Self-Propulsion by Directed Explosive Emulsification

Xuefei Wu, Han Xue, Gautam Bordia, Zachary Fink, Paul Y. Kim, Robert Streubel, Jiale Han, Brett A. Helms, Paul D. Ashby, Ahmad K. Omar, and Thomas P. Russell

An active droplet system, programmed to repeatedly move autonomously at a specific velocity in a well-defined direction, is demonstrated. Coulombic energy is stored in oversaturated interfacial assemblies of charged nanoparticle-surfactants by an applied DC electric field and can be released on demand. Spontaneous emulsification is suppressed by an increase in the stiffness of the oversaturated assemblies. Rapidly removing the field releases the stored energy in an explosive event that propels the droplet, where thousands of charged microdroplets are ballistically ejected from the surface of the parent droplet. The ejection is made directional by a symmetry breaking of the interfacial assembly, and the combined interaction force of the microdroplet plume on one side of the droplet propels the droplet distances tens of times its size, making the droplet active. The propulsion is autonomous, repeatable, and agnostic to the chemical composition of the nanoparticles. The symmetry-breaking in the nanoparticle assembly controls the microdroplet velocity and direction of propulsion. This mechanism of droplet propulsion will advance soft micro-robotics, establishes a new type of active matter, and introduces new vehicles for compartmentalized delivery.

1. Introduction

A liquid–liquid interface, the narrow boundary separating two immiscible liquids, can be locked into a specific shape, that is, structuring the liquids, to tailor transduction pathways for the transport of charges, ions, particulates, or fluids within a fluid medium.[1–3] Transport within a fluid environment can also be achieved by moving droplets within the medium. But, developing strategies to make the propulsion of fluid droplets autonomous, repeatable, and directional remains a challenge.[4–9] Indeed, the experimental realization of self-propulsion or “activity” is an area of intense current research. Achieving directed motion necessarily requires the flow of energy into the system to break time-reversal symmetry. The form of this energy can be chemical, as in the case of self-propulsion resulting from diffusiophoresis or chemotaxis.[10] Alternatively, this energy can be provided through an external field, as with electrophoresis or phototaxis.[11,12] For liquid droplets, owing to lack of an inherent anisotropy, self-propulsion is usually achieved through a surface gradient in the interfacial tension (IFT), typically realized by a solubilization, chemical reaction, or surface phase transformation.[13–17] Such propulsion, though, is limited to the system with a continuous injection of chemical/light energy or the need of specifically engineered or chemically reactive materials, and lacks control over reversibility and repeatability. Generating a new mode of self-propulsion for swimming droplets that can be used with a broader range of the materials and does not require the continuous injection of external energy remains an outstanding challenge in active liquid systems.

