

Charging Organic Liquids by Static Charge

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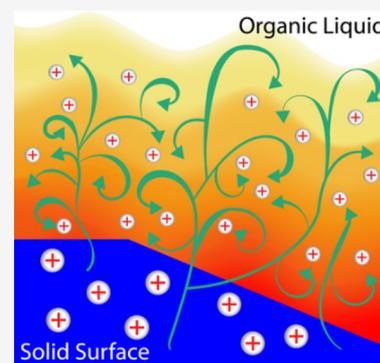


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ABSTRACT: Aqueous liquids can be charged effectively by a number of methods for many important applications. Organic liquids, however, cannot be charged effectively by existing methods due to their low conductivities, especially the insulating nonpolar organic liquids; hence, there has not been any significant application developed based on charged organic liquids. This study describes an effective fundamental strategy for charging organic liquids, including nonpolar organic liquids: static charge is simply mixed into the liquid. Analyses suggested that the charged species are molecular ions that reside in the bulk of the liquid after charging. This method is simple and general, and the amount and polarity of charge can be flexibly tunable. The effectiveness of this method gives rise to opportunities for the development of novel applications. Charged organic droplets are manipulated for the first time by an electric field for controlling organic reactions. Particles with charge embedded in their bulk matrices are fabricated for the first time (i.e., via polymerizing the liquid monomers mixed with static charge). The charge in this novel class of bulk-charged particles is stable and permanent, especially when compared to the typical surface-charged particles. Simultaneous bulk-charged and bulk-magnetic particles are fabricated for the first time via simply mixing both the static charge and magnetic nanoparticles into the liquid monomers. These highly versatile particles are responsive to both electric and magnetic fields for practical applications.



INTRODUCTION

Charging allows a liquid to acquire a number of useful fundamental properties, such as becoming responsive to electric fields (e.g., for control and manipulation) and self-dispersive. These desirable properties of charge form the basis for the development of many important applications of charged liquids, such as electrostatic coating, dispersion of chemicals (e.g., pesticides),^{1,2} mass spectrometry,³ high-resolution printing,^{4,5} fabrication of micro- and nanoscale materials (e.g., polymer scaffolds, crystals, and metallic particles),^{6–9} electrospinning of nanomaterials for different applications (e.g., chemical and biological sensors,¹⁰ superhydrophobic surfaces,^{11,12} and drug delivery^{13,14}), and generation of power.^{15–17} These applications, however, involved almost exclusively aqueous solutions. Due to their relatively high electrical conductivity, aqueous liquids can be charged easily by a number of methods, such as applying a high electric potential to the liquid, flowing the liquid across surfaces of solids (e.g., streaming current),^{15–18} or charging by electrostatic induction (e.g., Kelvin water dropper).^{19,20} On the other hand, it has been challenging to charge organic liquids due to their low conductivities. The methods investigated in previous studies are not effective even after many decades of research—hence, there has not been any significant application developed for these charged organic liquids.^{21,22} Organic liquids have many useful physical and chemical properties. The development of effective charging methods would give rise to plenty of opportunities for novel applications based on charged organic liquids.²¹

Due to the difficulties, however, there have only been very few published studies that explored ways of charging organic liquids. One of the few methods investigated involved applying a high electric potential (e.g., >10 kV) to the liquid via a high-voltage power supply. One important example is the ionization of organic liquids (e.g., electrospray) in mass spectrometry. However, this method is not effective for charging organic liquids, especially nonpolar liquids, because it requires a sufficient amount of electrical conductivity of the liquid for charging.²¹ Conductivities of organic liquids range from low to completely insulating for nonpolar organic liquids (e.g., $\sim 10^{-17}$ S/m for hexane and 7×10^{-16} S/m for cyclohexane).²³ Hence, many organic liquids cannot be charged adequately by a high electric potential for practical applications (e.g., electrospray requires solvents with sufficiently high dielectric constants).^{24,25} Substantial amounts of conductive additives (e.g., salts that are soluble in nonpolar liquids and ionic liquids) are thus routinely added to increase their conductivity (i.e., typically by several orders of magnitude) so that they can be charged effectively by a high electric potential (i.e., via transferring the charge generated at the solid–liquid interface of the high-potential electrode into the bulk volume of the

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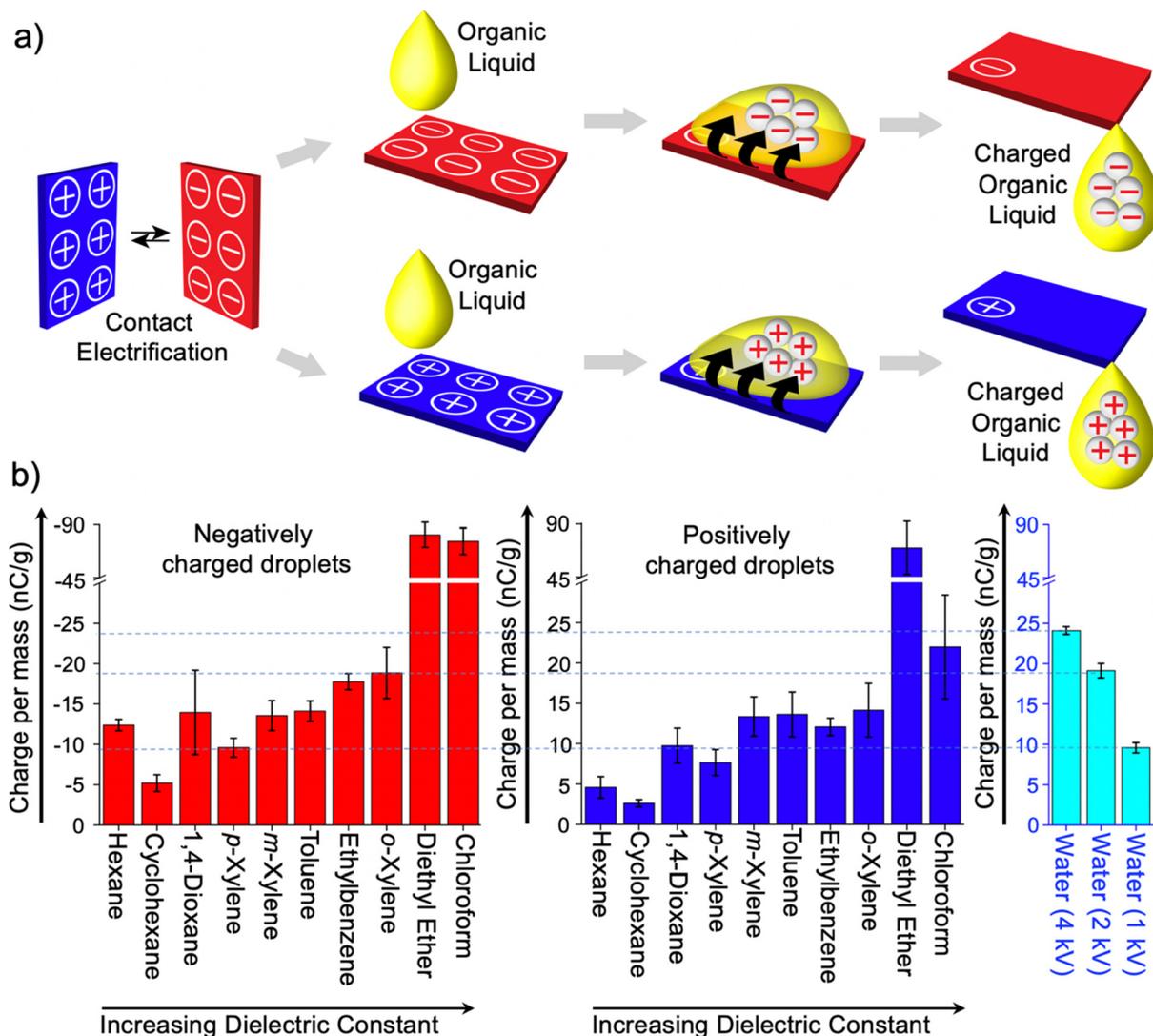


