

**Article****Surface effects of liquid metal amoeba**Liang Hu<sup>a</sup>, Jing Li<sup>a</sup>, Jianbo Tang<sup>b</sup>, Jing Liu<sup>a,b,\*</sup><sup>a</sup> Beijing Key Laboratory of Cryo-Biomedical Engineering and Key Laboratory of Cryogenics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China<sup>b</sup> Department of Biomedical Engineering, School of Medicine, Tsinghua University, Beijing 100084, China**ARTICLE INFO****Article history:**

Received 15 February 2017

Received in revised form 28 March 2017

Accepted 1 April 2017

Available online 20 April 2017

**Keywords:**

Surface effect

Liquid metal amoeba

Surface tension

Substrate materials

**ABSTRACT**

Liquid metals (LM) such as eutectic gallium-indium and gallium-indium-tin are important functional liquid-state metal materials with many unique properties, which have attracted wide attentions especially from soft robot area. Recently the amoeba-like transformations of LM on the graphite surface are discovered, which present a promising future for the design and assemble of self-fueled actuators with dendritically deformable body. It appears that the surface tension of the LM can be significantly reduced when it contacts graphite surface in alkaline solution. Clearly, the specific surface should play a vital role in inducing these intriguing behaviors, which is valuable and inspiring in soft robot design. However, the information regarding varied materials functions underlying these behaviors remains unknown. To explore the generalized effects of surface materials in those intriguing behavior, several materials including glass, graphite, nickel and copper oxides ( $\text{CuO}$ ) were comparatively investigated as substrate surfaces. Important results were obtained that only LM amoeba transformations were observed on graphite and  $\text{CuO}$  surfaces. In order to identify the proper surface condition for LM transformation, the intrinsic properties of substrate surfaces, such as the surface charge and roughness, as well as the specific interaction with LM like wetting behavior and mutual locomotion etc., were characterized. The integrated results revealed that LM droplet appears more likely to deform on surfaces with higher positive surface charge density, higher roughness and less bubble generation on them. In addition, another surface material,  $\text{CuO}_x$ , is identified to own similar ability to graphite, which is valuable in achieving amoeba-like transformation. Moreover, this study offers a fundamental understanding of the surface properties in realizing LM amoeba transformations, which would shed light on packing and structure design of liquid metal-based soft device within multi-material system.

© 2017 Science China Press. Published by Elsevier B.V. and Science China Press. All rights reserved.

**1. Introduction**

Gallium and its eutectic alloy such as gallium-indium ( $\text{GaIn}$ ) or gallium-indium-tin ( $\text{GaInSn}$ ), several typical non-toxic liquid-state metal materials at room temperature, are quickly gaining vast attention from academia and industry due to its unique and superior properties. Taking advantages of the high conductivity and remarkable deformability, extensive studies have been carried out on liquid gallium and its alloys in the investigation of soft devices and its components such as switch [1,2], pump [3,4], actuator [5,6] and motor [7–9] etc. By manipulating liquid metal in microfluidics, many of those functions can be achieved [10]. However, the capabilities of moving or deforming automatically and independently in free space are also quite desirable for soft devices especially when performing task in complex environment.

The liquid metal (LM) actuator self-fueled by aluminum electrochemical reactions independent of external energy has brought out a brand-new sight for the design of macroscale soft robotic devices [11]. Electrochemical oxidation by the oxygen in the air can also provide independent power supply for LM actuation [12,13]. Recently, our group investigated an intriguing transformation of LM droplet with striking external resemblance to amoeba (unpublished data), which arouses the provoking connection between physical and the vital. To achieve this amoeba-like transformation, LM droplet containing some Al (LM-Al droplet) is placed on graphite surface immersed in alkaline solution. Then the round LM droplet can transform even with the formation of pseudopodia-like extensions. This transformation is totally automatic without external power supply, which provides a multi-material strategy for the design of self-driven liquid metal soft actuators with more complicated behaviors.

The deformation of LM droplet has been observed in many recent studies. With the liquid-state soft body, LM can be deformed

\* Corresponding author.

E-mail address: [jliu@mail.ipc.ac.cn](mailto:jliu@mail.ipc.ac.cn) (J. Liu).

into diverse morphologies under certain circumstance with different mechanisms. For example, LM droplet can slightly elongate or deform in appropriate electric field [5,14], in imbalanced ionic solutions [1], or with bipolar electrochemical reactions [11,15] due to the induced surface tension gradient. When contacted with positive pole of electric power, LM droplet can spread into thin film due to formation of the surface oxide layer, which acts like a surfactant in reducing the surface tension [5,16]. In the amoeba-like transformation, apart from the aluminum reaction which acts as power supply to generate the surface tension gradient across the droplet, the graphite surface also plays important roles in achieving these transformations. It has been disclosed that the graphite surface can significantly reduce the surface tension of LM through electrochemically oxidizing the LM surface [15], which renders more deformability of LM droplet as well as further enhancement of the surface tension gradient. Such unique properties of graphite present great potential and value not only in LM actuation but also in LM shape patterning [15]. So far only graphite has been reported to own such properties and few other materials are reported to display similar properties. Therefore it requires further and comprehensive studies on various surface materials not only to generalize common roles of surfaces in these transformational behaviors but also to find other materials with such valuable properties.

In this study, several conductive or insulated surface materials were used based on preliminary experiments in order to investigate generalized role of substrate surface in LM amoeba transformations. The intrinsic properties of the surfaces as well as their interactions with LM were characterized by physical and optical measurements. The detailed experiments and results are described as follows.

