



Solid-to-Liquid Charge Transfer for Generating Droplets with Tunable Charge

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Abstract: Charged liquid droplets are typically generated by a high-voltage power supply. Herein, a previously unreported method is used for charging liquid droplets: by transferring charge from an insulating solid surface charged by contact electrification to the droplets. Charging the solid surface by contact electrification involves bringing it into contact with another solid surface for generating static charge. Subsequently, water droplets that flow across the surface are found to be charged—thus, the charge is readily transferred from solid to liquid. The charge of the droplets can be tuned continuously from positive to negative by varying the way the solid surface is charged. The amount of charge generated is sufficient for manipulating, coalescing, and sorting the water droplets by solid surfaces charged by contact electrification. This method of generating charged droplets is general, simple, inexpensive, and does not need any additional equipment or power supply.

Electrically charged droplets are useful in a wide variety of applications, including ink-jet printing, electrospray ionization for mass spectrometry, scrubbers for removing particulates in an air stream, and fabrication of materials (e.g., nano-scale materials and particles for drug delivery).^[1–8] In these applications, the liquid droplets are usually charged by a high-voltage power supply. Liquid can also be charged using other methods; examples include pressure-driven flows across initially uncharged channels (e.g., from millimeters to nanometers in size),^[9–12] electrostatic induction (e.g., the Kelvin water dropper), and electrostatic charging of jumping droplets.^[13] These methods, however, either require an external power supply, are technically challenging to operate, or are unable to control the charge of the liquid.

Herein, we describe a previously unreported method for charging water droplets: we transfer charge from a solid surface charged by contact electrification into the droplet (Figure 1). Contact electrification is the phenomenon in which static charge is generated when two surfaces are brought into contact and are then separated. After the contact, one surface charges positively, while the other charges negatively. The mechanisms that underlie the separation of charge in contact electrification is incompletely understood. Several mechanisms have been proposed in previous studies, including electron transfer,^[14,15] ion trans-

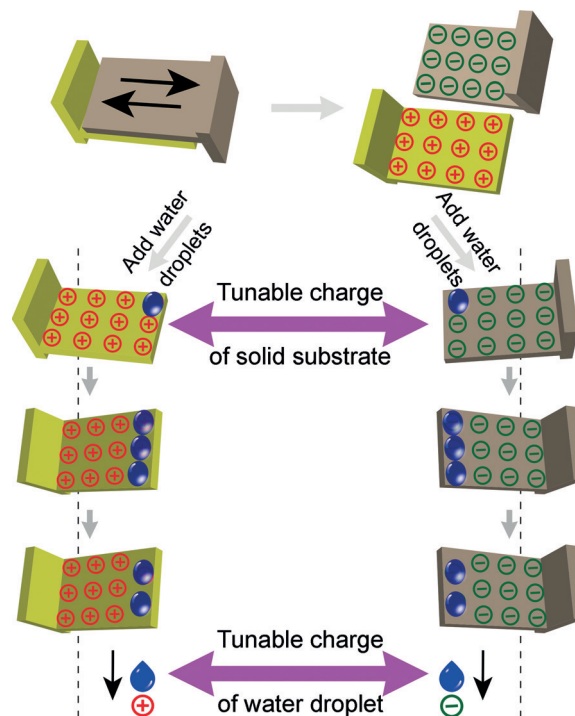


Figure 1. Generating water droplets with tunable charge. First, two solid surfaces are rubbed against each other such that one surface charges positively while the other surface charges negatively via contact electrification. Water droplets can be charged by flowing them across the charged solid surface. When the solid surface is positively charged, the droplet tends to charge positively; when the solid surface is negatively charged, the droplet tends to charge negatively. Different amounts of charge of the solid surfaces generate droplets of different amounts of charge.

fer,^[16] material transfer,^[17,18] and others (e.g., contact de-electrification^[19,20] and the stabilizing effect of radicals^[21]). Fundamentally, the identity of the charge species that is responsible for the generation of charge on surfaces is still under debate.^[16,22,23]

Although the mechanisms that underlie contact electrification and the identity of the charge species are not completely understood, we found from our experiments that it is possible to transfer charge from a solid surface charged by contact electrification to water droplets when they come into contact. A positively charged solid surface tends to charge the water droplets positively, while a negatively charged solid surface tends to charge the water droplets negatively (Figure 1). Importantly, the method is inexpensive, and does not require any external machinery or power supply.

