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Preprogramming Floating Time of Liquid Marble

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Non-sticking droplets wrapped with fine hydrophobic particles, namely liquid marbles, can be transported both on solid and water pool without an undesired spill of the inner encapsulated liquid. While the stimuliresponsive release of the inner liquid in the target area is proposed, the time-programmed release is not yet achieved. Herein, the hydrophobicity of nanoclay is modulated via a catalyst-free 1,4-conjugate addition reaction to form liquid marbles. This nanoclay liquid marble is robust and stable in air but collapses on the liquid pool with a specific lifetime. The lifetime of the liquid marble can be modulated over seconds to hours scale depending on the selection of chemically modulated wettability of the nanoclay. The critical mechanism of lifetime modulation is responsible for controlling the coalescence kinetics between the water pool and inner liquid by nanoclays' high diffusion length and chemically varied water spreading potential. The NC liquid marble's programmable lifetime to 'time-bomb' type drug release and cascade chemical reaction is applied-without requiring any external intervention.

1. Introduction

Solid particles in the nanometer to micrometer size range attach to liquid surfaces, which have led to the design of powder form,^[1] colloidosomes,^[2] dry water,^[3] Pickering emulsions,^[4] and liquid marbles.^[5] Liquid marble is a droplet covered with fine hydrophobic particles—and behave as non-wetting

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soft spherical solid, which can roll of the tilted surface or float on the water pool without a spill of inner liquid. This concept has potentially led to various applications by replacing the inner liquid with various fluidic media.^[6] Examples include droplet fluidics,^[7] sensor platforms,^[8] soft robotics,^[9] cargo transporter,^[10] healing agents,^[11] biosystems,^[12] and chemical reactors.^[13] Based on the demands, efforts have been made toward mainly two directions: i) tether functionality to liquid marbles such as stimuli responsivity for locomoting the liquid marble or releasing the inner liquid;^[14] and ii) improve multilevel robustness according to the application environment.^[15] The direction (i) is approached by the synthesis and/or interfacial design of responsive particles for liquid marbles.^[14] Various responsive liquid marbles have been reported including those response to light,^[16] elec-

tricity,^[17] magnet,^[18] temperature,^[19] ultrasound,^[20] chemical vapor^[21] or pressure.^[22] Even multi-responsive liquid marbles have been achieved by the integration of several functional particles on the liquid marbles.^[10] The direction (ii) is approached by the fundamental study of the liquid marble properties, for example, the effect of the particles' surface tension,^[23,24] shape,^[21] size,^[25] packing density on droplet,^[26] liquid surface tension^[18] on the mechanical,^[27] long-term stability,^[28] or robustness against stimuli have been studied.^[14,15]

In this progress, the liquid marble floating stability on the liquid pool is studied. Whether liquid marbles float on or sink in the liquid pool depends on the buoyancy and particles' hydrophobicity.^[29,30] In the floating regime, the lifetime of the liquid marbles has been studied. In the early-stage study by Quéré et al., the lifetime is typically 1 min for water marble and can be shortened to 0.3 s by surfactant addition.^[31,32] In 2010s, Cengiz et al. reported that the lifetime is varied with the particle size and surface tension.^[33] Moreover, the static state and collapse dynamics of liquid marbles on liquid pool have been studied.^[34,35] The liquid marble collapse is the result of the bridge of the inner liquid droplet and liquid pool like Cassie-Wenzel transition.^[11] Thus, the conventionally developed responsive liquid marbles release the inner liquid on the liquid pool in response to the external stimuli, as well as on the solid.^[36] However, the modulation of the liquid marble lifetime has not been achieved because of the difficulty in controlling the coalescence speed between the droplet and liquid pool.