Here, we show that a DC electric field can be used to oversaturate the surface of a liquid droplet with charged nanoparticle-surfactants (NPSs), agnostic to the chemical composition of the nanoparticles (NPs). The charges on the NPSs, coupled with the increased thickness of the interfacial assembly, increases the stiffness of the interfacial assembly[18–22] suppressing a spontaneous emulsification anticipated for such densely packed interfaces.[23] The increased dipole–dipole interaction also helps to stabilize the oversaturated packing of the interface. A Coulombic potential energy is stored in the oversaturated NPS assembly that upon rapid removal of the field, is released in the form of a plume of hundreds of thousands of charged microdroplets that are explosively ejected from the droplet surface, an event termed explosive...
emulsification. This event, accompanied with a sharp increase in the IFT, is two orders of magnitude more intense than that achievable by other means, indicating that the underlying mechanism is electrostatic in origin.\[^{24}\] The explosive emulsification described here is distinct from prior research that used magnetic or electric fields to demulsify the emulsions\[^{25}\] or tune their macroscopic properties by adjusting the emulsions interaction and microscale physical phenomena,\[^{26–28}\] and also different from conventional rapid emulsification processes, for example, spontaneous emulsification\[^{29}\] and electric emulsification.\[^{30}\] For spontaneous emulsification, various mechanisms have been reported, for example, ultralow/negative interfacial tension\[^{29–31}\] and supersaturation of surfactants/cosolvents at the interface.\[^{32–36}\] The velocity at which microdroplets are ejected during spontaneous emulsification is significantly slower compared to that in explosive emulsions, and this process continues spontaneously until the system reaches equilibrium. In electric emulsification, rapid emulsification occurs only under high voltage, facilitated by the use of strong electric fields. These fields increase Coulombic repulsion at the interface, overcoming IFT and leading to the generation and ejection of droplets from the surface. This process ceases immediately when the high voltage is turned off, showing behavior that is distinctly different from explosive emulsification, which can quench the out-of-equilibrium self-assemblies at the interface by applying the external fields, allowing for controlled release of the stored energy. Furthermore, explosive emulsification holds promise for propulsion provided the ejected plume of charged microdroplets can be directed. This is accomplished by placing the droplet between two parallel electrodes, where an applied DC electric field breaks the symmetry of the interfacial assembly making the explosive emulsification highly directional. The repulsive force between the charged parent droplet and the plume of ejected charged microdroplets propels a millimeter-sized parent droplet centimeters in seconds. The droplet velocity can be tuned by the strength of the applied field. This self-propulsion does not require the constant injection of a chemical fuel and the propulsion, while triggered by the field, occurs only after the field is removed. The propulsion is repeatable and the direction of propulsion is controllable, making it of use in soft micro-robotics, compartmentalized micro-delivery systems, and smart materials. The propelled droplets can also be used as a model active matter system that may deepen our understanding of these out-of-equilibrium materials.

2. Results and Discussions

2.1. Field-Direction Dependence of Explosive Emulsification

Initial experiments were performed using a 1 mg mL\(^{-1}\) dispersion of 30 nm diameter carboxylic acid functionalized iron oxide NPs (Fe\(_3\)O\(_4\)-COOH NP) in water at a pH of 7.5. Droplets of these dispersions were suspended from a stainless-steel needle connected to an external power supply in a 1 mg mL\(^{-1}\) toluene solution of polystyrene-triamine (PS-triNH\(_3\)) (Figure 1). The negatively charged NPs interact with the protonated PS-triNH\(_3\) at the interface forming NPSs that assemble at and irreversibly bind
to the interface, decreasing the IFT to an equilibrium value of 12 mN m$^{-1}$ (see Figure S1, Supporting Information). In addition to minimizing the interfacial energy, the NPSs significantly enhance both the binding energy of individual NP$^{17}$ and the bending modulus of the interface,$^{38}$ thereby capable of stabilizing the oversaturated packing assemblies and effectively preventing the electric emulsification, even when subjected to high voltage. A voltage was applied across the needle to the conductive walls of the container holding the PS-triNH$_2$ solution making the field lines nearly normal to the surface of the droplet. The sign of the applied voltage led to dramatically different behavior. With the needle as the cathode (Video S1, Supporting Information), the droplet is stable until the voltage is turned off, then a plume of hundreds of thousands of microdroplets are ballistically jettisoned from the droplet surface (Figure 1a,b), and the total released energy is on the order of hundreds of nJ (Figure S2, Supporting Information), where the majority of the jettisoned microdroplets are spherical with an average diameter of 3.0 $\pm$ 1.2 μm. Cylindrical microdroplets, with typical lengths of 18.5 $\pm$ 9.8 μm and diameter of ≈1.5 μm, are also seen (Figure S3, Supporting Information), demonstrating that NPS assemblies on the microdroplet surfaces are jammed, preventing them from relaxing to a spherical shape.$^{1,2}$ Reversing the field direction (Video S2, Supporting Information) makes the droplet interface unstable, leading to a continuous field-induced emulsification, also known as electric emulsification,$^{23,39}$ which affects the Columbic interactions between the NPSs and their interfacial activity. Under neutral pH conditions, there is a combination of both strong electrostatic repulsion and high interfacial packing density, capable of accumulating substantial potential energy at the interface and resulting in pronounced explosive emulsification.

