



# Porous liquid marble shell offers possibilities for gas detection and gas reactions

Junfei Tian, Tina Arbatan, Xu Li, Wei Shen\*

Department of Chemical Engineering, Monash University, Wellington Rd, Clayton, Vic. 3800, Australia

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## ABSTRACT

The hydrophobic shell of a liquid marble prevents direct contact of the liquid core of the marble with any condensed phases (i.e. solid or liquid) outside the marble, but allows gas and vapour to diffuse across the shell. This property of a liquid marble naturally enables it to discriminately absorb or emit gaseous and vaporous compounds across its shell while denying contact or transport of liquids. Liquid marbles can, therefore, be used to form micro-gas reactors for gas detection application when loaded with an indicator solution. Liquid marble can also be used as a gas emitter; the relatively thin liquid marble shell enables the gas dissolved in the liquid marble core to be emitted to the supporting surface from a very close range, making it possible to carry out chemical sensing using the emitted gas as an indicator. In this study we show the potential of liquid marbles as gas sensors in different arrangements, i.e. with dissolved indicator in the liquid core to sense gases diffusing into the liquid marble from outside, or with soluble gas in the liquid core that is emitted out of the liquid marble where it is sensed (or used to indicate chemical species outside of the liquid marble). An important implication of this study is that other types of superhydrophobic surfaces may also be used to design sensors for sensing gases and vapours, or to use emitted gases and vapours as indicators for chemical sensing.

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## 1. Introduction

Liquid marble is a natural phenomenon generally associated to the phenomenon of the lotus leaf; dust particles on the lotus leaf adhere to the surface of rolling water droplets on the lotus leaf and are removed from the leaf surface. Quéré and Aussillous [1] have reported the phenomenon of liquid marble based on his laboratory studies. Since then a number of research articles have appeared in the literature [2–5], providing a fuller understanding of the fundamental physics and the physical chemistry criteria of the formation of liquid marbles. Hydrophobic particles of regular or irregular shapes have been used to make liquid marbles by rolling liquid drops over a particle bed [5,6]. The hydrophobic particles, therefore, form a porous shell, covering the liquid core, preventing direct contact between the liquid core and any condensed material (i.e. solid or liquid non-wetting to the shell) outside the marble. Recently, Dandan and Erbil have shown that liquid marble can also be formed using solid particles that have  $<90^\circ$  contact angle with the liquid. They also reported that the water evaporation rate from the liquid marble is slower than that of the bare water droplet [7]. Quéré and Aussillous [1] and Eshtiaghi et al. [8] have shown, using optical microscopy, that the particle shell of liquid marbles are porous. Hapgood et al. [9] showed that the shell of a stable marble

has a structure consisting of multilayers of hydrophobic particles. Such a structure enables the liquid marble to withstand certain levels of mechanical impacts and deformation, since the porous shell is stretchable.

Recently, Nguyen et al. [10] used confocal microscopy technique to investigate the structure of the liquid marble shell using hydrophobic nano-silica particles, silica R974, and an aqueous rhodamine B solution. The confocal images reported by these authors showed that silica R974 particles formed a loosely packed multilayer shell consisting of small and relatively large lumps of primary particles [10]. The multilayer marble shell thickness varied from 50 to  $\sim 150 \mu\text{m}$  and the shell was porous.

The liquid marble phenomenon has attracted an increasing number of application studies exploiting the properties of the liquid marble. Hapgood et al. [9] investigated the hollow structure of dried liquid marbles and showed that such a structure can have useful properties in pharmaceutical applications. Zhang et al. [11] studied the use of liquid marble for DNA amplification using PCR microfluidic devices. Their work took advantage of the contamination-free liquid transport and the low transport friction offered by liquid marbles. Bormashenko et al. studied the floating of liquid marbles in terms of critical density, shape, response to vibration, and surface tension [2,12]. This group also formed liquid marbles with hydrophobic magnetic powder and demonstrated that such liquid marbles can be maneuvered by magnetic forces [13]. These researchers also reported comprehensive studies on the mechanisms of the floating and sliding of liquid marbles for manipulation

\* Corresponding author. Tel.: +61 3 99053447.

E-mail address: [Wei.shen@eng.monash.edu.au](mailto:Wei.shen@eng.monash.edu.au) (W. Shen).

purposes [3]. Fujii et al. [14] used pH responsible polymer to control the stability of liquid marbles. Zhao et al. [15] have shown that liquid marbles formed using hydrophobic  $\text{Fe}_3\text{O}_4$  nanoparticles can be manipulated and transported using magnetic fields. Kim et al. [16] used Janus microspheres to form liquid marbles with highly flexible and superhydrophobic shell; such marbles can withstand mechanical manipulation with tweezers. Gao and McCarthy [4] reported the formation of liquid marbles with ionic liquids. These authors carefully considered the surface chemistry criteria of marble formation and showed that a liquid with surface tension as low as 40 mN/m can form marbles with fine oligomeric tetrafluoroethylene particles.