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Herein, we report a liquid marble having nanoclay (NC) multilayered shell, which is robust and stable in air, but collapses on the liquid pool with programmed time. The controlled chemical modulation of NC wettability resulted in the variation in the lifetime from seconds to hours scale. We unraveled that the lifetime variation of liquid marble is due to the long vapor diffusion length and high advancing contact angle of the NC shell. We applied such programmable lifetime of the NC liquid marble to 'time-bomb' type drug release and cascade chemical reaction. Similar liquid response behavior is possible by capsulating the liquid into a non-dissolving solid film,[37] which can selectively dissolve into the liquid pool. However, the NC-derived liquid marble can release the inner liquid without relying on the dissolution, thus it is available even though the inner liquid and liquid pool has the same solubility parameter, and the outer particles can be recycled. Thus, we believe this work would likely to contribute toward the development of carrier materials and its circulation.

2. Results and Discussion

2.1. Synthesis of the Hydrophobic Nanoclay

In our current design, a catalyst-free 1,4-conjugate addition reaction between amine and acrylate is successfully applied for controlled modulation of NC surface at ambient condition (**Figure 1A**). As shown in Figure 1B, NC was first modified with a primary amine-terminated silane coupling agent to obtain NC–NH₂. Then, NC–NH₂ was reacted with alkyl acrylate to obtain alkyl chain modified NC– C_nH_{2n+1} , where alkyl chain length *n* is varied 6, 8, 12, or 18 for modulating hydrophobicity without changing the nanoscale structure of NC (Figure 1C,D), the pore of NC is clearly visible in FESEM image. The sequential chemical reactions on NC were confirmed by FT-IR spectra (Figure 1E). The appearance of IR peaks at 1570 and 1483 cm⁻¹for N–H and CH₂ bending, respectively, supports the NC–NH₂ formation. Further, the carbonyl



Figure 1. Synthesis of the hydrophobic nanoclay. A) Reaction scheme for the hydrophobic modification of the nanoclay by 1,4-conjugate addition reaction. B) Surface modification procedure of the nanoclay. The nanoclay (NC) was first activated by modification with amino-group (NC–NH₂). Then, the NC–NH₂ was hydrophobized to NC– C_nH_{2n+1} by 1,4-conjugate addition reaction, where *n* is the alkyl chain length on the NC surfaces. C,D) Scanning electron microscopic (SEM) image of the (C) NC and (D) NC– $C_{18}H_{37}$. E) Fourier transform infrared (FT-IR) spectrum of the NC, NC–NH₂, and NC– $C_{18}H_{37}$. F) Digital images and G) static contact angle θ_s of 5 µL water droplet on the modified NC powder surfaces.



