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Wetting-Induced Coalescence of Nanoliter Drops as Microreactors in Microfluidics

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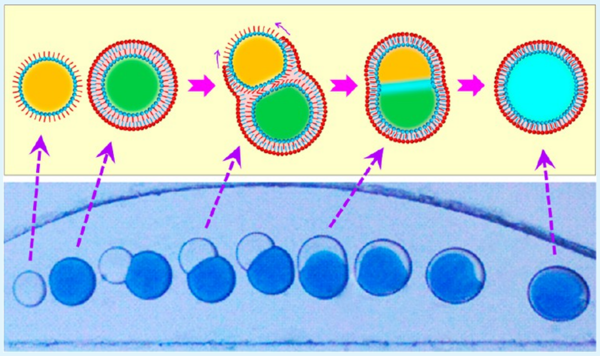
Supporting Information

ABSTRACT: Controllable one-to-one coalescence of surfactant-stabilized nanoliter water drops is successfully achieved from wetting-induced drop engulfing in microfluidics by surrounding one of the drops with a thin layer of immiscible wetting fluid. This wetting layer can spread over the other drop to drain away the liquid film between the two drops, thereby inducing coalescence. This innovative approach is totally spontaneous and highly potential in a myriad of fields, such as quantitative analysis, microreaction, and high-throughput injection. To demonstrate this potential, we successfully perform the drop-coalescence-triggered microreaction in microchannels for pH indicator and syntheses of functional materials including micro- and nanoparticles.



KEYWORDS: *drop coalescence, drop engulfing, wetting, microreactor, microfluidics*

INTRODUCTION

Microreactors, which benefit from better molecular diffusion and heat-transfer properties at the microscale level, perform chemical reactions faster and more selectively.[1,2] In particular, the controlled drop coalescence in microfluidics, as a promising platform for independently implementing numerous microreactions of well-defined volume,[3,4] has attracted increasing attention because of its potential use in various fields, such as nanoparticle fabrication,[5−7] chemical synthesis,[8,9] quantitative analysis,[10,11] and high-throughput injection.[12,13]

Drops dispersed in a matrix fluid are mainly coalesced via the rupture of the thin film between adjacent droplets, which leads two droplets to transform into only one.[14] Essentially, only if the thickness of the separate film is less than a certain critical value (on the order of nanometers) for some time (typically tens of milliseconds),[15] will the film become unstable for the increase of attractive van der Waals forces[15] and the undulation of interfacial tensions resulting from the Marangoni effect.[16] When two droplets approach, the drainage of liquid between them is retarded by the concomitant dilution of the emulsifier film, which leads to a gradient in interfacial tension (higher between the drops than elsewhere) to drag liquid back due to the Marangoni effect.[16] The fluctuations motivate the break of the thin film to initiate the whole fusion as a result of minimization of the total interfacial energies of the system. Thus far, reported methods for droplet coalescence in microchannels are mostly performed by either exploiting fluid dynamics through special channel geometry[12,17,18] and special channel treatment[19,20] or applying external energy sources such as electric fields,[6,21−23] magnetic fields,[24,25] or even focused lasers.[10,26] The special channel geometry method is typically performed through the design of an expanded chamber in the collection channel to enhance the collision of adjacent droplets and prolong their contact time, thereby promoting drop coalescence. This simple approach is mainly applied to surfactant-free drops, although surfactants are widely used to stabilize emulsions and to hinder undesired drop coalescence. Compared with the special channel geometry, the special channel treatment is available for merging surfactant-stabilized drops. For instance, Fidalgo et al.[19] and Liu and Ismagilov[20] designed a section of hydrophilic surface in a hydrophobic channel to capture and fuse water drops. Unfortunately, the attachment of water drops to the hydrophilic wall and the contamination issues between drops limit applications of this method. By contrast, the second type of method allows the fusion of surfactant-stabilized drops by applying external energies to breach the separate film, but the fusion efficiency is heavily dependent on the fluid constituents. For example, charged liquids are required when electric fields are applied. The microfluidic devices that integrate with electrodes or other elements are somewhat complicated to construct. Besides, the external forces might be harmful to the active ingredients contained within the droplets such as proteins, enzymes, or DNA, which limits applications. For example, it has been reported that magnetic fields can induce DNA strand breaks in cells because exposure to magnetic fields initiates an iron-mediated process that increases free-radical formation in cells, leading to DNA strand breaks and cell death.[27,28] Recently, we

