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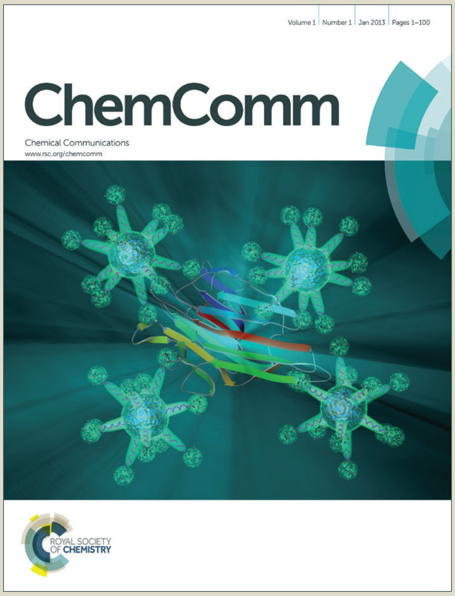

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ARTICLE TYPE

# Catalytic Liquid Marbles: Ag Nanowire-based Miniature Reactors for Highly Efficient Degradation of Methylene Blue

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**Ag nanowire-based catalytic liquid marbles are fabricated as miniature reactors which demonstrate highly efficient, support-free and rate-controllable heterogeneous degradation of methylene blue, with catalytic efficiency close to 100 %. Our miniature catalytic liquid marbles is essential for reactions involving highly toxic/hazardous or costly reactants, where small volume preliminary reaction is preferred.**

As a new approach to isolate and manipulate liquid,[1] liquid marbles have attracted increasing attentions on the study of their formation, properties and potential applications.[2] Liquid marbles are generally spherical structures formed by rolling sessile liquid droplets over a bed of hydrophobic micro- or nano-sized particles to form loosely packed and porous encapsulating shell at the liquid-gas interface.[3] This hydrophobic shell imparts liquid marble a non-wetting property that allows it to move easily on both solid and liquid platforms.[4] Liquid marble also demonstrates excellent mechanical stability imparted by hydrophobic powder attraction forces which maintain its structural integrity and flexibility, even when subjected to mechanical impact and deformation.[5] Thus, liquid marbles can be easily manipulated by external forces, such as gravity,[6] electrical,[7] and magnetic field without rupturing.[8] In addition, unique properties can be installed onto liquid marbles via the choice of encapsulating solid, making liquid marbles highly versatile platforms for a wide range of applications, such as chemical sensors,[4, 9] micro-pumps,[10] and miniature reactors.[11]

The application of liquid marbles as miniature reactors have been extensively explored due to their reduced use of chemical reagents and solvents, much confined micro-environment and precisely controllable reaction conditions. These unique properties render liquid marble useful for minimizing the usage of toxin, highly reactive and/or costly reagents in hazardous reactions and also fine analyses in chemical and biological processes.[12] For instance, Xue et al.[11a] showed that liquid marbles coated with fluorinated decyl polyhedral oligomeric silsesquioxane and magnetic $Fe_3O_4$ powder can be used as remotely-controllable chemical miniature reactors. However, current applications of liquid marbles as miniature reactors are limited because the encapsulating shells only act as inert isolating layers to provide confined environment and do not participate in the reactions. By using solid catalysts and/or reagents as the encapsulating layer, liquid marble can further enforce its suitability as miniature reactor, especially in the field of heterogeneous catalysis/chemical reactions.

Metal nanoparticles are promising candidates as the building blocks for the new generation liquid marble miniature reactor due to their superior catalytic ability for a wide variety of organic and inorganic reactions.[13] However, the direct use of free metal nanoparticles in heterogeneous catalysis is limited because they are susceptible to aggregation which reduces effective catalytic surface area. Moreover, metal nanoparticles freely dispersed in liquid media generally suffer from poor recovery and reusability, severely limiting their catalytic efficiency for multiple reactions. Existing strategies to enhance the efficiency and recyclability of catalysts in heterogeneous chemical reactions generally involved the immobilization of metal nanoparticles onto various solid supports such as carbonaceous materials,[14] metal oxides,[15] and polymeric materials,[16] and also formation of hierarchical metal nanostructures like hollow spheres or “yolk-shell” clusters.[17] However, these fabrication processes involved complex protocols and harsh conditions, such as hydrothermal treatment and strong acid etching, which make the construction of self-standing macrostructure of metal nanoparticles with high catalytic efficiency, easy manipulation and recovery still challenging. With the incorporation of solid catalyst and/or reagents as the encapsulating layer, the application of liquid marble as a catalytic platform therefore serves as an imperative approach in heterogeneous catalysis that allows both high catalytic efficiency and simple yet efficient recovery protocol.