2.2. Properties of Nanoclay Liquid Marble

bending frequency at 1468 cm⁻¹ confirmed the formation of NC-C₁₈H₃₇ through 1,4- conjugate addition reaction between NC liquid marbles are formed by covering water droplets the available amines of NC-NH2 and octadecylacrylate with NC-C₆ H₁₃, NC-C₈H₁₇, NC-C₁₂H₂₅, or NC-C₁₈H₃₇, as shown in Figure 2A. These liquid marbles rest on hydro-(ODAc). Thereafter, the surface modification effect on NC wetphilic glass substrates with complete spherical shapes with tability was studied by measuring the static contact angle θ_s for the beaded water droplet on the NC powder bed (Figure 1F,G). apparent contact angles ($\theta_{\rm app}$) \approx 170 to 180° like soft solid beads. These slight changes in θ_{app} are likely to attributed The droplet of water was soaked inside the NC or NC-NH₂ powder bed to exhibit superhydrophilicity. In contrast, NCto the NC liquid marbles' effective surface tension change $C_n H_{2n+1}$ ones exhibit highly hydrophobic behavior, and θ_s (Table S1 and Figure S3, Supporting Information) due to the increases with *n*, and eventually provided superhydrophobicity inter-NCs' hydrophobic interactions. Thereafter, the surface structure of NC liquid marbles is obtained by polymerizing for $n \ge 8$ (Figure S1, Supporting Information). In this case, the their air-water interface^[39] and then examined with FESEM air layer is entrapped beneath the water droplet owing to the nanostructure by NC aggregates, which can be explained by imaging (Figure 2B). The liquid marble surface is covered the heterogenous wettability of Cassie-Baxter model.^[38] In this with high-density NCs from the shell to prevent spillage of model, the contact angle is an average between the value on the core liquid. No apparent difference is observed in surface air (that is, 180°) and on the NC (that is Young contact angle structures between NC liquid marbles. Then, the NC shell porosity *P* is estimated by $P \approx 1 - m(6^{2/3}\pi^{1/3}\rho_C\Omega^{2/3}D_s)^{-1}$, where $\theta_{\rm Y}$), that is, $\cos \theta_{\rm s} = -1 + \varphi_{\rm s} (1 + \cos \theta_{\rm Y})$, where $\varphi_{\rm s}$ is a fraction of NC contact with the liquid. $\theta_{\rm Y}$ on the NC is substituted by m is adsorbed mass of the clay onto a droplet (Figure S4, the static contact angle on the flat glass substrate coated with Supporting Information), $\rho_{\rm C} \approx 2530$ kg m⁻³ is NC density, Ω the same chemicals used for modification of NC (Figure S2, is a core droplet volume, D_s is the thickness of the NC shell Supporting Information). We obtained (θ_{Y} , φ_{s}) \approx (81.3°, 0.229), (Figure S5, Supporting Information). The NC shell porosity (82.8°, 0.111), (88.2°, 0.113), and (92.3°, 0.081) for NC-C₆H₁₃, is roughly constant of $P \approx 0.7$ to 0.8, even after modifying NC-C₈H₁₇, NC-C₁₂H₂₅, and NC-C₁₈H₃₇, respectively. The the NC with various alkyl amines (NC- C_nH_{2n+1} Figure 2C). impact of such chemically modulated tailored water wettability Overall, NCs are roughly accumulated to form a porous of NC on the properties of liquid marble was further examined multilayered shell on the droplet. We then estimated the free energy change for a single NC transferring from the



Figure 2. Properties of nanoclay liquid marble. A) Side view photos of the liquid marbles by core liquid volume Ω = 5 μ L covered with NC-C₆H₁₃, NC-C₈H₁₇, NC-C₁₂H₂₅, or NC-C₁₈H₃₇. Their apparent contact angles (θ_{app}) are displayed under respective contact angle images. B) FESEM images of the NC liquid marble surfaces. C) Estimated porosity P of the NC liquid marble as a function of the alkyl chain length. D) Schematic illustration of the possible interfacial states of the NC against core liquid: i) single NC detached state; ii) the NC attached at the interface; and iii) the NC wet state. E) Free energy difference between state (ii) to (i) ΔE_{det} and that between state (ii) to (iii) ΔE_{wet} estimated with different liquid surface energy χ and Young contact angle θ_{Y} . F) Calculation of ΔE_{det} and ΔE_{wet} as a function of the alkyl chain length.

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(C=O) stretching peak at 1750 cm⁻¹ and the shift in the CH_2



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Figure 3. Stability of the nanoclay liquid marble. A) Schematic illustration of the compression test. B) Maximum compression of the NC liquid marbles keeping unbroken. C) Photos of the liquid marble by NC–C₁₈H₃₇ in a compression test. D) Liquid marble (NC–C₁₈H₃₇) stability against cyclic 50% compression assessed with apparent contact angle variation. E) Side view photos of the liquid marble (NC–C₁₈H₃₇) before and after cyclic compressions. F) Schematic illustration of the impact test. G) Critical drop height of the impacting liquid marbles ($\Omega = 10 \,\mu$ L) on glass substrate for breakage. H) Height change and I) Apparent contact angle (θ_{app}) evolution during evaporation of NC liquid marbles. J) Photos of the NC liquid marbles ($\Omega = 20 \,\mu$ L) at the time *t* = 0 and *t* = 121 min. in ambient conditions. K) Assessment of the liquid marble formation by apparent contact angles with the different core liquids ($\Omega = 5 \,\mu$ L): river water (Brahmaputra River, Guwahati, Assam, India), artificial seawater, HCl aq. (pH 1), NaOH aq. (pH 12), SDS (1 mM), and DTAB (1 mM).