## 2. Experimental

### 2.1. Materials

All the LM droplets used in the experiments were GaInSn alloy prepared from gallium, indium and tin with purity of 99.99%. These raw materials with mass ratios of 67:12:13 respectively were added into a beaker and then heated to 100 °C. A magnetic stirrer was used to stir the mixture uniformly after the metals were all melted. All NaOH electrolyte used in the experiment of this study was freshly made at 0.5 mmol/L.

Glass, graphite, nickel (Ni) and CuO were tested as material for substrate surfaces in the present study. The glass slides (72 mm × 26 mm) were used as glass surface. The graphite plate with purity of 99.9% took the size as 100 mm × 100 mm × 10 mm in length, width and height, respectively. Nickel plate (100 mm × 100 mm × 3 mm) with purity of 99.9% was used as surface. To prepare the CuO surface, Cu foils from a tape (0.1 mm thick) were stuck to the glass slide to make a Cu surface at first. Then the Cu surface was immersed in hydrogen peroxide (30%) for 24 h and was dried in the air. A layer of copper oxides should form on the copper surface. Then the CuO surface was examined by scanning electron microscopy (SEM) and energy disperse spectroscopy (EDS).

### 2.2. LM-Al droplet preparation and its transformation on substrate surfaces

Briefly, a piece of Al foil was placed on the LM droplet in NaOH electrolyte in the glass petri dish. Based on the quantification in preliminary studies, a piece of Al (around 0.8 mg) was dispersed in each LM droplet (200 μL) in NaOH to make the LM-Al droplet as LM would destroy the inter-granular bonds of Al foil and

penetrate into Al grain boundaries [17,18]. When the Al foil was dispersed into small granules without apparent big debris, the LM droplets containing Al (LM-Al droplet) were gently transferred by sucker onto the graphite surface immersed in NaOH solution. Then the transformations of LM-Al droplet were observed and recorded by digital video equipment (Sony HDR-PJ670). In the experiments, all the surfaces were ensured to be the horizontal to avoid interference factor from gravity.

### 2.3. Physical characterization of surface materials

#### 2.3.1. Contact angle measurement

The contact angle (CA) measurement of LM droplet on those surfaces was carried out in 0.5 mmol/L NaOH solution. In this study, we did not adopt the sessile drop method because the contact between small LM sessile drop and surface in electrolyte can be severely influenced by the buoyance. Thus we compared the wetting ability of macro droplet of LM on testing surfaces by their contact angles. The same LM droplet with the volume of 600 μL was placed on various surfaces and the CA at both sides was measured and averaged.

#### 2.3.2. Zeta potential measurement

The nanoparticles were purchased from DK Nano Technology Co. Beijing. The testing colloid solutions with nanoparticles were prepared by adding nanoparticles into deionized water. The pHs were adjusted by NaOH or HCl. The concentration of each conductive nanoparticle was 0.10 mg/mL SiO<sub>2</sub>, 0.10 mg/mL graphite, 0.3 mg/mL nickel and 0.3 mg/mL CuO, respectively. Then the zeta potential of those nanoparticles was measured by the Beckman Coulter Delsa Nano C Zeta Potential Analyzer.

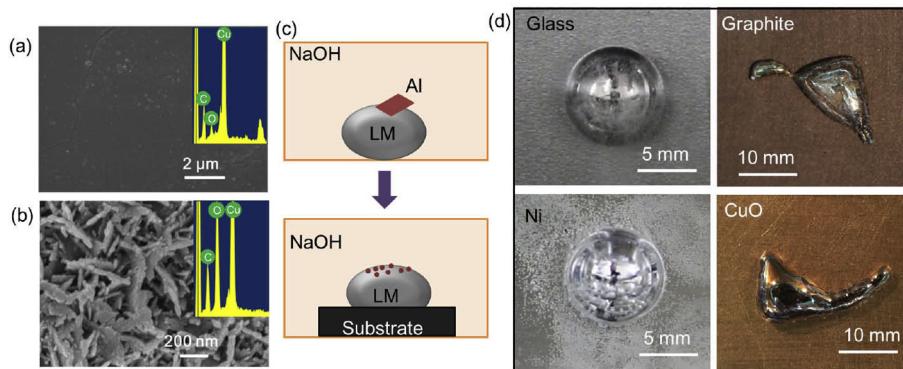
#### 2.3.3. Optical measurement of surface surfaces

Prior to all the measurement, the surfaces should be maintained clean and dry. The surface roughness of the testing surfaces was examined by optical profiler (Counter GT-K, Bruker Nano Inc.). The graphite surface was also examined by SEM.

## 3. Results and discussion

### 3.1. Amoeba transformation on various surfaces

The amoeba-like behavior of gallium-based LM has been observed on graphite surface. In this study, insulated and conductive surface materials were employed to study the surface conditions in the transformation. Initially, CuO surface treated by H<sub>2</sub>O<sub>2</sub> was examined by SEM and EDS. For original Cu surface, the component of oxygen was relatively low (1.84% in mass) (Fig. 1a). After H<sub>2</sub>O<sub>2</sub> treatment, the oxygen obviously increased as illustrated by the EDS (20.79% in mass). The results together indicate that a layer of copper oxides was formed on the original copper surface (Fig. 1b). Thus the CuO surface was successfully prepared. Then the LM-Al droplet was prepared and the transformation was monitored as shown in Fig. 1c. The experimental phenomenon of LM-Al droplet on these surfaces was characterized as shown Fig. 1d and Movies S1–S4 (online). From our observation, obvious transformation with LM extensions only appeared on graphite and copper oxide surfaces. During the amoeba-like transformation, the LM-Al droplet kept twisting and deforming with dark and grey oxide surface appeared on the droplets. The amoeba-transformation was observed on CuO surfaces prepared by magnetron sputtering (Fig. S1 online), which implies that CuO should participate in inducing such transformation. On the other surfaces, LM-Al droplets presented distinct behaviors. On the nickel surface, the LM-Al droplet still maintained the metallic color with abundant