The IFT for a pure water droplet suspended in toluene is ≈202 mN m$^{-1}$ (see Figure S1, Supporting Information). In addition to minimizing the interfacial energy, the NPSs significantly enhance both the binding energy of individual NP$^{17}$ and the bending modulus of the interface,$^{38}$ thereby capable of stabilizing the oversaturated packing assemblies and effectively preventing the electric emulsification, even when subjected to high voltage. A voltage was applied across the needle to the conductive walls of the container holding the PS-triNH$_2$ solution making the field lines nearly normal to the surface of the droplet. The sign of the applied voltage led to dramatically different behavior. With the needle as the cathode (Video S1, Supporting Information), the droplet is stable until the voltage is turned off, then a plume of hundreds of thousands of microdroplets are ballistically jettisoned from the droplet surface (Figure 1a,b), and the total released energy is on the order of hundreds of nJ (Figure S2, Supporting Information), where the majority of the jettisoned microdroplets are spherical with an average diameter of 3.0 $\pm$ 1.2 μm. Cylindrical microdroplets, with typical lengths of 18.5 $\pm$ 9.8 μm and diameter of ≈1.5 μm, are also seen (Figure S3, Supporting Information), demonstrating that NPS assemblies on the microdroplet surfaces are jammed, preventing them from relaxing to a spherical shape.$^{1,2}$ Reversing the field direction (Video S2, Supporting Information) makes the droplet interface unstable, leading to a continuous field-induced emulsification, also known as electric emulsification,$^{23,39}$ which affects the Columbic interactions between the NPSs and their interfacial activity. Under neutral pH conditions, there is a combination of both strong electrostatic repulsion and high interfacial packing density, capable of accumulating substantial potential energy at the interface and resulting in pronounced explosive emulsification.

The IFT for a pure water droplet suspended in toluene is ≈202 mN m$^{-1}$ (see Figure S1, Supporting Information). In addition to minimizing the interfacial energy, the NPSs significantly enhance both the binding energy of individual NP$^{17}$ and the bending modulus of the interface,$^{38}$ thereby capable of stabilizing the oversaturated packing assemblies and effectively preventing the electric emulsification, even when subjected to high voltage. A voltage was applied across the needle to the conductive walls of the container holding the PS-triNH$_2$ solution making the field lines nearly normal to the surface of the droplet. The sign of the applied voltage led to dramatically different behavior. With the needle as the cathode (Video S1, Supporting Information), the droplet is stable until the voltage is turned off, then a plume of hundreds of thousands of microdroplets are ballistically jettisoned from the droplet surface (Figure 1a,b), and the total released energy is on the order of hundreds of nJ (Figure S2, Supporting Information), where the majority of the jettisoned microdroplets are spherical with an average diameter of 3.0 $\pm$ 1.2 μm. Cylindrical microdroplets, with typical lengths of 18.5 $\pm$ 9.8 μm and diameter of ≈1.5 μm, are also seen (Figure S3, Supporting Information), demonstrating that NPS assemblies on the microdroplet surfaces are jammed, preventing them from relaxing to a spherical shape.$^{1,2}$ Reversing the field direction (Video S2, Supporting Information) makes the droplet interface unstable, leading to a continuous field-induced emulsification, also known as electric emulsification,$^{23,39}$ which affects the Columbic interactions between the NPSs and their interfacial activity. Under neutral pH conditions, there is a combination of both strong electrostatic repulsion and high interfacial packing density, capable of accumulating substantial potential energy at the interface and resulting in pronounced explosive emulsification.