In one experiment, we first charged the surface of a piece of polyamide (nylon) positively by rubbing it against a piece

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of polytetrafluoroethylene (PTFE). The charge of the piece of nylon was measured using a Faraday Cup connected to an electrometer (see Supporting Information, Methods and Materials). We placed a droplet of de-ionized water (0.1 mL) on the charged surface of the piece of nylon, and allowed it to slide down the surface under gravity. The droplet was then dropped into the Faraday Cup for measuring its charge. Since the piece of nylon was charged positively, the water droplet was found to charge positively as well (Figure 2a). In a separate experiment, we charged the piece of

two solid surfaces against each other with a larger force. Accordingly, we performed a series of experiments in which we rubbed nylon against either PTFE or PEGDA with a different force for each experiment. We then flowed droplets of water across the surfaces, and measured their charges. Results show that the charge of the water droplet is approximately linearly proportional to the charge of the nylon that it contacted with (Figure 2a).

To demonstrate the generality of the method, we repeated the experiments using a piece of polydimethylsiloxane (PDMS) and a piece of PTFE instead of nylon. For PDMS, we found that the results are qualitatively similar to the case of nylon—the charge of the water droplet is approximately linearly proportional to the charge of PDMS (Figure 2b). For PTFE, interestingly, the results show that when the surface was charged slightly negatively, the water droplets charged positively instead (Figure 2c). Previous studies have shown that an uncharged solid surface can charge water droplets positively.^[9,24] Hence, it seems that a water droplet can be charged either positively or negatively by a piece of negatively charged PTFE, depending on the amount of negative charge the piece of PTFE has.

After finding that charged water droplets can be generated by solid surfaces charged by contact electrification, the question is: is the amount of charge gained by the water droplet sufficient for practical applications related to charged droplets? We demonstrated that these charged water droplets can be manipulated simply by solid surfaces charged by contact electrification. Manipulation is important for microfluidic systems that are based on droplets flowing in an immiscible fluid. Droplet-based microfluidic systems have been introduced as an effective strategy for compartmentalizing chemicals and biomolecules for applications such as microreactors for performing multiple chemical reactions in parallel.^[25] Other applications include drug discovery, gene-expression analysis, protein crystallization, screening of catalytic activities, and the analysis of single cell and biomolecules.^[26–28] Operationally, the droplets need to be manipulated across the microfluidic channels for their intended purposes. Methods used to manipulate the droplets include channels with specific geometrical design, valves, electric field, magnetic field, thermocapillary effect, optical tweezer, or acoustic wave.^[29–32] These methods, however, cannot allow the droplets to be manipulated flexibly, or require the use of external machinery to operate. On the other hand, it is desirable to create systems that are low cost, portable, easy to use, and preferably, systems that operate without any external power supply.^[33–37] Such a method would be particularly useful for low-cost, point-of-care diagnostics.^[38]

To demonstrate that the charged water droplets can be manipulated flexibly, we first charged a water droplet (0.03 mL) positively by flowing it across an initially uncharged perfluoroalkoxy (PFA) tube (see Supporting Information, Methods and Materials). The droplet was placed on the air-liquid interface of a Petri dish filled with silicone oil (Figure 3a). We charged a piece of PTFE negatively by rubbing it against a piece of nylon, and placed it next to the positively charged droplet (distance ca. 3 cm). We observed that the