An interesting property of the liquid marble we are addressing in this study is its hydrophobic and porous shell structure. The porous liquid marble shell prevents direct contact between the liquid core and any surface outside the marble, but does not prevent the transport of gas or vapour. Tian et al. [17] proposed that, since the porous liquid marble shell allows gas or vapour to freely transport across the shell, liquid marble therefore has potential to detect gas when it diffuses from outside of the liquid marble into the liquid core of the marble. It is further realized that porous liquid marble shell also enables liquid marbles to be used as micro-reactors which can selectively react to gas component transported between liquid marbles. When a liquid marble is formed with an appropriate indicator solution and placed onto the surface of a gas/vapour-emitting solid or liquid, the indicator solution is at a very close distance from the gas/vapour-emitting source, but has no direct contact with the source. This makes the liquid marble an efficient sensor for the gas/vapour of interest. If the gas/vapour-emitting body is a liquid, liquid marbles can be placed onto the liquid surface and, after sensing, be recovered from the liquid surface. If the gas/vapour-emitting body is a solid, a suitable liquid vapour pressure may be required to slow down liquid evaporation from the marble in order to enable long-term sensing. Liquid marbles therefore allow the use of liquid indicators to detect or sense gas components from a liquid phase without the need to add the indicator into the liquid phase. Liquid marbles can also be used as a gas/vapour emitter; gases/vapours emitted by the liquid marble can either be sensed by some other detection mechanisms or be used as a gas/vapour indicator to indicate chemical species outside of the liquid marble. Following the same train of thoughts, gas transport between two liquid marbles is also possible. The gas transport between liquid marbles can be used for analysis purposes with very little preparation required. Proper selection of the hydrophobic powder and indicator means that the liquid marble system for gas or vapour detection can further improve the detection sensitive. In this paper we report an investigation of using liquid marbles as colorimetric and fluorescent gas detectors for ammonia and hydrochloride acid gases. The quantitative capabilities of the liquid marble sensors are also studied using conventional UV–vis spectrophotometry and paper-based colorimetry measurements.

## 2. Experimental

### 2.1. Materials

Polytetrafluoroethylene powder (100  $\mu\text{m}$ ) was obtained from Aldrich and was used to form liquid marble sensors. NaOH (AR),  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (AR),  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$  (AR) and Ammonia solution (AR, 25%) were obtained from Analar. Phenolphthalein (AR) was obtained from BDH. A fluorescent dye, 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS), was obtained from Sigma–Aldrich. Another fluorescent dye, rhodamine B, was obtained from Ciba, Switzerland. Millipore water (18 M $\Omega$ ) was used to prepare all solutions.

An acrylic-based water-borne flexographic printing ink was used as a real emission source of ammonia and amines. This ink was obtained from TMI, USA; it was formulated for printing of packaging polymer films and contained ammonia and low molecular weight amines [18].

Whatman filter paper #4 was used as the base to make indicator paper. Liquid marble of consistent size were generated using a 1 ml syringe with a Gauge 30 needle. A digital camera was used to capture photos of colorimetric changes of liquid marbles during vapour detection. An UV–vis spectrophotometer was used to quantify vapour detection.

### 2.2. UV–vis spectrophotometric measurement

A Shimadzu UV-1601 UV–vis spectrophotometer was used to quantify colour changes of the indicator solution caused by the absorption and dissolution of gaseous analytes. The maximum absorption wavelength of the indicator solution was first determined; light absorption data were then collected at this wavelength. Triplicate measurements were carried out for each sample.

### 2.3. Paper-based gas sensors

Circular paper discs ( $\varnothing = 2$  mm) were produced from Whatman No. 4 filter paper using a disc punching device (Facit 4070, Sweden). A 600 nL aliquot of 0.1 M  $\text{CuCl}_2$  solution was introduced onto each paper disc and allowed to dry. Five so-treated paper discs were then fixed onto a piece of sticky tape, which was placed in a Petri dish to form one gas sensing device. The five indicator-loaded paper discs allowed for five replicate colorimetric measurements to be made. Colour changes of the paper discs were quantified using a desktop scanner (EPSON perfection 2450 PHOTO) and the image analysis software (Adobe PhotoShop 7.0) following the procedure we reported previously [19].

