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Discovery of a Voltage-Stimulated Heartbeat Effect in Droplets of Liquid Gallium

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Chemomechanical effects are known to initiate fluid oscillations in certain liquid metals; however, they typically produce an irregular motion that is difficult to deactivate or control. Here we show that stimulating liquid gallium with electrochemistry can cause a metal drop to exhibit a heart beating effect by shape shifting at a telltale frequency. Unlike the effects reported in the past for mercury, the symmetry-breaking forces generated by using gallium propel the drop several millimeters with velocities of the order of 1 cm per second. We demonstrate pulsating dynamics between 0 and 610 beats per minute for 50–150 μL droplets in a NaOH electrolyte at 34 °C. The underlying mechanism is a self-regulating cycle initiated by fast electrochemical oxidation that adjusts the drop's surface tension and causes a transformation from spherical to pancake form, followed by detachment from the circular electrode. As the beat frequency can be activated and controlled using a dc voltage, the electrochemical mechanism opens the way for fluid-based timers and actuators.

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Liquid motion is vital in engineering and biological systems in order to transport matter, store energy, absorb shocks, and exert pressure. For this reason, many biological species have developed exquisite methods for controlling their internal fluid dynamics for a variety of functions (e.g., selective osmosis and propulsion) [1,2]. In contrast, most human fluidic technology still relies on mechanical flow controllers that seem inelegant by comparison. One route beyond this limitation is to utilize synthetic fluids that mimic the flexibility of biological counterparts [3–5]. In this context, liquids are needed that respond strongly to external stimuli such as electric fields by switching properties including volume, viscosity, or surface tension. Electrorheological and magnetorheological responses have been extensively investigated in the family of "smart fluids" consisting of ferromagnetic, ferroelectric, or liquid crystal particles suspended in dielectric solutions [6]. More recently, pioneering work has unveiled strong electrochemical-mechanical responses in liquid metal gallium alloys [7]. The combination of high electrical conductivity and programmable surface tension makes these attractive candidates for reconfigurable electronics, actuators, artificial muscles, soft robotics, and "lab-on-a-chip" microfluidic circuitry. Certain fluidic components such as oscillators or ac actuators necessitate a time-varying mechanical response with a controllable frequency. There have been no reports, however, indicating that it is possible to create a dc voltage-based self-regulating oscillator with gallium-based liquids. While analogous chemomechanical oscillations are well known using liquid mercury [4,8–15], as first reported by Lippman in 1873 [16], they do not permit practical utilization of the alternating motion. This is because the autonomous beating of mercury occurs at zero potential via a natural chemical reaction, making it difficult to deactivate or control, and the beat frequency is strongly determined by the drop's mechanical properties resulting in a limited dynamic range [12,17].

In this Letter, we report our discovery of a voltage-activated heartbeat effect in liquid metal gallium that inverts a direct current (dc) signal into a self-regulated autonomous oscillation with an adjustable frequency. In contrast to mercury heart systems, the gallium drop expands laterally while pressing against the electrode, generating a strongly asymmetric reaction force that overcomes gravity and ultimately enables an uphill displacement of the drop (see Supplemental Material, Sec. i [18]). This discovery is a striking implementation of the recent advances using the surface chemistry of gallium-based liquid metals to allow for strongly modified surface tension under an electric potential [19]. Recent studies have proven that the electrochemical oxidation in gallium greatly enhances the response compared to the standard electrocapillary effect known in mercury [19]. This allows gallium liquid metals to deform [19,25], self-actuate [3,26], self-propel [27], solidify [28], mimic the stretching motion of a biological body [29], move directionally or rotationally [5,30,31], and trace a voltage through a maze [32]. Achieving self-regulating control over oscillatory fluid dynamics for gallium remains attractive for a range of environments where its low toxicity is advantageous [33–35]. The additional periodic displacements produced by

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the gallium heart offer a promising avenue to increase the amount of work that the drop performs on the surrounding fluid via drag. Most recently, a promising proof-of-principle experiment demonstrated a continuous-flow pump using liquid gallium; however, this required active regulation with ac voltage [30]. To this end, we present a scheme that enables tunable, self-regulated oscillations using a liquid gallium droplet in a dc voltage.