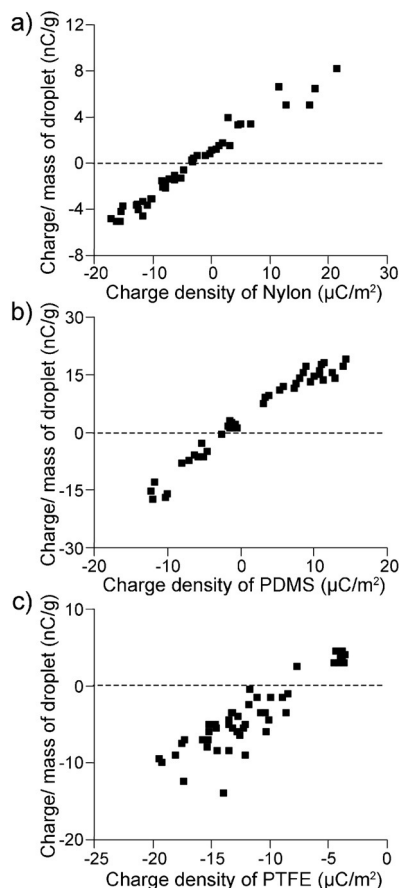


Figure 2. Tuning the charge of water droplets with solid surfaces of different charges and materials. Water droplets are charged when they flow across a) a polyamide (nylon), b) a polydimethylsiloxane (PDMS), and c) a polytetrafluoroethylene (PTFE) surface.

nylon negatively by rubbing it against a piece of poly(ethylene glycol) diacrylate (PEGDA). After sliding a droplet of water across the negatively charged surface and measuring its charge, we found that the droplet charged negatively (Figure 2a). Thus, although the identity of the charge species that is responsible for contact electrification of two solid surfaces is not known, we showed in this work that the charge on the solid surface is readily transferrable to a liquid phase.

In general, we found that it is possible to tune the charge of the droplet: when a droplet is in contact with a solid surface with a higher charge, the droplet gains a higher charge. The charge of the solid surfaces can be increased by rubbing the

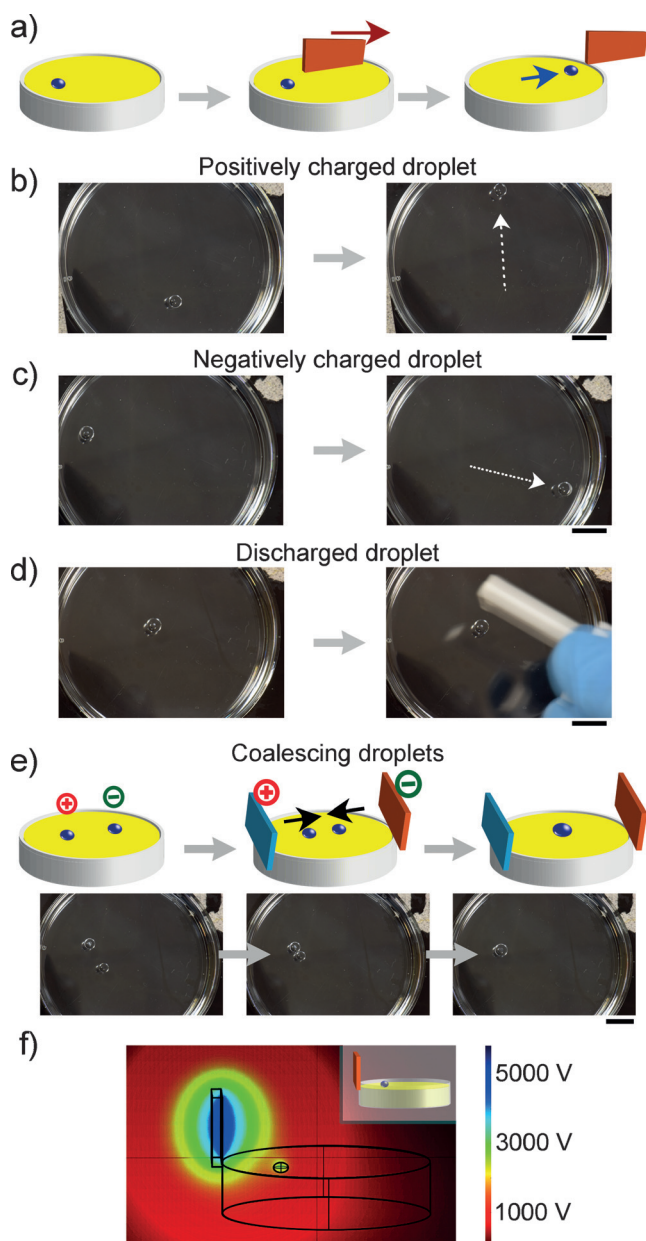


Figure 3. Manipulating and coalescing water droplets of different charges. a) Water droplets of different charges were placed in a Petri dish filled with oil. When a piece of charged solid was placed close to a droplet of opposite polarity, the droplet was attracted to the solid. When the piece of solid moved, the droplet followed accordingly. b) A positively charged water droplet moved under the influence of a piece of negatively charged PTFE. c) A negatively charged water droplet moved under the influence of a piece of positively charged nylon. d) For a discharged droplet, it remained stationary when a piece of negatively charged PTFE was placed close to it. e) When a piece of negatively charged PTFE was placed close to a negatively charged droplet and a piece of positively charged nylon was placed close to a positively charged droplet, the two droplets moved toward each other and coalesced. Scale bar: 1 cm. f) The electric potential around a piece of charged solid and a charged water droplet of the same polarity. The inset shows the geometry of the model, which includes the piece of solid, the droplet, and the dish filled with oil.