Here, we demonstrate the fabrication of Ag nanowire-based liquid marble as a support-free catalytic miniature reactor and its application in heterogeneous Ag-catalyzed degradation of methylene blue (Fig. 1A). Our strategy combines the superior catalytic property of Ag, large surface area-to-volume ratio of nanowires, and its ability to yield mechanically stable network-like porous liquid marble shell to achieve efficient catalytic reaction. Ag nanowire-based liquid marbles of various sizes are fabricated using sessile water droplets ranging from 5 to 80 μL and their catalytic activities are quantitatively monitored using UV-vis spectrometer. We then systematically demonstrate the kinetics modulation of Ag-catalyzed reactions and investigate on the recyclability and reusability of Ag nanowire catalyst.

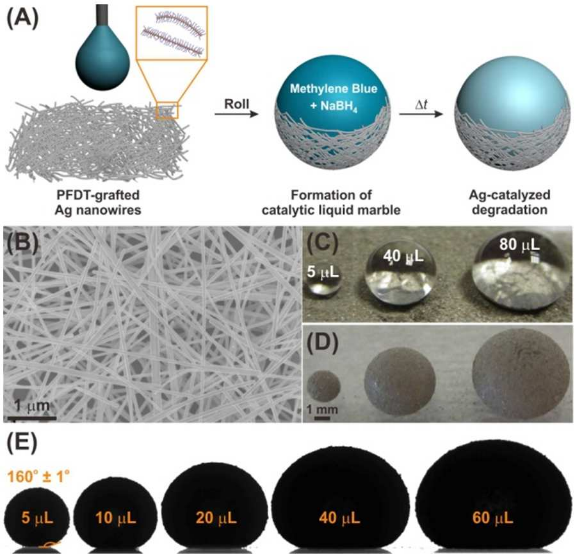

**Fig. 1** (A) Schematic illustration for the preparation of catalytic liquid marble. (B) SEM image of Ag nanowires. Digital images of 5, 40 and 80 µL of (C) water droplets deposited on the bed of perfluorodecanethiol-grafted Ag nanowires and (D) catalytic liquid marble. (E) Static contact angles of Ag nanowire-based catalytic liquid marbles fabricated using water volumes ranging from 5 to 60 µL.

Monodispersed Ag nanowires are synthesized in high yield using a modified polyol process,[18] with an average length over 10 µm and average diameter of 65 ± 14 nm (Fig. 1B).

To render hydrophobicity essential for supporting a spherical sessile droplet of water, 1H,1H,2H,2H-perfluorodecanethiol is grafted onto the as-prepared Ag nanowires via ligand exchange. No obvious change in the morphology of perfluorodecanethiol-grafted Ag nanowires is observed (Fig. S1A). The observation is further supported by the negligible change in extinction spectra after ligand exchange process (Fig. S1B), where the characteristic transverse plasmon peaks at 383 nm and 349 nm remain unchanged. These transverse surface plasmon peaks correspond to the out-of-plane quadrupole resonances of Ag nanowires with pentagonal cross-section.[19] When different sessile water droplets of volume ranging from 5 to 80 µL are dispensed on the bed of perfluorodecanethiol-grafted Ag nanowires, spherical water droplets are formed (Fig. 1C). This clearly illustrates the superior anti-wetting properties of the perfluorodecanethiol-grafted Ag nanowires, which is essential for subsequent catalytic liquid marble formation.

Catalytic liquid marbles are formed by rolling sessile water droplets over the hydrophobic perfluorodecanethiol-grafted Ag nanowires. The Ag nanowires are observed to assemble at the water/air interface spontaneously (Fig. 1D) and the resulting encapsulating shell is determined as a free-standing microstructure made up of loosely-packed Ag nanowires (Fig. S2). The length of pulverized Ag nanowires used for the formation of catalytic liquid marbles is also observed to be shorter compared to the un-pulverized Ag nanowires. Nevertheless, pulverization of Ag nanowire powder is essential for the formation of uniform catalytic liquid marble. These shorter Ag nanowires are able to provide a porous Ag nanowire network with potentially high catalytic surface area.