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have reported a surgery-like strategy for droplet coalescence by using a microlancet with suitable surface wettability.[29]

Herein, we report a brand new method for controllably achieving one-to-one coalescence of surfactant-stabilized water droplets in microchannels. Two different water drops dispersed in a continuous phase are coalesced by surrounding one of them with a thin layer of immiscible wetting fluid. By simple control of interfacial energies of the system, the wetting layer on one drop preferentially wets the other drop compared to the continuous fluid,[30] which causes the wetting fluid to spread rapidly over the other drop and drain away the liquid film between the two precursor drops. As a result, the two drops coalesce efficiently.

■ MECHANISM OF WETTING-INDUCED DROP COALESCENCE

Coalescence of drops is mainly driven by the interfacial tension, which creates a thermodynamic drive to minimize the total interfacial energies of the system. Drop coalescence relies on the film thickness that separates two interfaces. When the thickness of the separate film is less than a certain critical value h_c [$h_c = 0.22(AR_f^2/f\gamma)^{1/4}$, where A, R_f, f, and γ are the Hamaker constant, radius of separate film, numerical factor, and interfacial tension, respectively],[15] van der Waals forces start to play a role, then the film becomes unstable, and finally drops merge (Figure S1 in the Supporting Information, SI). The wetting-induced strategy for drop coalescence is dependent on exploitation of the interfacial energies of three immiscible liquids. Similar to what we have reported recently,[30] when two immiscible drops (drops i and j) are dispersed in a third immiscible fluid (k), drop i can completely engulf drop j to form a double emulsion drop only if the spreading coefficient (S_i) is positive. The spreading coefficient is defined as $S_i = \gamma_{jk} - (\gamma_{ij} + \gamma_{jk})$,[31] where γ_{ij} is the interfacial tension between fluids i and j. Inspired from the drop-engulfing-drop phenomenon, we design a thin layer of wetting oil over one of the drop pairs to trigger their coalescence. As Figure 1a shows, when $S_A = \gamma_{CD} - (\gamma_{AD} + \gamma_{AC})$ is positive, the thin layer of phase A outside drop B will preferentially wet the other drop C compared to the continuous fluid (D), resulting in the wetting oil spreading over drop C and draining away the liquid film of phase A between drops B and C. When the separate film is drained to the critical thickness, the instability of the film will take place, thereby inducing coalescence of drops B and C (Figure 1a). Additionally, the critical thickness also has a relationship with the innermost drop sizes, which is reflected as the radius of the separate film in the equation of h_c. Typically, the critical thickness h_c is about tens of nanometers. However, if the thickness of the separate film is still beyond the critical value after total engulfment, double emulsions with two inner drops will be formed instead of drop coalescence.[30]

■ RESULTS AND DISCUSSION

To demonstrate the novel wetting-induced strategy for drop coalescence, we utilize a glass microfluidic device[32] that comprises of two sequential flow-focusing drop generators to generate two different water drops (Figure 1b), one of which is covered with a thin layer of wetting fluid. To assist the contact between neighboring drops, an expanded chamber is designed in the collection microchannel of the device to slow down the local flow rates (Figure 1b). We use silicone oil containing 1.0 wt % Dow Corning 749 (DC749) as the continuous phase (D) in both generators and an aqueous solution containing 1.0 wt % sodium dodecyl sulfate (SDS) as the dispersed phase (B; dyed with 0.002 g mL^{-1} methylene blue trihydrate) and soybean oil (SO) consisting of 2.0 wt % polyglycerol polyricinoleate (PGPR 90) as the wetting phase (A; dyed with 1.0 mg mL^{-1} Lumogen F Red 300) in one generator to fabricate ultrathin-shelled B/A/D water-in-oil-in-oil (W/O/O) double emulsions from complete spreading of drop A over drop B, as illustrated in Figure 1b,c. In the other generator, another aqueous solution containing 1.0 wt % SDS is used as the disperses phase (C), which is sheared by the performed B/A/D double emulsions to generate C/D (W/O) single emulsions (Figure 1b,c), thereby directly forming one-to-one drop pairs of B/A/D double and C/D single emulsions. Because there is a considerably long distance between the second drop generator and the expanded chamber of the microfluidic devices, the flowing of drops has an impact on the drop pairing. Because of the inherent characteristics of the laminar flow field in the microchannel, smaller drops always flow faster than larger drops in microchannels (movie S1 in the SI). Therefore, when the single-emulsion drops are much smaller than the double-

