Rail-Assisted Dynamic Assembly of Metallic Nanowires

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Motion modulation of functional micro-/nanoparticles is a key challenge for biomedical science and development of optics and electronics. Herein, microrail-assisted reversible assemblies of nanowires remotely powered by acoustic waves are demonstrated. The microrails embedded into the ultrasound field can make the surrounding acoustic potential nonuniform distribution and cause nanowires to trap into and assemble along the microrails. The width of the microrail can determine the dynamic assembly of nanowires in parallel to or in perpendicular to the direction of the microrail, which is validated by numerical simulations. In addition, trapping and transportation of nanowires on microrails are also achieved by adjusting the microfluidic direction from the microrail. Such microrail-assisted capabilities of assembling and transporting nanowires provide great potentials in photonic crystals, cell collection, and nanoelectronic fabrication.

Inspired by natural biological micro-organisms, synthetic micro-/nanomotors have paved the way toward major advances in nanotechnology and nanoscience. The 2016 Nobel Prize in Chemistry was awarded jointly to Jean-Pierre Sauvage, Sir J. Fraser Stoddart, and Bernard L. Feringa for their design and synthesis of molecular-scale nanomachines.[1,1] Similar to their natural counterparts, man-made tiny machines at micro-/nanoscales (often referred to microswimmers, microrobots, colloidal motors, or micro-/nanomotors), manipulated and precisely controlled by external stimuli (e.g., chemical energy, light, magnetic, ultrasonic, or electric fields) in biologically relevant environments, are expected to help humanity in a variety of biomedical and environmental applications.[2–16] Recently, considerate efforts have been devoted to patterning and assembling functional micro-/nanoparticles triggered by different external stimuli, which has a profound impact on numerous applications including cell biology, tissue engineering, and medicinal science and the development of optics and electronics.[17–28]

Acoustic actuation is one of the most promising external stimuli that meets the strict requirements for manipulating microbubbles,[29] silica or polymer beams,[30–33] metallic nanowires[14–18] and cells[39–42] in liquid or air medium. Multiple proof-of-concept studies using acoustic propulsion for drug delivery[43,44] and effective biodegradation[45] have been presented over the past 3 years.[46] Recently, acoustic holograms were obtained by assembling the particles into arbitrary static shapes and simultaneously confining and propelling objects. The forces exerted within these holograms allow for particle patterning and trajectories controlling.[47–49] Herein, we demonstrate an innovative approach based on the use of ultrasound waves to modulate Au nanowires on the microrail in microchannel. Under ultrasound field, the presence of the microrail generates a nonuniform distribution of acoustic potential that induces the Au nanowires assembly in the microrail. In contrast, the Au nanowires display random Brownian motion when the ultrasound is off; such ultrasound-induced on-command assembling behavior is fully reversible. The experimental results are also supported by numerical simulation of the microrail and the acoustic pressure intensity using the finite element analysis method. We expect that microrail-assisted acoustic manipulation will provide new capabilities in assembly, transportation, and directional manipulation of micro-/nanoparticles, enabling unlimited possibilities in nanotechnology applications.

As schematically shown in Figure 1, the ultrasound experimental setup involves an acoustic wave generation module for ultrasound generation and a microfluidic device to provide a microfluidic environment for gold nanowires assembly (Figure 1a). The acoustic wave is generated from a piezoelectric transducer that is connected to an arbitrary waveform generator and a power amplifier. The power of the ultrasound wave can be adjusted by modifying the input voltages of the waveform generator, where increasing the input voltage will increase the power of the ultrasound wave. The microfluidic part includes a microrail on a tape layer for the formation of nonuniform acoustic potential and a polydimethylsiloxane (PDMS) microchannel for microfluidic environment. The continuous alternating electric field on the piezoelectric transducer results in continuous ultrasound radiation. Then, the ultrasound radiation passes through the steel sheet and then arrives at...
the microrail, which results in a nonuniform ultrasound potential distribution in the microrail, in which a high ultrasound pressure occurs. As a result, Au nanowires in the microfluidic environment tend to trap in a high-pressure microrail-like node along with the microrail as shown in Figure 1b,c. The trapping remains as the ultrasound is on. Such an ability of programmable nanowire aligning along the designed microrail could lead to a remarkably effective microsystem for the assembly of micro-/nanoparticles.