droplet moved toward the piece of PTFE. Moving the piece of PTFE across the Petri dish caused the droplet to move

accordingly (Figure 3b); hence, we are able to manipulate the droplet using a solid surface charged simply by contact electrification. Similarly, a positively charged nylon can be used to manipulate a negatively charged water droplet (Figure 3c). As a control experiment, we used a discharged water droplet and a piece of negatively charged PTFE; the droplet remained stationary (Figure 3d).

In droplet-based microfluidics, it is often important to coalesce droplets in a controlled manner. For example, controlled coalescence of droplets containing different reactants is needed for performing reactions (e.g., synthesis of molecules, or formation of particles) at the appropriate condition and time.^[39] To demonstrate controlled coalescence, we placed a positively charged droplet and a negatively charged droplet in a Petri dish filled with silicone oil. We then placed a piece of negatively charged PTFE and a piece of positively charged nylon at opposite sides of the Petri dish as shown in Figure 3e. Under the influence of the electric fields of the solid surfaces, the droplets moved toward each other, and coalesced (Figure 3e).

Subsequently, we performed an order-of-magnitude analysis to show that the electrostatic force, F_E , produced by the charged solid surface and the charged water droplet results in the motion of the droplet observed experimentally. For this analysis, we used a model system that involves a single piece of charged solid placed by the side of the Petri dish, and a charged water droplet (Figure 3f, inset). We first solved for the electric potential using COMSOL Multiphysics (Figure 3f), and determined that F_E is on the order of approximately 10 μN (see Supporting Information, Methods and Materials). At steady state, F_E is equal to the drag force, F_D , experienced by the water droplet moving in the silicone oil. F_D can be estimated by $F_D = 6\pi\mu RV_{ss}$, where μ is the viscosity of silicone oil (20 MPas), R is the radius of the droplet (ca. 2 mm), and V_{ss} is the steady-state velocity of the droplet moving in oil. Through this relationship, V_{ss} is calculated to be on the order of approximately 1 cm s^{-1} ; this value agrees with our experimental observations.

Another important type of manipulation that is needed for droplet-based microfluidics is sorting. Sorting allows the droplets to be isolated so that they can analyzed separately.^[39] Experimentally, we dropped a negatively charged water droplet into a container filled with paraffin oil (Figure 4a). At one side of the container, we placed a piece of negatively charged PTFE. Under the influence of the electric field imposed by the piece of PTFE, the water droplet was observed to deflect horizontally away from the piece of PTFE. By reducing the distance between the piece of PTFE and the side of the container, the droplet deflected more horizontally; thus, the droplets can move into different channels. Therefore, it is possible to sort the droplets by actively varying the distance between the piece of PTFE and the side of the container.

Alternatively, it is possible to sort the water droplets autonomously based on the amount of charge that they have. First, we dropped a positively charged water droplet into the container filled with paraffin oil. As it fell, the water droplet was attracted to the negatively charged PTFE, and moved to the edge of the container (top left image of Figure 4b). We

