Electrostatic tweezer for droplet manipulation

Jin, Yuankai; Xu, Wanghuai; Zhang, Huanhuan; Li, Ruirui; Sun, Jing; Yang, Siyan; Liu, Minjie; Mao, Haiyang; Wang, Zuankai

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Various physical tweezers for manipulating liquid droplets based on optical, electrical, magnetic, acoustic, or other external fields have emerged and revolutionized research and application in medical, biological, and environmental fields. Despite notable progress, the existing modalities for droplet control and manipulation are still limited by the extra responsive additives and relatively poor controllability in terms of droplet motion behaviors, such as distance, velocity, and direction. Herein, we report a versatile droplet electrostatic tweezer (DEST) for remotely and programatically trapping or guiding the liquid droplets under diverse conditions, such as in open and closed spaces and on flat and tilted surfaces as well as in oil medium. DEST, leveraging on the coulomb attraction force resulting from its electrostatic induction to a droplet, could manipulate droplets of various compositions, volumes, and arrays on various substrates, offering a potential platform for a series of applications, such as high-throughput surface-enhanced Raman spectroscopy detection with single measuring time less than 20 s.

tweezers | droplet manipulation | electrostatic induction | SERS

Since the emergence of optical tweezers that are capable of trapping and manipulating microparticles in a remote and noninvasive manner in 1986 (1), the tweezers have evolved to diverse forms, such as magnetic tweezers (2) and acoustic tweezers (3). These tweezers have been widely used to manipulate many kinds of micro-/nanometal particles, bioparticles, liquid droplets, and so on. In particular, well-controlled liquid droplet manipulation is essential to various practical fields (4–7), such as printing technology (8), heat management (9–11), water harvesting (12, 13), biological assays (14), chemical reactions (15, 16), and frost prevention (17, 18). Despite remarkable significances, the droplet manipulation using these physical tweezers has achieved less progress, probably owing to the fluidic nature of droplets, which are soft and deformable in diverse operating conditions and mediums. Current approaches to manipulating droplets mainly take advantage of surface force gradient (3, 4, 9, 19–27) or the force directly applied to droplets, which always demand the responsiveness of substrates or droplets for force sources. As one of the most important physical fields to generate driving force, the electric field offers the intrinsic advantage that it comprises an electrode tip connecting with a power source, droplet, and substrate that is electrically grounded.

Here, we report a versatile droplet electrostatic tweezer (DEST) for remote and noninvasive manipulation of droplets on the basis of electrostatic induction. Due to the inherent responsiveness of liquid droplets to the electrostatic field, the droplets on conductive superhydrophobic surfaces obtain temporary and adjustable induced charges, and therefore, they could be trapped and guided by a noncontact tweezer, which is further proven by the diverse droplet types on diverse substrates. Such a DEST allows us to maneuver the droplets with a wide volume range (from tens of nanoliters to several milliliters) and amount range (from one to seven or more droplets) on both open surface and closed channels, even under oil. DEST could also programatically manipulate droplets with high velocity (81.6 mm/s or faster), unlimited distance, agile direction steering, and a precise droplet stopping point without the need for any responsive agents in droplets and substrates, which offers a potential platform for the chemical reaction carrying solid cargo, surface-cleaning, and high-throughput surface-enhanced Raman spectroscopy (SERS) detection.

Results

Fig. L4 shows the schematic drawing of the DEST system, which comprises an electrode tip connecting with a power source, droplet, and substrate that is electrically grounded. Here, the superhydrophobic copper oxide substrates are used (characterized in SI Appendix, Fig. S1), aiming to reduce the