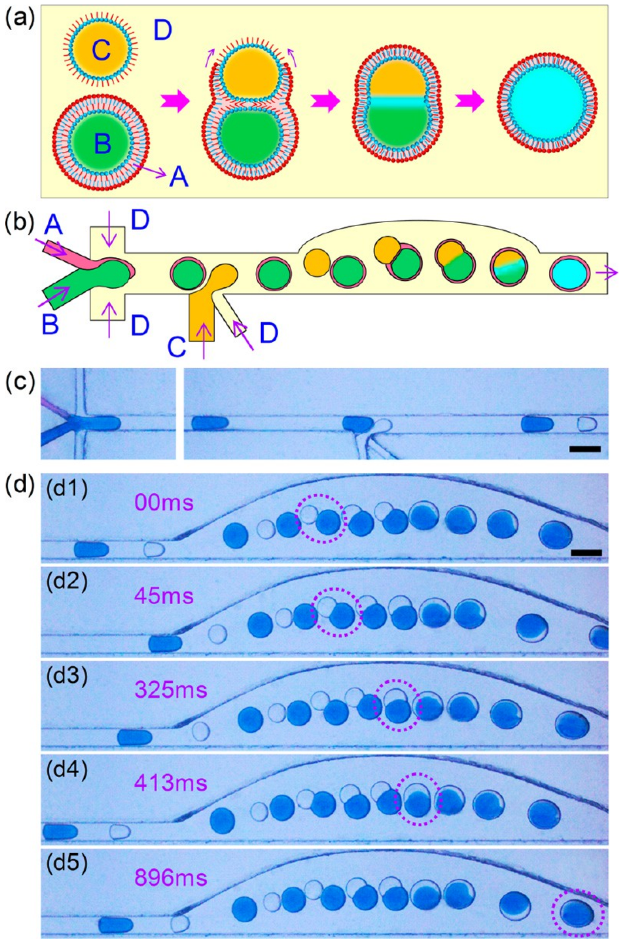

Figure 1. Wetting-induced coalescence of water drops. (a) Schematic illustration of coalescence of drops B and C induced by spread of phase A over phase C when the spreading coefficient S_A is positive. (b−d) Schematic and high-speed snapshots of the preparation of ultrathin-shelled B/A/D double and C/D single emulsions (b and c), as well as wetting-induced coalescence of drops C and B in continuous fluid D (d). The flow rates in c and d are $Q_A = 20\ \mu L\ h^{-1}$, $Q_B = 100\ \mu L\ h^{-1}$, $Q_C = 50\ \mu L\ h^{-1}$, $Q_{D(left)} = 250\ \mu L\ h^{-1}$, and $Q_{D(right)} = 200\ \mu L\ h^{-1}$. Scale bars, 200 μm.

emulsion drops, they will pair with the larger double emulsions ahead of them (Figures 1b and S2a in the SI); on the contrary, when the single-emulsion drops are larger than the double-emulsion drops, they will pair with the smaller double-emulsion drops following them (Figure S2b in the SI). When pairs of C/D single-emulsion drops and ultrathin-shelled B/A/D double-emulsion drops contact each other in the expanded chamber (Figure 1d1), they first form a doublet of drops (Figure 1d2,d3) because of the positive spreading coefficient S_A of phase A over phase C (S_A = 7.33, γ_{AC} = 0.28 mN m^{-1}, γ_{CD} = 8.82 mN m^{-1}, and γ_{AD} = 1.21 mN m^{-1}). Meanwhile, the oil film between them becomes thinner and thinner until the critical thickness ($h_c \approx$ 157 nm; see calculation of the critical thickness in the SI) as phase A is spreading over phase C, and finally coalescence of the two water drops of phases B and C is induced (Figure 1d4 and movie S1 in the SI). Similarly, this wetting-induced drop coalescence is also demonstrated in another glass microfluidic device, in which the B/A/D double emulsions are directly generated within a double-stage flow-focusing drop generator (Figure S3a−d in the SI). Importantly, the whole combination is such an expeditious process that it takes only less than 1 s (Figure 1d5), which is beneficial to initiate, modify, or terminate independent microreactions in droplets through the addition of new reagents to preformed droplets of defined volumes.