**Fig. 1.** (Color online) The SEM images of raw Cu (a) and CuO surface (b) treated by  $\text{H}_2\text{O}_2$ . The insets are the results of EDS. (c) The experimental procedure in observing LM transformation on testing surfaces. (d) The LM-Al droplet transformation on the glass, graphite, nickel and CuO surfaces.

gas bubbles generated right underneath and over the droplet, pushing droplets running around. Droplet appeared like a bouncing sphere due to the abundant bubbles generated under the droplet (Fig. S2 online). On the glass surface, hydrogen was generally generated on the top surface of the droplet because Al granules were usually distributed on the top of the droplet due to its light weight. The droplet still maintained the round shape.

In these multi-material interactions in NaOH electrolyte, galvanic reactions should take place among those materials. For all these four cases, the cathodic reactions are the same ( $\text{Al} + 4\text{OH}^- - 3\text{e} = \text{AlO}_2^- + 2\text{H}_2\text{O}$ ). However, the anodic reactions varied in different cases. For the insulate glass surface, Al would form galvanic cell with LM. Water received the electron and hydrogen was produced at LM ( $2\text{H}_2\text{O} + 2\text{e} = \text{H}_2 \uparrow + 2\text{OH}^-$ ). For other conductive surfaces, the Al in the LM droplet would form galvanic cell with surfaces through LM, since the LM droplet was conductively contacted with surfaces. Specifically, at graphite and nickel surfaces hydrogen was produced. The abundant bubbles generation on nickel surface should be due to the specific catalytic capability of nickel in hydrogen evolution reaction [19,20]. However, as graphite is a porous material and can store hydrogen [21], bubbles were not observed at initial stage. The hydrogen bubbles were observed after some time from the gaps of graphite surfaces (Fig. S3 online). While at CuO surface the copper oxides instead of water were reduced ( $\text{CuO} + \text{H}_2\text{O} + 2\text{e} = \text{Cu} + 2\text{OH}^-$ ,  $\text{Cu}_2\text{O} + \text{H}_2\text{O} + 2\text{e} = 2\text{Cu} + 2\text{OH}^-$ ) as the standard electrode potential of water is more negative than copper oxides or copper hydroxides [22]. Thus in our observation, no gas was observed on copper oxides surface. When the Al reaction continued, the LM can amalgamate with the reduced Cu at their interface, which could influence further transformation of the LM droplet (Fig. S4 online). Thus there was little interference of gas bubbles on the contact between the droplet and the graphite or the CuO surfaces, which may enhance the interaction between the surfaces and the LM-Al droplet.

### 3.2. Wetting capability of LM on testing surfaces

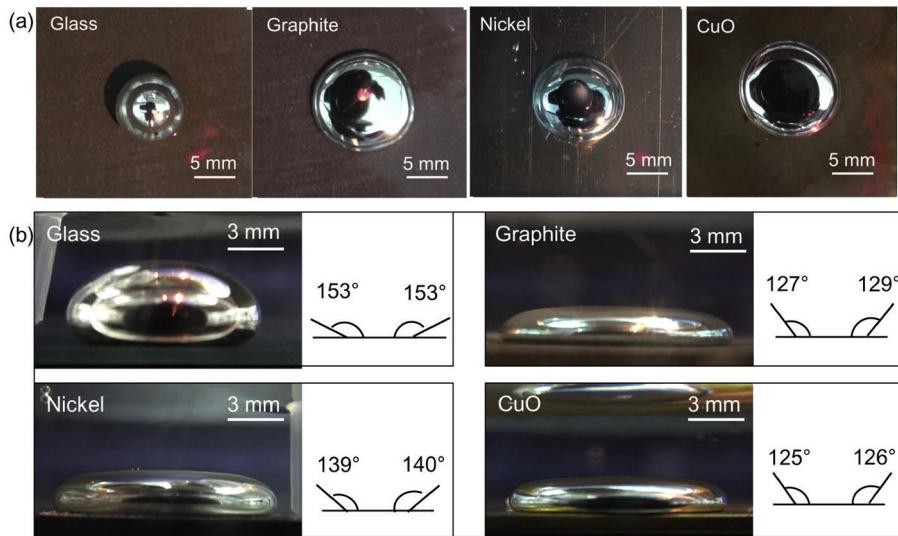
In the amoeba transformation of LM-Al droplet on the graphite surface, the LM droplet was oxidized by the interaction with graphite. The oxide layer formed on the LM droplet surface reduced the surface tension, making droplet spread to become flat and appear more wetting on the graphite surface (Figs. S5–S7 online). In our study, the diameter changes of the droplet on various substrate surfaces were also characterized as shown in Fig. 2a. The diameter of a 600  $\mu\text{L}$  LM droplet on glass was around  $(8.2 \pm 0.1)$  mm. On the conductive substrates, the diameter of some LM droplet increased to  $(12.2 \pm 0.2)$ ,  $(11.2 \pm 0.3)$ ,  $(12.3 \pm 0.2)$  mm on the

graphite, nickel and CuO surfaces, respectively. This result suggests that the LM droplets all became relatively flat on conductive substrates. Practically, LM droplet has largest deformation on the CuO surfaces, which is close to that on graphite. The result implies that the CuO surface have similar capability in reducing the surface tension of LM droplet, which is vital for inducing the LM amoeba-like transformation.