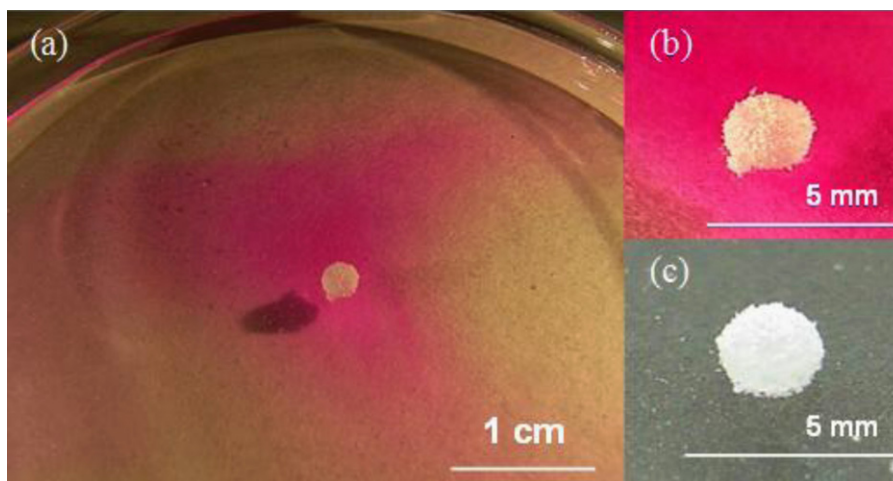
## 3. Results

### 3.1. Qualitative $\text{NH}_3$ sensing using liquid marble

When a liquid marble, made using a phenolphthalein indicator solution and Teflon powder, was placed onto the surface of an ammonia solution, ammonia gas penetrated through the liquid marble shell and dissolved into the indicator solution. The phenolphthalein indicator changed colour and the liquid marble became pink. Since the indicator solution in the liquid marble was in very close proximity to the  $\text{NH}_3$  solution and the volume of the liquid marble was small (4  $\mu\text{L}$ ), the colour change was rapid.

To confirm the colour change of the indicator was caused by the ammonia gas diffused across the marble shell and not by any direct liquid–liquid contact between the indicator solution and the ammonia solution, we reversed the experimental arrangement by placing two liquid marbles containing an ammonia solution and a sodium hydroxide solution, respectively, onto the surface of a phenolphthalein indicator solution contained in two separate Petri dishes (Fig. 1). While the  $\text{NH}_3$ -OH liquid marble caused immediate colour change of the indicator solution (Fig. 1(a) and (b)), the NaOH liquid marble does not cause any colour change (Fig. 1(c)). It was therefore confirmed that the indicator colour change was caused by ammonia gas transport across the marble shell and not by liquid contact.

Ammonia detection in this experiment is caused by pH change of the indicator solution. Ammonia sensing using pH indicators has a problem of colour fading; the colour gradually faded and eventually disappeared by the end of the experiment (2 h) as the  $\text{NH}_3$  dissolved in the indicator solution evaporated. To overcome

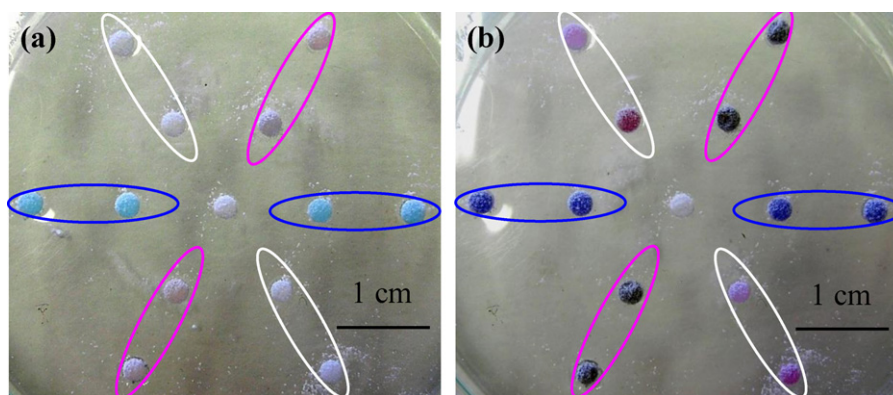
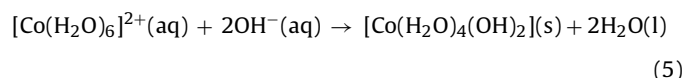
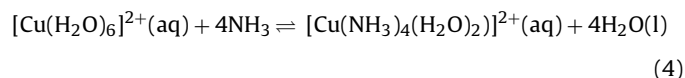
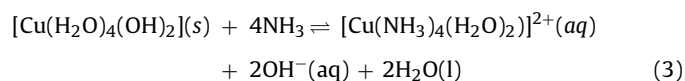
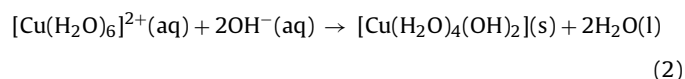
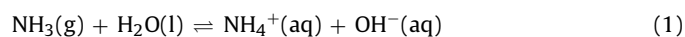