Fluorescently labeled SiO$_2$ NPs functionalized with carboxylic acid groups show a similar behavior under an applied electric field (Figures S5 and S6, Supporting Information), providing a means to probe NPSs behavior in situ. Laser scanning fluorescence confocal microscopy images of fluorescently labeled, carboxy-functionalized SiO$_2$ NPs aqueous droplet suspended in a toluene solution of PS-triNH$_2$ show the accumulation of the NPSs at the droplet interface (Figure 2). A positive bias applied to the needle holding the droplet brightens the interface initially, but then it dims while the droplet interior increases in brightness, as the field pulls NPs (that have not formed NPSs) away from the interface into the droplet interior (Figure 2a). There is an increase in the concentration of PS-triNH$_2$ at the interface, as evidenced by the reduction in the IFT. The reduced IFT, combined with the in-plane electrostatic pressure, amplifies the interfacial fluctuations, inducing an electric emulsification, where spikes are seen to form at the interface. This electric emulsification removes NPSs from the surface of the parent droplet causing the observed dimming (Video S5, Supporting Information). When the field is removed, the excess PS-triNH$_2$ and charge dissipate from the surface of the droplet, resulting in the increased IFT. This is followed by a gradual decrease in the IFT, as NPSs subsequently form and assemble at the interface (Figure S7, Supporting Information). The microdroplets located near the parent droplet surface are rapidly repelled from the droplet when the field is turned off, due to the like polarities of the microdroplets and droplet. No additional microdroplets form during this process (Video S2, Supporting Information).

A negative bias drives the negatively charged NPs to the interface where they interact with PS-triNH$_2$,$^{19}$ forming stable NPSs, increasing the effective stiffness of the interface that suppresses field-induced emulsification. The number of NPSs at the interface increases, oversaturating the interface, as evidenced by the brighter fluorescence intensity (Figure 2a), and an enhancement in the fluctuations at the interface is seen. The densification of the NPSs under negative bias is also evident in in situ X-ray scattering measurements (Figure S8c, Supporting Information), clearly showing an excess of NPs being driven to and adsorbing onto the interface. Equally important, the X-ray scattering studies show that the assemblies remain liquid-like with no development of ordering. Under a positive bias, no such densification is observed. The results of the in situ X-ray scattering measurements are treated in full in a forthcoming manuscript.$^{46}$ We note, though, that these experiments were not performed on a pendant drop due to the absorption of the X-rays, but at the interface between an oil–water bilayer. Attempts were made to replicate the conditions of the pendant drop studies. The increased

2.2. Oversaturation of the NPSs at the Interface

Fluorescently labeled SiO$_2$ NPs functionalized with carboxylic acid groups show a similar behavior under an applied electric field (Figures S5 and S6, Supporting Information), providing a means to probe NPSs behavior in situ. Laser scanning fluorescence confocal microscopy images of fluorescently labeled, carboxy-functionalized SiO$_2$ NPs aqueous droplet suspended in a toluene solution of PS-triNH$_2$ show the accumulation of the NPSs at the droplet interface (Figure 2). A positive bias applied to the needle holding the droplet brightens the interface initially, but then it dims while the droplet interior increases in brightness, as the field pulls NPs (that have not formed NPSs) away from the interface into the droplet interior (Figure 2a). There is an increase in the concentration of PS-triNH$_2$ at the interface, as evidenced by the reduction in the IFT. The reduced IFT, combined with the in-plane electrostatic pressure, amplifies the interfacial fluctuations, inducing an electric emulsification, where spikes are seen to form at the interface. This electric emulsification removes NPSs from the surface of the parent droplet causing the observed dimming (Video S5, Supporting Information). When the field is removed, the excess PS-triNH$_2$ and charge dissipate from the surface of the droplet, resulting in the increased IFT. This is followed by a gradual decrease in the IFT, as NPSs subsequently form and assemble at the interface (Figure S7, Supporting Information). The microdroplets located near the parent droplet surface are rapidly repelled from the droplet when the field is turned off, due to the like polarities of the microdroplets and droplet. No additional microdroplets form during this process (Video S2, Supporting Information).