Contact angles are also important macroscopic characteristics of the surface wettability and the interfacial free energy [23]. Generally larger contact angles usually indicate the more wetting capability of liquid on surfaces. For the examples shown in Fig. 2b, the averaged CAs of LM droplet on the glass, graphite, nickel and CuO surfaces were  $154.3^\circ \pm 0.7^\circ$ ,  $128.6^\circ \pm 1.7^\circ$ ,  $141.2^\circ \pm 4.5^\circ$  and  $126.3^\circ \pm 4.8^\circ$  respectively. Based on the CA results, the wetting ability of the LM droplets on those surfaces as ranked by CA was CuO, graphite, nickel and glass, which is consistent with the spreading deformation results in Fig. 2a. For glass surface, there should be no electrochemical interaction between LM droplet and the surface due to the insulation of glass. For those conductive surfaces, however, the quasi-spherical LM droplets became flat and spread out on those surfaces. The flattening behavior of LM on graphite surface was due to the electrochemical formation of oxide layer induced by the positive surface charge of graphite as described above. Thus it was speculated that other surfaces have been also positively charged in NaOH, which similarly induced electrochemical oxidation on LM and further reduced its surface tension. To testify this speculation, further investigations of the surface properties of these substrate materials were examined as presented in the following section.

### 3.3. Surface charge of surface materials in NaOH

In the flattening behavior of LM on graphite surface in NaOH electrolyte, the positive surface charge on graphite plays an important role in electrochemical oxidation of LM, which results in the surface tension reduction of the LM droplet [15]. Zeta potential was used to define the surface charge at the interface of material in non-interacting electrolyte [24]. Although the experimentally derived parameters are only approximate values, they are related to surface charge in such a way as to provide useful information regarding the source and magnitude of surface charge [25]. For graphite, the zeta potential of graphite particles was remarkably low at basic solutions, indicating a positive surface charge on the surface. It is widely known that the surface charge of LM in NaOH is negative [3,5,6]. When the LM contacts with graphite in NaOH, the negative potential drop across the LM-NaOH interface could be significantly increased in order to reach equal potential with graphite surface [15]. Thus LM was electrochemically oxidized

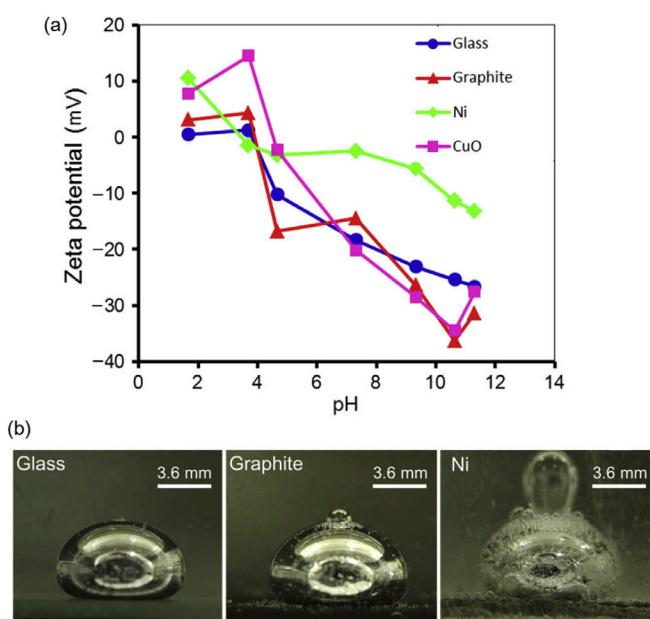


**Fig. 2.** (Color online) The wetting capability of LM droplet on various surfaces measured in 0.5 mmol/L NaOH. (a) The spreading of LM droplet (200  $\mu$ L) on glass, graphite, nickel and CuO surfaces. (b) Contact angle measurement of LM droplets (600  $\mu$ L) on glass, graphite, nickel and CuO surfaces.

with the formation of an oxide layer, which reduced the surface tension as a result (Fig. S7 online). As the surface charge may vary for different surfaces at different pHs, the zeta potential of those testing surfaces material nanoparticles were measured at various pHs in order to generally determine the surface charge properties of these surface materials. The results of zeta potentials shown in Fig. 3a revealed that when the pH was low, the zeta potentials were positive and that when pH increased, the zeta potentials generally decreased to negative. This result is consistent with common tendency of zeta potentials measurement that materials usually have low negative zeta potentials at high pHs due to absorption or attraction of cations or negatively charged groups [24]. The zeta potential at very basic pHs of all the four surface materials were all negative, indicating the materials themselves were positively charged in NaOH, which also confirmed our specu-

lation that it was the positive surface potential across the substrate surface-electrolyte that electrochemically oxidized the LM surface. More specifically, at very basic pHs (pH 10–12), the zeta potential of nickel nanoparticle is apparently higher than others, indicating less positive charge on nickel surface. This result is also consistent with the less wetting behavior of LM on nickel surface as shown in Fig. 2a. For glass surface (mainly composed of  $\text{SiO}_2$ ), although the zeta potential of  $\text{SiO}_2$  nanoparticles was also as low as other conductive metal nanoparticles, there was no electrochemical interaction between LM and glass. Thus LM still presented almost non-wetting behavior on glass, which further confirmed the previous conclusion that the LM oxidation was induced by the electrochemical reaction with substrate materials.