Minimal interaction between catalytic liquid marbles and underlying solid platform is also demonstrated by measurement of their contact angles. Static contact angles over 160° are generally observed for all catalytic liquid marbles, ranging from 5 to 60 µL, when deposited on a hydrophilic substrate (Fig. 1E). The high contact angle (≥ 150°) of the liquid marble is another indication of the non-wetting properties of Ag nanowires, which prevent the direct interaction of encapsulated water with the underlying platform. Although slight shape distortions from spherical structures are observed for liquid marbles with volume larger than 5 µL as a consequence of gravity, the intact, isolated and flexible puddle-like structures are still able to act as miniature reactors. Moreover, the result clearly demonstrates that the reaction capacities of liquid marble-based miniature reactors can be systematically modulated by accurately controlling the volumes of water droplet used for the formation of liquid marble. Hence, the versatility of liquid marble-based miniature reactor enables it to potentially accommodate a wide range of volumes of reaction mixture, ranging from 5 µL to 60 µL.

To investigate the performance of Ag nanowire-based liquid marble as a catalytic miniature reactor, the catalytic reduction of encapsulated aqueous methylene blue in the presence of sodium borohydride ($NaBH_4$) is studied.[20] Typically, 5 µL catalytic liquid marbles containing 2 mM methylene blue solution and 0.2 M $NaBH_4$ are prepared. The catalytic liquid marbles are then ruptured at pre-defined timings and the encapsulated aqueous methylene blue solutions are collected, diluted 100-folds, where the color intensity of the solution is first examined. Using 5 µL Ag nanowire-based liquid marbles, the intensity of the blue coloration of methylene blue solution is visibly reduced within the second min and eventually turns colorless by the tenth min (Fig. 2A). In contrary, no apparent color change is noted on the methylene blue solution in the absence of encapsulating Ag nanowire shell (Fig. 2B).

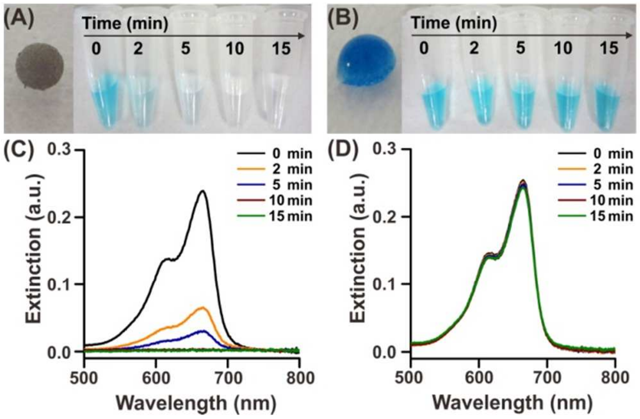

**Fig. 2** Digital images depicting the color change of aqueous methylene blue solutions (A) in Ag nanowire-based liquid marble and (B) without forming liquid marble at different time intervals. All setups use 5 µL of methylene blue solution. (C - D) UV-Vis spectra of methylene blue solutions measured at different time points of (A) and (B), respectively.