A negative bias drives the negatively charged NPs to the interface where they interact with PS-triNH$_2$,$^{19}$ forming stable NPSs, increasing the effective stiffness of the interface that suppresses field-induced emulsification. The number of NPSs at the interface increases, oversaturating the interface, as evidenced by the brighter fluorescence intensity (Figure 2a), and an enhancement in the fluctuations at the interface is seen. The densification of the NPSs under negative bias is also evident in in situ X-ray scattering measurements (Figure S8c, Supporting Information), clearly showing an excess of NPs being driven to and adsorbing onto the interface. Equally important, the X-ray scattering studies show that the assemblies remain liquid-like with no development of ordering. Under a positive bias, no such densification is observed. The results of the in situ X-ray scattering measurements are treated in full in a forthcoming manuscript.$^{46}$ We note, though, that these experiments were not performed on a pendant drop due to the absorption of the X-rays, but at the interface between an oil–water bilayer. Attempts were made to replicate the conditions of the pendant drop studies. The increased
Figure 2. Microscope imaging of the NPSs under different applied voltages. a) Top row: a time-series of confocal images of the SiO$_2$ NPs aqueous droplet in toluene phase before, during, and after applying positive bias voltages, $+500$ V; bottom row: a time-series of confocal images of the same droplets before, during, and after applying $-500$ V. $C_{\text{SiO}_2} = 1 \text{ mg mL}^{-1}$, $C_{\text{PS-triNH}_2} = 1 \text{ mg mL}^{-1}$; b) Confocal image of the water/oil interface right after switching off the voltage ($-1000$ V); c) Wavelength ($\lambda$) of the spikes formed after different negative voltages are turned off. The concentration of the SiO$_2$ varies from 0.1–10 mg mL$^{-1}$ and the ligand concentration is 1 mg mL$^{-1}$.

dipole–dipole interaction also helps to stabilize the oversaturated packing structure at the interface. However, upon removal of the field, the chemical potential of the NPSs at the interface changes, as do interparticle interactions. Dipole interactions between the NPSs are absent,$^{[47-49]}$ causing an increased in-plane interfacial pressure and lowering of the IFT (Figure 3a and Video S6, Supporting Information). Fluctuations at the interface are further amplified, leading to thin fingers that extend from the interface, rapidly budding off microdroplets that are ballistically ejected, as the system returns to its original state absent a field (Figure 2b and Videos S7 and S8, Supporting Information).

A characteristic wavelength, $\lambda$, of the large-amplitude fluctuations emerges that decreases from $\approx 47$ to $\approx 20 \mu$m as the applied negative voltage increases from 250 to $10^3$ V (Figure 2c and Figure S8, Supporting Information) and as the intensity of the explosive emulsification increases. The applied field across the
Figure 3. Electric field-driven oversaturation of NPSs at interface. a) Time evolution of the IFT under different applied voltages, 0 V (black) and −750 V (red), and the field is turned off at 5029 s. Inset is a magnified view of IFT plot within the designated rectangular area; b) Difference between the equilibrium IFT under 0 V and the minimum/maximum IFT after the field is switched off. The insets are the optical images of the droplet after the negative/positive bias voltage is turned off. c, d) The concentration of Fe₃O₄ and PS-triNH₂ are both 1 mg mL⁻¹; C₃Fe₃O₄ (c) and C₅Ps-triNH₂ (d) dependencies of stable interface (blue triangle), explosive emulsification (green circle), and spontaneous emulsification (red diamond) behavior for various PS-triNH₂ and Fe₃O₄ concentrations. The C₅Ps-triNH₂ is 0.1 mg mL⁻¹ in (c) and C₃Fe₃O₄ is 1 mg mL⁻¹ in (d).

interface produces an electrostatic pressure that amplifies fluctuations and, as the IFT decreases, λ decreases (Figure 3b).[50,51] However, by increasing the NP concentration to 5 and 10 mg mL⁻¹, λ increases to ≈70 μm due to the increase of effective stiffness of the interface at high NP concentrations (Figure S9, Supporting Information).[52,53]

The low areal density of NPSs formed at a fixed PS-triNH₂ concentration of 0.1 mg mL⁻¹ and with [Fe₃O₄-COOH NP] ≤ 0.1 mg mL⁻¹ suppresses an explosive emulsification at any of the applied voltages. For [Fe₃O₄-COOH NP] = 0.5 mg mL⁻¹, the achievable areal density increases, and explosive emulsification occurs for V_app < −500 V. Higher concentrations yield an explosive emulsification for V_app ≤ −250 V (Figure 3c). In contrast, [Fe₃O₄-COOH NP] = 1 mg mL⁻¹ and [PS-triNH₂] ≤ 0.01 mg mL⁻¹ prevent explosive emulsification and [PS-triNH₂] ≥ 5 mg mL⁻¹ triggers spontaneous emulsification (Figure 3d and Figure S10, Supporting Information) even without NPs and under no field.[54,55]

