Electronic Supplementary Information

Catalytic Liquid Marbles: Ag Nanowire-based Micro-reactors for Highly Efficient Degradation of Methylene Blue

Yue-E Miao,ab Hiang Kwee Lee,ac Wee Shern Chew,a In Yee Phang,c Tianxi Liu,*b and Xing Yi Ling*aa

a Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371.

b State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, P. R. China.

c Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), 3 Research Link, Singapore 117602.

* To whom correspondence should be addressed. Email: txliu@fudan.edu.cn, xyling@ntu.edu.sg
Experimental Section

Materials. Poly(vinyl pyrrolidone) (PVP, average Mw = 360000 and 55000), anhydrous ethylene glycol (EG, 99.8%), 1H,1H,2H,2H-perfluorodecanethiol (PFDT, ≥ 97 %), 1,5-pentanediol (PD, ≥ 97 %), and methylene blue (≥ 82 %) were purchased from Sigma Aldrich; silver (I) nitrate (AgNO$_3$, 99+ %) and copper(II) chloride (≥ 98 %) were purchased from Alfa Aesar; sodium chloride (NaCl, 99.5 %) was purchased from Goodrich Chemical Enterprise; ethanol (ACS, ISO, Reag. Ph Eur) was from EMSURE; acetone (AR) was purchased from P. P. Chemicals Sdn Bhd; n-hexane (AR, ≥ 95 %) was obtained from RCI Labscan; propan-2-ol (HPLC grade) was from Fisher Scientific UK. All chemicals were used without further purification. Milli-Q water (>18.0 MΩ.cm) was purified with a Sartorius Arium® 611 UV ultrapure water system.

Synthesis and purification of Ag nanowires. Ag nanowires were synthesized based on a modified literature procedure.$^1$ In a typical synthesis, the mixture of 7 mg of NaCl and 0.5 g of PVP was dissolved in 10 mL of EG and heated to 160 °C in a round-bottom flask. With the use of a syringe pump, 5 mL EG solution of 0.12 M AgNO$_3$ was added dropwise into PVP solution at a rate of 5 mL/h while keeping vigorous stirring at 1000 rpm. After the addition of AgNO$_3$, the reaction solution was further heated at 160 °C for 30 min and then cooled to room temperature. The as-obtained nanowire solution was washed several times using acetone and ethanol to remove small colloidal nanoparticles. Then, Ag nanowires were redispersed in ethanol and left to sediment overnight in the fridge. The sediment was discarded to remove large colloidal particles while the top suspension was transferred into a new vial for further use.

Synthesis and purification of Ag nanocubes. Ag nanocubes were prepared based on a literature procedure.$^2$ In a typical synthesis, 10 mL of PVP (20 mg/mL) and AgNO$_3$ (20 mg/mL) were separately dissolved in PD with adding 35 μL of CuCl$_2$ (8 mg/mL) solution into AgNO$_3$ solution. Then, 20 mL of PD was heated to 190 °C for 10 min, followed by adding 250 μL of PVP precursor every 30 s and 500 μL of AgNO$_3$ precursor every minute in the reaction duration of approximately 20 min. Upon formation of Ag nanocubes, the as-obtained nanocube solution was washed several times using acetone and ethanol to remove residual PD. After that, Ag nanocubes were re-dispersed in ethanol and added dropwise into 100 mL of PVP water solution (0.2 g/L), which was then vacuum filtered multiple times using PVDF filter membranes (Durapore®) with pore sizes ranging from 5 μm, 0.65 μm, 0.45 μm and 0.22 μm to remove any impurities. The purified Ag nanocubes were re-
dispersed in ethanol for storage and further use.

**Preparation of catalytic liquid marble.** Both the purified Ag nanowires (1.3 mg/mL) and nanocubes (2 mg/mL) were re-dispersed with 5 mM PFDT in the mixture solution of propan-2-ol and hexane with a volume ratio of 1/1 at room temperature for over 12 h to render hydrophobicity. Sessile water droplets of various volumes, ranging from 5 μL to 80 μL, were dispensed and subsequently rolled on the powder bed of PFDT-grafted Ag nanowires and nanocubes until complete encapsulation, typically less than 10 seconds, to form catalytic liquid marbles with controllable sizes.

**Catalytic degradation of methylene blue.** The degradation of methylene blue was carried out in the catalytic liquid marble. Firstly, same volume of aqueous NaBH₄ solution was added to aqueous methylene blue solution to obtain the mixture solution of NaBH₄ (0.2 M) and methylene blue (2 mM). Then, five 5-µL droplets of the as-obtained solution were dropped on the functionalized Ag nanowire or nanocube powder bed to form the catalytic liquid marbles. At selected time intervals, the methylene blue solution was respectively extracted out from one of the 5 catalytic liquid marbles and diluted 100 times in water for UV-Vis spectroscopy measurement (Cary 60 UV-Vis spectrometer). The catalytic efficiency, between liquid-marble state and dispersed state, was studied by deliberately breaking the 5 µL catalytic liquid marble upon its formation to ensure that a consistent amount of Ag nanowires was dispersed in an equal volume droplet of methylene blue solution. The degradation of methylene blue by NaBH₄ in solution droplets without Ag nanoparticles were also carried out as a reference sample.