The extinction of the reacting aqueous solution is then monitored over a duration of 10 min to quantitatively examine the degree of methylene blue degradation (Fig. 2C). Using the characteristic 665 nm absorption band of the methylene blue, a calibration plot relating methylene blue concentration and extinction is obtained (Fig. S3). Hence, the concentration of methylene blue at selected time can be easily interpolated based on the calibration plot. The methylene blue degradation rate is characterized by plotting $C/C_0$ against time, where $C_0$ and C represent the methylene blue at its initial concentration and its concentration at time t, respectively (Fig. 3A). The extinction-duration plot depicts an exponential decrease in extinction with time for the 5 µL Ag nanowire-based catalytic liquid marble, which indicates a drastic degradation of methylene blue to non-absorbing products.[21] Within 2 min of the reaction time, ≥ 75 % of the initial methylene blue molecules are degraded ($C/C_0$ = 0.25) and a further decrease in methylene blue concentration is observed as the reaction proceeds. At $t > 10$ min, the reduction efficiency of methylene blue reaches nearly 100 % ($C/C_0 = 0.02$), indicating that almost all methylene blue molecules have been degraded. The rapid degradation of methylene blue using Ag nanowire-based catalytic liquid marble can be attributed to two reasons. Firstly, the presence of Ag serves as an efficient electron relay between nucleophilic $NaBH_4$ and electrophilic methylene blue for the catalytic reduction/degradation process.[21] Secondly, the high surface area-to-volume ratio imparted by Ag nanowires and the aforementioned porous network structure allow the exposure of large amount of catalytic sites for efficient degradation reaction. The need for porous network structure for efficient catalysis is further affirm using compacted-shell Ag nanocube-based liquid marble (5 µL), which only provides a catalytic efficiency of 49 % after 10 min reaction time (Fig. S4), approximately halved the catalytic efficiency of Ag nanowire-based liquid marble (refer to Supporting Information for detailed discussion).

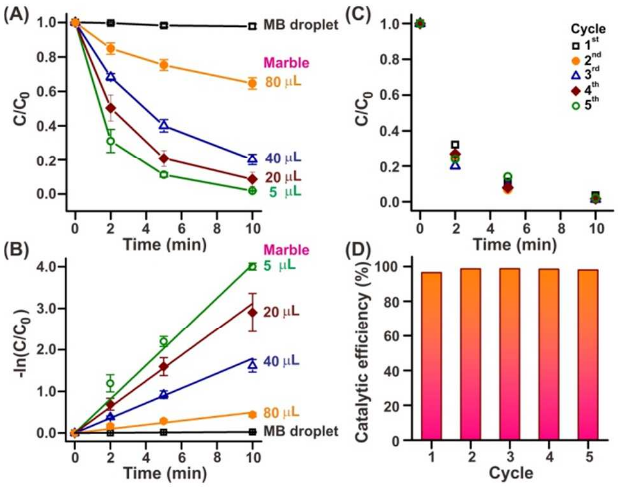

**Fig. 3** Plots of (A) normalized methylene blue concentrations ($C/C_0$) and (B) –$\ln(C/C_0)$ versus time using catalytic Ag nanowire liquid marbles of different sizes. (C) Correlation of methylene blue concentration with time using 5 µL Ag nanowire-based catalytic liquid marble for 5 degradation cycles. (D) Comparison of catalytic efficiency and reusability of Ag nanowires over 5 degradation cycles.

We further illustrate the necessity of the Ag catalyst by comparing with an identical experimental set-up but in the absence of encapsulating Ag layer. The non-encapsulated methylene blue solution exhibits no obvious degradation of methylene blue by $NaBH_4$ from its appearance and UV-vis spectra (Fig. 2B & 2D), with $C/C_0$ approximating 1 even after 10 min. Hence, it is evident that the heterogeneous Ag nanoparticle-based catalyst is essential for the degradation reaction and can be easily incorporated into the reacting mixtures in the form of liquid marble without the need of supporting platforms. Although the catalytic efficiency of liquid marble may be lower compared to an equal volume (5 µL) of aqueous methylene blue dispersed with approximately equal amount of Ag nanowires instead (Fig. S5), we emphasize that such dispersion cannot act as an isolated robust miniature reactor and the Ag catalyst cannot be recovered easily in comparison to the use of liquid marble.

The chemical kinetic of our catalytic liquid marbles can be easily modulated by systematically varying their sizes using different volume of aqueous reaction solution (5, 20, 40 and 80 µL). By monitoring the intensity of 655 nm extinction peak over time (Fig. 3A and Fig. S6), we observe a general exponential decrease of $C/C_0$ as the reaction proceeds for all reaction volumes. Hence, we assume the catalytic reaction as a pseudo-first order reaction where first-order reaction kinetics equation can be applied, i.e. $\ln(C_0/C) = k_{app}*t$, where $k_{app}$ is the degradation rate constant (Fig. 3B).[17b] The apparent rate constant $k_{app}$ values are 0.41, 0.31, 0.18, 0.05 $min^{-1}$ for 5, 20, 40 and 80 µL liquid marbles respectively. The results clearly indicate that kinetic rate of the catalytic reactions can be easily manipulated simply by controlling the size of the liquid marble. An increase in the liquid marble size leads to a significant decrease of catalytic reaction rate. Although the reaction rate of catalytic liquid marble of < 5 µL is expected to be faster, it is technically challenging to obtain accurate sessile droplets of < 5 µL using a pipette/ manual dispenser. Moreover, at volume < 5 µL, it is difficult to visibly differentiate between a liquid marble from its ruptured state.