interface to the air side (i.e., the energy for the detachment of the NCs from the interface: ΔE_{det}) or liquid side (i.e., the energy for the complete wetting of the NCs from the interface ΔE_{wet}) as schemed in Figure 2D. We assumed the NC to be a rod-like particle with rounded hemispherical ends (Figure S6, Supporting Information). By defining NC's long (short) semi-axis *L* (*R*), we obtain^[40]

$$\Delta E_{det} = \gamma_L \, \pi R^2 \left(1 + \cos\theta_Y\right)^2 \left[1 + \frac{4(L/R - 1)\left[\sin\theta_Y + (\pi - \theta_Y)\cos\theta_Y\right]}{\pi \left(1 + \cos\theta_Y\right)^2}\right] \quad (1)$$

and

$$\Delta E_{\text{wet}} = \gamma_L \, \pi R^2 \left(1 - \cos \theta_{\text{Y}}\right)^2 \left[1 + \frac{4 \left(L/R - 1\right) \left[\sin \theta_{\text{Y}} - \theta_{\text{Y}} \cos \theta_{\text{Y}}\right]}{\pi \left(1 - \cos \theta_{\text{Y}}\right)^2}\right] \quad (2)$$

where γ_L is the air–water interfacial energy of the inner liquid. Since the semi-axis *L* and *R* of NC are not varied with the surface modification (Figure 1C,D), ΔE_{det} and ΔE_{wet} are the functions by θ_Y and γ_L (Figure 2E). Thus, the interfacial behavior of NC can be controlled by the liquid property and the surface chemistry of NCs in this work. When the core liquid is water, ΔE_{wet} increases with the alkyl chain length, whereas ΔE_{det} decreases (Figure 2F). Thus important property of liquid marble is tailored through a simple and common chemical reaction, i.e., 1,4-conjugate addition reaction at ambient condition.

2.3. Stability of the Nanoclay Liquid Marble

The impact of controlled chemical modulation on the stability of the nanoclay liquid marble is investigated in detail. First,



Figure 4. Lifetime analysis on water pool. A) Photos of the liquid marble (NC-C₁₈H₃₇, $\Omega = 20 \,\mu$ L) on a water pool floating at t = 0 and broken at $t = 73 \,\text{min. B}$) Plots of the liquid marble lifetime $t_{L}(\Omega = 20 \,\mu$ L) floating on the water pool as a function of the ΔE_{wet} , where ΔE_{wet} varies with core liquid surface tension γ_L and NC alkyl chain length *n* (Figure S11, Supporting Information). C) The lifetime t_L variation with core liquid volume Ω with different NC modifications. D) The lifetime (t_L) plotted with ΔE_{wet} multiplied by the total adsorbed volume [$\approx \Omega^{2/3}D_s(1-P)$] of NCs of the liquid marble, where D_s is the thickness of the NC shell of the liquid marble. E) Schematic illustration of the gas barrier model. This model considers that the condensed water advances between the NCs with a much larger diffusion length (images of the diffusion orbitals are written by pink arrows) than D_s . F) Schematic illustration of the condensed water advances between NCs. G) Calculated vapor saturation time (t_{sat}) as a function of the diffusion length *D*. Plotted with the t_L for the NC liquid marble at water pool–NC temperature difference of $\Delta T = 10 \,^{\circ}$ C. The green highlighted area is the typical shell thickness D_s of NC liquid marble. H,I) The plot of the t_L as a function of (H) ΔT and (I) advancing contact angle (θ_{adv}) on the NCs.