The characteristic extinction peak of methylene blue at 665 nm peak is used as the reference extinction peak for the reaction kinetic study. The calibration graph of methylene blue at different concentrations was obtained by measuring the extinction of different predetermined concentrations of aqueous methylene blue solutions. The extinction intensity of the measured methylene blue solution was then converted to methylene blue concentration using a methylene blue extinction-concentration calibration graph. The size effect of catalytic liquid marbles on the catalytic reaction rate was investigated by accurately controlling the volume of solution droplets in the range of 5 to 80 μL. The recyclability and reusability of catalytic liquid marbles were obtained by withdrawing solution inside liquid marbles and re-rolling new droplets of methylene blue solution on the powder bed without additional treatment for over 5 cycles.
**Characterization.** Morphology of Ag nanowires and nanocubes was carried out by JEOL JSM-7600F scanning electron microscope (SEM) at an accelerating voltage of 5 kV. Static contact angles were measured with a Theta Lite contact angle measuring instrument equipped with a Firewire digital camera. Dark field image was obtained under dark field illumination using the Olympus BX51 microscope with a 100× (N.A. 0.9) objective.
Fig. S1 (A) SEM image of perfluorodecanethiol-grafted Ag nanowires. (B) UV-vis spectra of Ag nanowires before and after functionalization.

Fig. S2 (A) Dark field optical and (B) SEM images of a liquid marble formed by Ag nanowires upon drying.

Fig. S3 (A) Extinction spectra of various pre-defined methylene blue concentrations and (B) their corresponding calibration curve relating absorbance, at characteristic 655 nm, with the concentrations of methylene blue.
Fig. S4 SEM images of a liquid marble formed by Ag nanocubes upon drying at a (A) lower magnification and (B) higher magnification. (C) Digital images depicting color changes of aqueous methylene blue solutions in Ag nanocube-based liquid marble at different time intervals. (D) UV-Vis spectra of methylene blue solutions measured at different time points of (C).

The study on catalytic liquid marble is extended using Ag nanocube-based liquid marbles fabricated with the same volume of aqueous reactants (5 µL) to determine the effect of particle shape and corresponding packing behaviour of Ag nanoparticles on the catalytic efficiency. We observe that Ag nanocube-based liquid marble exhibits a slower reaction kinetics compared to Ag nanowire-based liquid marble, as illustrated from both the methylene blue solution color (Fig. S4C) and UV-Vis extinction spectra (Fig. S4D) with time. A catalytic efficiency of 49 % ((C/C₀ = 0.51)) toward the reduction of methylene blue is achieved after 10 min, which is significantly poorer than that of Ag nanowires (catalytic efficiency ~ 100 %). Such superior catalytic property of Ag nanowire over Ag nanocubes, in the form of liquid marble, can be primarily attributed to the higher catalytic surface area rendered by Ag nanowires and its porous network structure. In contrary, Ag nanocube-based liquid marble of equal volume are made up of a much more compacted shell of nanocubes (Fig. S4A - B), which may severely decrease the active surface area of Ag nanoparticles exposed and also hinder effective diffusion of probe molecules within the encapsulating catalytic shells. Hence, a great decrease of catalytic reduction efficiency of methylene blue is observed in Ag nanocube-based catalytic liquid marble. This again emphasizes on the necessity of high specific area of Ag nanowires and the associated porous network-structured shell on the liquid marble for efficient catalysis.
Fig. S5 UV-Vis spectra of 5 μL aqueous methylene blue solution catalyzed by the dispersion of same amount of Ag nanowires at selected time intervals.

We compare the catalytic efficiency of liquid marble to an equal volume (5 μL) of aqueous methylene blue dispersed with approximately equal amount of Ag nanowires instead. An enhancement in catalytic efficiency from 75% (C/C₀ = 0.25 using Ag nanowire-based liquid marble) to 100% (C/C₀ = 0.08) of methylene blue within 2 min using an Ag nanowire dispersion is observed (Fig. S5). This can be attributed to the presence of more catalytic sites available for the reaction. Despite a greater catalytic efficiency, this dispersion cannot act as an isolated robust micro-reactor and the Ag catalyst cannot be recovered easily in comparison to the use of liquid marble. Therefore, the design of liquid marbles as catalytic micro-reactors is appealing to effectively realize the function of metal nanoparticles with high catalytic efficiency, easy manipulation and recovery.

Fig. S6 UV-Vis spectra of aqueous methylene blue solution catalyzed with Ag nanowire-based liquid marbles prepared using (A) 5 μL, (B) 20 μL, (C) 40 μL and (D) 80 μL of aqueous methylene blue solutions at different time intervals. The insets are the corresponding photographs of methylene blue solutions at the same time when the UV−Vis spectra are taken.

The volume and surface area of a liquid marble structure can be defined as \( V = \frac{4\pi R^3}{3} \) and \( S = 4\pi R^2 \) where \( R \) is the radius of a sphere, the ratio of surface area between two liquid marbles with
different volume of $V_1$ and $V_2$ can be expressed as \( S_2/S_1 = \left( V_2/V_1 \right)^{2} \) where $S_1$ and $S_2$ are their corresponding surface area. Similarly, as the concentration of methylene blue in our experiment is fixed, the ratio of the amount of methylene blue in two liquid marbles with different volume of $V_1$ and $V_2$ can be expressed as \( M_2/M_1 = \left( V_2/V_1 \right) \) where $M_1$ and $M_2$ are their corresponding amount of methylene blue in each liquid marble. Thus, it can be observed that with increasing volumes of liquid marbles, the surface areas are increasing at a slower rate compared to the increase of the amount of methylene blue encapsulated in liquid marbles. Therefore, the increase in M/S ratio with increasing volumes of catalytic liquid marble can also contribute to a longer degradation time of methylene blue and a slower rate constant.

![Fig. S7 SEM images of the recycled Ag nanowire liquid marble upon recovery and subsequent drying after five repeated cycles at (A) lower magnification and (B) higher magnification.](image)

**References**