By adding salt the ionic strength of the aqueous phase is increased, charges are screened, and electrostatic repulsion between the NPSs on the interface are reduced allowing the areal density of the NPSs to increase and the IFT to decrease.[56,57] Consequently, electric emulsification is suppressed with a positive bias voltage, but, with a negative bias, explosive emulsification still occurs upon removal of the field, though at a significantly reduced ejection velocity (Figure S11, Supporting Information). We note that reducing the IFT typically promotes emulsification. However, the presence of salt screens the electrostatic interactions that are responsible for the explosive event, inhibiting electric emulsification and weakening the explosive emulsification.

2.3. Self-Propelled Droplets: Asymmetric Explosive Emulsification

In a uniform parallel electric field (Figure 4a), the droplet is polarized and the negatively charged NPs migrate to the side of the droplet closer to the positive electrode, promoting NPS formation on that side of the droplet (Figure S12; Videos S9 and S10, Supporting Information). Explosive emulsification is found to occur on that side of the droplet with ejected microdroplet velocities up to tens of mm s⁻¹. Upon ejection of the microdroplets the parent droplet is propelled in the opposite direction (Figure 4a). Similarly, if a plug of an aqueous NP dispersion is confined to a capillary tube (tilted at 3.3° from the horizontal) with PS-triNH₂ solutions on either side, the interface on the right moves ≈15 μm toward the negative electrode (Figure 4b), while an explosive emulsification pushes an entrapped air bubble downward, away from the interface. The interface on the left shows no observable displacement (Figure S13, Supporting Information).

Figure 5a shows an aqueous droplet (∼0.5 mm diameter) with dispersed NPs suspended in a toluene solution of PS-triNH₂
Figure 4. Asymmetric explosive emulsification. a) Left: Schematic of the experimental setup. A pendant aqueous droplet is immersed in the toluene phase and hung at the end of a stainless-steel needle. Two electrodes made of copper tape are attached to opposite walls of the container, enabling application of a uniform electric field across the droplet. Middle and right: aqueous droplet (C_{Fe3O4} = 1 mg mL\(^{-1}\)) immersed in the toluene phase (C_{PS-triNH2} = 1 mg mL\(^{-1}\)) in the presence of a parallel electric field (2.7 kV cm\(^{-1}\)) and after turning it off. Inset shows binary contrast processed with ImageJ to highlight the droplet and microdroplets; b) The displacement of the interface caused by explosive emulsification. Aqueous phase (C_{Fe3O4} = 1 mg mL\(^{-1}\)) in a glass capillary tube (tilted at 3.3° from the horizontal) and with a toluene phase on either side (C_{PS-triNH2} = 1 mg mL\(^{-1}\)); an air bubble is located at the right of the interface spontaneously due to the buoyancy. The optical microscopy images of the capillary tube, captured before and after the uniform electric field (3 kV cm\(^{-1}\)) turned off, are displayed in the left column. The gray value profile across the interface (red and blue boxes) as a function of horizontal distance is shown in the right column. The time values inserted in the images represent the duration that has passed after the electric field was turned off.
within a polypropylene capillary tube that is subjected to a parallel electric field along the axis of the capillary. When the field is removed, both the droplets with and without the NPs initially move toward the positive electrode, then stop, and reverse direction (Videos S11 and S12, Supporting Information). The initial retraction distance of the droplet without NPs is small and can be attributed to an electric emulsification arising from the accumulation of ligands on the negative electrode side. Removing the field causes the ligands to spread uniformly across the droplet surface, generating a Marangoni flow that moves the droplet toward the negative electrode. [13] However, the droplet, oversaturated with NPs on the side near the positive electrode, begins to redistribute some NPSs to the depleted side of the droplet, resulting in an electric emulsification on the droplet surface facing the negative electrode (Figure S14 and Video S13, Supporting Information). This model captures the experimental findings remarkably well, as shown in Figure 5d.

