Supplementary Information

Electrochemically Induced Actuation of Liquid Metal Marbles

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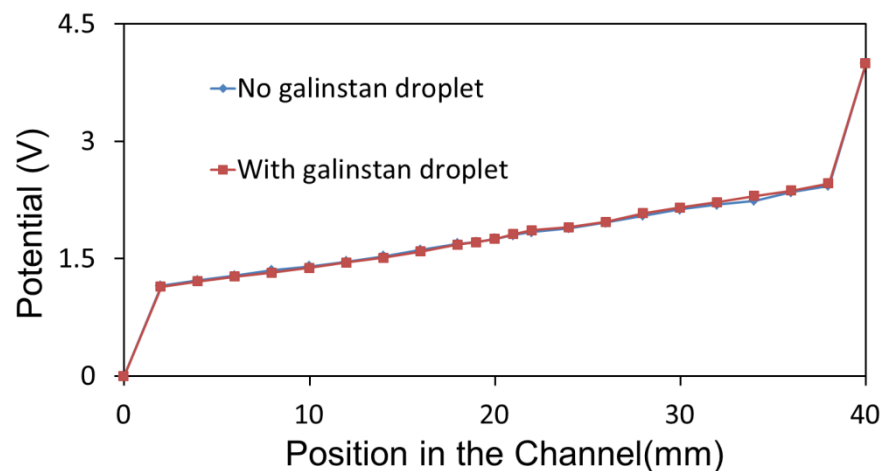
Supplementary Figure S1. Potential distribution along the channel when a DC voltage is applied. Position vs potential plots of the basic electrolyte (pH = 13.5) filled PDMS channel with or without a 2 mm diameter galinstan droplet placed inside when a 4 V DC voltage is applied across the two graphite electrodes, which are separated by 4 cm. The potential distributes linearly along the channel and galinstan droplet has no effect on the linearity of the distribution since the cross section of the channel (24 mm^2) is much larger than the galinstan droplet cross section (~ 3.14 mm^2).
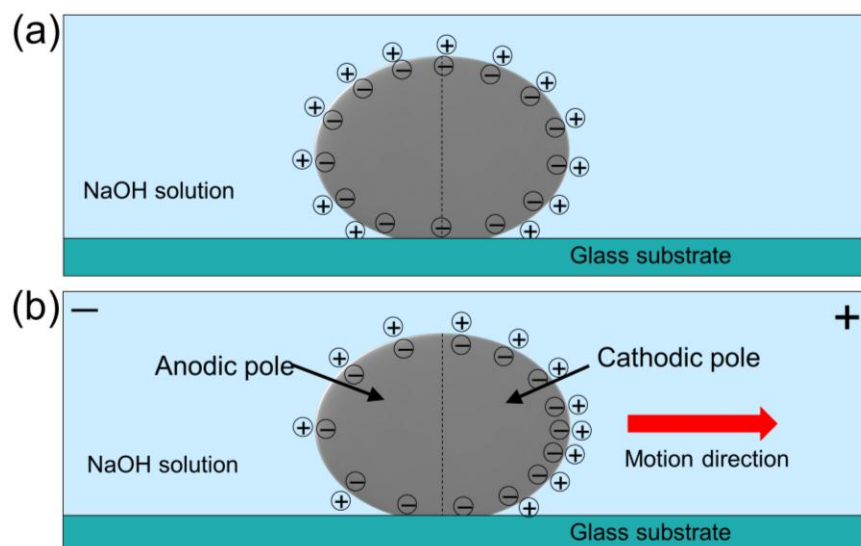
Supplementary Figure S2. Actuation mechanism of galinstan droplet in a basic solution.