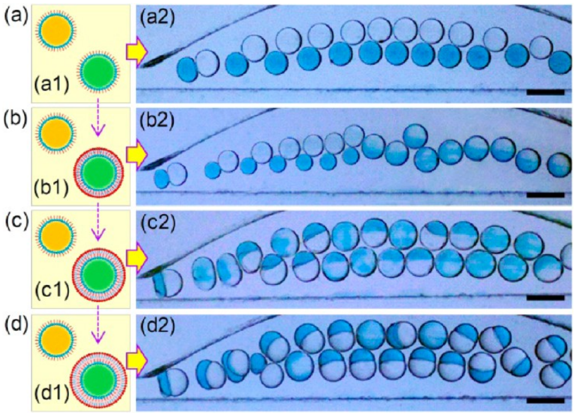

Figure 2. Effect of the thickness of the wetting layer on drop coalescence. (a) No coalescence of two drops without the wetting layer. (b and c) Coalescence of two drops by covering one of them with ultrathin wetting shells. (d) Dual-core double emulsions that form when the thickness of the wetting layer increases beyond the critical value. The flow rates are Q_A= 0 (a), 20 (b), 40 (c), and 60 (d) μL h^{-1}, Q_B = 100−150 μL h^{-1}, Q_C = 100−200 μL h^{-1}, $Q_{D(left)}$= 250−800 μL h^{-1}, and $Q_{D(right)}$= 100 μL h^{-1}. Scale bars, 200 μm.

To verify the function of the wetting layer in the coalescence of emulsion drops, we carry out the collisions of drops in microchannels without the wetting layer and with different thicknesses of wetting layers (Figure 2). First, the collision of two single water drops, B/D and C/D (without the wetting layer of phase A), is performed in microchannels by stopping the supply of phase A as a control experiment. Just as expected, no coalescence is observed because of stabilization of the surfactants (Figures 2a and S3e and movie S2 in the SI). Then, we pump the wetting phase A again at diverse flow rates to make the wetting layers over the drops of phase B different thicknesses. When the flow rate of phase A is fixed at 20 μL h^{-1}, as long as pairs of the prepared ultrathin-shelled B/A/D double and C/D single emulsions contact each other in the expanded chamber, the coalescence of drops of phases B and C is induced accurately (Figure 2b). When the flow rate of phase A increases to 40 μL h^{-1}, the prepared thin-shelled B/A/D double and C/D single emulsion drops form doublets first, and then the liquid film is drained away during the wetting process, inducing drop coalescence (Figure 2c and movie S2 in the SI). However, as the flow rate of phase A increases to 60 μL h^{-1}, the two water drops remain separate rather than combined together after the wetting, because the immiscible wetting liquid film is much thicker than the critical thickness (Figure 2d).[30] However, these nonspherical double-emulsion drops cannot keep their structures for a long time without proper surfactants or solidification of their shells because the nonspherical shell drives the interior drops approached because of capillary forces, which drains away the separate film, finally inducing coalescence. For example, when we use SO containing 1.0 wt % PGPG 90 as the wetting layer with a thickness of about 10 μm, it takes about 2 min until coalescence is induced (Figure S4 in the SI). Similar phenomena have also recently been observed by Lee et al.[33] With kerosene containing 8% PGPR 90 as the middle layer, dumbbell-shaped double-emulsion drops can maintain their structures for more than 1 day.[33] Besides, when the wetting liquid is excess, drop fusion also relies on the contact orientations of drops. For instance, a single-emulsion drop can be spread by a double-emulsion drop with asymmetrical shell thickness (Figure S5 in the SI). The main reasons for the anisotropic distribution of middle layer of double-emulsion drops in the microchannel are the shear forces and the Marangoni effect around the double-emulsion drops. As soon as the double-emulsion droplets are generated, they are carried by the continuous fluid to flow downward, and the shear forces and Marangoni effect around them make the distribution of the middle layer asymmetrical. The orientation of the drop contact can be controlled by adjusting the relative flow rates of the two drops. If the thicker part of the shell wets the single-emulsion drop, a dual-core double-emulsion drop forms without any coalescence (Figure S5a and movie S3 in the SI); however, when the thinner part of the shell wets the single-emulsion drop to make the separate film lower to the critical value, coalescence will be initiated (Figure S5b and movie S3 in the SI). As a result, there are still several drop pairs passing through the chamber without coalescence, as in movie S2 in the SI. Although the wetting liquid is limited, it takes different time to coalesce when drop pairs start the wetting processes from the different parts of shells. Additionally, it takes only about 1 s for drops to pass through the expanded chamber after they are generated (Figure 2). Judging from the state of drop pairs at the outlet of the expanded chamber, the percentages of drop coalescence in parts b−d of Figure 2 are respectively 100%, 88%, and 21% when the thicknesses of the wetting shells are 1.2, 2.5, and 3.8 μm, respectively. Therefore, the key point to wetting-induced coalescence is whether the thickness of the separate film is less than the critical value, which is not only decided by the volume of the wetting layer on one drop and the size of the to-be-wetted drop but also impacted by the drop-contact orientation.