**Fig. 1.** (a) A liquid marble made using a diluted  $\text{NH}_4\text{OH}$  solution was placed onto the surface of a phenolphthalein indicator solution. The diffusion of  $\text{NH}_3$  gas through the marble shell into the indicator solution was detected by the colour change of the phenolphthalein indicator; (b) a close-up view of (a); (c) a close-up view of a liquid marble made using a diluted  $\text{NaOH}$  solution placed on the surface of water containing phenolphthalein indicator. The lack of any colour change indicates that the liquid core of the marble has no contact with the indicator solution outside of the marble. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

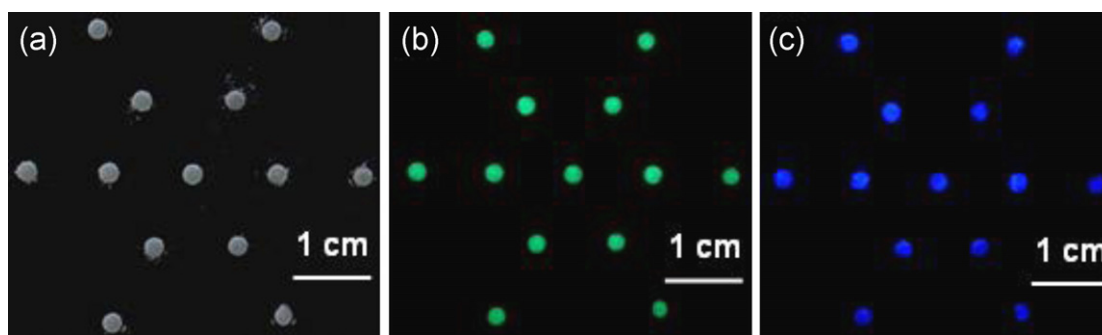
this problem, indicators with more permanent colour changes were used. Fig. 2(a) shows liquid marbles made using water, phenolphthalein, 0.1 M of  $\text{CoCl}_2$ , 0.1 M of  $\text{CuCl}_2$  solutions and Teflon powder. When these liquid marbles were exposed to ammonia gas, the transition metal salts showed strong and sustained colour changes (Fig. 2(b)).

Ammonia can act as a  $\sigma$ -donor to form metal complexes with transition metals such as copper (II). In aqueous solutions, ammonia exists as ammonium and hydroxide ions. Cu(II) in the form of hexa-aquacopper(II) ions reacts with hydroxide ions to form a pale blue Cu(II) hydroxide precipitate; the precipitate further reacts with ammonia molecules to form tetraamminediaquacopper(II) ions to give a deep blue colour. Cobalt chloride reacts with  $\text{NH}_3$  in a similar way to that of  $\text{CuCl}_2$ ; the only difference is that the final cobalt complex with ammonia contains six  $\text{NH}_3$  ligands. When  $\text{NH}_3$  concentration is low, the pH increase of the solution first leads to the precipitation of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  to  $[\text{Co}(\text{H}_2\text{O})_4(\text{OH})_2](\text{s})$ , which has a bluish green colour. Further exposure to sufficient  $\text{NH}_3$  will lead to the formation of the purple hexaammincobalt(II) complex. The reactions of copper and cobalt solutions are summarized below

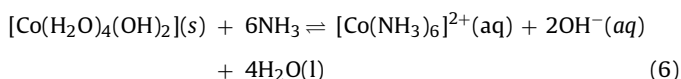
(schemes (1)–(6)).



**Fig. 2.** (a) Four groups of liquid marbles containing water (center), phenolphthalein,  $\text{CoCl}_2$ ,  $\text{CuCl}_2$  solutions, indicated by white, blue, purple circles, respectively. (b) The colour changes of those liquid marbles after exposing to the ammonia gas. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



**Fig. 3.** (a) Liquid marbles containing the HPTS indicator under ambient lighting before and after exposing to HCl vapour; (b) liquid marbles containing the HPTS indicator under UV light before exposing to HCl vapour; (c) liquid marbles containing HPTS under UV light after exposing to HCl vapour.



Since transition metal ammonia complexes are very stable (e.g. for reaction scheme (4),  $\lg K_{\text{stab.}} = 12$  [20]), these transition complexes did not fade within the time of the experiment (4 h).

The different colour changes of those transition metal salts triggered by  $\text{NH}_3$  suggest that liquid marbles containing different but chemically specific indicators can potentially be used to detect different gaseous species. Conversely, this phenomenon also promises the possible use of liquid marbles to detect chemical species in aqueous media using gas(es) as an indicator(s).