Significance

The manipulation of liquid droplets plays a crucial role in multidisciplinary applications. However, existing methods still face many challenges, such as short distance, low velocity, restricted operating conditions, the need for extra responsive additives in droplet, and so on. To circumvent these constraints, here we develop a droplet electrostatic tweezer to trap the liquid droplet or faithfully guide the droplet motion in a remote manner. Our method allows high flexibility and precision in manipulating droplets of different types, volumes, and numbers under different working conditions, such as in open and closed spaces and on flat and tilted surfaces as well as in oil medium, imparting various applications, such as high-throughput and high-sensitivity Raman detection.
When an external voltage is applied on the electrode tip, electrostatic induction causes the redistribution of charges in droplet and substrate, which is similar to the well-known classical electrostatic induction of conductive solid materials (Fig. 1B) (36, 37). In brief, the charged object X electrostatically induces the redistribution of charges in objects Y and Z when they are closing (step 1), and the charges stemming from electrostatic induction are defined as induced charges. The variation of induced charges in the water droplet (~7 μL) as a function of the applied voltage of the tweezer with a diameter of 2 mm. The positive and negative values denote the polarity of induced charges. The error bars are based on the SD values of five tests. Maxwell stress tensor exerting on the droplet in the lateral direction ($T_x$) and the vertical direction ($T_y$). These results are based on the finite-element analysis of the water droplet (~7 μL) under the tweezer voltage of 4 kV, and the tweezer diameter is 2 mm. Phase diagram showing different droplet dynamic behaviors under various applied voltages ($V$) and electrode diameters. In region I (black circles), the droplet is stationary. In region II (red triangles), the droplet moves horizontally toward the tweezer, and in region III (blue squares), the droplet finally detaches from the surface due to overlarge coulomb force. The red and blue dashed lines illustrate the minimum voltages for regions II and III, respectively, suggesting the agreement between the simulation and experimental results. Schematic drawing for electrostatic induction of water droplets on nongrounded substrates. In contrast to on grounded substrates, the magnitude of induced charges in droplets on nongrounded substrates is less. Time-resolved optical images showing the motion of a colored water droplet on the patterned polystyrene substrates with and without electrically conductive (gold) coating. The water droplet on the gold-coated region (conductive and being grounded) moves following the electrode (from 0.0 to 2.0 s), but the droplet on the non-coated region (insulating) is not faithful to the tweezer (from 2.2 to 3.6 s); therefore, it finally stops at a random position. The x-y position of the water droplet denoting the real-time droplet position when it moves from conductive to the insulating area.
droplets under the various applied tweezer voltages \(V\) could also be quantitatively measured by separating droplets and substrates (illustrated in SI Appendix, Fig. S2A), and Fig. 1C shows the linear relationship between \(Q\) and \(V\), expressed as \(Q = -0.02\ V\). Such a result suggests that the induced charges in droplets can be tailored by voltages applied to the tweezer, causing the adjustable electrostatic coulomb force between tweezer and droplet (SI Appendix, Fig. S3). Note that the generation of induced charges in droplets is reversible in an on-demand manner (SI Appendix, Fig. S4). In this system, the electrode tip that provides the electrostatic induction to the droplet is reminiscent of an invisible tweezer, in analogy to other physical modalities tweezers (1, 2).

The adjustable coulomb force \(F_C\) exerting on the droplet could be quantified via the following equation:

\[
F_C = \oint T_{ij} \cdot n dS, \text{ with } T_{ij} = \epsilon_0 \left( E_i E_j - \frac{\delta_{ij}}{2} E^2 \right), i,j = x,y,
\]

where \(T_{ij}\), \(n\), \(\delta_{ij}\), and \(E\) are the Maxwell stress tensor, the surface unit normal, the Kronecker delta function, and the magnitude of the electric field intensity, respectively (38). \(T_{ij}\) in the lateral direction \((T_x)\) and vertical direction \((T_y)\) is obtained by finite-element analysis using the COMSOL-Multiphysics simulation, demonstrated in Fig. 1D.

Note that the \(F_C\) in the direction perpendicular to the plane is symmetric, and thus, there is no actual force on the droplet.

On the basis of adjustable electrostatic interaction between the droplet and the tweezer, we determined three different scenarios of droplet dynamic behaviors by both theoretical analysis and experimental observation (Fig. 1E and SI Appendix, Fig. S5 and Note S1). In region I, the droplet remains stationary because the coulomb force is small relative to the lateral adhesion force. As the voltage increases (region II), the droplet moves horizontally and finally stabilizes at the position below the tweezer. This state is the main focus of our work, in which the voltage required for the steady droplet manipulation also depends on the diameter of tweezer (SI Appendix, Fig. S6). In region III, the droplet is lifted by the tweezer because of the strong electrostatic force (SI Appendix, Fig. S7). Note that the droplet dynamics are independent of the polarity of the applied voltages (SI Appendix, Fig. S8).

