping above 200 nm.

2.2. Water Induced Tensional Force Acting on a Nanowire

To manipulate a nanowire using the water meniscus, the force component along the substrate should be larger than the friction between the nanowire and the substrate. The lateral component of the meniscus force can be given from Figure 2(a):

$$F_{\text{nl}} = 2L \times \sigma \times \sin \psi \times \sin \theta$$

Figure 2(a) can now be interpreted as the cross-sectional view of a nanowire instead of a nanoparticle, if the axis of the nanowire is parallel to the meniscus edge. In this configuration, the water meniscus can give maximum force onto the nanowire, when the nanowire is in abeam mode, i.e., the direction of nanowire axis is along the water edge. (Fig. 4(a)) If a nanowire has an initial angle against the meniscus before it meets the meniscus, a point on the nanowire becomes a pivot and the nanowire starts rotating until it is in abeam mode. (Fig. 4(a)) Pivoting initiates when the nanowire is floating above the substrate (Fig. 5(a)-1), or it is lying on the substrate with an angle above some critical angle. During the abeam mode driving, due to local friction variation, the nanowire can have an anchor holding a portion of a nanowire acting as another pivot point. In this situation, the meniscus rotates the nanowire (Fig. 5(c)) The nanowire rotates until its driving force component along the meniscus direction balances the friction of nanowire. Then the nanowire stops pivoting and ceases to follow the meniscus (Fig. 5(d)) and is left behind with a critical angle, $\theta_c$. At this moment, the lateral meniscus force balances the friction.

$$F_{\text{nl}} = 2L \times \sigma \times \sin \psi \times \sin \theta = F_{\text{Friction}} = \mu L$$

where $\mu$ is the friction coefficient. If the nanowire initially had an angle less than this critical angle before meeting the meniscus, the meniscus will have no driving effect, just passing the nanowire. (Fig. 5(e) and (e)-1) The critical angle, $\theta_c$, will depend on two factors, including water-substrate contact angle, $\psi$, and length of the nanowire, $L$. The first factor can be controlled by the surface treatment using Teflon coating. The second factor can be controlled by the length of the nanowire. If the friction of a nanowire becomes small by reducing the length below a critical length, $L_c$, then the meniscus acting only at one tip of a nanowire has enough force to drive the nanowire, with the nanowire axis perpendicular to the meniscus edge; i.e., pole mode. (Fig. 5(f) and (f)-1)

If the length is longer than $L_c$, the angles of all the nanowires behind the meniscus are smaller than $\theta_c$, because the meniscus rotates the nanowires below the critical angle or the meniscus has no effect due to the small
Fig. 5. (a) When a water meniscus meets a nanowire in the water, which is floating above the substrate like (a)-1 or lying in an angle larger than critical angle, $\theta_c$, it forces the nanowire into abeam mode in (b) and (a)-2. (c) However, the nanowire can rotate around a stationary pivoting point, depending on the substrate’s local friction on a section of the nanowire. (d) At a critical angle $(\theta_c)$ the friction on the nanowire exceeds the meniscus, forcing the nanowire left behind the water edge. (e) If a nanowire was initially lying with an angle less than $\theta_c$, the meniscus does not drive it, leaving the nanowire unaffected. (f) If a nanowire’s length is shorter than a critical length, $L_c$, the meniscus can drive the nanowire by its one end only, overcoming the friction from the nanowire’s entire length.

initial lying angle. Therefore, the angular distribution must show a step around the critical angle in an ideal situation if a meniscus is swept across a substrate and the angles of all the nanowires left on the substrate are recorded. (The step in Fig. 7(a)). However, due to stochastic variations of friction among individual nanowires, only a gradual decrease must be observed above the critical angle. (The curve in Fig. 7(a)).

From the above arguments, one can expect that the measured $\theta_c$ depends on surface treatment, but not on the length of the nanowires, because both sides of Eq. (3) cancel out the length dependency. Also, the right hand side of the equation is a constant, and $\psi$ and $\theta$ affect each other; if $\psi$ becomes larger, then $\theta$ gets smaller and vice versa. Thus, the water contact angle and the critical angle have inverse dependence, and it is expected that the hydrophobic treatment yields a smaller critical angle.