### 3.2. Qualitative HCl sensing using liquid marble and fluorescent detection mechanism

Fluorescent pH indicator can be used as the core solution of liquid marbles for gas sensing. We use liquid marbles made of an aqueous fluorescent solution of 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS) (10 mg/L) and Teflon powder to elucidate the gas detection. HPTS is a strongly water soluble and pH dependent fluorescent dye with the  $\text{pK}_a$  of  $\sim 7.3$  [21]. HPTS has a pH dependent fluorescent colour change from blue (405 nm) at  $\text{pH} \leq 6$  to green (centered at 450 nm) at  $\text{pH} \geq 8$  [21]. The transition of the colour change occurs between pH 6.6 and 7.4.

HPTS liquid marbles show no specific colour under ambient lighting before and after exposing to HCl vapour (Fig. 3(a)), but show a green fluorescence under UV light before exposing to HCl vapour (Fig. 3(b)). This property of the fluorescent indicator allows it to be distinguished from colorimetric indicators. When HPTS liquid marbles were exposed to HCl vapour, HPTS showed a clear fluorescent colour change which can be observed under UV light (Fig. 3(c)). This result has an implication that different detection mechanisms (e.g. colorimetry and fluorescence) can be employed to carry out simultaneous detections of different vapours or gases.

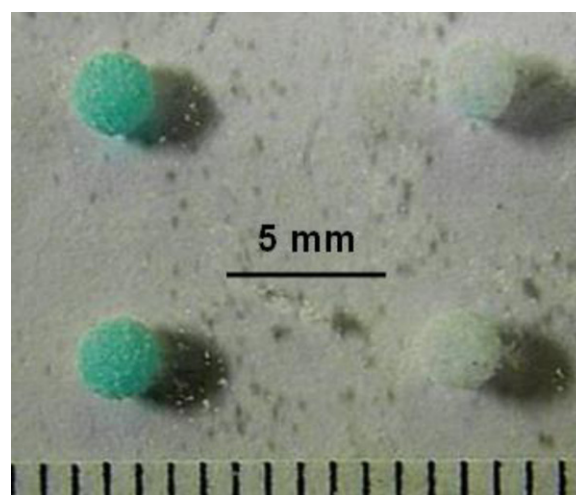
### 3.3. Practical work-place gas emission sensing with liquid marble

Liquid marble can potentially be used as a practical gas emission indicator in the work-place and in the environment. In this study we present an application of monitoring ammonia and amine emission in the printing industry. Flexography is a major printing process for production of a wide range of packaging materials including corrugated boxes and polymer films [22,23]. Water-based ink formulations for flexographic printing are widely used for polymer film printing. A current commercial water-based formulation is based on the acrylic resin system; inks formulated using the acrylic resin system are pigment suspensions stabilized by an elevated pH ( $\text{pH} = 8.0\text{--}9.5$ ) which is provided by the hydrolysis of ammonia and low molecular weight amines. Ink drying after printing is triggered

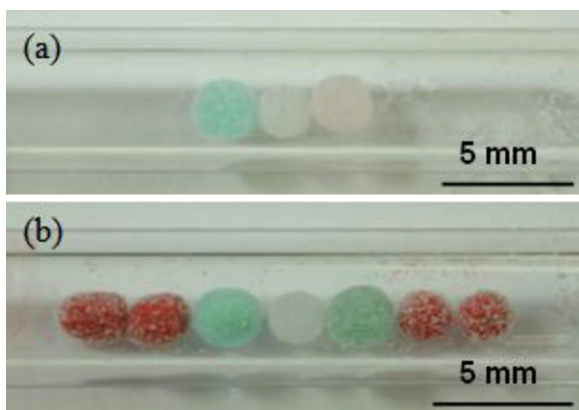
by the evaporation of ammonia and low molecular weight amines. The acrylic resin suspension system coagulates as the pH decreases to below 7.0 [18], allowing the coagulated ink to adhere to the substrate. However, the release of ammonia and low molecular weight amine during ink drying is a serious source of air pollution in the printing industry, since some printing presses have unsealed inking systems and the printed products also emits these gases during the drying process.

Liquid marbles made of a  $\text{CuCl}_2$  (0.1 M,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) solution and Teflon powder were used to detect the ammonia and amine release from the flexographic ink. Since the low molecular weight primary, secondary and some tertiary amines can form stable complexes with  $\text{Cu}(\text{II})$  ion [24],  $\text{CuCl}_2$  can be used as an indicator to detect ammonia and amine vapours in the air. Half a millilitre of acrylic resin based flexographic ink ( $\text{pH} = 9.4$ ) was placed into a Petri dish ( $\phi = 10$  cm); a smaller Petri dish ( $\phi = 5$  cm) carrying two  $\text{CuCl}_2$  liquid marbles was also placed into the larger Petri dish which was then capped. The liquid marbles changed colour within 15 min.