The well-controlled droplet manipulation in the DEST also demands that substrates should be grounded and electrically conductive to provide a free channel for charge release. The electrically conductive but nongrounded substrates could also obtain induced charges, causing the less induced charges in droplets (Fig. 1F and SI Appendix, Fig. S9A). As a result, the DEST’s control for droplets is weaker due to the reduced electrostatic force even totally collapsed, which is detailed in Fig. 2.
The importance of grounded and electrically conductive substrates is further revealed by comparing the droplet manipulation on grounded conductive substrates and insulating substrates. Briefly, we deposited a gold layer (~40 nm) on the left part of the insulating polystyrene surface and then sprayed a commercial superhydrophobic spray on the surface to make the whole surface superhydrophobic. When the tweezer is moved from the grounded gold-coated (conductive area) to the noncoated (insulating) area, the colored water droplet first moves following the tweezer from 0.0 to 2.0 s. However, upon moving to the insulating area, the droplet escapes from the control of the tweezer and stops at a random position at 3.6 s (Fig. 1G and Movie S1). The time-resolved x–y position of the water droplet (Fig. 1H) depicts that the droplet regularly moves on the gold-coated area but that it randomly moves on the noncoated area and finally stops at an unpredictable endpoint. Such undesired movement mainly results from the electrostatic interaction of droplets with randomly distributed triboelectric charges on the insulating surface (39).

**SI Appendix, Note S3.**

The DEST is generic to diverse types of droplets on electrically conductive substrates, larger or smaller droplets, droplet arrays formed by multidoplets, and various operating conditions. Given the vital roles of electrostatic induction in the DEST, we first considered the effect of the droplet's conductivity on induced charges in droplets. By adding various concentrations (0.01, 0.1, and 1 M) of NaCl into the droplets, we obtained droplets with various conductivity (SI Appendix, Fig. S10) and measured their induced charges under the DEST. In Fig. 2A, the amounts of induced charges in these droplets are almost the same under both 4- and ~4-kV tweezer voltages. In addition, Fig. 2A also demonstrates the induced charges in droplets are not affected by the salt types and their ionic valences, such as bivalent (CaCl$_2$, Na$_2$SO$_4$) and trivalent (FeCl$_3$, Na$_3$PO$_4$) ions. These results indicate that the magnitudes of induced charges of droplets and hence, their motion velocities are not sensitive to the salt concentration and ion types (SI Appendix, Fig. S11). Furthermore, we also demonstrated the manipulation of liquid noble on a copper surface, glycerol on a superhydrophobic alumina surface, and tris(hydroxymethyl)aminomethane hydrogen chloride (Tris-HCl) buffer on a superhydrophobic indium tin oxide (ITO)–coated glass surface (Fig. 2B and Movie S2). In all these cases, liquids are responsive to the electric field, as affirmed by the induced charge measurement (Fig. 2C). In comparison, liquid droplets with weak responsiveness to the electric field, such as apolar and insulating silicon oil, cannot be manipulated because of minimal interaction between the tweezer and the droplet (SI Appendix, Fig. S12).

Different from previously reported methods, the remote and spatially distributed coulomb force of the DEST allows us to manipulate the droplets with a wide range of volumes and even droplet arrays (Movie S3). Fig. 2C shows that droplets with volumes ranging from tens of nanoliters to several milliliters could be moved by the tweezer, demonstrating a broad volume range up to five orders of magnitude, which is three orders of magnitude higher than that reported in recent work (40). Furthermore, the DEST could also simultaneously manipulate multidroplets in an array because the droplets carry the same polarity of electrostatically induced charges, as shown in the lower part of Fig. 2C where seven droplets are manipulated without merging. This kind of multidroplet manipulation is rarely reported in the literature to the best of our knowledge. Indeed, more droplets could also be remotely manipulated by changing the applied voltage and diameter of the tweezer, and these droplets always spontaneously form an array. In addition to an open plane surface, the remote electrostatic force also allows us to precisely manipulate the droplet on a sloped surface (Fig. 2D), under oil environment (Fig. 2E), and in a closed channel with a zigzag track (Fig. 2F), which is shown in Movie S4. Another intriguing point of this manipulation method is that the electrode connecting with the power supply could be replaced by objects carried triboelectric charges. **SI Appendix, Note S4.**
Fig. S13 shows the droplet manipulation by glass rods with positive static charges and rubber rods with negative charges, demonstrating a low-energy consumption property of such a DEST.