the compression stability of NC liquid marble is assessed (Figure 3A). The NC liquid marbles remained stable even after incurring >50% compressions in height change of liquid marbles, the ability of liquid marble to sustain compressive strain is increased with the alkyl chain length of the NCs (Figure 3B,C; Figure S7, Supporting Information). Moreover, cyclic compression for the liquid marble by NC-C₁₈H₃₇ is provided in Figure 3D. This liquid marble breaks down after repetitively compressing with 50% strain for 35 cycles by cracking event (Figure S8, Supporting Information). Through cyclic compression, the detachment of NCs has not been observed. We guess the breakage may be due to the interaction between NCs being weakened by the NCs' rearrangement through mechanical stimuli.^[41,42] As a result, the apparent contact angle drastically decreases on a hydrophilic solid^[15] (Figure 3E). Qualitatively, this liquid marble is stable against picking up and squeezing (Figure S9 and Movie S1, Supporting Information). We also assessed the liquid marble stability by impacting (Figure 3F) on a hydrophilic planar substrate, i.e., glass slide. The NC liquid marbles were dropped into a glass substrate from a height (H) (Figure S10 and Movie S2, Supporting Information). In this case, the potential energy stored in the liquid marble $U \sim (\rho_w \Omega + m)gH$, where ρ_w is water density, and g is the gravitational acceleration constant. These liquid marbles ($\Omega = 10 \ \mu L$) are stable after dropping from >20 mm (U > 1.9 µJ), and the critical height is increased with the alkyl chain length of the adequately modified NCs (Figure 3G). Near the critical range, liquid marbles break down through formation of cracks on the shell.^[15] In this case, the shell tension plays a vital role in mechanical stability. We consider NC liquid marbles' tension increases with the alkyl chain length as the apparent contact angle increases (Figure 2A).

We then evaluated the long-term stability of liquid marbles. The change in the height of the NC liquid marble $(\Omega = 20 \ \mu L)$ and the apparent contact angle is monitored over time (Figure 3H,I). The height and contact angle decreased by inner water evaporation, and the degree of the reduction in both height and apparent contact angles was noticed to be lesser on increasing the alkyl chain length. However, as shown in Figure 3J, the shape of liquid marbles after inner liquid evaporation is top concaved. Thus, the difference in droplet height change is not due to the evaporation speed but the shell tension of NC liquid marbles. Overall, the apparent difference in the evaporation speed of the inner liquid is not observed. However, the NC liquid marbles are not broken until the evaporation of the inner liquid, as the apparent contact angles keep much greater than that of water on the glass substrate (Figure 3I).

The chemical stability of the NC liquid marble is assessed by changing the inner liquid with different aqueous contents

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Figure 5. Drug-releasing behavior of nanoclay liquid marbles compared with porous sponges by measuring the amount of drug release through UV-vis spectra recorded at 558 nm. A,B) Schematic illustration of the setups for monitoring the drug releasing of the (A) NC liquid marble and (B) Melamine sponge (MS) with the same surface modification as NC. C) Drug releasing behavior, and D) a time-lapsed photo of the NC— $C_{18}H_{37}$ liquid marble. E,F) Those of MS with different surface modifications.

(Figure 3K). The NC liquid marble remained stable with high apparent contact angles against water, including electrolytes (river or sea water), acid (pH 1), base (pH 12), and surfactant (SDS or DTAB). The surface tension range in encapsulating liquid for the NC liquid marbles is \geq 31.4 mN m⁻¹ (Figure S11, Supporting Information). Such nonfluorinated modification on NC also allowed to form liquid marbles with organic solvents, i.e., dimethyl sulfoxide and dimethylformamide. Thus, liquid marbles that are formed out of differently modified NC powder (NC-C₆H₁₃, NC-C₈H₁₇, NC-C₁₂H₂₅, and NC-C₁₈H₃₇) remained similar tolerance toward various complex aqueous phases as shown in Figure 3K.