Similar behavior was also observed when an ≈3 μL droplet of an aqueous dispersion of NPs placed at the interface between solutions of PS-triNH2 in CCl4 (bottom layer) and toluene (top layer). Two electrodes with a separation distance of 35 mm were used to apply a field parallel to the interface between the fluids. A top view of the droplet trajectory is shown in Figure 6a. The droplet rapidly moves toward the negative electrode, triggering an electric emulsification on the droplet surface facing the negative electrode (Figure S14 and Video S13, Supporting Information). The emulsification decreases the excess charge on the droplet and the Coulombic forces acting on the droplet balance, and the velocity of the droplet steadily decreases until it comes to rest. Upon removing the field (bright blue line), the droplet velocity abruptly increases to ≈8 mm s⁻¹, where an explosive emulsification occurs on the negatively charged side of the droplet propelling the droplet in the opposite direction. Even with
a larger ≈10 μL droplet, explosive emulsification efficiently propels the droplet (Video S14, Supporting Information). The force generated for propulsion increases with increasing field strength and so does the droplet velocity (Figure 6b and Figure S15, Supporting Information). It should be noted that the multi-curved trajectory of the self-propelled droplets at the toluene/CCl₄ interface mainly stems from the density gradient of the surrounding medium and the asymmetric overpacking of the NPSs. These factors lead to a deviation from the perfect spherical shape of the droplets. Moreover, the confined space within the container introduces a boundary effect, further influencing the movement of the droplets and resulting in a multi-curve trajectory. If we introduce a second droplet to the interface, when the field is applied and the droplets polarized, the droplets can be strongly attracted to each other, inducing an electro-coalescence. This attraction, if strong enough, can cause the formation of a liquid bridge between the droplets, a redistribution of the charges on the droplet surfaces, causing an electrostatic repulsion. Here the result shows electric emulsification occurring in the gap between the droplets. As the field is turned off, the charges on the surfaces of the droplets redistribute and the droplets repel each other (Figure 6c).

3. Conclusion

We have demonstrated an advanced form of active matter that can be programmed to repeatedly move at a specific velocity in a well-defined direction. A DC electric field is used to oversaturate the surface of a liquid droplet with charged NPSs, agnostic of chemical composition of the NPs, storing a Coulombic energy. On demand the field is released causing the formation of hundreds of thousands of charged microdroplets that are electrostatically repelled from the droplet in an explosive emulsification event. The explosive emulsification is made directional by breaking the symmetry of the interfacial assembly, propelling the droplet large distances in the opposite direction. The propulsion is autonomous and repeatable and the direction can be changed with each cycle. This propulsion can be leveraged for microactuation in soft micro-robotics compartmentalized micro-delivery systems, and smart materials. Since the explosive emulsification behavior is independent of the chemical nature of the NPs, the explosive emulsification can be harnessed to serve as a unique delivery mechanism for spray-coating surfaces of objects in situ, controlling chemical reaction, or enhancing delivery of water-soluble materials in organic environment.
4. Experimental Section

Sample Preparation: The negatively charged carboxylic acid-functionalized iron oxide NPs (Fe₃O₄-COOH) (Ocean NanoTech) and green fluorescently labeled silica NPs (SiO₂-COOH) (Micromod) with diameters of ~30 nm were dispersed in deionized water and suspended in a solution of (diethylene triamine)-terminated polyisoprene (PS-triNH₂). The concentration of 310 mg·L⁻¹ was added to the pH 7 solution (1 mL). After complete reaction, the residual NaOH, mol·L⁻¹, were measured by titration with HCl solution (pH 3.4), and the consumption of the HCl was denoted as "nHCl." Upon adding the acid solution that had a certain number of deprotonated carboxyl groups reacted with protons, and two pKa values were observed. These values arise from the two neighboring carboxyl groups. After one of the two carboxyl groups had completely reacted, the total consumption of HCl was denoted as "nHCl." Thus, the number of carboxyl groups on individual NP (NCOOH) could be calculated with the following equation

\[ N_{\text{COOH}} = \frac{2(n_{\text{HCl}} - n_{\text{Na}}) N_A}{N_{\text{Fe}_{3}\text{O}_{4}}} \]  

where \( N_A \) is Avogadro’s number, and \( N_{\text{Fe}_{3}\text{O}_{4}} \) is the number of the Fe₃O₄-COOH NPs used in the titration which can be identified by their mass concentration. To minimize the effect of CO₂ from the air, the open end of the vial was covered with parafilm during titration.