Galinstan is composed of gallium (68%), indium (22%) and tin (10%). It is likely that a chemical reaction can slowly occur between gallium (the more dominant metal) and strong alkalies such as sodium hydroxide solution, to produce gallates, such as $[Ga(OH)_4]^-$, which appear as anions. These anions make the surface negatively charged, which results in an accumulation of positively charged ions in a diffuse layer of the EDL as shown in (a). If an electric field is applied, the surface charge on the galinstan droplet will be redistributed. In this case, we can assume that the charge on the surface take a distribution similar to that of shown in (b). Since the body of the galinstan droplet is at equipotential, the electric potential across the EDL (V), in equation (1) in the main manuscript, is greater on the cathodic pole than the anodic pole. Therefore, the surface tension on the cathodic pole, according to equation (1), is less than the anodic pole of the droplet. As a result, this surface tension gradient induces motion of the galinstan droplet towards the anode. The mechanism of the motion can alternatively be interpreted as a tendency to minimize the surface energy by wetting more to the area where the surface tension is lower, i.e. the cathodic pole of the droplet.
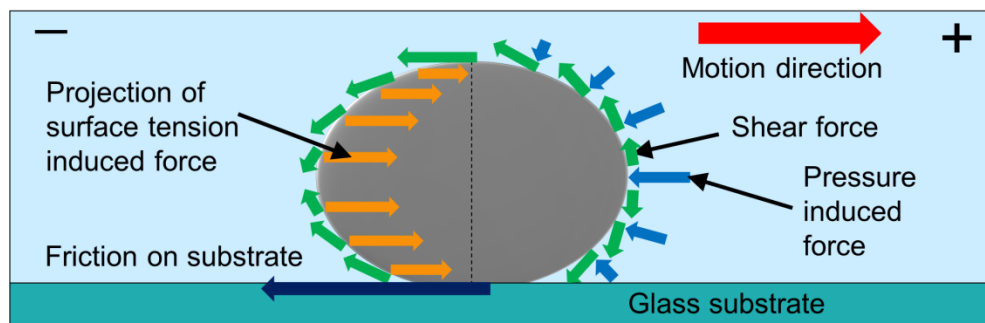
Supplementary Figure S3. Schematic of force components influencing the motion of galinstan droplets in a basic solution. Forces influence the motion of a galinstan droplet in a basic solution include the surface tension gradient induced driven force (towards the anode), the retardation forces such as the frictional force between the droplet and the surface of the substrate (towards the cathode), and the viscous friction between the droplet and its surrounding electrolyte (towards the cathode), in which the viscous friction between the droplet and its surrounding electrolyte is composed of the shear force (green arrows) and the pressure induced force (light blue arrows) during motion.
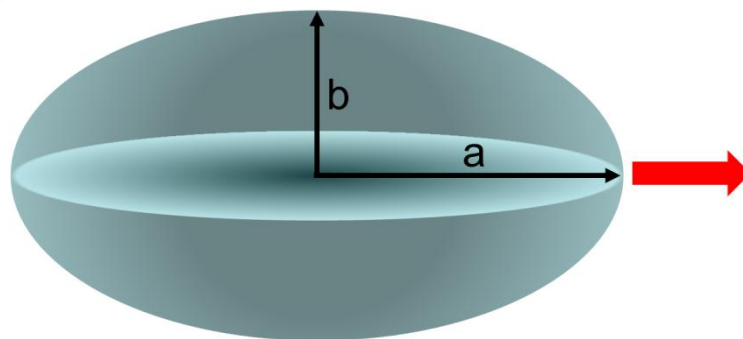
Supplementary Figure S4. Correction factor corresponding to an ellipsoid droplet.

Schematic of an ellipsoid droplet. The correction factor k_1 corresponding to an ellipsoid droplet when moving in the PDMS channel is given by:

$$k_1 = \frac{\frac{8}{3}(\alpha^2 - 1)}{\frac{\alpha(3\alpha^2 - 2)}{(\alpha^2 - 1)^{1/2}} \tan^{-1}(\alpha^2 - 1)^{1/2} - \alpha} \tag{S3.1}$$

$$\alpha = \frac{a}{b} \tag{S3.2}$$

where α is the ratio of semi- major axis and semi-minor axis of ellipsoid, a represents the semi-major axis and b represent the semi-minor axis.
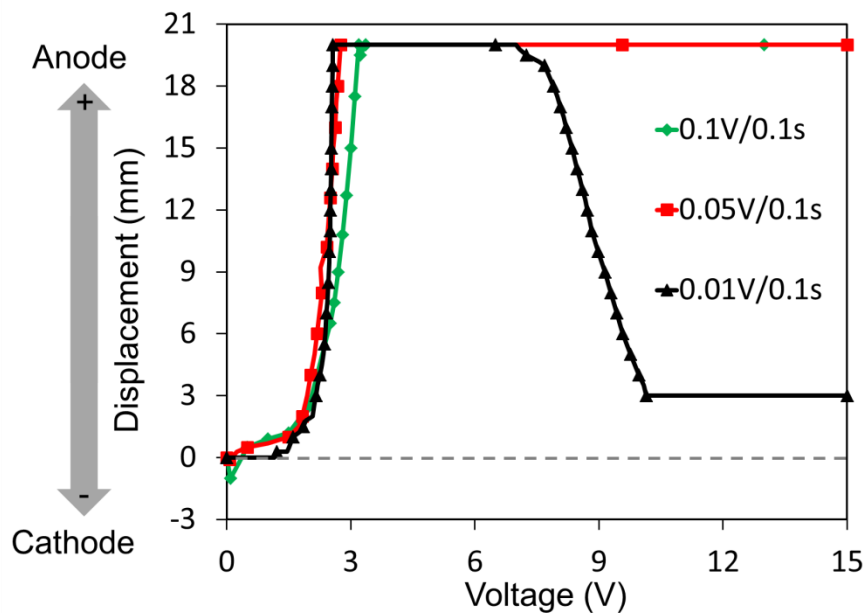
Supplementary Figure S5. Actuation of galinstan droplets in a basic electrolyte under the influence of ramped applied voltages. Voltage-displacement plots for voltage ramping tests at 1, 0.5 and 0.1 V s^{-1} from 0 to 15 V in a basic solution of pH 13.5.