The reversible assembly and disassembly of Au nanowires on microrails is achieved by modulating the ultrasound field. First, the fabricated Au nanowires are added to the PDMS microfluidic device by pumping injection. The speed of the microfluids is controlled by the injection pump. The bottom piezoelectric ceramic transducer (PZT) transducer generates a vertical acoustic wave that passes through the PDMS microfluidic channel. The presence of the microrail along the vertical direction on the bottom of the PDMS channel breaks the symmetry of pressure distribution of the rectangular water-filled channel and results in a high-pressure area on the microrail, which further leads to the assembly of the nanowires. The microrail-induced uneven pressure distribution is also confirmed by numerical simulations. As shown in Figure 2a, numerical simulations show that the rail line causes the distribution of acoustic pressure intensity along the $x$-$y$ plane so that the high-pressure node occurs at the center of the microrail. Such ultrasound-assisted pressure distribution is also clearly visualized through reversible dispersing of Au nanowires. In the absence of ultrasound irradiation, the Au nanowires display a random Brownian motion near the surface at a speed of about 1 μm s$^{-1}$ as shown in Figure 2b (ultrasound is off, as shown in Video 1, Supporting Information). Upon turning on the ultrasound field, the ultrasound wave passes across the microrail and induces high ultrasound pressure intensity on the microrail. Finally, the interaction between Au nanowires and the ultrasound pressure gradient leads to the migration of Au nanowires toward the microrail and results in assembling in one line as shown in Figure 2b (ultrasound is on, as shown in Video 1, Supporting Information). Such assembly behavior is highly switchable and can be repeated with multiple cycles (two cycles are shown here). Therefore, it is anticipated that the assembling behavior can be moved in a controlled manner by switching the applied ultrasound input "on/off.”

Previous reports have verified that sharp-edge structures could generate acoustic streaming in a fluid [50–52]. The interaction of irregular geometrical-shaped structures with the ultrasound field is much more complicated, which cannot be easily solved by simple acoustic wave equations. Here, we exploit one of the most widely used finite element methods to obtain the numerical simulations of specific geometrical shapes in the liquid domain. In finite element method analysis, the Helmholtz equation for the whole-liquid pressure can be expressed as

$$\nabla^2 p(t) = -\frac{\omega^2}{c_1^2} p(t)$$

where $c_1$ is the speed of sound in liquid, $p(t)$ is the time-dependent sound pressure, and $\omega$ is the angular frequency. To discretize this equation, the liquid domain is divided by a mesh into small free triangular units; thus, the pressure distribution of whole-liquid domain ($M$) is represented by the linear combination of functions of each individual units ($m$) with their own coefficients. By partial integration of Equation (1), only first derivatives are left in the integrand. The boundary conditions are applied as follows

$$n \cdot \nabla p(t) = M(r)$$

Using this approach, any shape of acoustic cavities with any boundary condition can be calculated. In our case, $x$ direction is
an open far-field boundary, it is recommended to construct a boundary such that the incidence angle is near to normal; a lossy-wall condition can be adopted as follows

$$M(r) = -iknp(r)$$  \hspace{1cm} (3)$$

where $n$ is the outward-pointing surface normal of the individual unit, $k$ is a constant related to intensity of liquid and boundary. However, the soft-wall boundary and normal acceleration boundary can be obtained by setting $M(r) = 0$ or $M(r) = a_\nu$, respectively.

The nonuniform distribution of acoustic potential results in acoustic radiation forces that propel micro-/nano-objects toward maximum or minimum pressure areas. The nanowire–nanowire interactions were neglected in the much-diluted nanowire solution. The nanowires experienced steady (time-averaged) hydrodynamic forces, which cause their drifting or clustering at certain space points due to the scattering of waves on the nanowires as described by previous research.\(^{[53]}\) Considering that the dimensions of the nanowires are much smaller than the wavelength $\lambda$, and taking into account of acoustic pressure amplitude $p_0$ and the volume of nanowires $v$, the radiation force acted on nanowires ($F_w$) in $x$–$y$ plane can be expressed as

$$F_w(x, y) = -\frac{\pi}{2\lambda} p_0^2 V \beta_0 \phi(\beta, \rho) \sin \left(\frac{\pi}{\lambda} x\right) \sin \left(\frac{\pi}{\lambda} y\right)$$  \hspace{1cm} (4)$$

where $x$ is the distance of one nanowire from a pressure node. Equation (4) is dependent on mass density ($\rho_w$) and compressibility ($\beta_w$) of the nanowire, which is related to the corresponding properties of the surrounding medium ($\rho_\nu, \beta_0$).

$$\phi(\beta, \rho) = \left(\frac{5\rho_w - 2\rho_\nu}{2\rho_w + \rho_\nu} \right) \frac{\beta_w}{\beta_0}$$  \hspace{1cm} (5)$$

Based on the aforementioned finite element method analysis, numerical simulations of the acoustic potential of microrail inside a microchannel are performed. To investigate the influence of the microrail widths on the assembly of Au nanowires, two kinds of microrails (narrow microrail: rail width $<\ll$ nanowire length, wide microrail: rail width $\approx$ nanowire length) are prepared, as shown in Figure 3a,b. As for the narrow microrail, numerical simulation results in $x$–$z$ plane (Figure 3c) based on the aforementioned finite element method that indicates that the pressure level near the $x$-axis in the microrail area is high. Such high pressure in the microrail enforces the nanowires to move toward the microrail and assemble into one line in parallel to the microrail as shown in Figure 3e (see Videos, Supporting Information). In contrast, numerical simulation results of the wide microrail show that the pressure level next to bottom of the microchannel ($x$–$z$ plane, Figure 3d) in the microrail area separates into two high-pressure nodes. Such pressure gradient in the microrail forcibly drags the Au nanowire toward two high-pressure areas and results in assembly of Au nanowires in perpendicular to the direction of the microrail, as shown in Figure 3f (see Video 2, Supporting Information).