2.4. Lifetime Analysis on Water Pool

The liquid marbles that were dropped directly on the water pool is also remained stable (Movie S3, Supporting Information). However, the NC liquid marble breaks down on its own to release the inner liquid depending on its lifetime (t_1) on the liquid pool (**Figure 4A**). For our system, the lifetime can be controlled by customizing the NC–liquid interfacial chemistry (Figure 4B).The liquid marble breaks in a stripping event.^[43] The breakage starts from the bottom side of the liquid marble. In this breakage event, models of the liquid immersion inside the liquid marble shells are proposed.^[32] Thus, we varied single NCs' wetting energy ΔE_{wet} by changing the inner liquid surface tension and NCs' surface chemistry (Figures S12 and S13, Supporting Information) and measured the lifetime in Figure 4B. The positive correlation between ΔE_{wet} and t_L is roughly obtained. Then, the droplet volume for the liquid marble was varied. The lifetime increased with the increase of the droplet volume for the liquid marbles by NC–C₆ H₁₃, NC–C₈H₁₇, NC–C₁₂H₂₅ (Figure 4C). As the increase of the droplet volume for the liquid marble, the number of adsorbed NCs is expected to increase as well as the total ΔE_{wet} . We estimated the total wetting energy, multiplying the ΔE_{wet} with NC numbers adsorbed on the liquid marble $\approx \Omega^{2/3} D_s(1-P)$, as shown in Figure 4D. We experimentally obtained $t_1 \approx \Omega^{2/3} D_s(1-P) \Delta E_{wet}$. However, this relation cannot explain enough the effect of surface chemistry on the lifetime.

We consider the model that the liquid marble breaks when the core water and the water pools are bridged by the vapor filling (Figure 4E). We assumed that the vapor condensates and advances inside the NCs driven by a diffusive flux of water (Figure 4F). Based on this hypothesis, we estimated how the vapor saturation speed changes with the diffusion length D. This estimation is equivalent to calculating the water saturation time t_{sat} inside the air pocket with the height of *D*, which yields: $t_{\text{sat}} \approx \rho_{\text{w}} D^2 J^{-1} \Delta c_{\text{sat}}^{-1,[44]}$ where $J \approx 20 \text{ mm}^2 \text{ s}^{-1}$ is the diffusion coefficient of vapor in the air, and Δc_{sat} is the difference in vapor mass concentration between the core water and the water pool, which is the function of the water temperature difference ΔT . In the case of the water, the pool temperature is 10 °C higher than the room temperature ($\Delta T = 10$ °C), we have $\Delta c_{\text{sat}} \approx 10 \text{ gm}^{-3}$. We get the relationship between the t_{sat} and D (Figure 4G). In Figure 4G, we estimated the $t_{sat} \approx t_L (\Delta T = 10 \text{ °C})$ and calculated the diffusion length for NCs' liquid marble $(D_{\rm NC})$. We find $D_{\rm NC}$ >100 mm for all NC liquid marbles, which is much larger than the shell thickness of the NC liquid marble ≈20–30 μ m. It means the diffusion length of the vapor is ≈1000 times longer than the direct distance between the water pool

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Figure 6. Programmed cascade liquid release and chemical reaction. A,B) Time programmed, cascade inner liquid releasing the NC liquid marbles on the water pool. A) Schematic illustration. Four liquid marbles with different NC break down in the order of clockwise. The background watch means the passing time after floating the liquid marbles. B) Time-lapsed photo images. C-E) Cascade chemical reaction by NC liquid marbles. C) Floating position, NC surface modification, and dissolved and selected chemicals in the core liquid of the NC liquid marbles. D) Photo of the setups. E) Photo of the broken NC liquid marbles induced the chemical reaction.

and core water. Thus, the vapor detours inside the accumulated NCs (pink arrow in Figure 4E), akin to the gas barrier model of clay coatings preventing vapor transmission.^[45] Overall, the diffusion length of the NC shell plays a critical role in the liquid marble's lifetime. Figure 4H plots the lifetime as a function of ΔT . The lifetime decreases with the increase of ΔT ; the increase of the vapor mass concentration speeds up the vapor saturation. Moreover, we dissolved salt in aqueous phases to decrease vapor pressure (Figure S14, Supporting Information). The lifetime increases with the salt concentration. However, solely with the vapor transmission, liquid marbles do not break (Figure 3J). The other critical factor of water advancing between the clays is quantified with the advancing contact angle θ_{adv} of water on the NCs. As shown in Figure 4I, the positive correlation of the advancing contact angle with the lifetime is obtained, which supports our model in Figure 4E,F. We confirmed that the advancing contact angle was consistent with the testing temperature (Figure S15, Supporting Information). Thus, the

temperature change influences the vapor concentration speeds rather than the water advancing contact angle. Overall, the origin of the lifetime of the floating liquid marble comes from the long diffusion length and the large advancing contact angle of the hydrophobic NCs.