The key factor to achieve controllable oscillations in gallium liquid metals is a novel circular graphite electrode design, inclined at an angle in an electrolyte bath [see Fig. 1(a)]. The cavity provides a constraint on the liquid metal, while the graphite electrode enables electrochemical oxidation through a range of contact angles [36]. Further details of the experimental conditions are given in Supplemental Material, Sec. ii [18]. Using a 30-mm ring, with a 11.1 mm inner diameter with height $h = 20$ mm, as shown in Figs. 1(a)–1(e) on a slightly inclined Petri dish ($\theta = 0.5°$), our results demonstrate how metal droplets with volumes (50 μL) can beat continuously in a NaOH electrolyte with a 1 molar concentration. This is caused by the drop periodically making electrical contact with the electrode, as shown in the sequence of images recorded using photography [see Fig. 1(h)]. Movies of the visually striking effect are available in Supplemental Material [18].

To understand the mechanism, it is useful to consider the repetitive heart beat [see Fig. 1(h)] in six steps: contact, oxidation, wetting, loss of contact, etching, and downhill drift. In the first phase [see Fig. 1(h), $\Delta t = 0$], the liquid metal droplet docks with the inner wall of the ring. This brings it to the same electric potential as the positively charged electrode and facilitates current flow through the liquid metal into the electrolyte. The voltage enables electrolysis and reactions to proceed at the surface of the gallium. Above a threshold voltage, anodic surface oxidation of liquid gallium into Ga_2O_3 becomes possible via the nonspontaneous reaction [3,37],

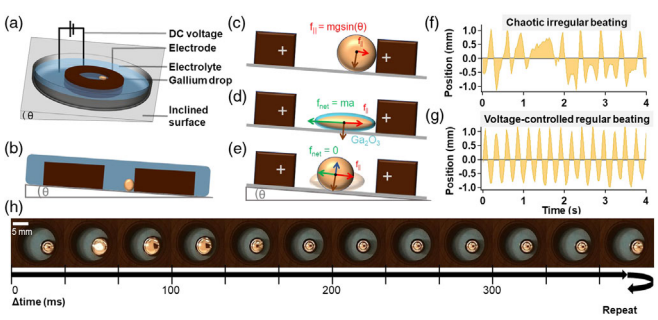

FIG. 1. (a) Schematic diagram of experimental setup for the gallium oscillations. (b) Cross section of the inclined apparatus. [(c)–(e)] Force diagram of the gallium heart beat sequence. (f) Chaotic motions can occur for certain drop sizes, or once the stabilizing voltage is removed. (g) Under a constant applied dc voltage, regular oscillations can be observed for the 50 μL drop. (h) The series of photographs captured from the video shows the cycle of a heartbeat for the 50 μL drop.

$$2Ga + 3H_2O \leftrightarrow Ga_2O_3 + 6H^+ + 6e^-.$$

The newly formed metal oxide behaves like a surfactant [19]. It is now well established that this leads to significant change in the surface tension from $\sim 500\ \mathrm{mJ/m^2}$ to almost 0 [7,25]. Consequently, the droplet begins to spread into a filmlike form [see Fig. 1(h), $\Delta t = 33$ ms] as the contact angle is reduced [19]. Pressure is exerted as the drop pushes against the electrode edge causing the center of mass to move away as the drop spreads. This "electrowetting" proceeds until the pancake-shaped gallium loses contact with the edges of the electrode [see Fig. 1(h), $\Delta t = 132$ ms]. The mechanical decoupling also breaks the connection between the droplet and the external power supply. The drop continues to move away from the electrode under the influence of linear momentum and gravity, until it approaches the center ($\Delta t = 198$ ms). Throughout its free trajectory, the apparent diameter begins to shrink, since without the applied voltage, hydroxyl ions can quickly etch the oxide layer surrounding the liquid metal surface [37] leading to the recovery of a state with high surface tension [19,38]. Consequently, in the final phase (from $\Delta t = 264$ ms), the droplet returns to a spherical shape, and under the influence of gravity, ultimately drifts downhill back to the inner wall of the electrode to begin the next cycle.

A comparatively special feature of the gallium-based liquid oscillator is that the electrochemistry allows the beating to be activated or deactivated just using an applied dc voltage. Figure 2(a) shows the trajectory of a 50 μL drop for 100 seconds where the displacement of the center of the drop is recorded relative to the center of the electrode before and after the voltage is applied. To analyze the numerous photographic frames, and accurately extract the beating frequency, our computational method took advantage of automatic image recognition and particle-tracking algorithms [39] (see details of the image analysis in Supplemental Material, Sec. iii [18]). Without the applied voltage, the drop docks with the inner side of the electrode due to the electrode inclination. The voltage causes the drop to self-actuate and a stable periodic motion is obtained soon afterward. An enlarged region [Fig. 2(b)] illustrates the sinusoidal displacements towards the center of the electrode. The oscillations stop after the voltage is removed. The motion can end abruptly; although in some cases, slower irregular beats persist for a few more cycles after the voltage is removed, indicating stored charges on the drop. Despite some background mechanical vibrations in the apparatus, the liquid metal itself shows a behavior that is self-correcting and self-regulating, governed by a well-defined characteristic frequency, as shown from the Fourier transform of the entire trajectory [Fig. 2(c)]. This indicates that the phenomena occur at a steady-state frequency that is relatively robust against mechanical perturbations.

The drop also undergoes a shape shifting transition during the cycle from spherical to pancake form, changing

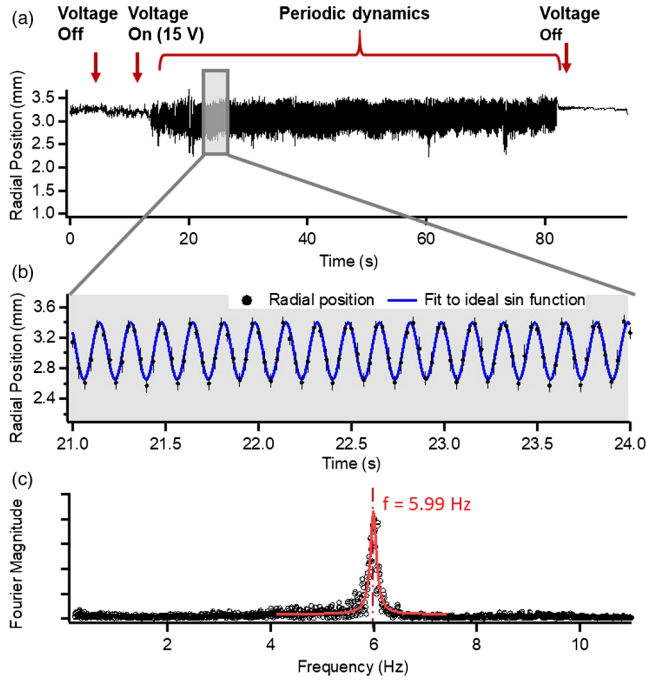

FIG. 2. (a) The translational motion of the 50 μL droplet begins when the voltage is applied and is deactivated after the voltage is removed. (b) The displacement of the 50 μL drop is close to that of an ideal sinusoid with a frequency of 5.99 ± 0.01 Hz. (c) The characteristic frequency dominates in the entire minute-long trajectory as is clear in the Fourier transform. The red line is a Lorentzian fit.

cross-sectional area as it spreads (Fig. 3). As with the displacement, the transformation is caused by the formation of the oxide layer, shown schematically [Fig. 3(a)]. By fitting a circular region to the visible area in each frame, the shape transformation can be tracked throughout the time sequence. Unlike the displacement that has a sinusoidal form, the shape undergoes abrupt steplike jumps for the 50 μL drop [Fig. 3(b)] producing a signal that is reminiscent of an electrocardiogram. Drops containing 100 μL

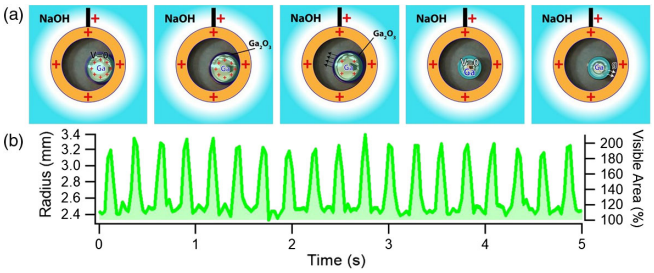

FIG. 3. (a) The motion and shape of the drop can be rationalized by considering the electrochemical reaction that forms a gallium-oxide interface and produces a net charge on the droplet to induce displacement. Subsequent etching in the electrolyte removes the oxide and neutralizes residual charge. The arrows on the drop indicate the motion direction of the liquid gallium. (b) 50 μL drops show abrupt shape transformations evident in their visible radius.

require two times longer than that of a 50 μL gallium droplet to return to their spherical form (see Fig. S2 in Supplemental Material [18]) indicating there is a volume-dependent time cost associated with the shape transformation. Close inspection reveals that the drop motion also affects the fluid dynamics in the surrounding electrolyte as periodic ripples appear on the electrolyte surface. Furthermore, by tracking the position of the center of drop, and assuming this corresponds to the center of mass, it is possible to estimate the force on the droplet from the second derivative of the displacement (Fig. S3). The driving acceleration can be divided into two regimes, depending on whether the drop is in contact with the electrode. If the drop is in contact, the net radial forces are -0.25 mN moving the drop away from the electrode edge. While not in contact, the forces are 0.037 μN, as expected for the gravitational component at the angle of 0.7°. For every single beat, the maximum instantaneous velocity of the liquid metal can be measured. The maximum instantaneous velocities are of the order of 1 cm/s.

In addition to the dominant electrochemical and mechanical effects, we directly verified that the drop also has a small net charge, and experiences Coulomb repulsion after it is detached from the graphite electrode. This is clear because inserting a wire as an additional control electrode can either repel or attract the drop without physical contact and without noticeable effects on the surface tension. Such Coulomb interactions are absent in pure chemomechanical phenomena, but can potentially enhance the force experienced by the droplet in the region of the strong electric field. Furthermore, the drop induces mirror currents measurable in a nearby neutral copper wire. Given the high conductivity and fast electronic response, the liquid metal can be treated as an ideal conductor under electrostatic equilibrium such that Maxwell's equation $\nabla \cdot \mathbf{E} = 0$ applies. The mechanism for the electromagnetic repulsion is then analogous to the motion of metallic electrostatic bells [40], the most famous example being Benjamin Franklin's bell designed to detect an approaching thunderstorm. This involves a process whereby any residual charge is redistributed at the surface, producing a dipole that balances the external potential. In the electrolyte, this involves forming the electrical-double layer on the liquid metal, structured with negative hydroxyl groups terminating the metal oxide counterbalanced by external positive ions [37], providing a capacitance that leads to a long-lived charge on the drop for several seconds [19].

To investigate the intriguing interplay of forces that determine the frequency of the motion, systematic experiments were conducted at constant electrolyte pressure. The following parameters were investigated: applied dc voltage, the angle of incline, drop volume, and choice of electrolyte. Three volumes of droplets were examined (50, 100, and 150 μL). In situations where steady-state beating could be obtained, a point is recorded in Fig. 4 detailing the

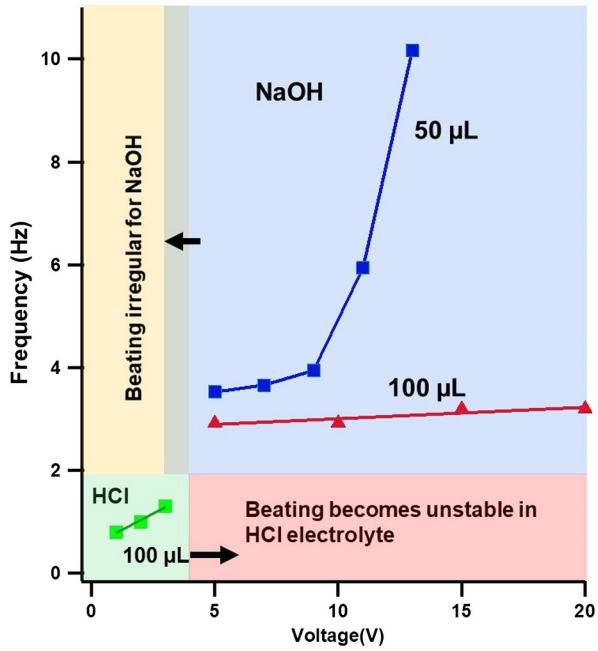

FIG. 4. The beating frequency for NaOH and HCl electrolytes. Different threshold voltages are required to initiate beating in the acid or base electrolyte.

maximum frequency achievable for a given set of conditions. Experiments were conducted for 1–2 minutes to evaluate stability and reproducibility. Although some initial motion invariably occurs, we omit discussion of conditions that exhibit chaotic trajectories, with no well-defined periodicity, or do not sustain beating for more than few cycles. Figure 4 summarizes the states that support stable beating for different volumes, voltages, and electrolytes under a fixed angle of $\theta = 0.7°$.

The simplest way to adjust the steady-state frequency in the heart beat is to apply different voltages (see Fig. 4). Higher voltages tend to increase the beat frequency in acid and alkaline electrolytes. The largest dynamic response results from using the smallest droplet (50 μL) producing a maximum frequency of 10.16 Hz. For the NaOH solution, a threshold voltage of at least 4 V is required to initiate the reaction and sustain the oscillation. For the HCl solution, the beating was observed for a 100 μL drop between 1–3 V, albeit with a much lower frequency. The efficient alkaline electrolyte appears to act as "adrenaline" to speed up the reaction compared to the acidic solutions. The fact that beating occurs in both acidic and alkaline solutions confirms the well-established fact that the Ga_2O_3 forms in a wide variety of liquid solutions and pH levels [37]. Gravity also has a strong effect on the frequency, as a small incline is essential to generate reproducible beating [see Fig. S4(a)]. The beating is experimentally stable for angles up to 2.5 degrees, and higher angles correspond to faster frequencies, as expected since the component of gravitational force is enhanced in the latter case. The beat frequency is also related with the volume of the gallium droplet. Under a fixed voltage, the frequency is inversely proportional to the volume of the droplet [Fig. S4(b)]. For larger drops (150 uL) and high voltages, the patterns of oscillation deviate from regular frequencies and behave increasingly randomly, as the droplets expand completely to fill the cavity, suffer "cardiomegaly," and enter cardiac arrest [see inset Fig. S4(b)]. The large changes in reflective area scale up to 200% during the transformation, which is much larger than the mercury-based systems, and has been exploited previously to produce high contrast light valves in optical systems [41].

In conclusion, this Letter unveils an easily implemented liquid oscillator using electrochemical oxidation of gallium in a graphite ring. The heart beatlike response has many similarities with the previously known mercury oscillators. However, without a viable control mechanism, the chaotic motion of liquid mercury has proven to be merely an academic curiosity. An important conceptual difference is that, unlike the spontaneous mercury heart [42], the gallium oscillations can be turned on or off using an external voltage even while the drop is in contact with the electrode, thus providing a route to control the underlying mechanism. The gallium drop can be tuned over a range of frequencies using a dc voltage, whereas the frequency of mercury beating is fixed at certain discrete values governed by the topological modes regulated by the external ac voltage [8,13,17]. Unlike the mercury heart that shape shifts around its center of mass, the experiment on gallium generates strong forces that drive a net displacement in the drop position, therefore increasing the drag as it moves through the surrounding carrier fluid. Collectively, these findings represent a significant step forward to adding new functionality for dynamic fluid controllers, stretchable electronics [43], and composite materials [44] using mechanically robust liquid metals [45]. The uniquely controllable heart beating rheological response of gallium liquid metals could drive central biomimetic vascular units in a variety of contexts, such as soft robots and microfluidic chips. To date, we have demonstrated beating frequencies between 2.3 and 10.17 Hz. However, this is not an intrinsic limitation but only reflects the limitations of our proof-of-principle apparatus. Optimized electrode geometries are now being investigated to determine the ultimate limit on the down scaling to microscale systems.