To further testify our speculation that positive surface charge is the key reason for the electrochemical oxidation of LM droplet, the wetting behavior of droplets on the testing surfaces was also examined at low pHs. 200  $\mu$ L LM droplets on various surfaces immersed in 1 mmol/L HCl was shown in Fig. 3b. On all the three surfaces (glass, nickel and graphite), the LM droplet generally also appeared spherical. CuO surface was not examined in this experiment because CuO could chemically interact with HCl. Specifically, few bubbles were observed on droplet on glass surface. However, abundant bubbles were generated all over the LM droplet on nickel surface, which should be due to the strong catalytic ability of nickel in hydrogen evolution reaction [19,20]. There were also some bubbles on droplet on graphite, which should be due to the galvanic effect. In the acid solution, the LM surface should be positively charged due to the production of  $\text{Ga}^{3+}$  [26]. According to the zeta potential results, the surfaces should be negatively charged. When the LM contacts with graphite or nickel surface, the negatively charged surface could not electrochemically oxidize the LM. Thus the LM droplet still maintained the spherical shape with metallic color. This result in this section further confirmed our speculation that it is the surface charge of substrate material that electrochemically oxidized the LM and reduced its surface tension.



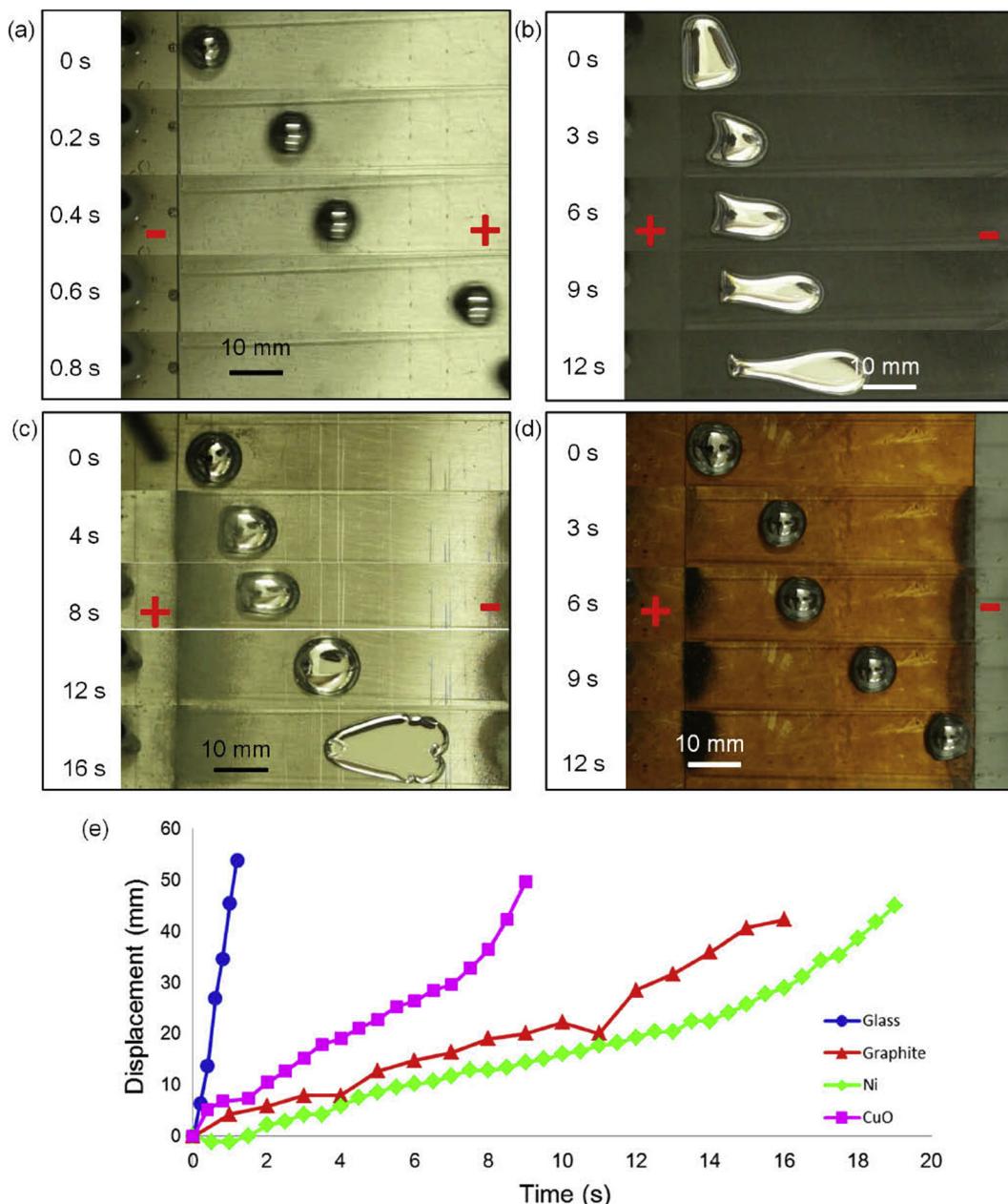
**Fig. 3.** (Color online) (a) The zeta potentials of surface materials in electrolyte solution at various pHs. (b) 200  $\mu$ L LM droplet on glass, nickel and graphite surface in 1 mmol/L HCl.