2.5. Drug Release Application

The NC liquid marble exhibits different drug-release properties compare to porous solids that were embedded with similar hydrophobicity (Figure S16, Supporting Information). We loaded rhodamine B (as a model drug) inside the liquid marble and observed % of the absorption intensity change (I/I_0) (Figure 5A) over the time (Figures S17 and S18, Supporting Information). We also prepared hydrophobic melamine sponge through association of adequate surface modification as similar to the NC ones (MS- C_nH_{2n+1}) for comparison (Figure 5B).

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Figure 5D.

the step response (Figure 5C,D; Movie S4, Supporting Information), without any external intervention at the threshold of $t \approx t_L$, while the MS-C_nH_{2n+1} release drug continuously and the releasing speed is decreased with the increment of the embedded hydrophobicity (Figure 5E,F). Moreover, the hydrophobic sponges failed to load soluble form (in aqueous phase) of small molecules inside, rather selected small molecule loaded and stored in its solid form in the prepared hydrophobic sponges prior to demonstrate the release study. Thus, the current approach is not only provided a distinct method of loading & storing model drug molecule, but it also allowed to pre-set the time of releasing the encapsulated small molecules through selection of appropriate chemical modulation of from the author. NC used for LM formation as shown in Figure 5C,D. The NC liquid marble can release inner liquids even though the inner and floating liquid is the same, and the NC is not dissolved in the liquid pool-rather remained floating on top as shown in U.M. thanks

2.6. Programmed Chemical Reaction Using Nanoclay Liquid Marble

The NC liquid marble releases the model drug molecule with

We applied the NC liquid marble for the programmed cascade liquid release (Figure 6A,B) and chemical reaction (Figure 6C-E). Different liquid-loaded NC liquid marbles floating on the water pool break to release the inner liquid from the NC-C₆ H₁₃, NC-C₈H₁₇, NC-C₁₂H₂₅ to NC-C₁₈H₃₇ (Figure 6A,B; Movie S5, Supporting Information) at distinct time, without having any external intervention. Thus, the current approach allowed to demonstrate the programmed release of loaded dye molecules at specific time at different location of same water pool. Moreover, in a separate demonstration, we dissolved the reactants, i.e., metal ions (either ferric chloride (FeCl₃ 57 mм) or copper sulphate (CuSO₄, 38 mм)) into the core liquid and floated them on the pool of aqueous solution of a selected ligand, i.e., potassium thiocyanate (KSCN, 19 mm) to form respective metal complexes through mutual reaction between selected metal ions and ligand, at different part of the water pool at pre-determined time. Depending on the chemical modification of NC through 1,4-conjugate addition reaction, the liquid marbles busted at a specified time to release selected metal ions and immediately formed the metal complex in the water pool on reaction with KSCN-as indicated by the appearance of intense color of respective metal complexes, i.e., Fe(SCN)₃ (red color) and Cu(SCN)₂ (light green color; Figure 6C-E; Figure S19 and Movie S6, Supporting Information) Since liquid marbles are non-sticking droplets, the reactant transportation efficiency is ≈100%. Thus, this system is promising for loss-less and spatially selective cascade chemical reactor.

3. Conclusion

In summary, NC liquid marbles are robust in air but collapse on the water pool due to coalescence between the inner liquid and water pool. The coalescence speed depends on the vapor condensation-induced water advancement inside the NCs. Thus, controlling the advancing contact angle on NCs following the chemical modulation of the surface hydrophobicity resulted in the programmed lifetime. The wide range variation in the liquid marble's lifetime is not solely owing to the surface hydrophobicity but the high diffusion length of the NCs as the multilayered NC is used for the vapor barrier coating. While previous works utilized external stimuli to release the inner liquid, this work is advantageous from the viewpoint of handling and energy consumption.

Supporting Information

Supporting Information is available from the Wiley Online Library or

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

1,4-conjugate addition reaction, liquid marbles, nanoclay, programmed life times, superhydrophobicity

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