To visually compare the colour change, two fresh  $\text{CuCl}_2$  liquid marbles were placed near the liquid marbles that had been exposed to the ink vapour (Fig. 4). The unambiguous colour development of the liquid marbles exposed to the ink vapour, therefore, demonstrates the potential to use liquid marbles for the practical vapour emission detection.



**Fig. 4.** Liquid marbles of  $\text{CuCl}_2$  shelled with Teflon powder changes colour after being exposed to vapour of the water-based flexographic ink. Two fresh liquid  $\text{CuCl}_2$  liquid marbles (right) were placed in the same Petri dish for comparison. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



**Fig. 5.** (a) Liquid marbles made using Teflon powder and  $\text{CuCl}_2$  solution (left), water (middle) and  $\text{CoCl}_2$  solution (right) were placed in a glass tube; (b) four liquid marbles made using flexographic inks were placed from both sides into the glass tube, which was then sealed.  $\text{CuCl}_2$  marble changed from light blue to greenish;  $\text{CoCl}_2$  marble changed from light pink to green. Water does not show colour change. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

#### 3.4. Gas transport and sensing between liquid marbles

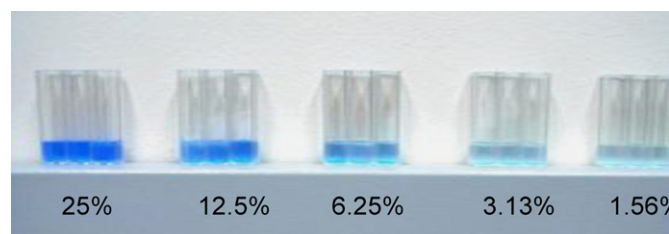
In the above experiments we have shown the transport of gas/vapour across a single liquid marble shell. It is obvious that gases and vapours can also transport through two layers of liquid marble shells, as long as they both are porous. This enables gas transport between individual or separate liquid marbles; an application of this concept would be to perform gas sensing between liquid marbles. An easily perceivable experiment may be to use one liquid marble containing a liquid sample and a desirable number of liquid marbles that contain indicator solutions and then house all marbles in a small space such as within a small beaker or a glass tube that can be easily sealed.

Fig. 5 shows four liquid marbles containing flexographic ink (red) and three other liquid marbles containing the indicator solutions,  $\text{CuCl}_2$  (light blue),  $\text{CoCl}_2$  (light pink) and water (white), all placed inside a sealed glass tube. All liquid marbles were made using the Teflon powder. Colour changes of  $\text{CuCl}_2$  and  $\text{CoCl}_2$  solutions after exposing to the ink liquid marbles were caused by reactions (2) and (5), respectively. Colour changes of the indicator liquid marbles confirm that gas transport and sensing between liquid marbles is viable and can be further developed for practical applications.

#### 3.5. Quantitative monitoring of gas emission from liquid marble

The potential to use the gas transport property of the liquid marble shell to quantitatively determine gaseous and vaporous analytes was explored. Our aim in this study was to establish correlations between the sensing signal of the gaseous analyte and its concentration in aqueous samples so as to prove the concept of the quantitative gas sensing using liquid marbles. Ammonia was used as the gaseous chemical species of interest. The experimental arrangement was made so that the solution with dissolved  $\text{NH}_3$  gas was encapsulated inside the liquid marbles and a quantitative ammonia signal was collected from outside the liquid marbles.

Ammonia solutions of different concentrations (25%, 12.5%, 6.25%, 3.13% and 1.56%) were used to form liquid marbles. Two colorimetric detection methods, i.e. the UV–vis spectrophotometry and a paper-based gas sensing method, were used to each obtain a calibration curve for signal quantification. For the UV–vis spectrophotometric method,  $\text{CuCl}_2$  solution (800  $\mu\text{l}$  of 0.1 M) was introduced onto a watch glass. Eight liquid marbles of  $\text{NH}_3$  solution

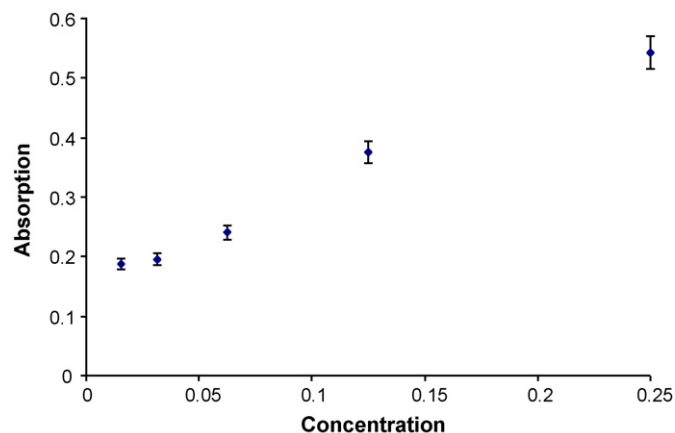


**Fig. 6.** Visual appreciation of colour changes of the  $\text{CuCl}_2$  indicator solutions after the controlled exposure to  $\text{NH}_3$ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