Figure 1. Charging organic liquids by static charge. (a) The fundamental approach involves first charging solid surfaces with static charge by contact electrification and then bringing the charged surface into contact with the organic liquid. (b) Charge per mass of organic liquids that were charged negatively (red bars; plot on the left) or positively (blue bars; plot in the middle) to saturation by the fundamental approach. Plot on the right shows the charge of water droplets charged to a high electric potential of 1, 2, or 4 kV via a high-voltage power supply. The organic liquids are ordered according to increasing dielectric constants along the *x*-axis.

liquid).^{26–30} However, additives change the chemical composition and properties of the liquids; thus, this method is not suitable for many types of applications (e.g., organic reactions may be influenced by additives). In addition, the application of high electric potential can cause molecular degradation of the organic liquids. Besides being ineffective, the use of high electric potential for charging the liquids requires expensive and bulky equipment, dangerous operations, and complicated engineering of the system.²¹ Another method discussed in previous studies involved flow electrification (e.g., flow in pipe or spraying); however, the net charge produced is usually negligible and can only reach measurable quantities when substantial amounts of additives are added.^{31–33}

This article describes a previously unreported fundamental approach for charging organic liquids—including insulating nonpolar organic liquids—by the addition of static charge. The approach first involves generating static charge on the surfaces of solids via contact electrification. Specifically, the surfaces of two pieces of insulating solids are brought into contact and are

then separated (Figure 1a). After contact, one of the surfaces charges positively, whereas the other surface charges negatively. By bringing the charged surface into contact with the organic liquid (e.g., allowing a droplet to flow across the charged surface), we found that the liquid becomes charged. This method is thus extremely simple: it involves simply mixing the static charge from the charged surface directly into the organic liquid. Despite its simplicity, the fundamental approach is found to be effective. Organic liquids can surprisingly gain substantial amounts of charge via this method, including insulating nonpolar organic liquids (i.e., even when their conductivities remained low). Because of its effectiveness, we are able to use the highly charged organic liquids for developing novel practical applications, such as droplet manipulations, controlled organic reactions, and the fabrication of the novel class of bulk-charged particles (i.e., particles with their charges stably and permanently embedded in their bulk matrices). One main evaluation criterion that we used for determining the effectiveness of our method for the develop-

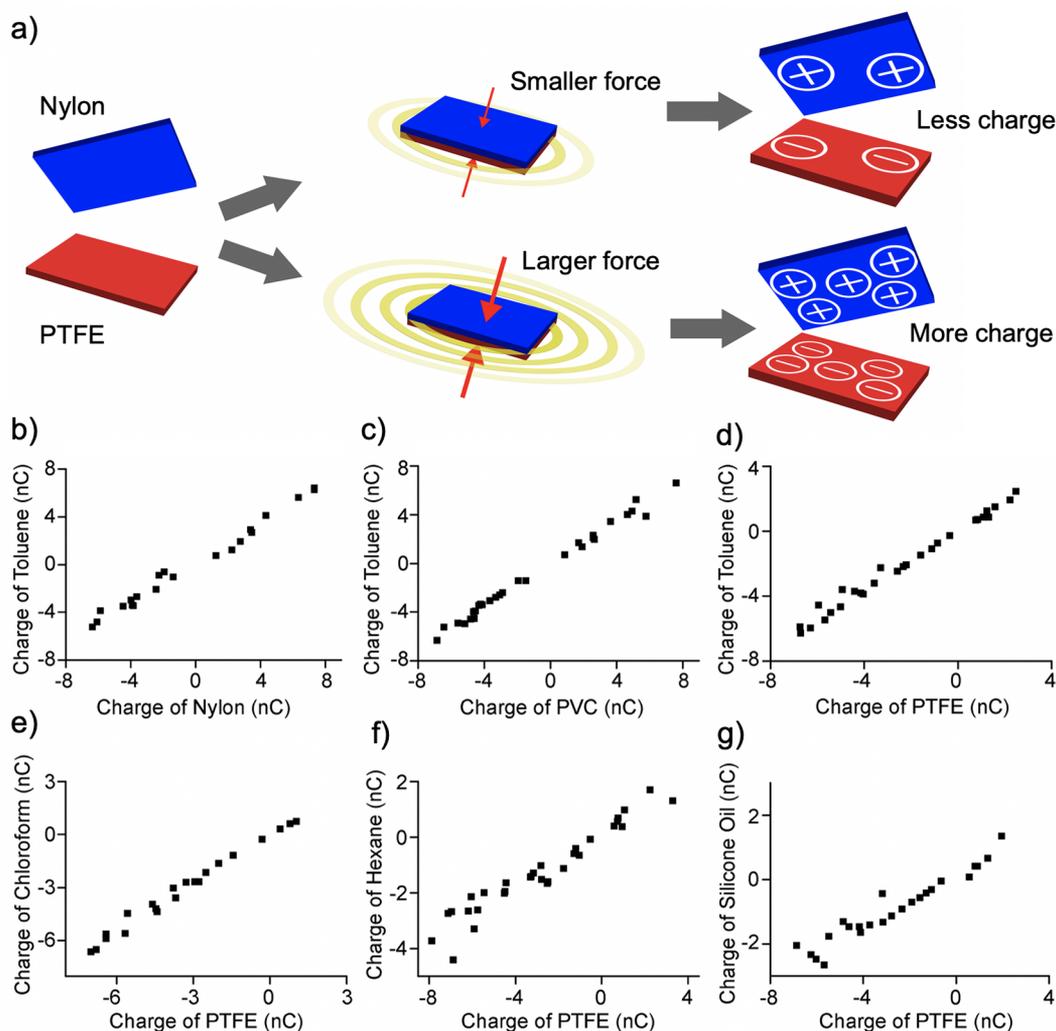


Figure 2. Charging organic liquids flexibly with a desired polarity and a tunable amount of charge. (a) Surfaces are first charged with variable amounts of positive or negative charge by contact electrification of different types of solid with different amounts of force. The static charge is then mixed into the organic liquid for the desired polarity and amount of charge. Charging toluene with a piece of charged (b) polyamide (nylon), (c) poly(vinyl chloride) (PVC), or (d) poly(tetrafluoroethylene) (PTFE). Charging (e) chloroform, (f) hexane, or (g) silicone oil with a piece of charged PTFE. *x*-axis represents the static charge of the solid before contacting the liquid. *y*-axis represents the charge of the liquid after contacting the solid.

ment of these novel applications is to test if the charged substances respond actively to an electric field. For example, we were able to verify that the organic liquids were substantially charged by static charge and the charge in the bulk-charged particles was stable by showing that they responded to an electric field. This evaluation criterion is essential because many important applications of charged substances require the substances to respond actively to an electric field (e.g., electrostatic coating and high-resolution printing).

Fundamentally, the chemical identity of the static charge generated by the contact electrification of two insulating solids is still not known despite a long history of research.³⁴ Previous studies have proposed that the type of charged species transferred from one surface to another during contact electrification is either an electron,^{35,36} an ion,^{37,38} or a small quantity (e.g., nanosized) of charged materials.^{39,40} Regardless of the identity of the static charge generated on the surfaces, however, our analyses suggested that the charged species present in the organic liquid charged by our fundamental

approach are molecular ions. On the other hand, there were no detectable changes in the chemical compositions of the liquids even after the addition of the static charge.