### 3.4. LM droplet locomotion on various surfaces

Although the zeta potential measurement reveals some information of surface charge for surface materials from the nanoparticle, it is still insufficient for understanding the specific interaction between LM droplet and surfaces in the macro level. In order to

further characterize the surface properties of LM droplets on the testing surfaces, electric field was employed to study the locomotion of droplets on surfaces, which could be regarded as an analogy in the macro level to the zeta potential measurement for macro particles like LM droplet in this study. In the present experiment, the electrodes of the electric field were placed at a distance of around 65 mm with the electrical potential applied at 10 V. LM droplet was placed at a distance of 10 mm close to one electrode. The sequential images of LM droplet locomotion were displaced in Fig. 4a and their displacement vs. time was plotted in Fig. 4b. On the glass surface, the LM droplet quickly ran to the positive pole of the electric field, which is consistent with previous studies [3,5]. While on other conductive surfaces, the LM droplet all ran to the negative pole of electric field, suggesting the LM was positively charged on those surfaces, which is also consistent with previous speculation that the negative surface charge of LM has turned to positive pulled up by the surface potential of substrate surfaces.

In regard to their velocity, LM droplet ran fastest on glass surface. For other conductive surfaces, the velocity of droplet ranked from high to low was on CuO, graphite and nickel surfaces, respectively. On the nickel surface, the droplet ran the slowest, which should be related to the less surface charge of nickel in NaOH solution. In regard to the CuO and graphite surfaces, it seems the surface charges on graphite and CuO were in similar level based on the CA and zeta potential results. However, the apparently higher velocity of LM droplet on the CuO suggested that there were still significant distinctions between graphite and CuO surfaces. More detailed, on the graphite surface the LM droplet gradually elongated like dragging a tail in its way to negative pole, while on the other conductive surfaces, the droplet are more likely to move as a whole with much less deformation. Only when moved close to negative pole, the LM droplet obviously deformed on nickel surface, which should be due to strong electrochemical reaction induced by electrode pole. It is supposed that the larger deforma-



**Fig. 4.** (Color online) The locomotion of LM droplet on glass (a), graphite (b), nickel (c) and CuO (d) surfaces induced by electric field with the application of electric potential at 10 V. (e) The displacement of droplet on those surfaces. Particularly, on graphite the displacement indicates that of the head end of the droplet.

tion of droplet on graphite may be related to the roughness of the surface, since the more rough the surface, the larger friction the droplet has to overcome. Moreover, the surface topography may influence the wetting behavior of LM on surfaces, which may also affect the amoeba transformation of LM-Al droplets. Hence the surface topography of the testing surfaces in this study was examined in the following section.

### 3.5. Surface roughness

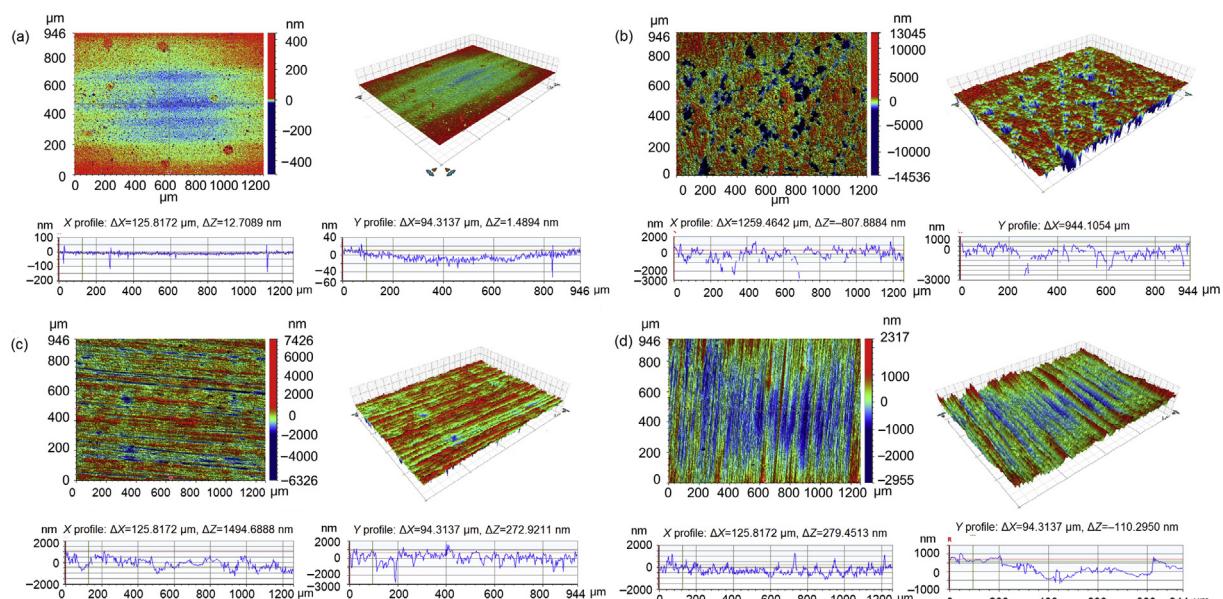
The roughness of the testing surfaces examined by optical profiler (Counter GT-K, Bruker Nano Inc.) was shown in Fig. 5. The profile of sample areas in X and Y directions were also displayed. The roughness parameters RMS roughness  $R_q$  (root mean square) is used to define the roughness of surfaces. For a three-dimensional surface,  $R_q$  is calculated by including all surface heights from the reference plane. The  $R_q$  of surfaces tested in this study were  $15.475 \pm 4.332$ ,  $773.382 \pm 14.631$ ,  $594.287 \pm 13.332$  and  $489.233 \pm 10.426$  for glass, graphite, nickel and CuO, respectively. This result indicates that the graphite has the roughest surface among those testing surfaces. Nickel surface was a little rougher than the CuO surface and the glass surface is the smoothest. The higher roughness of the graphite surface than the CuO should explain the slow velocity of LM droplet on the graphite surface though graphite and CuO both have similar surface charge levels. Besides, although graphite has the roughest surface, the droplet has the lowest velocity on the nickel rather than the graphite surface. It suggests that the surface charge plays a more important role than the surface roughness does in determining the droplet velocity in the same electric field.

