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Ultraviolet-light-responsive Liquid Marbles

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Photoresponsive liquid marbles were prepared using spiropyran (SP) powder. The liquid marbles were transferred to a Petri dish containing water and remained stable on the water surface for more than a week in the dark. The liquid marbles disintegrated immediately upon irradiation with ultraviolet (UV) light.

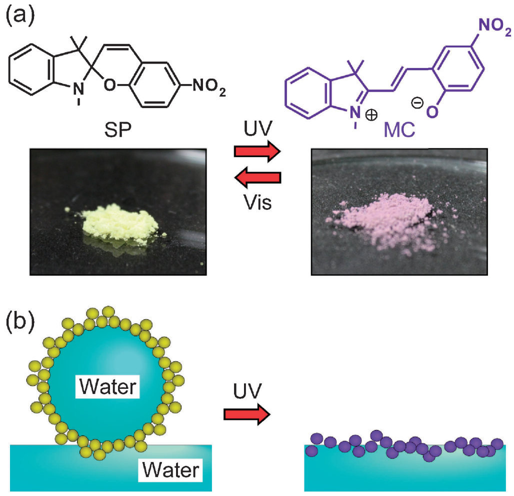
Liquid marbles, which are liquid droplets (typically of millimeter-sized diameter) encapsulated by relatively hydrophobic self-assembled particles at the air–liquid interface, constitute a novel approach for handling droplets and conducting reactions within droplets.[1] Liquid marbles have been shown to be promising for applications in material-based devices such as chemical sensors,[2] micropumps,[3] and microreactors.[4] They are considered to be a perfect nonwetting system; in addition, they work as liquid microcarriers, capable of moving quickly without any leakage, because the hydrophobic particles on the liquid marble surface form a nonstick interface between the droplet and the substrate, reducing motion resistance. In order to exploit liquid marbles as microcarriers, both stability and remote movement control are highly desirable. Recently, stimulus-responsive liquid marbles that are sensitive to pH,[5] electric fields,[6] and magnetic fields[7] have been fabricated. We previously reported pH-responsive liquid marbles stabilized by polymer particles carrying pH-responsive hairs, of which the surface wettability by water could be changed through pH control.[5a–5c]

Herein, we report light-responsive liquid marbles prepared using a spiropyran (SP) powder, of which the wettability by water changed upon external light stimulus (Scheme 1). These new liquid marbles were stable on substrates (solid and water) in the dark but disintegrated under ultraviolet (UV) light.

Photoresponsive isomerization of SP was confirmed by UV–visible absorption spectroscopy in homogeneous solution. Changes in the UV–vis absorption spectrum of SP in ethyl acetate upon UV irradiation for 10 min were examined (Supporting Information (SI), Figure S1).[8] Before UV irradiation, no absorption peak was observed at 580 nm; however, the absorbance at 580 nm increased upon UV irradiation; this was attributed to the formation of the corresponding merocyanine (MC). The color of the solution changed from clear to purple upon UV irradiation.

Figure 1a shows changes in the diffuse reflectance spectrum of SP powder due to UV irradiation. Upon irradiation with UV light, the reflectance at ca. 590 nm decreased owing to the photoisomerization of SP to the MC isomer. The fraction of the MC isomer (f_{MC}) at irradiation time t can be calculated from the reflectance by using the following equation:

$$f_{\mathrm{MC}} = \frac{[\mathrm{MC}]_t}{[\mathrm{SP}]_0} = 1 - \left(\frac{R(t) - R_\infty}{R(0) - R_\infty}\right) \qquad (1)$$



Scheme 1. (a) Light-induced isomerization between spiropyran (SP) and the corresponding merocyanine (MC) by alternating irradiation with ultraviolet (UV) and visible light. Also shown are digital photographs of SP and MC powder. (b) Schematic illustration of a liquid marble prepared using SP powder on the surface of a pool of water, and subsequent disintegration upon exposure to UV light.