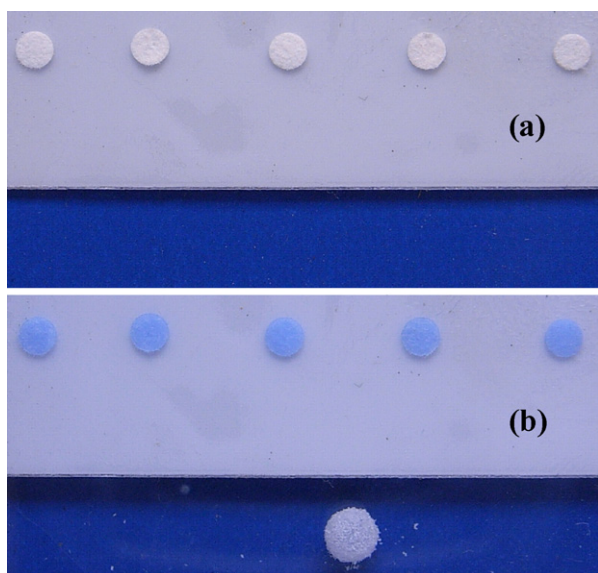
were then placed onto the watch glass and in contact with the  $\text{CuCl}_2$  solution. The volume of the liquid marbles was controlled to be 4  $\mu\text{l}$ . The watch glass was then sealed to allow controlled exposure of the  $\text{CuCl}_2$  solution to the  $\text{NH}_3$  gas released from the liquid marbles for 10 min. After the controlled  $\text{NH}_3$  release, the  $\text{CuCl}_2$  indicator solution was removed from the watch glass into UV–vis cells with a micropipette; the solution was further diluted with 200  $\mu\text{l}$  of water to make 1 ml solution for UV–vis measurement. Three repeated measurements were performed for each ammonia solution. Fig. 6 visually shows the colour change of the indicator solutions after exposure to the ammonia released from the liquid marbles. Fig. 7 shows the UV–vis calibration curve of the  $\text{CuCl}_2$  indicator solutions after reaction with ammonia.

For the paper-based gas sensing method, five liquid marbles containing  $\text{NH}_3$  solution of the same concentration were introduced into each paper-based gas sensing device. The device was then capped to allow the controlled exposure of the indicator-loading paper discs to  $\text{NH}_3$  for 10 min. Circular movement of the sensing device was provided to allow the free rolling motion of the liquid marbles around the paper discs. At the end of the 10 min period the liquid marbles were removed from the Petri dish. Fig. 8 shows the visual appreciation of colour changes of the paper discs; Fig. 9 shows the colorimetric measurements using the scanner and the colour analysis software Adobe PhotoShop 7.0.

Comparing the two quantitative methods, the UV–vis method provides an almost straight line calibration curve for high gas exposure levels, but the first two low concentration points show large deviation from the trend line (not shown) that passes the origin. There may be two contributing reasons for the error: First, when hexaaquacopper(II) ions react with hydroxide ions, the product is a pale blue precipitate (scheme (2)); this product may contribute to light absorption, giving a higher absorption reading. Second, the fine particles form stable colloidal suspended when  $\text{NH}_3$  con-

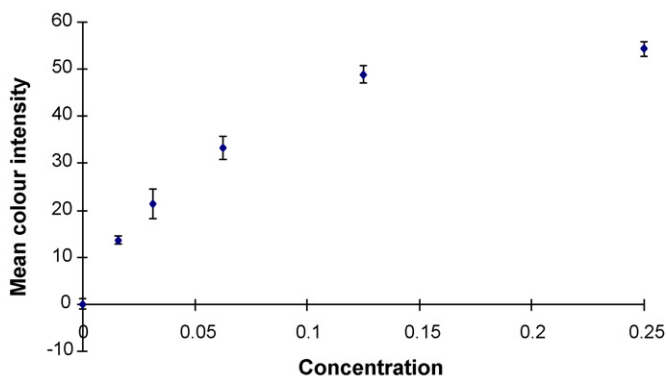


**Fig. 7.** UV–vis calibration curve of the absorption of  $\text{CuCl}_2$  indicator after reaction  $\text{NH}_3$  exposure versus the  $\text{NH}_3$  concentration of the liquid marble core solution.