The distinctive features of the DEST are further revealed by different droplet manipulation modes in response to the actuation of tweezer, including the guiding mode, the trapping mode, and the continuous trapping mode. Fig. 3A shows that the droplet moves faithfully under the guidance of the tweezer, referred to as the guiding mode. Unlike other reported methods in which a predetermined pathway for droplets is required (27, 34, 35), the manifestation of the guiding mode enables the droplet to move to any desired position simply by programming the motion of the tweezer. However, at a higher average velocity (∼81.6 mm/s) (Fig. 3B and Movie S5), the droplet still synchronously follows the motion of the tweezer, benefiting from its fast responsiveness for electrostatic induction (∼16 ms) (SI Appendix, Fig. S14). Such spatiotemporal precision in the guiding mode is of great importance for many applications where liquid droplets are involved, such as a microreactor. In the trapping mode, a droplet moves in a manner of damping oscillation and is finally trapped by the tweezer (SI Appendix, Fig. S15), which is analogous to the trapping of nanoparticles by the optical tweezer. As shown in Fig. 3C, by sequentially activating the state of individual tweezer in an on-demand manner, a droplet can be manipulated to the preferred position (Movie S6). In contrast, in the continuous trapping mode, all tweezers are “on,” and a droplet continuously moves along with the tweezer arrays (Fig. 3D and Movie S7). Taken together, our DEST demonstrates overwhelmingly collective performances over other counterparts in the aspects of droplet motion behavior, manipulating condition, and less limitation for the droplet itself (Fig. 3E).

Fig. 4. The applications of the DEST. (A) Sequential images showing the electrostatic manipulation of droplets for chemical reaction. (A1 and A2) A 0.1 M AgNO₃ aqueous droplet is guided by the DEST to merge with the 0.1 M FeCl₃ aqueous droplet, and the coalescing droplet becomes muddy due to the formation of AgCl. (A3) The muddy droplet containing Fe⁺⁺ is further manipulated to react with the 0.05 M KSCN aqueous droplet, generating the red Fe(SCN)₂⁺. (B) The transportation of a solid sphere driven by two water droplets. (B1 and B2) The cargo carrier system moving toward the right is mainly driven by the colored water droplet. (C) Surface-cleaning application of the DEST. (C1 and C2) W-shape track is cleaned by the droplet. (D) Schematic drawing of the DEST-based SERS platform. The superhydrophobic substrates are functionalized by successively depositing parylene C and silver nanoparticles on a carbon soot-coated glass slide. The droplet carried with analyst obtains the plasmonic silver particle during its movement to the laser point, therefore showing an enhanced sensitivity of Raman detection. After the measurement, the first droplet is moved away, and then, the second droplet is moved to the detected position by the DEST. (E) The SERS spectra of an R6G aqueous droplet (1 × 10⁻⁸ M), MG (1 × 10⁻⁷ M), and the blank substrates after removing these droplets at the same detected point. The Raman shift (cm⁻¹), intensity (a.u.), and the colored area denotes the typical peaks of R6G and MG.
the tweezer. Furthermore, the unlimited direction in droplet manipulation allows us to clean the contaminants on the surface with any wanted route by programming the motion of the droplet. Fig. 4C shows that the “W”-shaped area is cleaned by the droplet under the guidance of the tweezer, illustrating precise control of the DEST on droplet motion.

The superhydrophobic substrates in our DEST system can also be functionalized with specific probes as amplification agents, imparting enhanced performances for chemical/biological analysis. As a demonstration, a superhydrophobic parylene C-coated carbon soot surface was first prepared, followed by depositing a thin silver layer made of silver nanoparticles for high-sensitivity and high-throughput SERS detection. On such a substrate, droplets carrying highly diluted aqueous analyte could pick the silver nanoparticles during motion (Fig. 4D), therefore showing an enhanced sensitivity in Raman measurement due to the plasmonic properties of silver nanoparticles (42). Such a method dramatically increases the detecting efficiency and sensitivity (SI Appendix, Fig. S14) in comparison with the traditional method, which adds plasmonic nanoparticles into the solutions of analytes, especially for the measurement of multiple analytes. In addition, DEST-based SERS eliminates the need for precise laser focusing, analytic enrichment, and substrate replacement (43–45), offering high throughput. As a result, the whole measurement process, including moving the droplet to the detecting spot, measuring, and moving the droplet away, only costs less than 20 s. Fig. 4E depicts the Raman signals of low concentration of rhodamine 6G (R6G; 1 × 10−6 M) (Fig. 4E, red line) and malachite green (MG; 1 × 10−7 M) (Fig. 4E, blue line), and two blank signals prove that there is no residual on the surface after the droplet is moved away, which demonstrates the feasibility of the DEST in high-throughput and high-detection sensitivity.