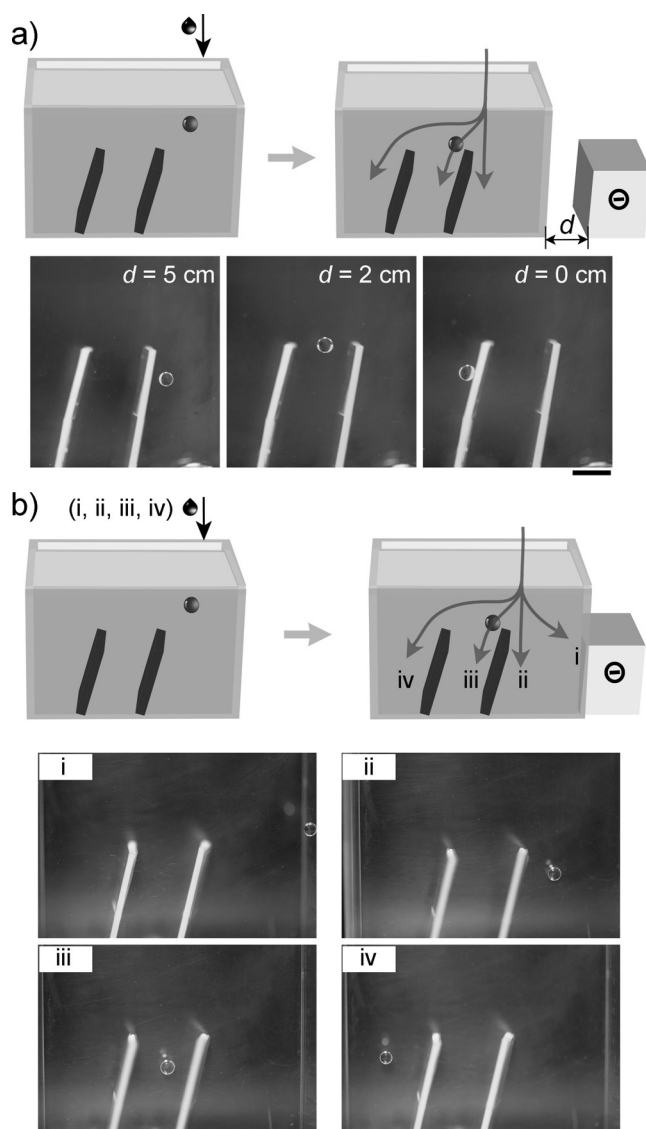


Figure 4. Sorting water droplets. a) Water droplets of the same charge and polarity can be sorted into different channels by placing a piece of charged PTFE at varying distance, d , away from the side of the container. When d was reduced, the droplet deflected more to the left. Different amounts of horizontal deflection caused the droplets to move into different channels. b) Water droplets can also be sorted autonomously according to their charge. In this case, d was kept constant at $d = 0$. (i) A positively charged droplet was attracted to the piece of negatively charged PTFE, and moved to the right side of the container (top left photo). (ii) A discharged droplet fell vertically downward (top right photo). A negatively charged droplet deflected to the left, and moved into the middle channel (bottom left photo). A droplet that was charged to a higher negative charge deflected more to the left and moved into the left channel (bottom right photo). Scale bar: 1 cm.

repeated the experiment for droplets of different charges. A discharged droplet fell vertically downward (top right image of Figure 4b). A negatively charged water droplet (ca. -0.15 nC) deflected horizontally away from the piece of PTFE, and entered a middle channel (bottom left image of Figure 4b). When a water droplet was charged even more negatively (ca. -0.35 nC), it deflected more horizontally, and

entered the channel that was farthest away from the piece of PTFE (bottom right image of Figure 4b).

We analyzed the three types of water droplets that we used in this study: the positively charged, the negatively charged, and the discharged droplet. The charged water droplets were flowed across either a PTFE, nylon, or a PDMS surface. Results from FTIR and NMR spectroscopy did not show any difference for these three types of water samples (see Supporting Information). Hence, at least at the limit of detection of these instruments, they seem pure.

In conclusion, we discussed a general method for generating charged droplets by transferring charge from a solid surface charged by contact electrification to the droplets. This method allows droplets to be charged continuously from positive to negative. The method is general because different solid materials can be used for generating the charged droplets. We demonstrated that the amount of charge generated is sufficient for manipulating, coalescing, and sorting the water droplets; importantly, we used solid surfaces charged simply by contact electrification for controlling the motion of the water droplets. Previous studies that use electric field to manipulate the droplets require a high-voltage power supply to charge the droplets. In addition, a high-voltage power supply is also needed to maintain a high potential on an electrode for manipulating the droplets.^[32] Our method is thus simple to implement, inexpensive, and does not require any additional external machinery or power supply. Because of this combination of advantages, the method may be useful for manipulating droplets in microfluidic systems that need to be low cost and simple to use (e.g., for low-cost and/or point-of-care diagnosis).^[38]

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