RESULTS AND DISCUSSION

In our experiments, we investigated different types of organic liquids, including hexane, cyclohexane, 1,4-dioxane, *p*-xylene, *m*-xylene, toluene, ethylbenzene, *o*-xylene, diethyl ether, and chloroform. These liquids included insulating nonpolar organic liquids with low dielectric constants (i.e., <4.5; see Table S1) as demonstrations that even liquids with low conductivities charged substantially using our fundamental approach. For generating the static charge, we charged a piece of poly(tetrafluoroethylene) (PTFE) negatively by rubbing it against a piece of nylon (see Supporting Information, Section 1, for details on the methods and materials). We then placed a droplet (50 μ L) of one of the organic liquids onto the piece of charged PTFE and allowed it to slide 20 cm down the charged surface under gravity until the amount of charge reached saturation (i.e., a longer length of the surface did not charge

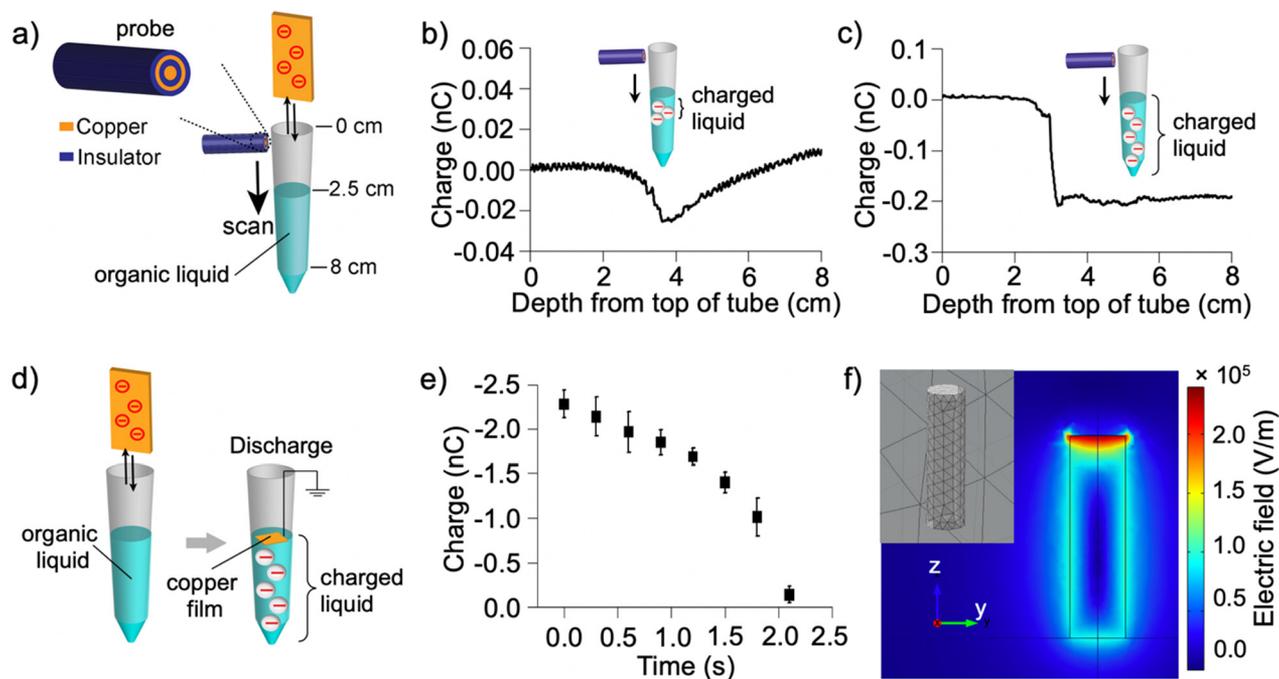


Figure 3. Mobility of the charged species in the organic liquid charged by static charge. (a) Experimental setup for determining the spatial distribution of the charge in the organic liquid within a tube using an electrostatic probe. Measurements of charge as the probe scanned down the charged liquid in the tube for the case when (b) only the top layer of around 1.5 cm of the liquid was charged (i.e., a depth of ~ 4 cm from the top of the tube) or (c) the whole depth of the liquid was charged. (d) Experimental setup for determining the mobility of the charged species in the organic liquid via placing a grounded piece of metal on the surface of the charged liquid. (e) Dissipation of the charge in the organic liquid with time via the grounded metal. (f) Calculation of the electric field strength from simulation of the space charge in the liquid and the grounded metal on top of the liquid.

the droplet more). This droplet was collected in a Faraday cup connected to an electrometer (Keithley, model 6514) for measuring its charge. Results showed that the organic droplets charged highly negatively (on the order of magnitude of -10 nC/g) after contacting the negatively charged surface for all the types of organic liquids investigated (Figure 1b; plot on the left). We repeated the experiment by sliding droplets of the organic liquids down a piece of positively charged poly(vinyl chloride) (PVC) (i.e., by rubbing it against PTFE) instead. In this case, the droplets charged highly positively (Figure 1b; plot in the middle). As a comparison, we charged water droplets to a high electric potential of either 1, 2, or 4 kV by a high-voltage power supply and measured their charges. In general, the absolute amounts of charge generated in the organic liquids by this fundamental approach were found to be on the same order of magnitude as that of water charged to a high potential of a few kilovolts by the high-voltage power supply. Notably, diethyl ether and chloroform charged far higher than that of water charged to 4 kV. The organic liquids thus gained surprisingly large amounts of charge through this simple method even for nonpolar organic liquids.

This fundamental approach is flexible: the organic liquid can be charged with a desired polarity and amount of charge by adding the appropriate type and amount of static charge into it. This flexibility is based on generating a variable polarity and amount of static charge on a solid surface via contact electrification. The desired polarity can be generated by contact-charging the surface against a specific material that has a specific ranking in the triboelectric series or a particular Lewis basicity/acidity.⁴¹ The amount of static charge generated can be varied by rubbing the surfaces with different pressures; a

higher pressure of rubbing generally produced a larger amount of static charge on the surface (Figure 2a). As a demonstration, we charged a piece of nylon either positively via rubbing it against a piece of PTFE or negatively via rubbing it against a piece of PEGDA. We repeated the experiment by rubbing the surfaces with different pressures for generating different amounts of static charge. After charging, we immersed the piece of charged nylon into initially uncharged toluene (40 mL) and mixed the static charge into the liquid. We measured the amount of charge of nylon after rubbing. We also measured the amount of charge of toluene after immersing the piece of charged nylon into it. Results showed that the polarity and amount of charge gained by the toluene corresponded to the polarity and amount of static charge on the solid surface before mixing (Figure 2b). The amount of charge of toluene was approximately linearly proportional to the amount of charge of the nylon before immersing it into the organic liquid. Other variations of this method also showed a similar type of flexibility for charging the organic liquids; one example involved flowing the organic droplets down different lengths of different types of charged solid surfaces.