Discussion

In summary, we demonstrate that the largely neglected electrostatic charges can be harnessed as the driving force of the invisible tweezer, imparting the versatile and remote manipulation of the droplet of different types, volumes, and numbers under different working conditions, such as in the closed tortuous channel and in oil medium. We also identify the critical conditions to achieve the tweezer-like functionalities. Compared with other techniques, our method endows high flexibility and precision in droplet motion, including achieving high average velocity, long distance, and agile direction maneuverability. We envision that the technology developed by us can find a wide range of applications where droplets are involved: for example, high-throughput biological/chemical analysis.

Materials and Methods

Sample Preparation. 1H, 1H, 2H, 2H-perfluorodecanethiol (97%; Sigma-Aldrich), perfluorooctanoic acid (95%; Sigma-Aldrich), glycerol (99.0%; Sigma-Aldrich), Mg (J&K), R6G (J&K), and salts purchased from Sigma-Aldrich, including NaCl, NaClO3, NaOH, Na2PO4·12H2O, FeCl3, KSCN, and AgNO3, were used without further purification.

The nanogroove structure of copper oxide was obtained by chemically etching the cleaned copper in a hot (96 °C) alkaline solution including NaClO3, NaOH, Na2PO4·12H2O, and deionized water (at 3.755:10:100 wt ratio) for 15 min. Then, the immersion of copper oxide in a 0.5 mM 1H, 1H, 2H, 2H-perfluoro-octanoanethol solution for 2 h could make the copper oxide superhydrophobic. The superhydrophobic alumina substrates were obtained by successively immersing the cleaned aluminum in a 2.5 M HCl solution for 15 min, hot water (100 °C) for 5 min, and a 0.01 M perfluorooctanoic acid aqueous solution for 1 h. To render ITO-coated glass, polystyrene, gold-coated polystyrene, and other substrates superhydrophobic, these substrates were first sprayed using a commercial superhydrophobic spray, Glaco (purchased from Soft99 Corporation), followed by heating at 60 °C for 5 min. The SERS surface was prepared using the combined candle soot and thin-film deposition processes (42). Briefly, a candle soot layer was first formed by placing a freshly prepared glass above a burning candle flame for 15 s. Then, the candle soot-coated substrate was deposited by a thin parylene C film (~150 nm) using specialized vacuum deposition equipment (Specialty Coating Systems, Inc.) as well as a thin silver film (~30 nm) composed of nanoparticles using a vacuum sputter coating apparatus (Denton Vacuum LC).

Instrument and Characterization. The induced charges in droplets were measured using a Faraday cup connected to a nanocoulomb meter (Monroe; Model 284) using the method shown in SI Appendix, Fig. S2. The nanogroove morphology of CuO was observed by a scanning electron microscope (Quanta TM 450; FEG). The motion of the droplet, programmatically controlled by a stepper, was recorded by a high-speed camera (Fastcam SA4; Photron Limited) and analyzed using the software ImageJ. The gold coating on the polystyrene surface was coated with a dual-target sputtering system (Q150TS; Quorum). The electric conductivities of NaCl aqueous solution were directly measured by directly immersing the probe of the handy conductivity meter (LC-DDB1M and CT-20; Lichen Tech.) into the solutions for 10 s. The static and dynamic contact angles of water droplets on superhydrophobic surfaces were measured by a Kruss DSA100 contact angle goniometer at ambient temperature, and the results are shown in SI Appendix, Table S1. Here, the dynamic contact angles (θa and θr) were measured by gradually increasing or decreasing the volume of droplets until the baseline of the droplet started to move.

Data Availability. There are no data underlying this work.

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