2.3. Nanowire Manipulation: Data Collection and Analysis

For the manipulation of nanowires, the same setup as in Figure 3 was used again. The gold nanowires were grown by an anodized aluminum oxide membrane template. Their length could be controlled by growth time in the electrolyte bath and their diameters are 250 nm. A water suspension containing various length gold nanowires (2 to 10 microns long) was dropped onto substrates. We used two kinds of substrates, PMMA coated silicon oxide substrate and Teflon-treated PMMA substrate. Unlike gold nanoparticles, gold nanowires could be driven on top of the PMMA surface, due to increased exposure length. After sweeping, angles of the nanowires were measured individually using optical microscopy pictures (Fig. 6(a)). Figures 6(b) and (c) show the top view of
Fig. 7. (a) Schematic histogram for ideal angular distribution represented by the black step and expected distribution by the blue curve. (b) Angle measurement histogram from PMMA surface. (c) Angle measurement histogram from Teflon-treated PMMA surface. (d) There was no length dependency in the distribution, either on PMMA surface or Teflon-treated PMMA surface. 

A meniscus containing nanowires in various lengths and another meniscus containing 1 μm long nanowires. Unlike Figure 6(b), in Figure 6(c), there was no slippage of nanowires from the meniscus. As stated in Section 2.2, the angular distribution of nanowires will show a step-like threshold after the meniscus passes over the substrate. However, the threshold angle will not be a step function, but rather a smooth curve around the angle (Fig. 7(a)) due to the stochastic nature of friction between nanowires and the substrate. Figure 7(b) shows an actual angular distribution on a PMMA substrate after a meniscus containing nanowires in various lengths (2 to 10 μm) swept through. The critical angle was near 70 ± 10°. Figure 7(c) was obtained from Teflon-treated PMMA substrate, which has a smaller critical angle around 20 ± 10°. This result follows the expectation in the previous subsection, because Teflon-treated PMMA surface has a larger water contact angle, θ, thus larger driving meniscus force. All the distributions in Figure 7(d) obtained from Teflon-treated PMMA substrate show a consistent trend regardless of nanowire lengths, as expected from the previous subsection argument. This non-dependency on the length was also observed on the PMMA substrate. (Not shown)

Using Eq. (3), one can calculate the friction coefficient of nanowires on PMMA or Teflon-treated PMMA substrates, using σ = 7.1 × 10⁻² N/m and φ = 42°,

\[ F_{\text{friction}}(\text{PMMA})/L = 2\sigma \times \sin \varphi \times \sin \psi_{\text{PMMA}} \times \sin \theta_{\text{PMMA}} \]

\[ = 14.2 \times 10^{-2} N/m \times \sin 42° \times \sin 30° \times \sin 70° \]

\[ = \mu_{\text{PMMA}} = 4.4 \times 10^{-2} N/m \] (4)

To manipulate the nanowires without any slipping out of the meniscus; i.e., pole mode on a Teflon-treated surface, \( F_{\text{friction}} \) (Eq. (2)) should be larger than friction.

\[ F_{\text{friction}} = \frac{2\pi R \times 0 \times \sin \varphi \times \sin \psi > F_{\text{friction}} = \mu_{\text{Teflon}}L} \]

Here the length of a nanowire is replaced by the radius. If a radius of 120 nm is inserted into Eq. (6), the left hand side of equation is 23 nN, which produces a length of 0.7 μm. Thus, this suggests that if the length of the nanowire is limited to around 1 micron or less, a water meniscus can drive all the nanowires without slipping, regardless of their angle against the meniscus. We experimentally verified this claim using a 1 micron long gold nanowire suspension over Teflon-treated PMMA surface as was shown in Figure 6(c).

This driving technique can be applied to longer nanowires if the friction between nanowires and the substrate can be further reduced, either by using low friction substrates such as mica or graphite, or by surface treatment, as shown with Teflon. Alternatively, if the surface is treated with super-hydrophobic material, then the water contact angle is expected to be more than 90° and the meniscus will apply an upward force when it contacts a nanowire. Such a lifting force may reduce the friction resulting in driving of longer nanowires in pole mode.
3. SUMMARY

The manipulation parameters to drive nanoparticles and nanowires were studied. It was confirmed that the water contact angle should be larger than a threshold angle to drive the nanoparticles. The friction between the nanowires and substrate was estimated by the nanowire angle measurements. To overcome the friction and to drive the nanowires without slipping, the length of nanowires should be limited and the water contact angle control should be increased by hydrophobic treatment. This method will ultimately enable parallel self-assembly of individual nanoparticles over a substrate with control over location and orientation.

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References and Notes


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