This wetting-induced coalescence of diverse drops in microchannels provides a facile and promising platform that has potential applications in a myriad of fields, such as quantitative analyses, microreactions, and high-throughput injections. To show the potentials, we perform the drop-coalescence-triggered microreactions in microchannels for pH indicator and syntheses of functional materials including micro-

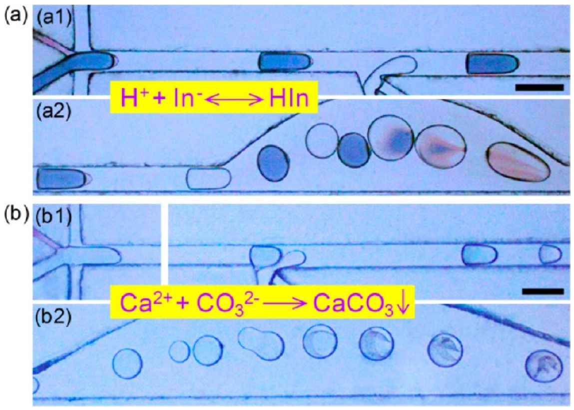

Figure 3. Drop-coalescence-triggered microreactions in microchannels. (a) Acid−base titration achieved by combining an acidic droplet and a droplet containing a litmus pH indicator. (b) Synthesis of $CaCO_3$ nanoparticles via wetting-induced coalescence of sodium carbonate (Na_2CO_3, 0.2 M) W/O/O drops and calcium chloride ($CaCl_2$, 0.2 M) W/O drops for synthesizing $CaCO_3$ nanoparticles. Scale bars, 200 μm.

and nanoparticles. As Figure 3a depicts, we first achieve acid−base titration by combining two different droplets, one with 10.0 wt % citric acid and the other containing 2.0 wt % litmus pH indicator. The volumes of the two precursor drops are almost the same, and the indicated drops (pH 9.0) are covered with SO consisting of 2.0 wt % PGPR 90 as the immiscible wetting layer (Figure 3a). As soon as coalescence is triggered by the wetting layer in the expanded chamber, the blue drop immediately turns brick-red (pH 2.0), and the whole coalesced drop becomes brick red within 0.3 s (movie S4 in the SI). That is, the drop-coalescence-triggered microreaction for quantitative analysis is reliable and speedy.