Here, $[\mathrm{MC}]_t$ is the amount of the MC isomer at time t, $[\mathrm{SP}]_0$ is the initial amount of the SP isomer, $R(t)$ and $R(0)$ denote the reflectances at ca. 590 nm at time t and at the beginning of the coloration process, respectively, and R_∞ represents the reflectance at ca. 590 nm after the photostationary state is reached. The fraction of MC was plotted against the irradiation time (Figure 1b). About 80% of the SP powder changed to MC within 10 s of UV irradiation. The first-order kinetic rate constant (k) for the conversion of SP to MC in the powder state was $5.31 \times 10^{-1}\,\mathrm{s}^{-1}$, as estimated from the initial slope (SI, Figure S2).[8]

Figure 2 shows water droplets on the pellet surface before and after UV irradiation. The contact angle of the SP pellet with pure water was 85° (Figure 2a), while that of the MC pellet after UV irradiation was 64° (Figure 2b). The pellet surface became more hydrophilic than the original SP pellet after UV irradiation because MC is hydrophilic owing to the presence of charged groups. This observation suggested that the surface polarity of the SP powder might be increased by conversion to MC upon UV irradiation. Rosario et al. reported a similar photoresponsive change in the water contact angle on SP molecules covalently bound to a glass surface.[9]

Liquid marbles were prepared by rolling a droplet of water over SP powder. The powder coated the water droplet

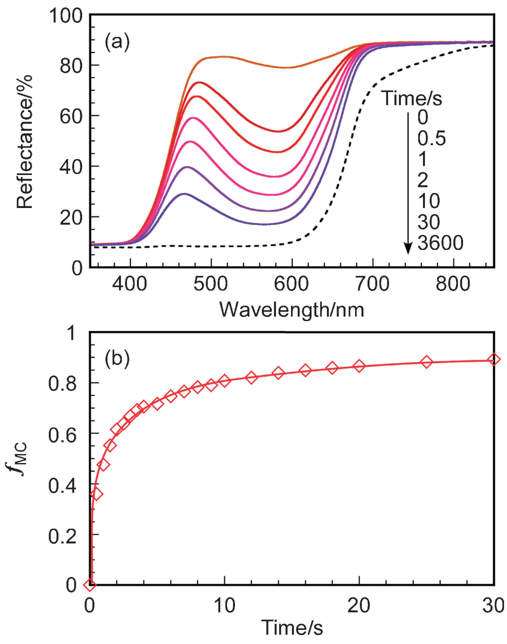


Figure 1. (a) Changes in the diffuse reflectance spectrum of SP powder upon UV irradiation. The irradiation times are indicated in the figure. (b) Changes in the MC fraction (f_{MC}) of the powder as a function of irradiation time upon photo-isomerization of SP to MC.

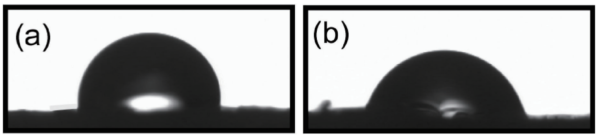


Figure 2. Water contact angles of the pellet surface of (a) SP before UV irradiation and (b) MC after UV irradiation.

immediately, rendering it both hydrophobic and nonwetting. These liquid marbles remained intact after transfer onto a glass slide (Figure 3a) and onto water (Figure 4b). The liquid marbles clearly had significant surface roughness, which suggested that they were coated with irregular powder clusters.[10] The shape of the irregular SP powder clusters could be observed by SEM (SI, Figure S3).[8] These powder clusters may trap air to form the liquid marble, allowing Cassie–Baxter wetting at the cluster–liquid interface.[11]

A liquid marble was examined through fluorescence microscopy (Figure 3b). The liquid marble was prepared with fluorescein (0.01 wt %) dissolved in an aqueous solution (10 µL) of gelatin (20 wt %) in combination with SP powder at 60 °C. After being cooled to room temperature, the liquid marble was sectioned with a scalpel. This was only possible because of the nature of gelatin, which is a free-flowing aqueous solution at 60 °C but forms a gel at room temperature. UV irradiation was applied for 10 min to transform the SP to MC, which emits fluorescence.[12] The fluorescein within the gel gave rise to a yellow color, which was surrounded by heterogeneous orange aggregates ranging from 180 to 5 µm; these were clusters of MC powder. The double-layered fluorescence image clearly showed

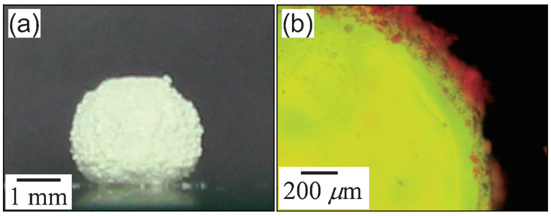


Figure 3. (a) Digital photograph showing a liquid marble containing 10 µL of water covered with SP powder on a glass slide. (b) Fluorescence microscopic image of a liquid marble prepared using SP powder and a 10-µL aqueous solution containing gelatin (20 wt %) and fluorescein (0.01 wt %) at 60 °C. After cooling to room temperature, UV irradiation was applied for 10 min to transform SP to MC, which emits fluorescence. The liquid marble was sectioned with a scalpel, and one of the hemispheres was placed on a glass slide. Note the yellow region due to fluorescein and the orange powder aggregates.