After the actuation onset, the galinstan droplets move towards the anode. The speeds are measured to be 3.3, 1.85 and 0.36 body lengths per second for 1, 0.5 and 0.1 V s^{-1}, respectively. Only for the smallest ramp rate used (0.1 V s^{-1}), the direction of motion is eventually reversed towards the cathode when the voltage reaches 7 V and the droplet ceases to move any further after 10 V. This can be explained due to the low ramping rate that is slow enough to enable a thick oxide layer to form, which accumulates continuously on the anodic pole of the galinstan surface. Electrolysis of the electrolyte also causes the solution close to the anode to become less basic (due to the oxygen evolution reaction) and hence decreases the reduction rate of the oxide layer. This causes the surface tension to decrease dramatically on the anodic pole, finally allowing the galinstan droplet to move towards the cathode.
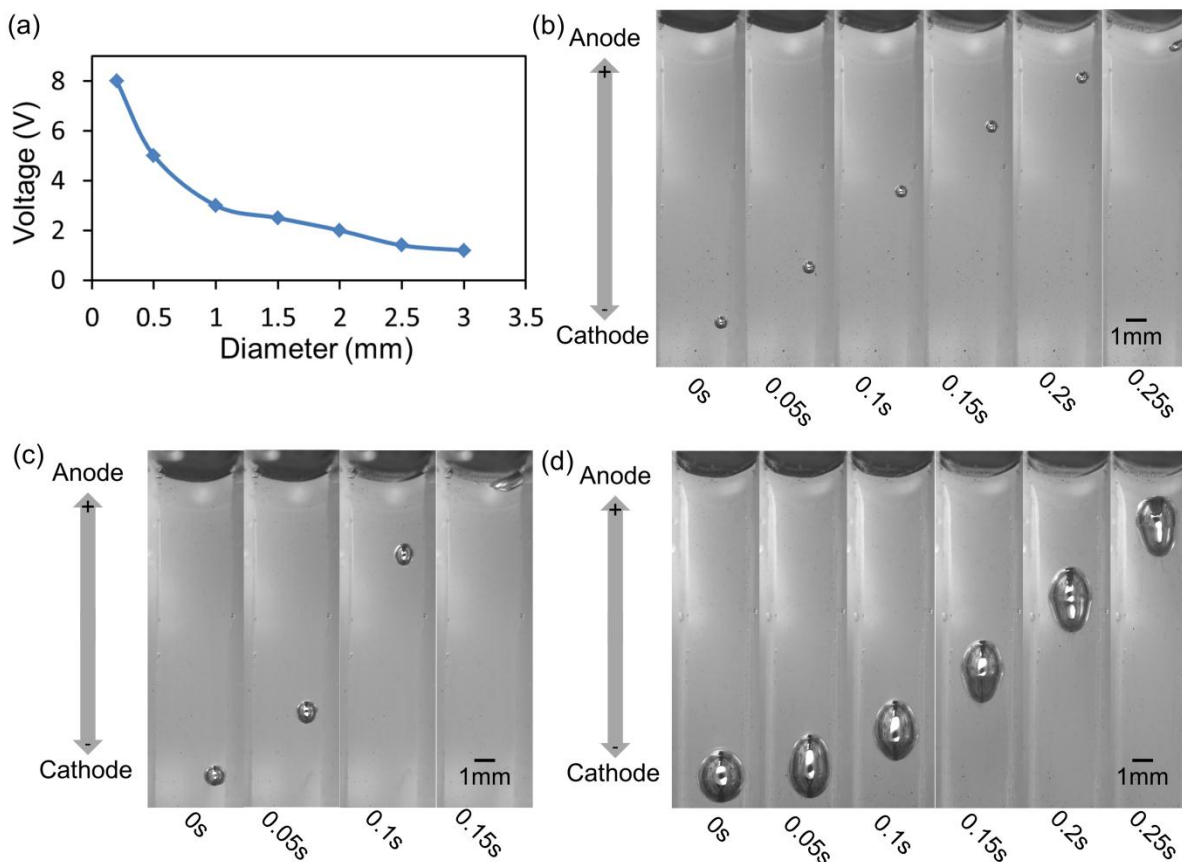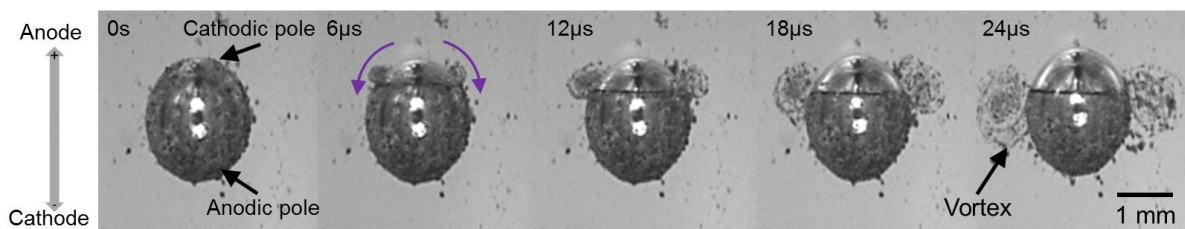
**Supplementary Figure S6. Actuation of galinstan droplets of different diameters in a basic electrolyte.** The actuation of galinstan droplets with the diameter ranging from 0.2 to 3 mm is investigated and (a) presents the minimum voltages required to actuate galinstan droplets of different sizes in a NaOH solution with the pH of 13.5. Beyond these voltages, galinstan droplets move towards the anode. It seems that larger voltages are required to induce enough surface tension difference in order to drive smaller droplets. Figures (b), (c) and (d) present sequential snapshots for the actuation of galinstan droplets with the diameters of 0.5, 1 and 3 mm, respectively, in NaOH solution with the pH value of 13.5 when a 15 V DC voltage is applied.