To illustrate the potential of our approach for preparation of functional materials, we synthesize calcium carbonate ($CaCO_3$) nanoparticles by wetting-induced coalescence of two different water drops, one with calcium chloride ($CaCl_2$, 0.2 M) and the other with sodium carbonate (Na_2CO_3, 0.2 M) (Figure 3b). Similarly, the microreaction is initiated instantly as fusion is induced; meanwhile, the precipitate generates rapidly within the coalesced drop (Figure 3b2 and movie S5 in the SI). The coalescence-triggered reaction is fast and reliable. Owing to the defined small volume and flowing condition, the prepared $CaCO_3$ precipitates in the coalesced emulsion drops (Figure 4a) are uniform nanoparticles (Figure 4b). By introduction of this method, a lot of functional materials can be easily synthesized in microfluidics. For further demonstrations, we successfully fabricate microscale hydroxyapatite powders (Figure 4c) and chitosan microspheres (Figure 4e−h) by the wetting-induced method of coalescence of two diverse precursor drops. Compared with multiform and irregular hydroxyapatite powders prepared by precipitation reaction in bulk solution (Figure 4d), the hydroxyapatite powders generated in the coalesced drops in microfluidics show flowerlike structures and remarkable homogeneity (Figure 4c), which could notably improve their performances in applications including artificial bone, tooth, and cosmetic surgery. Likewise, the prepared chitosan microspheres exhibit good monodispersity and highly spherical shape (Figure 4e−h). Importantly, because the micro- and nanoparticles are generated within the drops, any clogging of the microchannels by the synthesized particles can be effectively avoided. Besides, this method also enables one to combine premade emulsion drops and new droplets for injection of contents by coating the premade emulsion drops with a thin layer of wetting fluid at first, and then mixing the covered drops and new drops together for fusion (Figure S6 in the SI).

■ CONCLUSIONS

In summary, we have demonstrated a novel and reliable wetting-induced droplet-engulfing method for drop coalescence in microfluidics. Coalescence of two different drops is triggered by surrounding one of them with a thin wetting layer of immiscible fluid. The wetting-induced coalescence process is totally spontaneous and requires no external triggering stimuli. This novel strategy is highly potential in a myriad of fields, such as quantitative analysis, microreaction, and high-throughput injection. To demonstrate the potentials, we have successfully

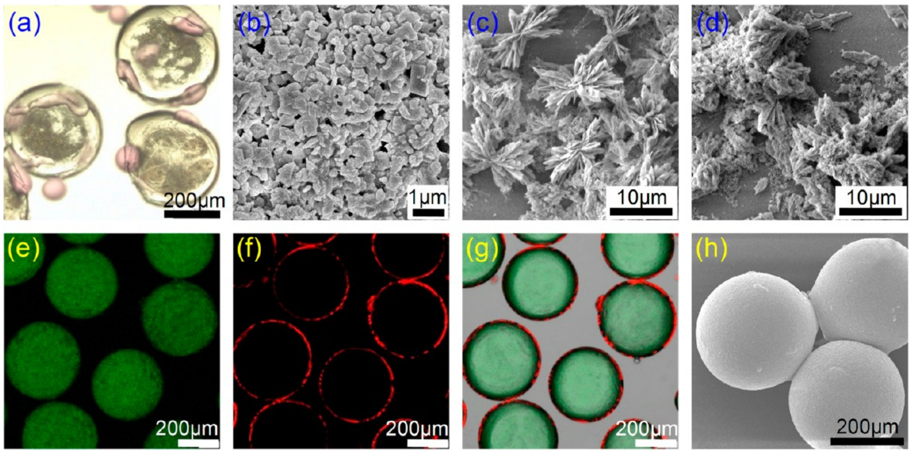

Figure 4. Characterization of as-prepared particles. (a) Optical micrograph of synthesized $CaCO_3$ particles in emulsion drops. (b) Scanning electron microscopy (SEM) image of dried $CaCO_3$ nanoparticles. (c and d) SEM images of dried hydroxyapatite powders prepared by wetting-induced coalescence of emulsion drops (c) and those prepared in a bulk solution (d). (e−h) Confocal laser scanning microscopy images (e−g) and SEM image (h) of the chitosan microspheres prepared by the wetting-induced method of drop fusion. Scale bars are 200 μm in parts a and e−h, 1 μm in part b, and 10 μm in parts c and d.

performed the drop-coalescence-triggered microreactions in microchannels for pH indicator and syntheses of functional materials including micro- and nanoparticles.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, supplementary figures, and movies showing wetting-induced drop coalescence and its applications in pH indicator and syntheses of functional materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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