Particularly, the discrete profile in X and Y direction as well the 3D image of the surface profile of graphite surface (Fig. 5b) suggest that there were some holes which are too deep to measure on graphite surface. While for other surfaces, the surface profiles were generally continuous. The SEM image of graphite surface also illustrates this porous topography on surface (Fig. S8 online). The unique porous graphite surface could increase the wetting and surface friction between droplet and surface, which verified our assumption in some degree that the larger deformation of LM

droplet during the locomotion on graphite may be related to high surface roughness and this specific surface topography.

From the above surface characterization, it seems although there are distinction in exact values, the nickel surface shares many similarities with graphite and CuO. Most importantly, surface tension of LM droplet could also be reduced on nickel surfaces, which is a vital factor in inducing amoeba transformations. In regard to the amoeba-like deformation, it should be noted that the Al is added into LM droplet. For the graphite and CuO surfaces, although there are some distinctions in surface roughness between both, the amoeba transformation of LM-Al droplet can be still achieved on both surfaces. Such distinctions may have some effects on the deformation extent of the LM-Al droplets, however, they may not be the key roles in inducing the emergence of the amoeba transformation. On the nickel surface, the deformation of LM-Al droplet did not take place even if nickel has rougher surface in this study. The key reasons should be the abundant gas bubble generation due to the specific catalytic ability of nickel in HER, which easily make the droplet detach from the substrate surface. As the droplet gets detached from the substrate, it cannot interact with the substrate surface and the oxide surface could be quickly dissolved by NaOH. Therefore the surface properties have little influence on the LM-Al droplet behavior. So the nickel surface properties including the surface roughness have little influence on the LM-Al droplet transformation on nickel surface. Sometimes when the CuO surface is relatively smooth, the LM droplet did not become oxidized and flat and still maintained the spherical shape at initial due to the thin layer of liquid beneath the droplet (Fig. S9 online). Thus the good contact between LM-Al droplet and substrates is another important factor in amoeba-like transformation.

Due to the intrinsic physical or chemical properties, the substrates examined in our study obviously have different influences on the LM transformation and locomotion, which provide a valuable insight for the design of LM-based devices or components. In another way, when combining the LM and those substrate materials together in certain ways, the liquid may present certain desirable behaviors due to the interaction with substrate materials. To develop and broaden this idea, other materials may be also combined in various forms with LM, which may also give the liquid



**Fig. 5.** (Color online) The surface profiles of test surfaces. (a) Glass, (b) graphite, (c) nickel, (d) CuO. The surface profiles were plotted as color-coded images in two-dimensional (2D) and three-dimensional (3D). The profiles in X and Y direction were also provided below the images.

metal special properties to achieve certain function or behavior. For example, researchers have designed a series of LM marbles, which are the LM droplets encapsulated in insulating or semi-conducting nanoparticles, and have achieved the function as electrochemical ion sensor by taking advantages of special physical properties of LM marble [27]. Besides, jumping behavior of LM has been observed by forming the point-contact with the nickel nanoparticle on glass surface [28]. These studies all shared the common essence that the combination with other materials can endow liquid metal more abundant properties, which is significantly valuable in LM-based soft device design and manufacture.

#### 4. Conclusion

Generally, apart from the Al reaction induced LM surface tension increase, the surface tension reduction induced by the interaction with surface material is the key factor in achieving amoeba transformation. In the present study, several common surface materials were investigated to evaluate their surface properties in achieving LM amoeba-like transformations. Among those substrate surfaces, LM amoeba transformations were only observed on graphite and CuO surfaces. The wetting behavior, surface charge, electric field induced locomotion and surface roughness of the testing surfaces were investigated and evaluated. Integrated from all those results, several general factors related to surface materials were characterized and summarized in achieving LM amoeba transformation. Firstly, the positive surface potential drop across the surface-electrolyte played the most important role in reducing the LM surface tension by electrochemically oxidizing the LM droplet. Secondly, the good contact between LM-Al droplet and substrates is another important factor in amoeba-like transformation. The bubbles generated through galvanic reaction can significantly impede the contact between LM-Al droplet and substrate surface, which can prevent the electrochemically induced surface tension reduction. The specific ability of hydrogen adsorption of graphite material improved the contact between LM-Al droplet and substrate surface. For the CuO surface, no bubbles were ever generated. Thirdly, the higher surface roughness could increase the wetting of LM droplet on surface, which should also improve the contact between droplet and surface. The amoeba-like transformation of LM-Al droplet requires the combination of those factors together. In this study, CuO surface is found to own similar ability to graphite surface in inducing the amoeba behavior, which provides a novel option of material in LM actuation and transformation. Above all, this study generalizes the common roles for surface materials in achieving the amoeba-like LM transformation as well provides fundamental and valuable knowledge for interfacial interactions between LM and various surface materials, which has great significance in the design and manufacture in LM-based soft devices.