Electric Field Experiment: Aisymmetric electric fields were applied to the pendant droplet suspended from stainless-steel needle (15 Gauge) by connecting the latter to a high-voltage generator (Treklab 615-10). The voltage supply was grounded to the outer surface of cuvette (12.5 mm x 12.5 mm x 45 mm), which was covered on two opposite sides and the bottom with conductive copper tape and the remaining two opposite walls were made of glass and clear view. A constant bias voltage was applied to the needle without any current. The microdroplets in the electric field experiments were imaged using an Olympus DSX1000 microscope. To apply a parallel electric field on the suspended droplet, two opposite sides of the cuvette were covered by a copper tape, connected to the bias voltage, and grounded separately.

IFT Measurement: A pendant drop tensiometer (Krüss DSA30) was used to measure the IFT. The time dependence of IFT was recorded after the aqueous droplet (~30 μL) was injected into the oil phase until the IFT reached equilibrium. An asymmetric electric field was applied to the pendant droplet during the measurement to investigate the influence of applied voltage on IFT.

Confocal Measurement: A Zeiss LSM710 confocal microscope was used to investigate the behavior of the NPSs under an electric field. The temporal evolution of microdroplets was identified and tracked with ImageJ/Scion Image software. The velocities of the microdroplets were calculated using OpenPIV (Particle Image Velocimetry).

Supporting Information

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

Acknowledgements

X.W. and H.X. contributed equally to this work. This work was supported by the U.S. Department of Energy, the Office of Science, the Offoce of Basic Energy Sciences, the Materials Sciences and Engineering Division under Contract No. DE-AC02-05-CH11231 within the Adaptive Interfacial Assemblies Towards Structuring Liquids program (KCTR16). R.S. acknowledges support to the beam for scattering measurement on a Pilatus area detector. The notable discrepancy in electron density between Au and the tolune oil phase induced significant scattering from the NPSs assembled at the interface. Horizontal averaging of scattering profiles showed maxima at a characteristic q² value, indicating the center-to-center distance between NPSs at the interface, d = 2π/λ q². The mobility of the droplet was studied using a capillary tube. A droplet of an aqueous dispersion of NPs was placed in a 1.5 mm diameter glass capillary tube forming a liquid plug in the capillary. Toluene solution of PS- triNH₂ was placed on both sides of the aqueous plug and an air droplet was placed on one side of the plug using an inclination angle of 3° to force the air droplet to the water/oil interface. Electrodes at the ends of the capillary tube were used to apply a parallel electric field across the components. In a separate experiment, a droplet of an aqueous dispersion of the NPs was placed in a larger polycarbonate capillary tube (2.4 mm diameter) in a toluene solution of PS-triNH₂. The diameter of the droplet was smaller than the inner diameter of the capillary to allow the droplet to freely move.

Analysis on the Explosive Emulsification: The jettisoned microdroplets during the explosive emulsification were identified and tracked with ImageMagick, an imaging processing tool. The optical images were converted into a black and white format, a process that is exemplified in Figure S17 (Supporting Information). For quantifying the microdroplets, the areas occupied by the needle and the parent droplet were first subtracted from the overall white area in the image. The total number of the jettisoned microdroplets was then estimated by dividing the projection area of each individual microdroplet from the remaining white area. It should be noted that this estimation did not account for overlapping microdroplets due to the absence of 3D imaging capabilities in the current experimental setup, which makes the authors’ estimate a lower bound. The velocities of the microdroplets were calculated using OpenPIV (Particle Image Velocimetry).
Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available in the supplementary material of this article.

Keywords
charged nanoparticle-surfactants, directed explosive emulsification, liquid–liquid interface, self-assembly, self-propulsion

Received: October 8, 2023
Revised: February 15, 2024
Published online: