Mechanical compression to characterize the robustness of liquid marbles

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KEYWORDS: Liquid marble, mechanical robustness, liquid interface, particles

Submitted to Langmuir on 29.7.15; revised 17.9.15

ABSTRACT

In this work, we have devised a new approach to measure the critical pressure that a liquid marble can withstand. A liquid marble is gradually squeezed under a mechanical compression applied by two parallel plates. It ruptures at a sufficiently large applied pressure. Combining the force measurement and the high speed imaging, we can determine the critical pressure that ruptures the liquid marble. This critical pressure, which reflects the mechanical robustness of liquid marbles, depends on the type and size of the stabilizing particles as well as the chemical nature of the liquid droplet. By investigating the surface of the liquid marble, we attribute its rupture under the critical pressure to the low surface coverage of particles when highly stretched. Moreover, the applied pressure can be reflected by the inner Laplace pressure of the liquid marble considering the squeezing test is a quasi-static process. By analyzing the Laplace pressure upon rupture of the liquid marble, we predict the dependence of the critical pressure on the size of the liquid marble, which agrees well with experimental results.

1. INTRODUCTION

Liquid marbles are droplets coated by non-wetting particles.¹⁻⁵ The geometries and chemical properties of these non-wetting particles can either be isotropic or anisotropic.⁶ They adsorb on the liquid-air interfaces, resulting from the minimization of the surface energy,⁷ similar to that of Pickering emulsions.^{8,9} The presence of particles on the surface prevents the direct contact between liquid droplet and substrate, making liquid marbles non-stick to the substrate. Thus, liquid marbles can be transported and manipulated conveniently as the adhesion and friction on the substrate is significantly reduced. These properties enable the liquid marbles to be a promising template for various droplet-based applications including chemical reactions,^{10,11} biomedical sensors,¹² micro pumps¹³ and optical detection.^{6,14}

The mechanical robustness, representing the capability to resist high pressure, shocks, impact and deformation, is particularly crucial for the transportation and manipulation of liquid marbles in these applications.^{2,15} The robustness of liquid marbles can be characterized either dynamically or statically.² Dynamic measurements usually involve impact of the liquid marbles at a controlled velocity or dropping them onto a substrate from a certain height.² The mechanical robustness is then characterized dynamically using the critical velocity or the critical height leading to rupture.^{2,16} Statically, the robustness of a liquid marble can be investigated through a quasi-static compression. At small mechanical compression, the liquid marble will initially demonstrate elastic property with reversible deformation of up to 30%.¹⁷ The spring constant during the reversible deformation is on the order of 10^2 mN/m, which is identical to that of a pure water droplet of the same size.¹⁷ This elastic property can be well interpreted by a model based on the growth of the marble surface and the conservation of the marble volume.^{18,19} However, at high mechanical compression, there exists a critical pressure P_c that a liquid marble can sustain.^{2,15} A pressure applied on liquid marbles exceeding this critical value can cause their rupture. To date, the study of the critical pressure is rare despite its great practical importance in applications involving the manipulation and transportation of liquid marbles. In particular, in-depth knowledge of how the liquid marble size and the properties of the particles influence the critical pressure has not been systematically gained. A previous approach proposed to use a micrometer screw to squeeze the liquid marble until rupture.² The critical pressure was then estimated indirectly based on the surface tension of the pure liquid and the shape of the liquid marble. However, the surface tension of the liquid marble instead of that of the liquid should be used in the calculation. Recent research indicates that the presence of the particles reduces the surface tension of the marble below that of the pure liquids.²⁰⁻²⁴ Moreover, the micrometer screw used in this approach induces a shear stress on the liquid marble, which may affect the result.

In this work, we have devised a new approach to measure the critical pressure that a liquid marble can withstand directly. We squeeze the liquid marble using two parallel plates at a controlled speed. The critical pressure prior to the rupture of the liquid marble is determined by combining the force measurement and the high speed imaging. Using this approach, we have systematically investigated the influence of the type and size of the particles as well as the type of liquid comprising the marble on the value of the critical pressure. Apart from determining the critical pressure, our approach enables us to monitor the particle-coated surface of the liquid marble in response to the mechanical compression, which helps us to understand the rupture mechanism. Our new approach is simple and feasible; it can facilitate accurate testing of the robustness of liquid marbles.

2. EXPERIMENTAL

2.1. Materials

In order to prepare the liquid marbles, we use a syringe pump (Longer Pumps, China) to deposit the liquid phase to a glass substrate covered with a layer of powdered particles. The droplets are released from a height of 2 cm. The radius R_0 of the droplets formed is precisely tuned from 0.9 mm to1.6 mm by varying the diameter of the dispensing needle *d* from 0.2 mm-1 mm (see Figure S1 for the control of the liquid droplet size). To form water marbles, we coat aqueous droplets containing 2 wt.% sodium alginate (Sigma Aldrich) of viscosity 576 mPa s (μ VISC, Rheosense Inc.) with the particles which include polytetrafluorothylene (PTFE) particles (average particle size: 35 μ m and 200 μ m; Sigma Aldrich), silica particles of uniform size (Tospearl 2000B*, 6 μ m, Momentive), fumed silica particles (primary particle size: 7 nm, Aerosil R812, Evonik) and particles of fumed fluorosilica possessing 50% SiOH (primary particle size: 20-30 nm, Wacker Chemie).²⁵ Microscopic images of all the particles are given in Figure S2. Sodium alginate is added to the water phase to increase its viscosity and the mechanical

robustness of the liquid marble² (see Figure S3 for the influence of viscosity on mechanical robustness). To generate oil liquid marbles, liquid paraffin (Aladdin, China) is used as the droplet phase which is covered by particles of fumed fluorosilica.²⁵ After the droplets make contact with the powder layer, we roll them for 5 times to ensure that the liquid marbles are covered with particles to the same extent.

2.2. Squeezing apparatus

After formation of the marbles, we carefully transport them onto a glass substrate placed on an electronic balance (BSA224S-SW, Sartorius) as shown in Figure 1. A squeezing plate made of glass, which is parallel to the bottom substrate, gradually moves down at a speed controlled by two syringe pumps to squeeze the liquid marble. The approach speed of the squeezing plate is set to be 45 μ m/s, which is low enough to determine the critical pressure (see Figure S4 for the influence of squeezing speed on the critical pressure). During the squeezing process, we use a high speed camera (Phantom v9.1) to capture the morphology of the liquid marble viewed from the top. The frame rate of the camera is set to be 100 *f s*⁻¹, which is sufficiently fast to determine the contact area between the liquid marble and the substrate. In the meantime, we monitor the mass reading of the electronic balance in order to determine the applied force on the liquid marble. All the experiments are carried out at a temperature of 24 °C.



Figure 1. Schematic of the experimental setup. A liquid marble is squeezed by two parallel plates at a constant speed which is controlled by the syringe pumps. An electronic balance and a high speed camera are used to monitor the compression force and morphology of the liquid marble respectively.

3. RESULTS AND DISSCUSSION

3.1. Formation of liquid marbles

When a spherical particle adsorbs at a flat air-liquid interface, the energy required to detach it is:⁷

$$\Delta G = \pi a^2 \gamma (1 - |\cos \theta|)^2, \tag{1}$$

where *a* is the radius of the particle, γ is the surface tension of the liquid and θ is the contact angle (measured through the liquid). Assuming *a* \approx 10 nm, $\gamma \approx$ 40 mN/m and $\theta \approx$ 90°, the detachment energy can be of the order 10³ k_BT,^{26,27} which makes the particle very difficult to be detached from the liquid/air interface once absorbed. Latest work indicates that, due to the increased curvature of the interface, a particle on the liquid droplet needs an even larger energy to be detached than the one on the flat interface.²⁷ The good stabilization effect of the particles makes the formed liquid marbles to be mechanically robust. A liquid marble placed on a substrate experiences the gravitational force, which tends to lower the center of the droplets and deform the liquid marble to a non-spherical shape, and the surface tension which opposes such deformation and tries to maintain the liquid marble as spherical.¹ The competition between the two forces can be characterized by the Bond number:

$$B_0 = \rho g R_0^2 / \gamma, \qquad (2)$$

where ρ is the density of the liquid, *g* is the gravitational acceleration, R_0 is the initial radius of the liquid marble and γ is the effective surface tension of the liquid marble.²⁸ By making the Bond number unity, we can define a capillary length:

$$\kappa_c = \sqrt{\gamma / \rho g} , \qquad (3)$$

Equation (3) characterizes the situation when the gravitational force and the surface tension are comparable.² For instance, the capillary lengths κ_c of water marbles and oil marbles used in our experiments are 2.7 mm and 2 mm respectively. If $R_0 < \kappa_c$, the surface tension effect dominates over the gravitational effect and the shape of the liquid marble remains largely spherical.¹ If $R_0 > \kappa_c$, the gravitational effect is dominant and the liquid marble will deform to a puddle-like shape.² To generalize the effect of droplet size on our results, we denote R_0 as the volume-averaged radius of the liquid marble:²

$$R_0 = \sqrt[3]{3V / 4\pi} ,$$
 (4)

where V is the volume of the droplet. In our experiments, liquid marbles are formed by dripping the liquid phase through a nozzle at a low flow rate. The volume of the droplet V can be precisely controlled by tuning the diameter of the nozzle (see Figure S1 and discussion for more detail).

3.2. Critical pressure P_c of liquid marbles

After forming the liquid marble of the required size, we zero the electronic balance and start the syringe pump to squeeze the liquid marble (see the movie demonstrating the squeezing test in the Supporting Information). The upper plate gradually approaches the liquid marble at a constant speed. Upon contact, the liquid marble is squeezed and flattened, leading to an increase in the contact area between the marble and substrate, as seen in Figure 2(a) for t = -13 and 0 s. The squeezing process is also reflected by the reading of the electronic balance. Prior to contact, the balance reading is zero. The balance reading gradually increases as the upper plate contacts the marble (Figure 2(a)). Eventually, the liquid marble ruptures when it is squeezed beyond a certain extent (Figure 2(a) for t = 0.9 s). Correspondingly, the

balance reading decreases dramatically (Figure 2(a)), which indicates the moment of rupture of the liquid marble (indicated by the gray arrow). Combining the high speed images and the mass balance readings, we can calculate the mechanical compression applied on the liquid marble during squeezing:

$$P = \Delta \mathrm{mg}/S , \qquad (5)$$

where *P* is the compression pressure, Δm is the change in the balance reading and *S* is the contact area which can be measured from the high-speed image. The calculated compression applied on the liquid marble increases during squeezing, as shown in Figure 2(b). It reaches a critical value *P*_c (indicated by the dashed line) prior to the rupture of liquid marble. We repeat the experiment several times and the value of *P*_c deduced causing rupture is highly reproducible. For instance, the liquid marble (2 wt.% sodium alginate aqueous solution coated by 35 µm PTFE particles) of size *R*₀ = 1.56 mm ruptures upon a critical pressure of 137 ± 14 Pa at the same condition for 5 independent tests, as shown in the inset of Figure 2(b).



Figure 2. (a) Evolution of mass balance reading during the squeezing of a liquid marble. The maximum represents the rupture of the liquid marble at t = 0 s. Inset: series of high speed images taken from above showing the morphology of the liquid marble under squeezing. Scale bar = 3 mm. (b) Evolution of compression pressure applied on the liquid marble prior to rupture. The dashed line represents the critical pressure P_c leading to rupture. Inset: measured critical pressure for the same liquid marble in 5

separate tests. For all the data, the liquid marbles of $R_0 = 1.56$ mm contain 2 wt.% aqueous sodium alginate coated by PTFE particles of size 35 μ m.

3.3. Influence of particle type and size and liquid core on P_c

The critical pressure P_c , representing the mechanical robustness of a liquid marble, depends crucially on the type of the particles coating the liquid droplets. To study the influence of the particle type on P_c , we form water marbles of the same radius ($R_0 = 1.28$ mm) by coating 2 wt.% aqueous sodium alginate droplets with fumed silica particles coated with hydrocarbon groups (Aerosil R812) or fumed fluorosilica particles possessing 50% SiOH and measure their corresponding P_c values given in Table 1. The results indicate that a water marble coated by fumed silica particles with hydrocarbon groups has a larger P_c than a water marble stabilised by fumed fluorosilica particles possessing 50% SiOH. The difference in mechanical robustness between these two kinds of water marbles may be attributed to the different contact angles of particles on the liquid interfaces. Recent studies demonstrate that the mechanical properties of particle layers at the liquid-air interface, including compression and shear moduli as well as the yield and melt strains, are more robust when the contact angle is around 90°.^{26,28} The dependence of the mechanical properties on the contact angle can be related to themay have a bearing on the inherent robustness of liquid marbles, which may depends depend on the energy of detachment ^{26,28}. At a contact angle closer toof 90°, the detachment energy is maximized, larger according to equation (1). Thus, the this could potentially enhance the robustness of the liquid marbles are more robust as the stabilizing particles can adsorb onto the liquid interface more readily. The contact angles between water and fumed silica particles with hydrocarbon groups²⁹ or fumed fluorosilica-50% SiOH²⁵ particles are 118° and 145° respectively. Therefore, the water marble stabilized by fumed silica

particles with hydrocarbon groups should be more robust as it has a contact angle closer to 90°. This is in agreement with our result that a water marble stabilized by such particles indeed has a larger P_c .

Apart from the particle type, the size of the particle should also play a significant role in relation to the robustness of the liquid marble. Previous studies indicate that smaller particles can actually produce more stable Pickering emulsions.⁷ Similarly, our results have shown that smaller particles make more robust liquid marbles. We have verified this by measuring the critical pressure for water marbles coated by silica particles of two different sizes. One is uniform micro-particles (6 µm, Tospearl 2000B*) whilst the other is fumed nanoparticles (primary size: 7 nm, Aerosil R812). The results shown in Table 1 indicate that the P_c for water marbles coated by nanoparticles (199 ± 22 Pa) is much larger than that coated by micro-particles (100 \pm 16 Pa). In addition, we compared the P_c between water marbles coated by PTFE particles of different sizes. The results in Table 1 show that the liquid marble fabricated using particles of 35 μ m has a larger critical pressure (156 ± 26 Pa) than the one formed using particles of 200 μ m (118 ± 19 Pa), agreeing with the previous result that smaller particles indeed make more robust liquid marbles. The influence of particle size on mechanical robustness may be attributed to pores/defects in the particle layers as well as to the interactions between the particles. When the liquid interface is packed with particles, some pores/defects exist in the particle layer. The size of the defects increases with the particle size.³⁰ When the particles are smaller, the mechanical robustness of a liquid marble will be enhanced as the surface tension effect to prevent the bare liquid droplets from touching the substrate through the pores/defects is more significant.³⁰ In addition, nanoparticles can form a network due to the capillary attraction between particles.^{31,32} Such a particle network can enhance the mechanical properties of liquid marbles against compression making them more robust than those stabilized by microparticles.¹⁵

Liquid	Particle	P _c ^c /Pa
Water ^a	PTFE (35 μm)	156 ± 26
	PTFE (200 μm)	118 ± 19
	Silica: Aerosil R812 (7 nm)	199 ± 22
	Silica: Tospearl 2000B* (6 µm)	100 ± 16
	Fumed fluorosilica-50% SiOH (25 nm)	157 ± 16
Oil ^b	Fumed fluorosilica-50% SiOH (25 nm)	93 ± 10

Table 1. Critical pressure for different types of liquid marble.

^a Water phase is 2 wt.% sodium alginate of radius = 1.28 mm.

^b Oil phase is paraffin, marble radius = 1.12 mm.

 c The critical pressure is measured at a constant squeezing speed of 45 μ m/s.

In addition to these effects, the critical pressure of a liquid marble is also greatly influenced by the type of liquid comprising the core. For instance, the oil marble formed by coating a liquid paraffin droplet with fumed fluorosilica-50% SiOH particles has a critical pressure of around 93 ± 10 Pa, which is much smaller than that of a water marble coated by the same particles (157 ± 16 Pa). We attribute the influence of liquid core on mechanical robustness to the large difference in surface tension between water (72 mN/m) and oil (around 20 mN/m).

3.4. Surface coverage of liquid marbles

In order to understand why a liquid marble would rupture upon application of a critical pressure, we monitor the surface of the liquid marble during squeezing. Under a compression, the liquid marble is stretched and adopts a pancake-like shape. Correspondingly, the air-liquid surface area of the liquid marble increases, leading to a lower coverage of particles on the surface. The high speed images in Figure 3 indicate that the surface is poorly covered and cracks appear (t = -8 s) when the liquid marble is squeezed to a certain extent. These cracks gradually grow in size upon further squeezing (from t = -8 s to t = -2 s). Eventually, the liquid touches the substrate at one of the largest cracks and leads to the rupture of the entire liquid marble. We thus attribute the rupture of the liquid marble to the poor coverage of particles on its surface.



Figure 3. High speed images from the top view demonstrating the appearance and evolution of the cracks on the surface when a liquid marble is squeezed. The rupture starts at the position of a big crack indicated by the red circle when t = 0 s. Scale bar = 3 mm. The liquid marble is 2 wt.% aqueous sodium alginate coated by 35 µm PTFE particles.

To characterize the surface coverage of a liquid marble under squeezing, we define a relative surface coverage ϕ which represents the surface coverage of a deformed liquid marble relative to that of the liquid marble before deformation. The value of ϕ will decrease when the liquid marble is gradually squeezed. We hypothesize that there will be a critical value of the relative surface coverage ϕ below which rupture occurs. Bearing in mind that the total amount of particles remains the same during the squeezing, we can calculate ϕ by comparing the corresponding surface areas of the liquid marble before and after deformation: $\phi = S_0/S_{max}$, where S_0 is the initial surface area of the liquid marble ($4\pi R_0^2$) and S_{max} is the surface area of the liquid marble just prior to rupture. Assuming the radius of the liquid marble is squeezed to R_{max} upon rupture as indicated schematically in Figure 4(a), the surface area of the liquid marble can be written as:²

$$S_{\max} = 4\pi R_0^2 + 32\pi (R_{\max} - R_0)^2 / 5.$$
(6)

Inputting the equations for S_0 and S_{max} into that for ϕ_c , we have:

$$\phi_{\rm c} = R_0^2 / (R_0^2 + 1.6(R_{\rm max} - R_0)^2, \tag{7}$$

Using this formula, we can calculate ϕ_c upon rupture of the liquid marble. Indeed, for the same type of liquid marble under many tests, we found a constant value of ϕ_c upon rupture of the liquid marble at P_c , which confirms our hypothesis as shown in Figure 4(b).



Figure 4. (a) Schematic diagram showing a liquid marble before squeezing and during squeezing. (b) Relative surface coverage S_0/S_{max} for five tests of a water marble under squeezing. The water marble of $R_0 = 1.28$ mm is formed by coating 2 wt.% aqueous sodium alginate droplets with 35 µm PTFE particles.

We systematically determine the value of $\phi_{\rm t}$ for different liquid marbles and find that the magnitude of $\phi_{\rm t}$ changes the most with the size of the particles. Generally, liquid marbles coated by small particles have small $\phi_{\rm t}$. For instance, the water marble coated by the microparticles of PTFE (size: 35 µm) has a $\phi_{\rm t}$ of 0.85±0.02 (Figure 5, green dots). This decreases to 0.69 ± 0.02 (Figure 5, blue dots) when the water marble is coated by the nanoparticles of silica Aerosil R812 (primary size: 7 nm). In addition, we find that $\phi_{\rm t}$ is virtually independent of the marble size. For instance, $\phi_{\rm t}$ of marbles coated with 35 µm PTFE particles remains almost constant when the radius of the liquid marble varies from 0.96 mm to 1.57 mm, as indicated by the green points in Figure 5. Also, $\phi_{\rm t}$ of marbles coated with silica nanoparticles (Aerosil R812) remains largely the same for marbles of different size, as shown by the blue points in Figure 5. We have also characterized $\phi_{\rm t}$ for the water and oil marbles of the same size (R_0 = 1.28 mm) and coated by fumed fluorosilica-50% SiOH particles. They are 0.66 ± 0.02 (red square) and 0.62 ± 0.04 (red circle) respectively, which are quite close.



Figure 5. Critical value of the relative surface coverage $\phi_c = S_0/S_{\text{max}}$ at rupture for different liquid marbles *versus* the initial marble radius (normalized by the capillary length κ). Three types of water marble are investigated. They are 2 wt.% aqueous sodium alginate droplets coated by either PTFE microparticles (green points), fumed silica Aerosil R812 nanoparticles (blue points) or fumed fluorosilica nanoparticles (red square). The oil marble (red circle) is formed by coating a liquid paraffin droplet with fumed fluorosilica nanoparticles. The error bars are the standard deviation of results from at least five measurements.

*3.5. Determining P*_c *by Laplace pressure*

It's interesting that the water and oil marbles coated by fumed fluorosilica-50% SiOH particles have significantly different P_c while their ϕ_c are similar. We attribute the P_c difference to the different surface tensions of water and oil marbles. When a liquid marble is squeezed, its deformation is resisted by the surface tension. By considering the squeezing as a quasi-static process, the mechanical compression should equalize the Laplace pressure of the liquid marble. Upon rupture, we can estimate the P_L of the liquid marble by the Young-Laplace equation:

$$P_{\rm L} = \gamma (1/R_{\rm max} + 2/h), \tag{8}$$

where γ is the surface tension of the liquid marble and *h* is the height of the liquid marble of pancakelike shape (Figure 4(a)). According to the volume conservation of the liquid, the height of the liquid marble can be estimated as: $h \approx 4R_0^3/3R_{\text{max}}^2$. Inputting this relationship into the equation for P_{L} , we have:

$$P_{\rm L} = \gamma (1/R_{\rm max} + 3R_{\rm max}^2/2R_0^3). \tag{9}$$

Combining equation (7) and (9), we have:

$$P_{\rm L} = \frac{\gamma}{R_0} \left(\frac{1}{\sqrt{(1/\phi_{\rm C} - 1)/1.6} + 1} + 1.5 \left(\sqrt{(1/\phi_{\rm C} - 1)/1.6} + 1 \right)^2 \right).$$
(10)

Equation (10) indicates that the critical pressure P_c which equalizes the P_L should relate to the surface tension (γ), initial radius (R_0) as well as the critical surface coverage (ϕ_c) of the liquid marble. Normally, an oil marble has a lower γ than a water marble. Therefore, the P_c of the oil marble should be smaller than the water marble with the same R_0 and ϕ_c , which is consistent with our previous results that the oil marble indeed has a smaller P_c , as shown in Table 1. In addition, the ϕ_c for the water marble coated by Aerosil R812 particles is smaller than the water marble coated by PTFE particles (Figure 5). If we assume the γ and R_0 of these two marbles are similar, the Aerosil R812-coated marble should have a larger P_c than the PTFE-coated marble according to equation (10), which agrees with our previous results of critical pressure (Table 1).

Moreover, if the liquid marbles have the same γ and ϕ_c , P_c can be significantly influenced by the initial size R_0 of the marble. According to the previous results (Figure 5), the liquid marbles fabricated by PTFE particles have a constant critical relative surface coverage $\phi_c = 0.85$ which is independent of R_0 . By inserting this condition and the appropriate surface tension value (60 mN/m)²⁰ into equation (10), we can predict the dependence of P_c on the marble size R_0 : $P_c = 204/R_0$, as shown by the dotted line in Figure 6. To examine this prediction, we systematically measured P_c for different marble radii R_0 using our squeezing apparatus. The experimental results of P_c (filled points) agree very well with our predicted values of P_c (dashed line) shown in Figure 6.



Figure 6. Influence of the initial liquid marble radius R_0 on the critical pressure P_c (experimental points for water marbles coated by 35 µm PTFE particles). The dashed line is the P_c predicted by the calculation of capillary pressure: $P_c = 204/R_0$.

CONCLUSIONS

In this work, we have devised an approach to squeeze a liquid marble and investigate its mechanical robustness. We have determined the critical pressure P_c leading to the rupture of the liquid marble using high speed imaging and force measurement. The value of P_c , representing the mechanical robustness of the liquid marble, changes with the properties of the marbles including the type and size of the particles as well as the type of the liquid droplet. In addition, we found that the rupture of a liquid marble occurs mainly due to the poor coverage of particles on its surface when a marble is highly squeezed. Based on Laplace pressure analysis, we accurately predict the critical pressure for different sizes of liquid marbles.

Our work extends the knowledge of liquid marbles and provides a simple and reliable method for characterizing their robustness.

SUPPORTING INFORMATION

(1) Controlling the liquid droplet size by changing the diameter of the needle; (2) Microscopy of the surface of liquid water marbles coated with different particles; (3) Influence of the viscosity of the liquid core on P_c ; (4) Influence of the squeezing speed on P_c ; (5) A movie demonstrating the squeezing test of a liquid marble using our technique.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Zhou Liu and Xiangyu Fu contributed equally to the experimental work.

ACKNOWLEDGMENT

This research was supported by the Early Career Scheme (HKU 707712P) and the General Research Fund (HKU 719813E and 17304514) from the Research Grants Council of Hong Kong, the General Program (21476189/ B060201) and Young Scholar's Program (NSFC51206138/E0605) from the National Natural Science Foundation of China as well as the Seed Funding Programme for Basic Research (201211159090, 201311159105) from the University of Hong Kong.

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