#### Author contributions

Liang Hu performed most of the experiments, analyzed the data and wrote the manuscript. Jing Li prepared the CuO surfaces and made relevant characterizations. Jianbo Tang performed the surface roughness measurement experiment. Jing Liu conceived the project, interpreted the data and wrote part of the manuscript. All authors discussed the results and commented on the manuscript.

#### Conflict of interest

The authors declare that they have no conflict of interest.

#### Acknowledgments

This work was supported by the Dean's Research Funding from the Chinese Academy of Sciences, Beijing Municipal Science and Technology Funding (Z151100003715002), the National Natural Science Foundation of China (61307065) and the National Key Research and Development Program of China (2016YFA0200500).

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.scib.2017.04.015>.

#### References

- [1] Zavabeti A, Torben D, Chrimes AF, et al. Ionic imbalance induced self-propulsion of liquid metals. *Nat Commun* 2016;7:12024.
- [2] Sen P, Kim CJ. A fast liquid-metal droplet microswitch using EWOD-driven contact-line sliding. *J Microelectromech Syst* 2009;18:174–85.
- [3] Tang SY, Khoshmanesh K, Sivan V, et al. Liquid metal enabled pump. *Proc Natl Acad Sci USA* 2014;111:3304–9.
- [4] Gao M, Gui L. A handy liquid metal based electroosmotic flow pump. *Lab Chip* 2014;14:1866–72.
- [5] Sheng L, Zhang J, Liu J. Diverse transformations of liquid metals between different morphologies. *Adv Mater* 2014;26:6036–42.
- [6] Tang SY, Sivan V, Petersen P, et al. Liquid metal actuator for inducing chaotic advection. *Adv Funct Mater* 2014;24:5851–8.
- [7] Yuan B, Tan S, Zhou Y, et al. Self-powered macroscopic Brownian motion of spontaneously running liquid metal motors. *Sci Bull* 2015;60:1203–10.
- [8] Zhang J, Guo R, Liu J. Self-propelled liquid metal motors steered by a magnetic or electrical field for drug delivery. *J Mater Chem B* 2016;4:5349–57.
- [9] Tan SC, Gui H, Yuan B, et al. Magnetic trap effect to restrict motion of self-powered tiny liquid metal motors. *Appl Phys Lett* 2015;107:13424.
- [10] Khoshmanesh K, Tang SY, Zhu JY, et al. Liquid metal enabled microfluidics. *Lab Chip* 2017;17:974–93.
- [11] Zhang J, Yao Y, Sheng L, et al. Self-fueled biomimetic liquid metal mollusk. *Adv Mater* 2015;27:2648–55.
- [12] Yi L, Ding Y, Yuan B, et al. Breathing to harvest energy as a mechanism towards making a liquid metal beating heart. *RSC Adv* 2016;6:94692–8.
- [13] Gough RC, Dang JH, Moorefield MR, et al. Self-actuation of liquid metal via redox reaction. *ACS Appl Mater Interfaces* 2015;8:6–10.
- [14] Tang SY, Sivan V, Khoshmanesh K, et al. Electrochemically induced actuation of liquid metal marbles. *Nanoscale* 2013;5:5949–57.
- [15] Hu L, Wang L, Ding Y, et al. Manipulation of liquid metals on a graphite surface. *Adv Mater* 2016;28:9210–7.
- [16] Zhang J, Sheng L, Liu J. Synthetically chemical-electrical mechanism for controlling large scale reversible deformation of liquid metal objects. *Sci Rep* 2014;4:7116.
- [17] Flaminio D, Saidman S, Bessone J. Aluminium activation produced by gallium. *Corr Sci* 2006;48:1413–25.
- [18] Ilyukhina A, Kravchenko O, Bulychev B, et al. Mechanochemical activation of aluminum with gallium for hydrogen evolution from water. *Int J Hydrogen Energy* 2010;35:1905–10.
- [19] Brewer L. Bonding and structure of transition metals. *Science* 1968;161:115–22.
- [20] Hall DE. Electrodes for alkaline water electrolysis. *J Electrochem Soc* 1981;128:740–6.
- [21] Züttel A. Materials for hydrogen storage. *Mater Today* 2003;6:24–33.
- [22] Zoski CG. *Handbook of electrochemistry*. Amsterdam: Elsevier; 2006.
- [23] Dimitrov AS, Kralchevsky PA, Nikolov AD, et al. Contact angle measurements with sessile drops and bubbles. *J Coll Interface Sci* 1991;145:279–82.
- [24] Hunter RJ, Ottewill RH, Rowell RL. *Zeta potential in colloid science*. Pittsburgh: Academic Press; 2013.
- [25] Grundke K. Characterization of polymer surfaces by wetting and electrokinetic measurements – contact angle, interfacial tension, Zeta potential. *Poly Surface Interfaces* 2008;103–38.
- [26] Kim D, Thissen P, Viner G, et al. Recovery of nonwetting characteristics by surface modification of gallium-based liquid metal droplets using hydrochloric acid vapor. *ACS Appl Mater Interfaces* 2013;5:179–85.
- [27] Sivan V, Tang SY, O'Mullane AP, et al. Liquid metal marbles. *Adv Funct Mater* 2013;23:144–52.
- [28] Tang J, Wang J, Liu J, et al. Jumping liquid metal droplet in electrolyte triggered by solid metal particles. *Appl Phys Lett* 2016;108:223901.