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[1] S. Vogel, *Life in Moving Fluids: The Physical Biology of Flow* (Princeton University Press, Princeton, 1981).

[2] J. Tu, K. Inthavong, and K. K. L. Wong, *The Human Cardiovascular System, Computational Hemodynamics—Theory, Modelling, and Applications* (Springer, New York, 2015), pp. 21–42.

[3] R. C. Gough, J. H. Dang, M. R. Moorefield, G. B. Zhang, L. H. Hihara, W. A. Shiroma, and A. T. Ohta, ACS Appl. Mater. Interfaces **8**, 6 (2016).

[4] S. Nakata, H. Komoto, K. Hayashi, and M. Menzinger, J. Phys. Chem. B **104**, 3589 (2000).

[5] J. Zhang, Y. Yao, L. Sheng, and J. Liu, Adv. Mater. **27**, 2648 (2015).

[6] R. Stanway, Mater. Sci. Technol. **20**, 931 (2004).

[7] M. D. Dickey, ACS Appl. Mater. Interfaces **6**, 18369 (2014).

[8] D. K. Verma, H. Singh, P. Parmananda, A. Q. Contractor, and M. Rivera, Chaos **25**, 064609 (2015).

[9] J. Keizer, P. A. Rock, and S.-W. Lin, J. Am. Chem. Soc. **101**, 5637 (1979).

[10] C. W. Kim, I.-H. Yeo, and W.-K. Paik, Electrochim. Acta **41**, 2829 (1996).

[11] P. Kumar, D. K. Verma, P. Parmananda, and S. Boccaletti, Phys. Rev. E **91**, 062909 (2015).

[12] S.-W. Lin, J. Keizer, P. A. Rock, and H. Stenschke, Proc. Natl. Acad. Sci. U.S.A. **71**, 4477 (1974).

[13] E. Ramírez-Álvarez, J. L. Ocampo-Espindola, F. Montoya, F. Yousif, F. Vázquez, and M. Rivera, J. Phys. Chem. A **118**, 10673 (2014).

[14] D. K. Verma, A. Q. Contractor, and P. Parmananda, J. Phys. Chem. A **117**, 267 (2013).

[15] D. K. Verma, H. Singh, A. Q. Contractor, and P. Parmananda, J. Phys. Chem. A **118**, 4647 (2014).

[16] G. Lippmann, Ann. Phys. (Berlin) **225**, 546 (1873).

[17] S. Smolin and R. Imbihl, J. Phys. Chem. **100**, 19055 (1996).

[18] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.121.024302 for comparison of mercury and gallium heart beat system, details of the experimental conditions, details of the image analysis, and experimental images and videos, which includes Refs. [9,10,12–14,17,19–24].

[19] M. R. Khan, C. B. Eaker, E. F. Bowden, and M. D. Dickey, Proc. Natl. Acad. Sci. U.S.A. **111**, 14047 (2014).

[20] R. W. Smithwick and J. A. M. Boulet, J. Colloid Interface Sci. **150**, 567 (1992).

[21] S. Castillo-Rojas, J. L. González-Chávez, L. Vicente, and G. Burillo, J. Phys. Chem. A **105**, 8038 (2001).

[22] S. Castillo-Rojas, G. Burillo, and L. Vicente, Chem. Educ. **7**, 159 (2002).