Collection and transportation of artificial micro-/nanoparticles in microfluidic solutions are particularly attractive for a wide range of applications.\(^{[22]}\) Figure 4a shows the ultrasound-assisted collection ability along the microrail with a microfluidic direction of 75° from the microrail. Initially, all the nanowires move along with the flow crossing the microrail. Turning on the acoustic field leads to rapid trapping of the nanowires toward the microrail. Such behavior is based on the acoustically generated uneven distribution of pressure that triggers spontaneous migration of Au nanowires toward high-pressure regions. The tracking trajectories of four Au nanowires are shown in Figure 4b. Nanowires are trapped by the ultrasound-generated rail-assisted radiation force and are transported along with the microrail. As expected from simulations, most of the Au nanowires are trapped by the microrails. Time-lapse images in Figure 4c (see Video 3, Supporting Information) show the trapping and transportation of the four Au nanowires in deionized water under an ultrasound field with a transducer voltage of 2 V and a frequency of 655 kHz. Such attractive behaviors hold great promise for nanoscale delivery applications.
In conclusion, we demonstrate the ability of using acoustic fields to trigger the assembly and transportation of Au nanowires on microrails. The application of ultrasound radiation generates an ultrasound pressure gradient along the microrail and results in trapping Au nanowires in microrail. Based on the finite element method analysis, the validation of pressure distribution is achieved using numerical simulations of acoustic potential inside microrails with different widths. High pressure is found in the narrow microrail that leads to the assembly of the nanowires in parallel to the direction of the microrail, whereas the two high-pressure nodes in the wide microrail could drag Au nanowires toward two high-pressure areas, resulting in the assembly of Au nanowires in perpendicular to the microrail. Such ability of programmable nanowire assemblies along predetermined paths could lead to a remarkably effective microsystem for micro-/nanoparticles assembly, providing possibility in cell collection, enrichment detection, and low-cost production of nanoelectronics.

Experimental Section

Synthesis of Nanowires: The gold nanowires were prepared by electrodeposition of Au into alumina membrane template ( nanopores size: ...
\[ \phi = 200 \text{nm} \times 60 \mu \text{m}, \text{Whatman} \], followed by the next steps. First, working electrode on the membrane was papered by sputtering a thin gold film. Then, the alumina membrane with aluminum foil serving as an electrical contact for the electrodeposition was assembled in a Teflon plating cell. Au nanowires were plated (CHI 660D, CH Instruments, Inc.) using a chloroauric acid solution (HAuCl₄·3H₂O, Segema) with a total charge of 1.5 C and a potential of −0.9 V (vs Ag/AgCl), along with platinum wire as the counter electrode. Then, Au nanowires were released by immersing the membrane in a 3 M NaOH solution for 30 min. Finally, the nanowires were separated from the solution by centrifugation at 10,000 rpm for 5 min and washed repeatedly using ultrapure water (18.2 MΩ cm). All chemicals were analytical-grade reagents and were used as received without any further purification and diluted in Milli-Q ultrapure water when not otherwise specified. Experiments were conducted at room temperature. Microscope images and videos were taken with digital complementary metal oxide semiconductor (CMOS) camera (Andor Zyla 4.2).

Ultrasound Equipment and Microfluidic Channels: The ultrasonic experiments were conducted in a microfluidic channel, which is similar to previous reports.[34,35] The piezoelectric transducer (\( \phi = 25 \text{mm} \times 1.2 \text{mm} \), Wuxi Huifeng PiezoElectric Co., Ltd., China) was attached to the bottom center of a steel sheet (thickness: 0.5 mm), which was connected to a 160 MHz arbitrary waveform generator (SDG5000, Siglent, China) and a power amplifier (MWPA, Mwstore, China). The waveform generated from the generator was a continuous sine wave with variable frequencies (500–700 kHz) and variable voltage amplitudes (0–100 V) for different requirements. The steel sheets were covered by one tape layer and the microrail on the tape layer was simply obtained by scratching. The PDMS microchannel (length: 1 cm and width: 0.1 cm) was fabricated using standard soft-lithography and mold-replica techniques. The silicon substrate for the microchannel was first patterned by photoresist (Shipley 1813) and etched by deep reactive ion etching. Then, Sylgard 184 Silicone Elastomer Base (1:10 weight ratio) was casted onto the silicon mold at 65 °C for 30 min to obtain the microchannel.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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