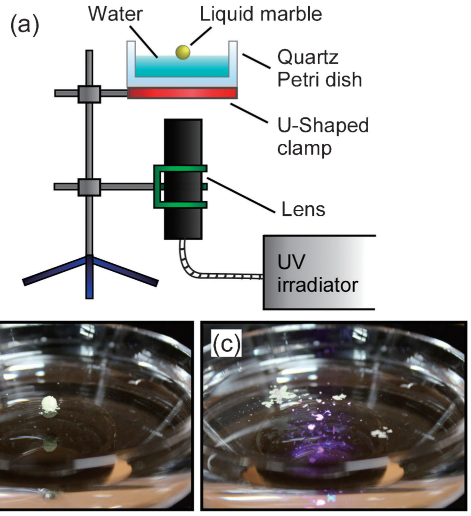


Figure 4. (a) Experimental setup for measuring light-induced disintegration of the liquid marble, and photographs of a floatable liquid marble consisting of 7 µL of water covered with SP powder on the surface of water in a quartz Petri dish (b) before and (c) after UV irradiation for 20 s from below.

that the powder acted as a liquid-marble stabilizer and was present only as a coating on the surface of the water droplet.

Liquid marbles were prepared by rolling a 7-µL water droplet over ground SP powder. For the investigation of the effect of UV irradiation, the liquid marbles were transferred to the surface of water in a quartz Petri dish, and UV light was applied from below the dish (Figure 4). Enhanced stability was achieved in the dark, which indicated that the SP powder was sufficiently hydrophobic to adsorb strongly at the air–water interface. The liquid marbles were stable for more than a week on the water surface, under humid conditions without UV irradiation. However, the liquid marbles on water were always unstable in the presence of UV light, disintegrating immediately. The disintegration time, defined as the time required for the liquid marble to break after UV irradiation, was measured. After five measurements, the average disintegration time for a liquid marble containing 7 µL of water was calculated to be 14.5 s (SI, Figure S4).[8] When UV irradiation was applied, the hydrophobic SP was converted to ionic MC. Therefore, the MC powder was wetted spontaneously, and disintegration of the liquid marble followed. Although liquid marbles containing 7 µL of water remained stable for more than one week on the water surface, they collapsed immediately upon UV irradiation. A video of the photoresponsive behavior of the liquid marbles is provided as Supplementary Video S1 in the SI.[8]

Recently, Wang et al.[13] reported the preparation of UV-responsive liquid marbles composed of a silica-coated magnetite core and a mesoporous silica shell grafted with a pH-responsive block copolymer, poly(2-vinylpyridine-*b*-dimethylsiloxane) (P2VP-*b*-PDMS), known as core–shell-structured pH-responsive magnetic particles (RMPs). The silica shell is loaded with a photo acid generator (PAG). Liquid marbles containing water droplets can be prepared by using RMPs. Upon UV irradiation, the PAG generates hydrogen ions, which induce the protonation of the P2VP chains on the particle surface and cause a hydrophilic transition of the RMPs, leading to disintegration of the liquid marbles. In this study, the photoresponsive liquid marbles prepared with SP powder do not require the addition of PAG, and disintegration of the liquid marble is caused by the photoresponsive nature of the SP molecule.

For the investigation of the relationship between the volume of water in a liquid marble and the average disintegration time of the marble on the water surface due to UV irradiation (SI, Figure S5),[8] liquid marbles containing 50 µL of water were prepared and transferred to a water surface. It was found that the disintegration time of ca. 10 s was almost independent of the volume of water used. It is thought that because around 80% of the SP powder changes to MC within 10 s (Figure 1b) and the hydrophobic SP powder in contact with the surface of a pool of water changes to hydrophilic MC, the disintegration of the liquid marbles is independent of the water content.

In conclusion, we have demonstrated the preparation of photoresponsive liquid marbles composed of SP powder and water droplets. The liquid marbles prepared using hydrophobic SP powder were transferred to a water surface, where they remained stable for more than a week under humid conditions in the dark. Upon UV irradiation, however, the liquid marbles burst immediately.

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8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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