**Fig. 8.** (a) Paper discs loaded with  $\text{CuCl}_2$  indicator; (b) colour change of the indicator paper discs after the controlled exposure to  $\text{NH}_3$ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

centration is low; the scattering of light by these particles may contribute to the loss of light intensity; this scattering is stronger in shorter wavelength range. The scattered light is interpreted by the spectrometer as “light absorption”. The scattering of light by colloidal particles is not as significant at higher  $\text{NH}_3$  concentrations, due to the formation of the final tetraamminediaquacopper(II) ions (scheme (3)). The UV–vis method can, however, differentiate higher levels of  $\text{NH}_3$  release. The paper-based gas sensing device gives a smooth calibration curve for low  $\text{NH}_3$  release. Since this method does not rely on the Beer’s law, it effectively avoids the interference of colloidal suspension of  $[\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2](\text{s})$ , and it is therefore more suitable for sensing vapour emitted from low concentration solutions. These quantitative gas sensing experiments show that the gas permeable and liquid impermeable characteristics of the liquid marble shell (and also other porous and superhydrophobic materials) can be used to design sensors to obtain quantitative gas sensing data. It should be noted that in this sensing design the gas released by the liquid marble can also be used as an indicator for the presence of the chemical species of interest on the supporting surfaces.



**Fig. 9.** Colour intensity versus the concentration of the aqueous solutions of  $\text{NH}_3$ . Colour intensity values were obtained using the software Adobe PhotoShop 7.0.

#### 4. Discussion

The porous structure of the liquid marble shell and its hydrophobic nature offer a realistic means to use liquid marbles to sense gaseous and vaporous components in the environment. The rough outer layer of the liquid marble shell generate a Cassie condition which completely prevents any contact between the liquid inside the marble and the liquid (or solid) outside the marble, while allowing the free transport of gases and vapours across the shell. The relatively small shell thickness of liquid marbles allows the core indicator solution to be in very close proximity of a gas/vapour-emitting liquid or solid. The close proximity of the indicator solution to the gas/vapour-emitting source, together with the high porosity of the marble shell, minimizes the gas diffusion resistance, therefore allowing the sensitive detection of the gaseous and vaporous species of interest.

The careful selection of hydrophobic powder materials to form liquid marbles may reduce the adsorption of gas and vapour by the liquid marble shell, therefore reducing chemical interference to gas and vapour sensing. We used Teflon powder to form liquid marbles for  $\text{NH}_3$  and  $\text{HCl}$  sensing because that Teflon has excellent chemical resistance to these gases and therefore, any chemical interference is negligible [25].

Liquid marble enable several chemical sensing possibilities to be exploited. While a liquid marble loaded with an indicator solution can be used as a gas or vapour sensor, a liquid marble loaded with one (or several) water dissolvable gases can be used as a gas emitter. The close range gas emission of the liquid marble to a solid or a liquid phase containing chemical species that are reactive to the emitted gases can be used as the detection chemistry. In this sensing design, the gas is used as an indicator. Liquid marbles loaded with different indicator solutions can be used to simultaneously detect different gases and vapours emitted from the same source. Fluorescent and colorimetric reactions can be used to further enhance the capabilities of gas sensing. Liquid marbles therefore provide flexible and versatile designs for chemical sensing.

Combining liquid marbles with appropriate detection methods, it is possible to gain quantitative signals which correlate to the concentrations of gases and vapours in their emitting sources. The ability of liquid marble to produce quantitative chemical sensing is particularly attractive and worth pursuing.

It is expected that, liquid marbles with strengthened shell mechanical properties will significantly widen the capability of this novel type of sensor for field sensing applications, including water and soil gas emission evaluation. This study shows that it is also possible to use other types of porous superhydrophobic surfaces to fabricate low-cost gas and vapour sensors for various applications, particularly as novel packaging materials that have the ability of monitoring the content of the package.

#### 5. Conclusion

In this work, we focused on the gas permeability property of the liquid marble shell and exploited this property for gas sensing applications. The superhydrophobic liquid marble shell completely prevents any contact between the core liquid and the liquid or solid outside of the marble, but allows gas transport across the shell. Liquid marble offers flexibility to achieve different designs for chemical sensing. These include gas sensing, and to use gas as an indicator for chemical sensing. It is possible to use liquid marbles loaded with different indicators to sense different gases from the same emission source. The use of colorimetric and fluorescent indicators further enhances the sensing capability of liquid marbles. Our future investigations will focus on the kinetic details of gas transport through the marble shell; this will enable liquid mar-

ble to be used for more practical engineering purposes. A further important implication of this study is that superhydrophobic surfaces of other kinds can also be used to design low-cost gas sensing devices provided that they are porous and inert to the gas to be sensed.

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