[23] J. L. Ocampo-Espindola, E. R. Álvarez, F. Montoya, P. Parmananda, and M. Rivera, J. Solid State Electrochem. **19**, 3297 (2015).

[24] J. L. Ealy, J. Chem. Educ. **70**, 491 (1993).

[25] C. B. Eaker, D. C. Hight, J. D. O'Regan, M. D. Dickey, and K. E. Daniels, Phys. Rev. Lett. **119**, 174502 (2017).

[26] S.-Y. Tang, V. Sivan, K. Khoshmanesh, A. P. O'Mullane, X. Tang, B. Gol, N. Eshtiaghi, F. Lieder, P. Petersen, and A. Mitchell, Nanoscale **5**, 5949 (2013).

[27] A. Zavabeti, T. Daeneke, A. F. Chrimes, A. P. O'Mullane, J. Zhen Ou, A. Mitchell, K. Khoshmanesh, and K. Kalantar-zadeh, Nat. Commun. **7**, 12402 (2016).

[28] Z. Yu, Y. Chen, F. F. Yun, and X. Wang, Adv. Eng. Mater. **19**, 1700190 (2017).

[29] L. Sheng, J. Zhang, and J. Liu, Adv. Mater. **26**, 6036 (2014).

[30] S.-Y. Tang, K. Khoshmanesh, V. Sivan, P. Petersen, A. P. O'Mullane, D. Abbott, A. Mitchell, and K. Kalantar-zadeh, Proc. Natl. Acad. Sci. U.S.A. **111**, 3304 (2014).

[31] Z. Yu, F. F. Yun, and X. Wang, Mater. Horiz. **5**, 36 (2018).

[32] M. R. Khan, C. Trlica, and M. D. Dickey, Adv. Funct. Mater. **25**, 671 (2015).

[33] M. D. Dickey, Adv. Mater. **29**, 1606425 (2017).

[34] Y. Lu, Q. Hu, Y. Lin, D. B. Pacardo, C. Wang, W. Sun, F. S. Ligler, M. D. Dickey, and Z. Gu, Nat. Commun. **6**, 10066 (2015).

[35] S. A. Chechetka, Y. Yu, X. Zhen, M. Pramanik, K. Pu, and E. Miyako, Nat. Commun. **8**, 15432 (2017).

[36] L. Hu, L. Wang, Y. Ding, S. Zhan, and J. Liu, Adv. Mater. **28**, 9210 (2016).

[37] Y. Chung and C.-W. Lee, J. Electrochem. Sci. Te. **4**, 1 (2013).

[38] S. C. Hardy, J. Cryst. Growth **71**, 602 (1985).

[39] J.-Y. Tinevez, N. Perry, J. Schindelin, G. M. Hoopes, G. D. Reynolds, E. Laplantine, S. Y. Bednarek, S. L. Shorte, and K. W. Eliceiri, Methods **115**, 80 (2017).

[40] A. J. Croft, Eur. J. Phys. **5**, 193 (1984).

[41] J. T. H. Tsai, C.-M. Ho, F.-C. Wang, and C.-T. Liang, Appl. Phys. Lett. **95**, 251110 (2009).

[42] J. Wang, B. Zheng, J. Xiao, X. Liu, H. Ji, J. Du, Y. Guo, and D. Xiao, RSC Adv. **7**, 32552 (2017).

[43] L. Ren, J. Zhuang, G. Casillas, H. Feng, Y. Liu, X. Xu, Y. Liu, J. Chen, Y. Du, L. Jiang, and S. X. Dou, Adv. Funct. Mater. **26**, 8111 (2016).

[44] N. Kazem, T. Hellebrekers, and C. Majidi, Adv. Mater. **29**, 1605985 (2017).

[45] Y. Chen, Z. Liu, D. Zhu, S. Handschuh-Wang, S. Liang, J. Yang, T. Kong, X. Zhou, Y. Liu, and X. Zhou, Mater. Horiz. **4**, 591 (2017).