The fundamental approach is general: it can be used to charge different types of organic liquids by using different types of solids. Experimentally, we showed that toluene could be charged by different types of charged solids, including nylon, PVC, and PTFE (Figure 2b–d). We further showed that a single type of charged solid material can be used for charging different types of organic liquids; specifically, pieces of charged PTFE were used to charge toluene, chloroform, hexane, and silicone oil (Figure 2d–g). In all cases, the polarity and amount of charge of the organic liquids were found to be flexibly

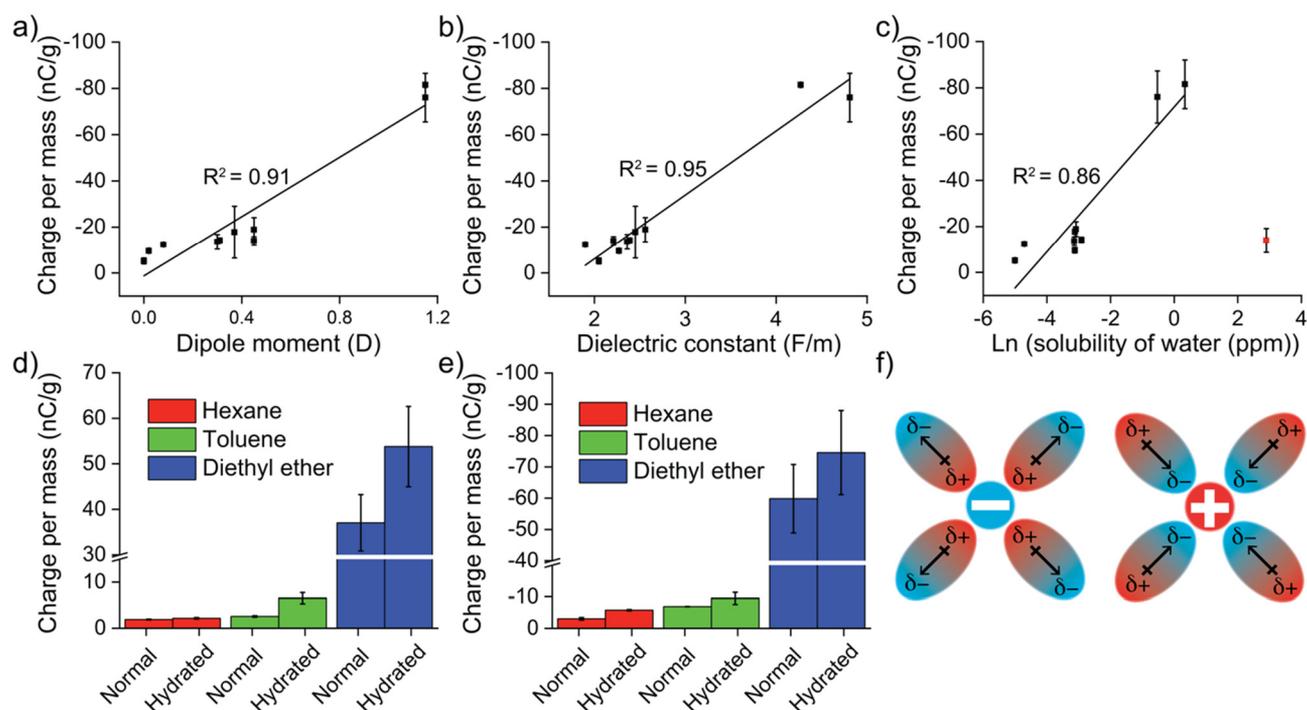


Figure 4. State of the charged species in the organic liquid. Correlations between the amount of negative charge gained by the organic liquids at saturation and (a) dipole moment, (b) dielectric constant, or (c) (natural logarithm of) solubility of water in the organic liquid. The linear fit of the solubility of water in the organic liquid does not include the red data point, which represents 1,4-dioxane (i.e., due to its ability to form hydrogen bonds with water that makes the solubility exceptionally high). Comparing the (d) positive or (e) negative charge gained (below saturation) by either the organic liquid (i.e., hexane, toluene, or diethyl ether) unmixed with water (i.e., “normal”) or mixed vigorously with water (i.e., “hydrated”). (f) Scheme illustrating the stabilization of the charged species in the organic liquid by the specific orientation of the dipole moment of the solvent molecules.

tunable by using solid surfaces with the corresponding polarity and amount of static charge. For charging toluene or chloroform, the gradients of the plots shown in Figure 2 are close to 1 (i.e., ~ 0.9 for Figure 2b–e); this result indicated that almost all the static charge from the solid surface transferred to the organic liquid. The transfer was less effective for hexane probably due to its low polarity and for silicone oil probably due to its high viscosity that prevented effective circulation of the liquid for the transfer of the charge. In general, we found that the total amounts of charge on the solid and in the liquid before and after immersing the solid into the liquid were conserved.

We investigated the state of the organic liquid after mixing the static charge into it. First, we analyzed the spatial distribution of the charge in the liquid by an electrostatic probe. The experiment involved filling a long cylindrical tube (10 cm in height) with hexane until the liquid level reached 2.5 cm below the top of the tube (Figure 3a and Supporting Information, Section 1). We then charged a portion of the hexane by immersing a piece of negatively charged PTFE into only the top ~ 1.5 cm layer of hexane. Immediately after charging the hexane, we scanned the charge throughout the depth of the liquid in the tube using an electrostatic probe connected to an electrometer (Keithley, model 6514). The probe was placed close to the external surface of the tube (i.e., at a distance of ~ 0.5 mm) and moved from the top of the tube (i.e., 0 cm) vertically downward by 8 cm. The measurement showed that only the top layer of the liquid (~ 2 cm) was significantly charged (Figure 3b). This result indicated that the charged species resided in the bulk of the organic liquid immediately after charging: if the mobility of the charged

species was instantaneous (e.g., electrons in a conductor), then the charged species would be present throughout the depth and not just at the top layer of the liquid. We then performed a control experiment in which we immersed the charged PTFE into the entire depth of the liquid. In this case, the charge was approximately homogeneously distributed throughout the depth of the liquid in the tube (Figure 3c).

For understanding the nature of the charged species, we analyzed its mobility in the liquid. We first charged toluene (6 mL) in a centrifuge tube by immersing a piece of negatively charged PTFE into the entire depth of the liquid (Figure 3d). Immediately thereafter, a grounded piece of copper film (1 cm \times 1 cm) was placed on the surface of the liquid in the tube. Through measuring the charge of the toluene with time, we found that the toluene discharged in around 2 s (Figure 3e). The speed at which the charged species migrated from the bulk of the liquid to the metal film (that subsequently allowed the charge to dissipate to ground) indicated the mobility of the species. As an order-of-magnitude analysis of the mobility of the charged species, we calculated the electric field computationally within the liquid by assuming that the liquid was charged initially uniformly with a space charge density (i.e., charge of toluene at ~ -2 nC divided by the volume of liquid) of around -3×10^{-4} C/m³, and the top surface of the liquid had a grounded boundary condition (Figure 3f). The result of the simulation showed that the electric field strength was on the order of $\sim 10^{-5}$ V/m within the liquid. By taking an average distance of migration of the charged species from the bulk liquid to the metal film to be half of the depth of the liquid (i.e., ~ 3 cm) and the time taken for the migration to be ~ 2 s, the order of magnitude of the mobility of the charged species

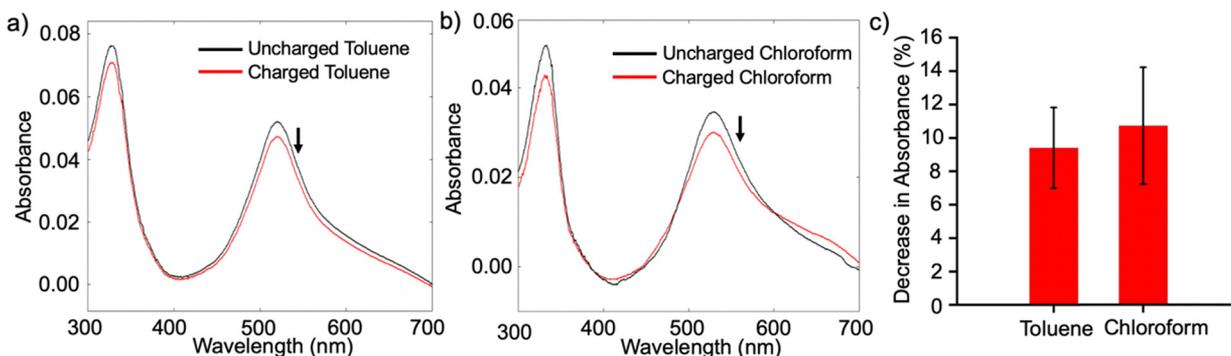


Figure 5. Presence of radicals in the charged organic liquid. Decrease in absorbance of the solution that consisted of the radical scavenger, 2,2-diphenyl-1-picrylhydrazyl (DPPH), dissolved in either (a) charged toluene or (b) charged chloroform compared to the respective uncharged organic liquids as analyzed by UV-vis spectroscopy. (c) Percentage decrease in absorbance of the charged toluene and charged chloroform compared to the respective uncharged organic liquids.

was calculated to be 10^{-3} cm²/V·s. This mobility corresponds to the same order of magnitude of small molecular ions migrating within (e.g., nonpolar) organic liquids. In any case, the species is probably not electrons due to their extremely short lifetime in organic liquids as reported in previous studies (e.g., roughly microseconds).^{22,42} In comparison, the charged species was found to remain in the organic liquid for more than half an hour (i.e., without placing the piece of grounded copper film on the surface of the liquid).

We examined the mechanism by which the different organic liquids are able to store the charge. We plotted the amount of charge that the different organic liquids gained up to saturation (i.e., Figure 1) with three properties of the organic molecules: dipole moment, dielectric constant, and solubility of water in the organic liquid (Figure 4a–c). Significant correlations are found for these three properties (i.e., $R^2 \sim 0.9$) when plotted against the negative charge gained by the organic liquids (although the correlations are weaker when plotted against the positive charge gained by the organic liquids; see Supporting Information, Section 2, for more details). All these three properties are related to the polarity of the organic liquid. Hence, the correlations suggest that organic liquids with a higher polarity have the ability to gain more charge from the charged solid surface.

To investigate this relationship, we performed an experiment that involved introducing polar molecules into the organic liquids. Specifically, we mixed the nonpolar organic liquid vigorously with water for hydrating the organic liquid. Droplets of the hydrated organic liquid were slid down a short length of 5 cm across a positively or negatively charged solid surface so that they did not charge to saturation. This experiment was performed for hexane, toluene, and diethyl ether. Results showed that the hydrated organic liquids gained a larger amount of charge compared to the organic liquids that were not mixed with water (Figure 4d–e). These results further indicated that organic liquids that consist of more polar molecules tend to gain more charge from the charged surface.

Molecules usually align themselves in a specific orientation toward a charged molecule. This effect allows the organic molecules to surround and form the solvation shell around the charged species (i.e., in a way that is similar to the hydration of ions by water molecules). This solvation shell of organic molecules with their dipole aligned in energetically favorable orientations stabilizes the charged species (Figure 4f). Therefore, organic molecules with a higher dipole moment

can stabilize the charged species more; in other words, a higher polarity of the organic liquid allows the liquid to gain more charge from a charged surface. On the other hand, it seems from our results that the organic liquids were nevertheless able to gain practically significant amounts of charge even for very nonpolar liquid molecules (e.g., toluene and xylene).

This charged molecule that resides in the organic liquid may be the same charged molecular species on the surface of the solid generated by contact electrification that transferred directly from the charged surface to the organic liquid. One possibility involves the small molecular ions that have previously been hypothesized to be the charged species of static charge (e.g., the aqueous OH[−] and H⁺ ions due to water molecules adsorbed on surfaces).⁴³ When the charged surface comes into contact with the organic liquid, these ions may simply transfer from the surface into the liquid. Alternatively, reactions may have occurred when the charged surface comes into contact with the organic liquid; thus, the charged species in the organic liquid is the product of the reactions that is different from the species on the charged surface. To further understand the mechanism, we analyzed the charged organic liquids for radicals. Radicals are known to be present on the surfaces of solids charged by contact electrification^{44,45} and are likely also present in the organic liquid after contacting the charged surfaces. For detecting the presence of radicals, we performed the standard test that involved the radical scavenger, 2,2-diphenyl-1-picrylhydrazyl (DPPH). In the presence of radicals, the dark-colored DPPH solution reacts with the radicals and produces the light yellow 2,2-diphenyl-1-picrylhydrazine (DPPH-H). This bleaching effect causes a decrease in absorbance at 517 nm that can be detected using UV-vis spectroscopy. For this test, we first prepared two types of liquids: an organic liquid that was charged by dipping a piece of negatively charged PTFE into it and the same organic liquid that was not charged (see Supporting Information, Section 3 for a more detailed discussion of the methods of this experiment). DPPH was then added immediately into these two liquids. Analysis from the UV-vis spectroscopy showed that there was a decrease in absorbance by $\sim 10\%$ for both the charged toluene and chloroform compared to the uncharged toluene and chloroform respectively (Figure 5). Based on the calibration curves established by measuring the absorbance of different concentrations of DPPH in toluene and chloroform (Figure S2), we found that the decrease in absorbance corresponded to ~ 0.5 μM of radicals present in either of

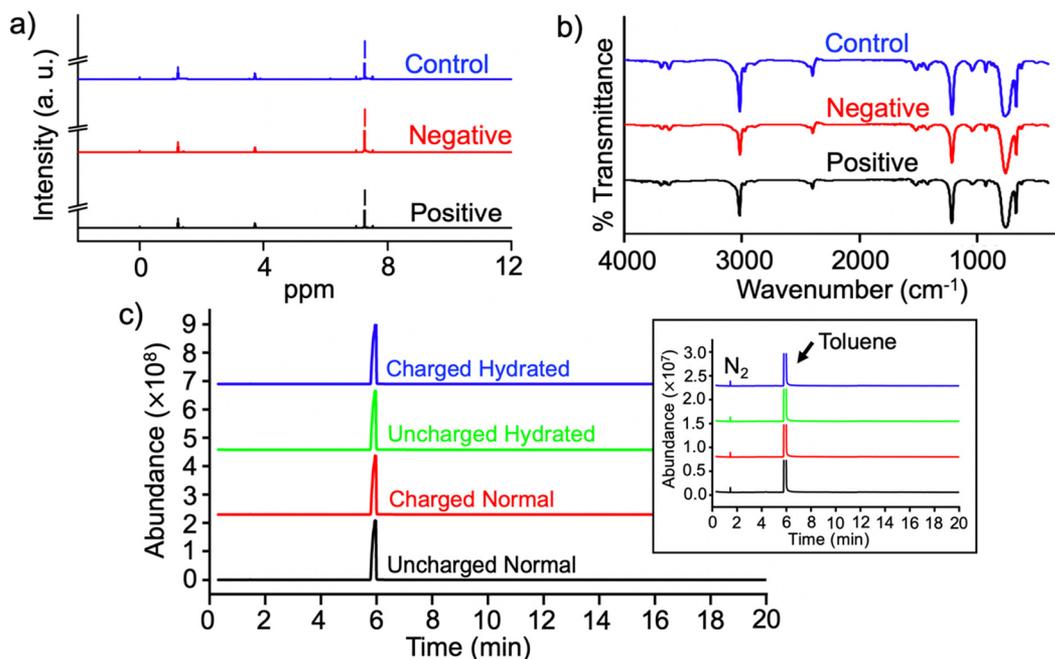


Figure 6. Organic liquids remained pure after charging by static charge. Analyses of both the positively and negatively charged liquids by (a) ^1H NMR with chloroform-*d* and (b) FTIR with chloroform showed that the charged liquids have the same chemical composition as the uncharged liquid (“control”). (c) Four types of toluene were analyzed by GC-MS: uncharged toluene (“uncharged normal”), negatively charged toluene (“charged normal”), uncharged toluene mixed with water (uncharged hydrated”), and negatively charged toluene mixed with water (“charged hydrated”). Analyses of all the four types of samples showed the same chemical composition. The inset shows the magnified plot of the analysis by GC-MS.

these two types of charged organic liquids. More analysis will be needed to identify the molecular species of the radicals (see Figure S3). These radicals may have taken part in reactions that occurred when the charged surface comes into contact with the organic liquid (e.g., for toluene, the radical anion of toluene may be produced when an electron transfers from the charged surface to toluene).

We were, however, not able to identify the charged molecule in the organic liquids. We analyzed the chemical compositions of the uncharged, positively charged, and negatively charged droplets of chloroform (i.e., the organic liquid that charged much higher than the other nonpolar organic liquids investigated) by NMR and FTIR. We also analyzed the chemical compositions of uncharged and charged toluene using GC-MS. In addition, we analyzed the chemical compositions of uncharged and charged toluene that were mixed vigorously with water using GC-MS; this analysis was performed because our results showed that hydrated organic liquids were able to gain more charge (i.e., see Figure 4d–e). In all cases, the results showed that the chemical compositions of the charged liquids were the same as that of the uncharged liquids within the limits of detection of the equipment (Figure 6). Theoretically, it is possible to add a substantial amount of charge to the liquid for practical applications but without actually changing its chemical composition significantly. For example, a charge of 10 nC/g of liquid corresponds to only on the order of 0.1 nM of the charged species in the liquid—a concentration that is negligible for practical purposes.

On the other hand, these results indicated that the organic liquids remained pure after charging. Our approach is thus fundamentally different from the method that involves the addition of substantial amounts of additives for increasing the conductivity of the organic liquid by orders of magnitude. To

show that our approach is fundamentally different, we measured the conductivities of toluene before and after charging it with a piece of negatively charged PTFE. We found that the conductivities remained at the same order of magnitude of $\sim 10^{-9}$ S/m before and after charging it by static charge (see Supporting Information, Section 1 for methods).

Because previous methods investigated for charging organic liquids are ineffective, there have been very few proposed applications of charged organic liquids in general reported in the literature. Hence, the effectiveness of our fundamental approach gives rise to opportunities for developing novel ways of using the charged organic liquids. One important application is in flow chemistry: the manipulation of charged liquid droplets by an electric field for different types of operations in fluidic systems (e.g., microfluidics and microreactors), including separation, sorting, mixing, and coalescence.⁴⁶ However, manipulation by an electric field has only been shown for charged aqueous droplets—the manipulation of charged organic droplets has not been demonstrated before. In addition, previous studies that manipulated aqueous droplets used a high-voltage power supply for charging both the droplets and the electrodes used for manipulation. On the other hand, it is desirable for many applications of fluidic systems (e.g., point-of-care diagnostics) to operate without any tethered power supply or expensive and bulky equipment.^{22,47–51}

We showed that organic liquids are effectively charged by our fundamental approach for manipulation by an electric field. In this experiment, we charged two droplets of organic liquid. The first droplet (3 μL) was composed of 5 mM of 2,2-diphenyl-1-picrylhydrazyl (DPPH) in 1-decanol and was charged positively by flowing it across a positively charged PTFE. The second droplet was composed of 50 mM of (\pm)- α -

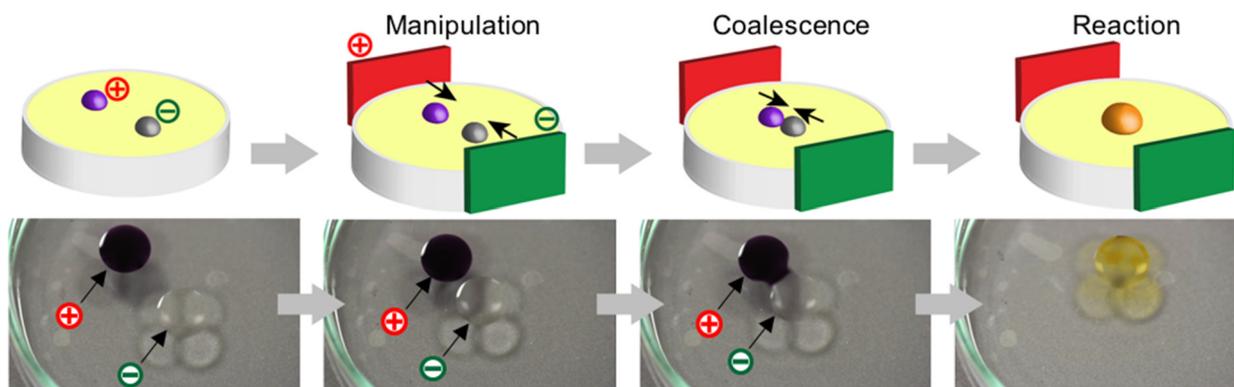


Figure 7. Manipulating the charged organic droplets for controlled organic reaction. The top row shows the scheme illustrating the process of manipulation, and the bottom row shows the corresponding experimental images. The positively charged droplet consisted of the dark purple 2,2-diphenyl-1-picrylhydrazyl (DPPH) in 1-decanol. The negatively charged droplet consisted of the colorless vitamin E in 1-decanol. A piece of positively charged nylon (red) and negatively charged PTFE (green) was used to control the coalescence of the charged droplets as illustrated in the scheme on the top row. After coalescence, the chemicals in the droplets reacted to produce the yellow-colored 2,2-diphenyl-1-picrylhydrazine (DPPH-H). Scale bar: 1 cm.

tocopherol (vitamin E) in 1-decanol and was charged negatively by flowing it across a negatively charged PTFE. The two droplets were placed on the air–water interface in a Petri dish filled with ultrapure water. We then charged a piece of nylon positively and a piece of PTFE negatively by contact electrification. The positively charged nylon was placed close to the positively charged droplet containing DPPH, and the negatively charged PTFE was placed close to the negatively charged droplet containing vitamin E in a configuration as shown in Figure 7 (scheme on top). Due to the electrostatic repulsive force from the pieces of charged polymers, the droplets moved toward each other and coalesced. The coalescence allowed the reaction between DPPH and vitamin E to occur and produced 2,2-diphenyl-1-picrylhydrazine (DPPH-H). The reaction of DPPH was immediately observable due to the bleaching of the dark purple droplet to a slight yellow coalesced droplet. This bleaching of DPPH is useful for the quantification of vitamin E (i.e., a natural antioxidant) in food substances.^{52–54} This experiment thus demonstrated that charged organic liquids can be used for controlling organic reactions and manipulation. Importantly, the experiment was performed entirely without the use of any tethered power supply or equipment, including charging both the droplets and the polymers. In addition, the ability of the charged organic liquids to actively respond to an electric field showed that the liquids were substantially charged in general for practical applications.

We further demonstrated a completely novel application using our fundamental approach for charging organic liquids: we fabricated a novel class of bulk-charged particles. The procedure involved first charging a piece of PTFE either positively or negatively (Figure 8a and Supporting Information, Section 4) and then dipping it into a highly viscous prepolymer silicone liquid for mixing the static charge into the liquid. After a droplet of the prepolymer liquid was polymerized, charged silicone particles ($\sim 500\ \mu\text{m}$ to $\sim 5\ \text{mm}$ with charge that ranged from ~ 0.02 to $\sim 5\ \text{nC}$) were obtained. The organic nature of the silicone particles was analyzed by FTIR (e.g., the Si–CH₃ groups; Figure S4). The mobility of ions in a liquid is inversely proportional to the viscosity of the liquid; hence, the charge was possibly trapped within the highly viscous bulk liquid during polymerization. After

polymerization, the charge was embedded in the hydrophobic bulk matrix of the silicone particle (i.e., the “bulk-charged particle”).

In comparison, charged particles fabricated by previous methods are charged only at the surface. Methods for charging particles include the spontaneous separation of charge at the solid–liquid interface (e.g., by functionalization of ionic functional groups on the surface), contact electrification, corona discharge, electron beam, or plasma,^{35,43,55–57} however, the charge is generated only at the surface after charging. The main disadvantage of these surface-charged particles is that the charge is not stable on the surface: they are highly susceptible to changes in the conditions of the surrounding medium and/or dissipate naturally with time. For example, the pH of the medium greatly affects the zeta potential of particles. On the other hand, we showed experimentally that the charge embedded in the hydrophobic matrix of the bulk-charged particle was stable and permanent. For testing the stability of the charge, we used the evaluation criterion that involved determining if the particle responded to an electric field under different conditions. The experiment involved first placing the bulk-charged particle at the air–liquid interface of an aqueous solution of extreme pH: either pH 1 or pH 14. When a piece of charged PTFE was placed close to the particles, we found that the bulk-charged particles moved on the surfaces of the solutions of both pH values (Figure 8). This result indicated that the charge remained in the particles regardless of the pH of the solution. Both the positively and negatively charged particles moved as expected based on their polarities by the negatively charged PTFE; hence, the polarity of the particles did not change due to the different extreme pH of the medium. As a control experiment, we found that the bulk-charged particle also moved on the surface of deionized water (i.e., neutral pH) by the charged PTFE (Figures S5 and S6). In addition, we found that the bulk-charged particle remained permanently charged for months. The last time we performed the experiment, it could still be moved by the charged PTFE at the air–water interface after more than four months since it was fabricated.

A clear validation of the stability of the charge embedded in the particle can be established by comparing bulk-charged particles and surface-charged particles that are both charged by

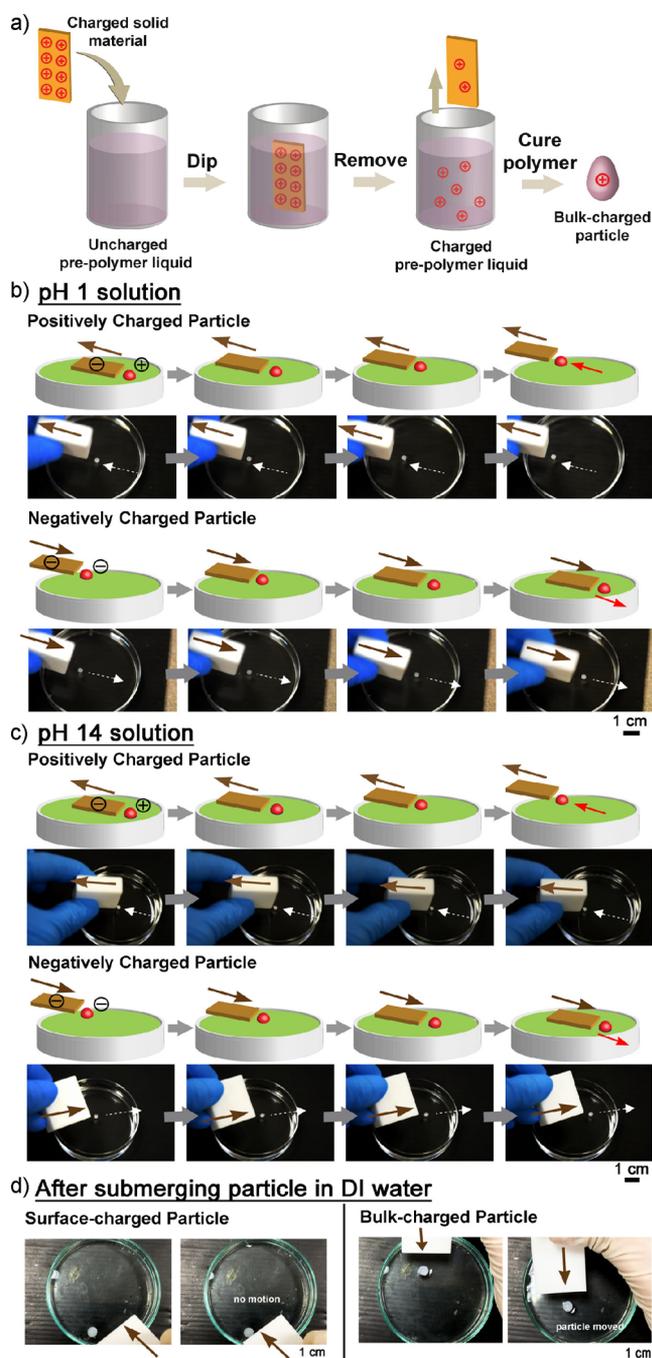


Figure 8. Permanently bulk-charged particles. (a) Scheme illustrating the fabrication of the novel class of bulk-charged particles. Manipulation of the bulk-charged silicone particle (~ 3 mm) on the surface of (b) highly acidic (pH = 1) or (c) highly alkaline (pH = 14) medium by a piece of negatively charged PTFE. Both the positively and negatively bulk-charged silicone particles moved accordingly as expected under these extreme conditions. The positively charged particle was attracted and moved according to the movement of the negatively charged PTFE. On the other hand, the negatively charged particle was repelled and moved away from the movement of the negatively charged PTFE. (d) After the particle was submerged in water and then placed back on the surface of the water, the surface-charged particle (i.e., particle charged only at the surface) stopped moving, whereas the bulk-charged particle continued to be able to move under the influence of the charged PTFE.

static charge. This comparison is useful because particles charged with static charge on their surfaces (e.g., by contact electrification) are very commonly found in nature and in industry. For a fair comparison, the surface-charged particle was prepared in a similar way as the bulk-charged particle, except that we did not charge the prepolymer liquid. After polymerizing the liquid into a particle (~ 3 mm), we then contact-charged the surface of the particle against glass to a charge of around -0.3 nC. We also prepared the bulk-charged particles of a similar size and a similar amount of charge for comparison. When placed on the surface of deionized water, we were able to move both the surface-charged and bulk-charged particles by a piece of charged PTFE as expected (Figure S7). Subsequently, we submerged both the particles into the deionized water for 1 s and then placed them on the surface of the water again. In this case, the bulk-charged particles continued to be able to move by the charged PTFE; however, the surface-charged particle did not move (Figure 8d). We repeated the experiment by submerging the particles in methanol instead of deionized water. The same result was observed: the bulk-charged particle continued to be able to move by an electric field, whereas the surface-charged particle did not move (Figure S7). These experiments showed that the charge remained stable in the core of the bulk-charged particles regardless of the type of the surrounding medium, whereas it dissipated readily for the surface-charged particle (i.e., and also regardless of the type of charged species present in the bulk-charged or on the surface-charged particle). In addition, solid objects with static charge on their surfaces (e.g., generated by contact electrification) are known to discharge quickly (e.g., seconds to minutes).

It is worth noting that stable and permanently magnetic particles that can be manipulated by a magnetic field have been fabricated easily via many methods for use in practical applications. One common method involves embedding magnetic nanoparticles into the bulk matrix of another material (e.g., a polymer)—trapping the magnetic components in the bulk of the particle ensures their stability in the particle. Hence, these stable bulk-magnetic particles are fabricated in a similar way as our bulk-charged particles. Because of this similarity, we used the same approach for fabricating another novel class of particles: the bulk-charged, bulk-magnetic particles. Our experiment involved first simply mixing magnetic iron oxide nanoparticles (~ 30 nm) homogeneously into the prepolymer silicone liquid (Supporting Information, Section 6). We then mixed static charge from a negatively or positively charged PTFE into the prepolymer liquid in the same way. After polymerization, both the charged species and the magnetic nanoparticles were embedded in the bulk of the hydrophobic silicone particle. These highly versatile particles were responsive to both an electric field and a magnetic field. Experimentally, we showed that both the negatively and positively charged magnetic particles moved under the influence of magnets, a positively charged surface, and a negatively charged surface (Figure 9).

CONCLUSION

The nonconductive nature of the organic liquids—especially the insulating nonpolar organic liquids—has made charging these liquids extremely challenging. The only way to facilitate the charging of the organic liquids requires the addition of conductive additives; however, additives change the chemical composition of the liquids significantly and are not suitable to

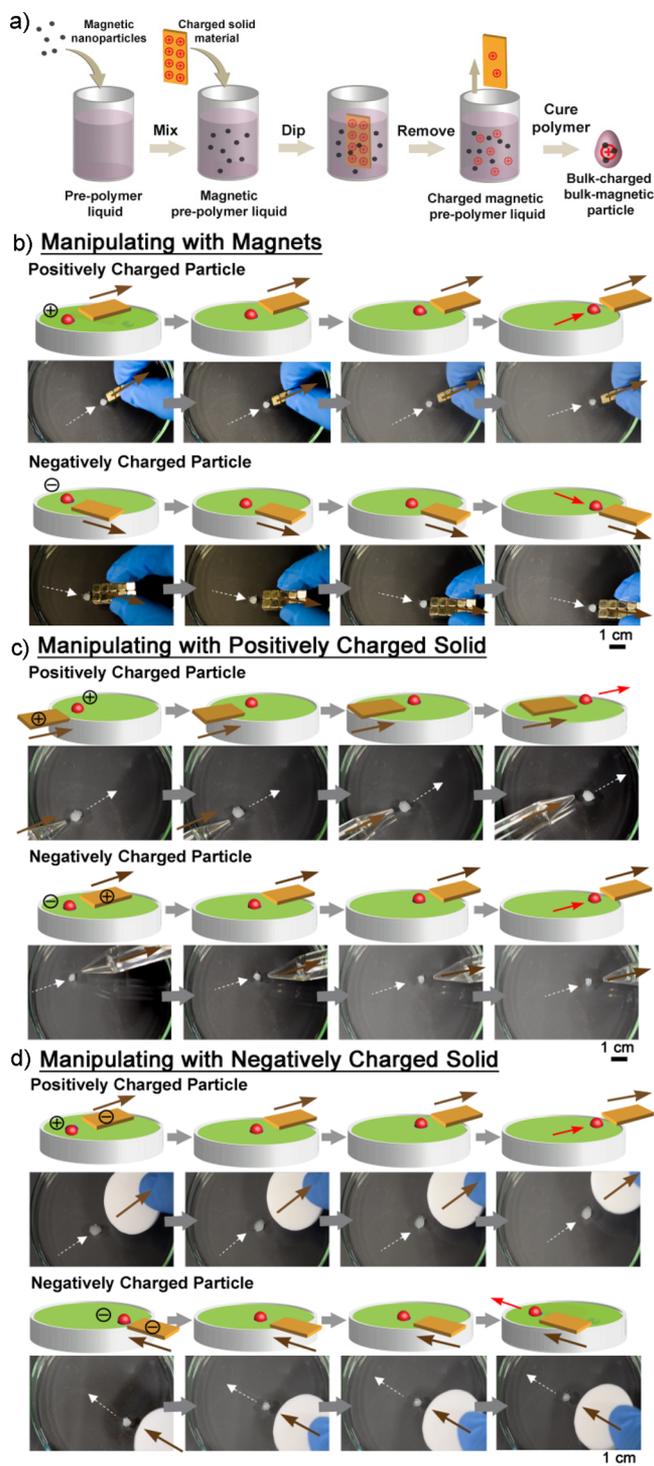


Figure 9. Highly versatile bulk-charged and bulk-magnetic particles. (a) The fabrication of the particle involved simply mixing magnetic nanoparticles and static charge into the liquid prepolymer solution and then polymerizing the liquid. Both the positively and negatively bulk-charged and bulk-magnetic particles (~ 5 mm) were responsive to (b) magnetic fields (via magnets), (c) electric field via a positively charged poly(dimethylsiloxane) (PDMS), and (d) electric field via a negatively charged PTFE.

be used in many applications. Without additives, there has not been any significant application developed based on charged organic liquids with low conductivities in general. This study describes a novel fundamental approach for charging organic

liquids effectively—including insulating nonpolar organic liquids—by the addition of static charge. This approach has a number of important features. (1) The method is simple. Similar to many operations in chemistry in which chemicals are simply added and mixed into reaction flasks, our method involved simply mixing static charge into the organic liquid. (2) The method is general. Different types of solid materials can be used for charging different types of organic liquids. (3) The method is versatile. It can be flexibly tuned to produce the desired polarity and amount of charge in the organic liquid. (4) Organic liquids can be charged effectively with substantial amounts of charge (i.e., on the order of ~ 10 nC/g) despite using this simple method. Notably, this method charged nonpolar organic liquids to amounts that are equivalent to that obtained by charging water with a high-voltage power supply operated at a high electric potential of a few kilovolts. (5) No change in the composition of the charged liquid was detected. (6) Due to the simplicity of the method, it does not require any additives, sources of high energy, power, equipment, or (complicated) engineering of the systems. (7) It is a safe and green method. Fundamentally, our results suggested that the chemical species of the static charge mixed into the organic liquids are molecular ions that resided in the bulk of the liquids immediately after charging. Although static charge has been used in many applications (e.g., performing chemical reactions in aqueous solutions),³⁵ our study reports for the first time that static charge can be used for charging organic liquids.

Due to the lack of effective methods for charging organic liquids, applications based on charged organic liquids have remained largely unexplored in literature. Hence, our method for effectively generating charged organic liquids has led to plenty of opportunities for the development of novel applications. Specifically, (i) we showed for the first time that organic liquid droplets, when charged by our method, can be manipulated by an electric field. The demonstration involved the on-demand coalescence of the droplets for controlling organic reactions. Manipulation of charged droplets by an electric field has been reported only for aqueous droplets but not for organic droplets; the manipulation of aqueous droplets is important for droplet flow chemistry (e.g., microfluidics).⁵⁸ On the other hand, previous studies have discussed the importance of the organic medium in flow chemistry for many applications, such as performing organic reactions, biochemical assays, self-assembly of colloidal particles, and synthesis of materials;^{59,60} hence, it will be useful to be able to manipulate charged organic droplets for these applications. (ii) We fabricated for the first time bulk-charged particles (via polymerization of charged prepolymer liquid). Methods reported in previous studies charged materials only at the surface (e.g., corona discharge), close to the surface (e.g., via electron beam and photon irradiation to ~ 10 μm into the bulk of the material), or within surfaces by sandwiching the surface-charged materials together.^{61,62} Compared to surface-charged particles, this novel class of bulk-charged particles is stably and permanently charged: they retained their charge regardless of the condition (e.g., different extreme pH) of the surrounding medium and for long periods of time (e.g., at least months). Stability of the charge is important for practical applications. An analogous example involved bulk-magnetic particles. The stability of the magnetic components embedded in bulk-magnetic particles allowed the particles to be used successfully in a number of biomedical applications (e.g., targeted imaging and drug release in the

human body).^{63–65} (iii) We fabricated for the first time bulk-charged and bulk-magnetic particles. The particles were fabricated by simply mixing both the magnetic nanoparticles and static charge into the prepolymer solutions, followed by polymerization. We demonstrated that these highly versatile particles were responsive to both electric and magnetic fields for maneuver with high degrees of freedom. In addition, previous studies have demonstrated that surface-charged and magnetic particles are used in many applications, including catalysis,⁶⁶ controlled release,⁶⁴ and as an adsorbent.⁶⁷ Therefore, due to the advantage that the charge is stably and permanently embedded in the bulk matrix of the particle, this novel class of bulk-charged and bulk-magnetic particles can thus potentially be used in a wide range of applications.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.0c06000>.

Methods and materials; factors that correlate with the charging of the organic liquids; detecting radicals in the charged organic liquids; preparing and manipulating particles charged by static charge; preparing and manipulating surface-charged particles and charged magnetic particles (PDF)

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Notes

The authors declare no competing financial interest.

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