Considering the temperature, pressure and initial reactants concentration are kept constant throughout the reactions, the decreasing rate constant $k_{app}$ with respect to the increase in volume/size of liquid marble can be attributed to a decrease in the efficiency of mass transfer of reactant to the catalytic active sites at the surface, which is a major factor affecting the kinetics of a heterogeneous catalytic reaction. In addition, the increase of analyte-to-surface area ratio with increasing volume of reaction solution can also contributes to a longer degradation time of methylene blue and a slower rate constant (or reaction kinetics) (see Supporting information for more discussion on volume-controlled reaction kinetics). Therefore, the catalytic liquid marbles have clearly demonstrated its ability to modulate chemical kinetics just simply by changing its size, which can be potentially applied as rate-controllable catalytic miniature reactors.

We also examine the recyclability and reusability of perfluorodecanethiol-grafted Ag nanowires by measuring its catalytic performance for multiple degradation cycles. The Ag nanowire powder on catalytic liquid marble can be easily recycled by removing the interior aqueous solution and re-rolling new droplets of methylene blue solution on the powder bed to form catalytic liquid marbles without additional treatment. We observe that the morphology of the recycled Ag nanowire powder (Fig. S7) exhibits negligible wear and tear, which is essential in the maintenance of the integrity of porous network liquid marble shell during the recycle test. Using the recycled Ag nanowires for the subsequent formation of catalytic liquid marbles, catalytic efficiencies of > 95 % towards the degradations of methylene blue are still consistently obtained even after five reaction cycles (Fig. 3C-D). Hence, the catalytic liquid marble has been heretofore demonstrated to be a promising cost-effective, highly efficient miniature reactor that is equipped with rate-modulating capability and long cycle life without losing its catalytic efficiency.

In summary, Ag nanoparticle-based catalytic liquid marbles have been fabricated as support-free, rate-controllable catalytic miniature reactor with high methylene blue reduction efficiency close to 100% and excellent reusability over 5 catalytic cycles. The ensemble of benefits therefore enables catalytic liquid marble an attractive alternative miniature reactor, which is highly appealing for providing support-free heterogeneous catalysis of small volume reaction. This is especially important in fields involving highly toxic and costly reactants and/or hazardous reaction where preliminary reaction involving small volume is preferred. Our protocol for the fabrication of catalytic liquid marble is also generic and can be extended to micro- and nanoparticles of different morphology and material to tailor its reactivity for a wide range of chemical reactions.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, SEM images and UV spectra of prepared samples. See DOI: 10.1039/b000000x/

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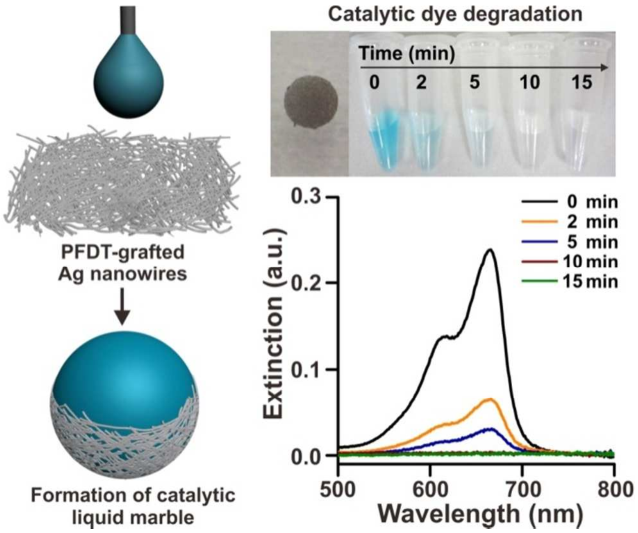

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