For comparison, the actuation speed is 152 body lengths per second (76 mm s^{-1}), 127 body lengths per second (127 mm s^{-1}) and 24 body lengths per second (72 mm s^{-1}) for the droplet diameters of 0.5, 1 and 3 mm, respectively. As can be seen, the absolute speeds for the small and

large droplets are smaller than the droplet with the diameter in the middle of the range. Interestingly, for a small droplet, the surface tension difference generated on both sides of the droplet is small, which results in a smaller speed. If the diameter of the droplet is large, the retardation forces such as the viscous friction between the droplet and its surrounding electrolyte as well as the friction between the droplet and the substrate also increase, which eventually result in a reduction in speed. A moderate droplet size, which is able to generate enough surface tension difference, together with relatively small retardation force effects, achieves the highest actuation speed. In our case, the droplets with the diameter of 1 mm provide the highest actuation speed.

Supplementary Figures S7. Ejection and migration of nanoparticles on the cathodic pole when a voltage is applied in a basic solution. When the marble is polarized in a basic solution, the surface of galinstan on the cathodic pole of the marble attempts to wet the surrounding liquid and consequently generate a flow on the surface, as evidenced by the vortices shown in the figure, to push away the nanoparticle coating towards the anodic pole. This process takes place in only 24 μs.
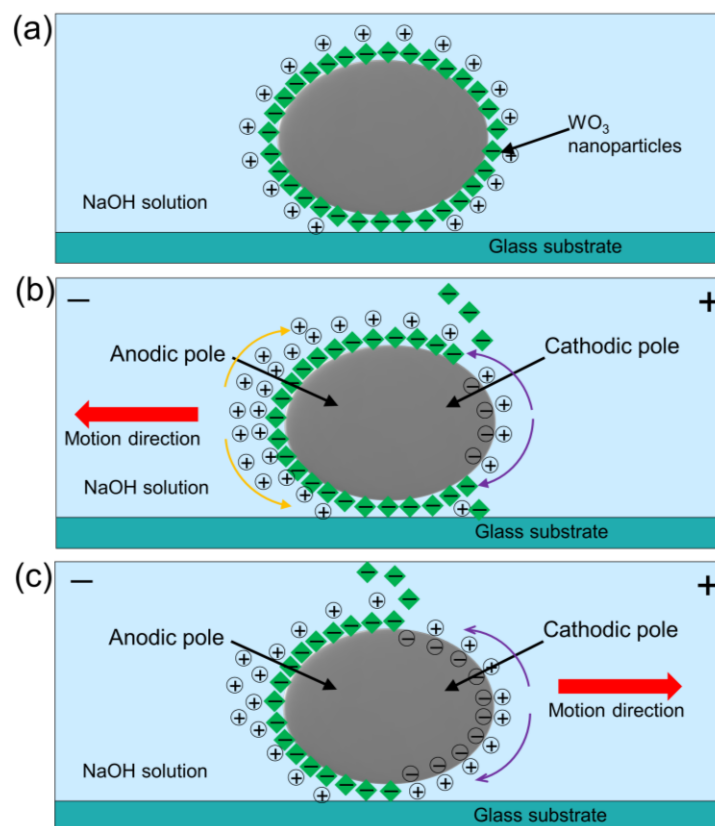
Supplementary Figure S8. Surface charge distribution of WO_3 nanoparticle coated liquid metal marbles in a basic solution. (a) presents the surface charge distribution for a liquid metal marble in a basic solution without the application of an electric field. (b) and (c) present the surface charge distribution for a marble when a small voltage (≤ 7 V) and a large voltage (> 7 V) are applied across the anode and cathode, respectively.
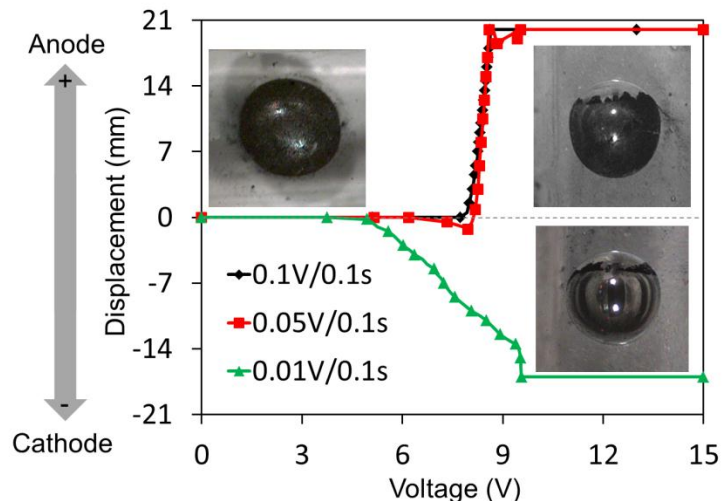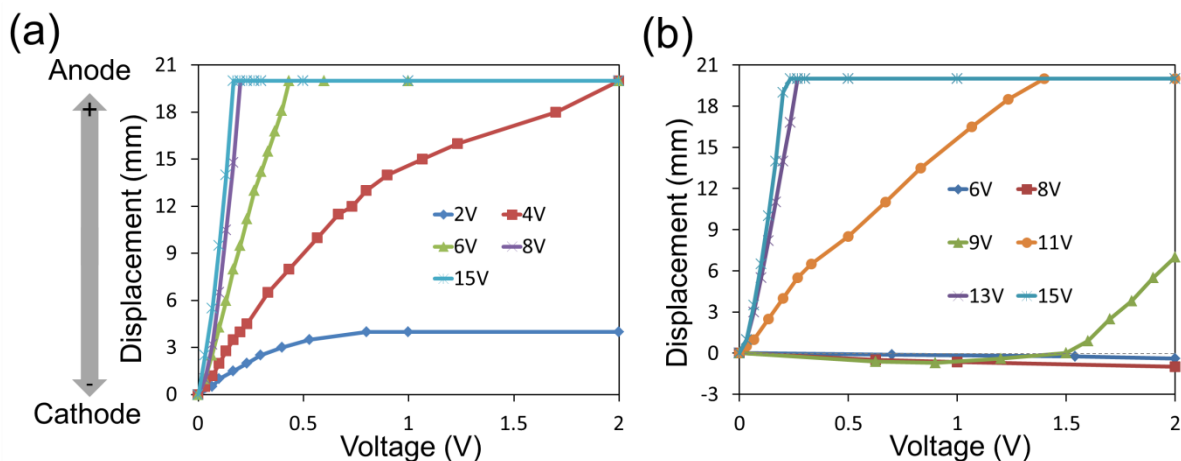
Supplementary Figure S9. Actuation of WO$_3$ nanoparticle coated liquid metal marbles in a basic electrolyte under the influence of ramped applied voltages. Voltage-displacement plots for voltage ramping tests of liquid metal marbles at different ramping rates of 1, 0.5 and 0.1 V s^{-1} from 0 to 15 V in a basic solution of pH 13.5. Marbles are obtained by rolling galinstan droplets over nanoparticles powder beds.

With a ramping rate of 1 V s^{-1}, the liquid metal marble remains immobile until the voltage exceeds 8 V, at which point it move directly towards the anode with speed of about 10 body lengths per second. For a smaller ramping rate of 0.5 V s^{-1}, the liquid metal marble initially remains immobile and then, at a potential of around 5 V starts to move slowly towards the cathode, and then when the voltage reaches 8 V it reverses direction and moves rapidly towards the anode with a similar speed for the case of 1 V s^{-1}. At a reduced ramp rate of 0.1 V s^{-1}, the liquid metal marble remains immobile until the potential reaches 5 V at which point it moves towards the cathode at a steady speed equivalent to 0.2 body lengths per second. Similar to Figures 3c and 3d in the main text, the inserts show that majority of WO$_3$ nanoparticles accumulate on the hemisphere of the liquid metal droplet, which is opposite to the actuation direction.
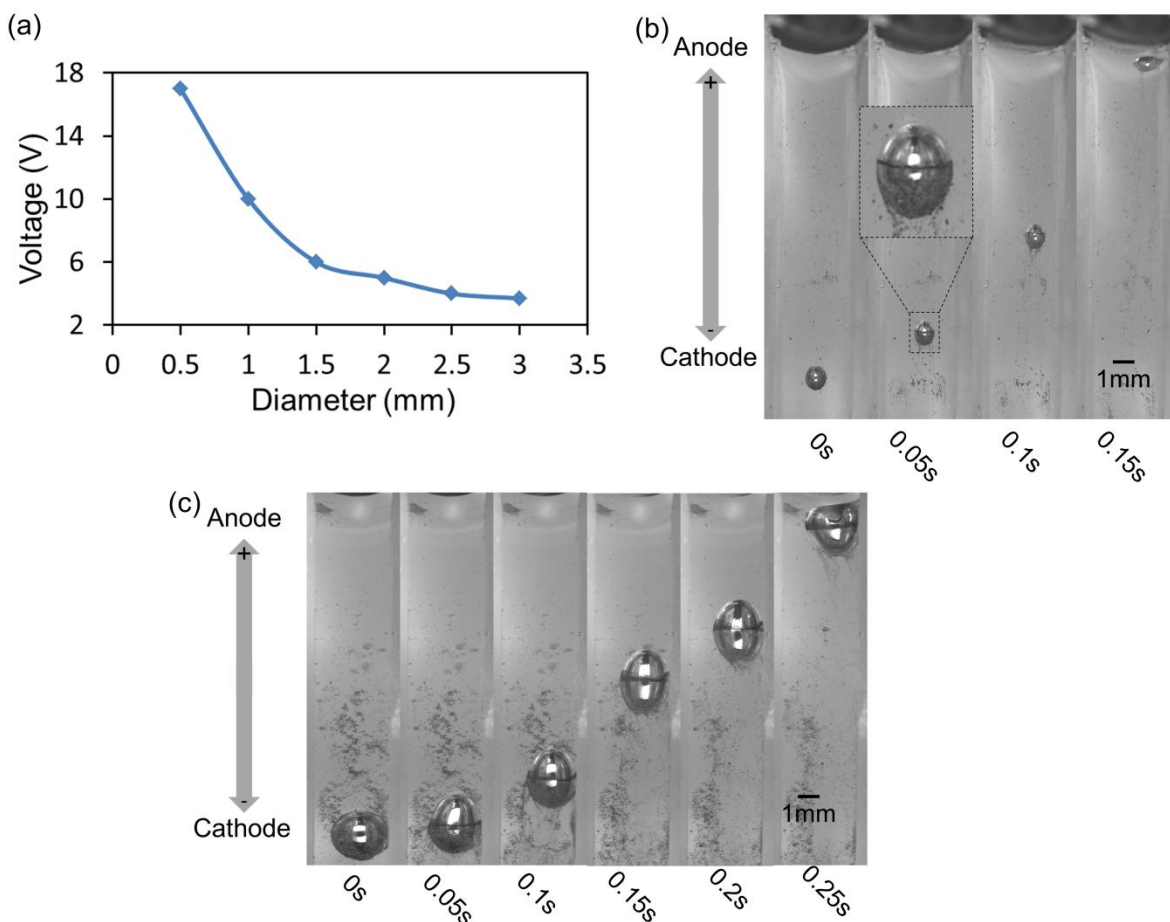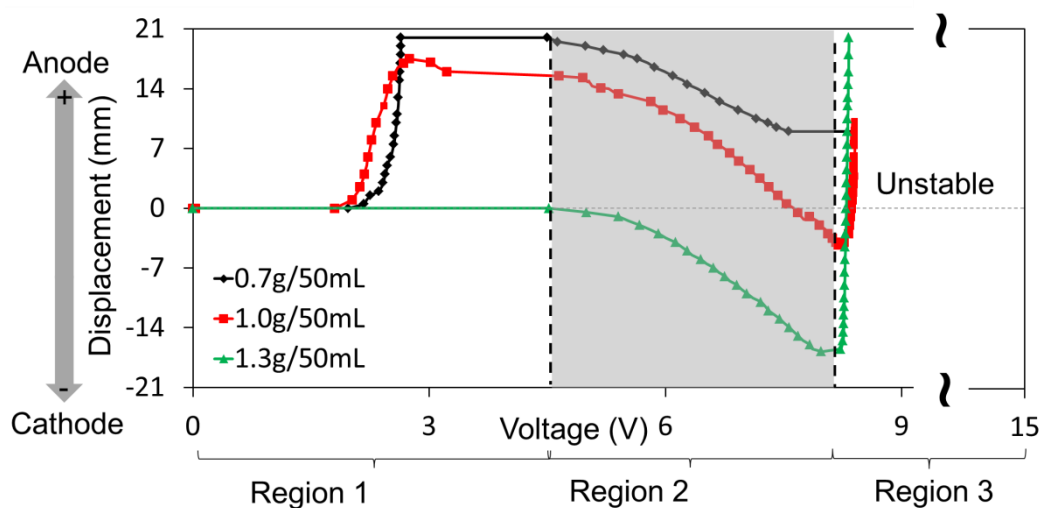
Supplementary Figure S10. Actuation of WO₃ nanoparticle coated liquid metal marbles with different diameters in a basic electrolyte. Actuation of liquid metal marbles with the diameter ranging from 0.5 to 3 mm are investigated and (a) presents the minimum voltages required to actuate galinstan droplets with different diameters in NaOH solution with the pH value of 13.5. Once this threshold voltage is reached, the coated galinstan droplets move towards the cathode. Similar to the bare galinstan case, higher voltages are required to induce enough surface tension differences in order to drive smaller marbles. Figures (b) and (c) present the sequential snapshots for the actuation of liquid metal marbles with the diameters of 1 and 3 mm, respectively, in NaOH solution with the pH value to 13.5, when a DC voltage 15 V DC is applied (15 V DC is chosen for direct comparison with the bare galinstan measurements - 0.5 mm is not

shown as it requires an actuation voltage higher than 15 V DC). The actuation speed is 128 body lengths per second (128 mm s^{-1}) and 27 body lengths per second (80 mm s^{-1}) for the droplets with the diameters of 1 and 3 mm, respectively. Compared to bare galinstan droplets, liquid metal marbles require a larger voltage in order to generate enough surface tension to initiate the actuation. However, once the marbles start the actuation, their speeds are slightly larger than that observed for the bare galinstan droplets with the same diameters due to the larger surface tension difference generated by the nanoparticle coating.
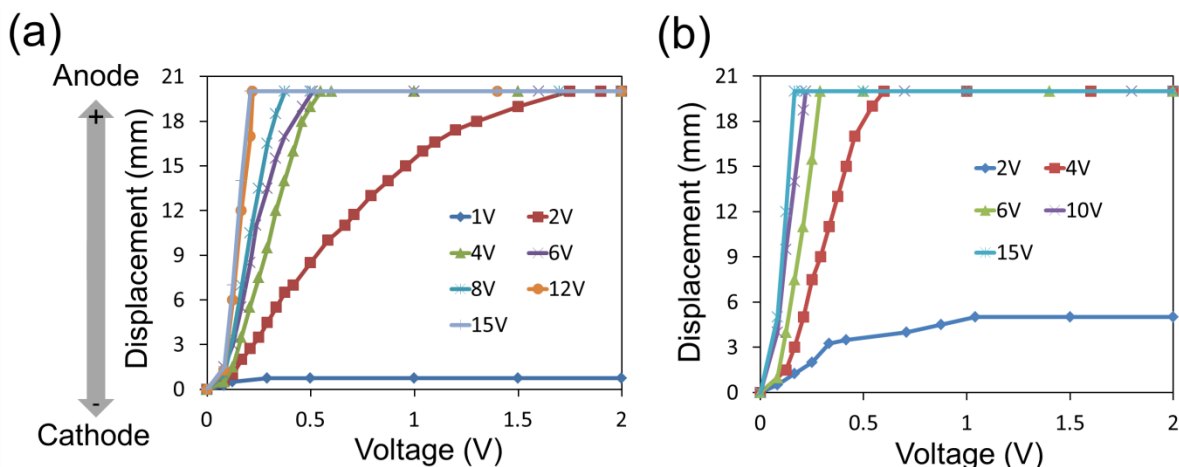
Supplementary Figure S11. Actuation of colloidal suspension coated liquid metal marbles in a basic electrolyte at DC applied voltages. Time-displacement plots for marbles made by immersing galinstan droplets in (a) 0.7 g and (b) 1.3 g of WO_3 dispersed in 50 mL DI water - various applied DC voltages (step functions) at a basic solution of pH 13.5.

For marbles coated in 0.7 g/50 mL suspension, the actuation performance is similar to that of bare galinstan droplets due to the less density of nanoparticle coating. No movement is observed when the applied voltage is less than 2 V. For marbles coated in 1.3 g/50 mL suspension, no movement is observed when the applied voltage is less than 6 V. With the applied voltage is between 6 and 8 V, the liquid metal marbles move slowly towards the cathode. If 9 V is applied, the marble begins moving slowly towards the cathode, then after about 0.9 s reverses its direction to move towards the anode. The liquid metal marble moves directly and rapidly towards the anode if the applied voltage is larger than 9 V. The distribution of nanoparticles on the surface depends on the marble actuation direction, which is similar to the case described in Figure 4 in the main text.

Supplementary Figure S12. Actuation of colloidal suspension coated liquid metal marbles in a basic electrolyte under the influence of ramped applied voltages. Voltage-displacement plots for ramping test at a ramping rate of 0.1 V s^{-1} in a basic solution of pH 13.5 for galinstan droplets immersed in 0.7, 1.0 and 1.3 g of WO_3 dispersed in 50 mL of DI water.

Actuation of marbles is classified into three different regions, denoted as Regions 1, 2 and 3. In Region 1, the marbles coated with 0.7 and 1.0 g/50 mL move towards the anode when the ramping voltage reaches 2 V, while no movement is observed by the marble coated with 1.3 g/50 mL. In Region 2, all marbles actuate towards the cathode at a voltage of 4.5 V. In Region 3, the 0.7 g/50 mL coated marble stops moving, while the 1.0 and 1.3 g/50 mL move back and forth in the channel and show significant instability in their movement. The distribution of nanoparticles on the surface depends on the marble actuation direction, which is similar to the case described in Figure 4 in the main text.

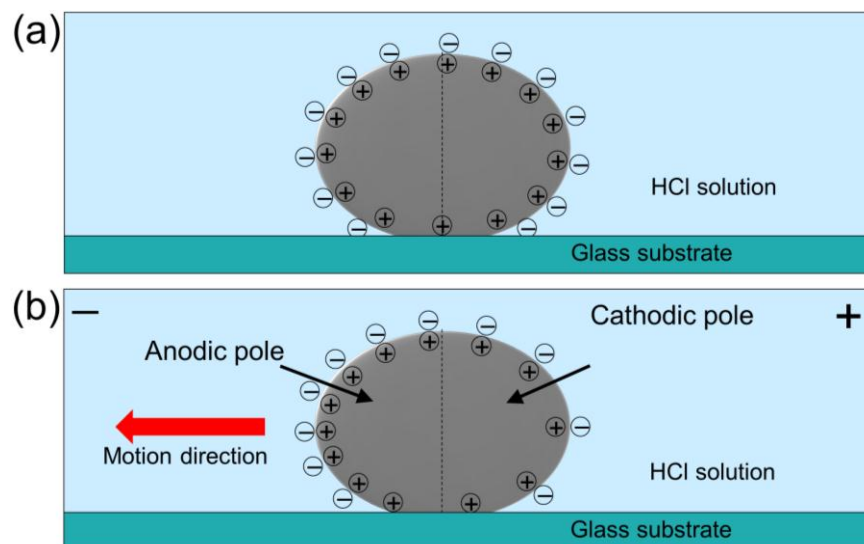**Supplementary Figure S13. Actuation of liquid metal marbles with different nanoparticle coatings.** Time-displacement plots for (a) In_2O_3 and (b) ZnO nanoparticle coated liquid metal marbles at various applied DC voltages (step functions) in a basic electrolyte of pH 13.5. Marbles are obtained by rolling galinstan droplets over nanoparticles powder beds.

No movement is observed when applied DC voltage is smaller than 1 V and 2 V for In_2O_3 and ZnO nanoparticle coated marbles, respectively. For both In_2O_3 and ZnO coated marbles, only the anodic hemispheres remain coated when the voltage is applied, and all marbles move towards the anode.
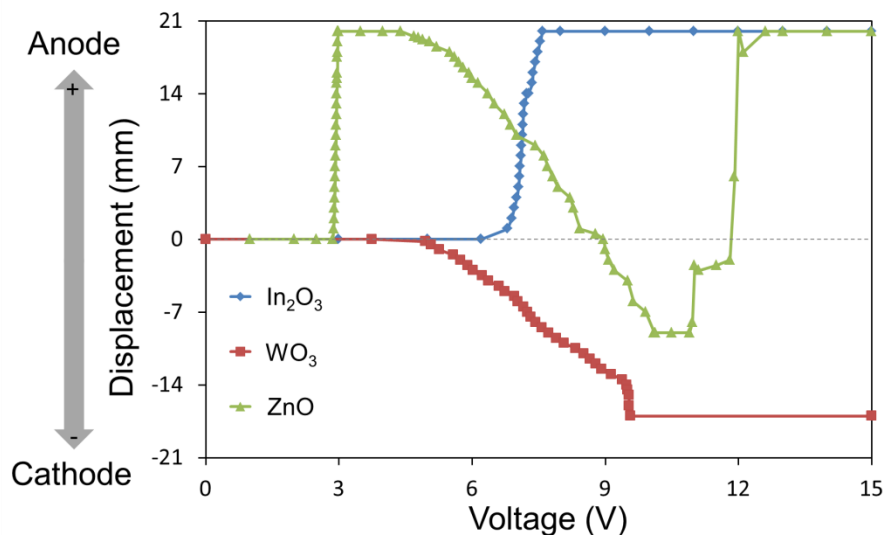
Supplementary Figure S14. Actuation of liquid metal marbles with different nanoparticle coatings in a basic electrolyte under the influence of ramped applied voltages. Voltage-displacement plots for In_2O_3 and ZnO nanoparticle coated liquid metal marbles at a ramping rate of 0.1 V s^{-1} from 0 to 15 V in a basic solution of pH 13.5. Marbles are obtained by rolling galinstan droplets over nanoparticles powder beds.

The In_2O_3 nanoparticle coated liquid metal marble remains immobile until the potential reaches 6 V at which point it moves towards the anode at a speed equivalent to 0.67 body lengths per second. The ZnO nanoparticle coated liquid metal marble start moving toward the anode when the potential reaches 3 V at a speed equivalent to 2.5 body lengths per second, then after ramping voltage reaches about 4.5 V reverses direction to move towards the cathode with the average speed of 0.25 body length per second. After ramping voltage reaches 11 V, the marble actuation becomes unstable.

Supplementary Figure S15. Actuation mechanism of a galinstan droplet in an acidic solution. In an acidic electrolyte, the surface of the liquid metal is positively charged while the outer layer is negatively charged[1] as shown in (a). If an electric field is applied, the surface charge on the galinstan droplet will be redistributed (the charge distribution along the EDL on the surface is shown in (b)). Since the body of galinstan droplet is equipotential, the electric potential across the EDL (V), in equation (1) in the main manuscript, is greater on the anodic pole than the cathodic pole. Therefore, the surface tension on the anodic pole, according to equation (1), is less than the cathodic pole of the droplet. As a result, this surface tension gradient induces motion of the galinstan droplet towards the cathode, which is in the opposite direction for a galinstan droplet actuated in a basic solution.

Supplementary reference

1.   M. Kosmulski, in *Chemical Properties of Material Surfaces*, CRC Press, 2001, pp. 731-744.