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TECHNICAL NOTE

Reduced UV light scattering in PDMS microfluidic devices

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Microfluidic devices which consist of polydimethylsiloxane (PDMS) are used extensively for the production of polymer microparticles through the use of droplet templating and on-chip photopolymerization. However, in existing methods, spatial confinement of the photochemical droplet solidification is impaired by UV light scattering inside the PDMS elastomer. We present a technique to load PDMS microfluidic devices with a fluorescent dye that absorbs the scattered UV light and shifts it to longer wavelengths. By this means, the stray light is no longer harmful, and UV exposure can be limited to a desired region on the microfluidic chip.

Droplet-based microfluidics is a powerful tool to form monodisperse emulsion droplets with sophisticated morphologies such as those with anisotropic compositions,[1–4] core–shell structures,[5–9] or non-spherical shapes.[10–12] These droplets can be used as templates to synthesize microparticles with complex architecture; this is typically achieved through droplet solidification by polymerization or gelation of monomers or macromolecular precursors.[13,14] To retain the complexity of the pre-particle droplets, it is essential to cure them immediately after their formation, which is typically achieved by rapid UV-induced photopolymerization or photogelation on the microfluidic chip.[13]

This strategy requires the light-induced droplet solidification to be confined to a defined area on the microfluidic device to avoid undesired solidification of the precursors prior to their emulsification. To achieve such a spatial confinement, various masking techniques have been used.[13] However, even though masking minimizes unwanted primary exposure of the microchannels, light can be propagated to remote regions inside the microfluidic device by scattering through the device material. In many cases, microfluidic devices are fabricated from elastomers such as polydimethylsiloxane (PDMS) through the use of soft lithography,[15] because this approach maximizes flexibility of the microchannel design. These PDMS devices consist of a rubbery polymer network, which gives rise to marked light scattering. This situation is exacerbated because PDMS elastomer kits contain silica nanoparticles, which strongly enhances light scattering. Hence, the use of photocurable fluids in PDMS microfluidic devices is markedly impaired by uncontrolled, stray-light-induced solidification of these fluids in the microchannels.

To circumvent this limitation, we present a way to load PDMS microfluidic devices with a fluorescent dye that absorbs the scattered UV light and shifts the stray light inside the elastomer to longer wavelengths. Thus, the stray light is no longer harmful, and UV exposure can be limited to a desired region using masking or light-focusing methods. Since many dyes are immiscible with PDMS, we link the fluorophore to silica nanoparticles, which can be mixed with PDMS over a wide range of compositions. To demonstrate the utility of this approach, we compare the UV-assisted fabrication of polymer microgel particles in PDMS microfluidic devices loaded with the fluorescent additive to those which have no additive: only the devices with fluorescent additives provide viable production of microgel particles and eliminate undesired clogging due to spurious UV illumination.

We synthesize fluorescent silica nanoparticles by a modified Stoeber process.[16] To link a fluorophore to these particles, we perform this reaction in the presence of a dapoxyl-functionalized silane. This reagent is obtained by dissolving a succinimidyl ester derivative of dapoxyl carboxylic acid (Invitrogen, 5 mg) in anhydrous dimethyl sulfoxide (VWR, 500 μL) and conjugating it with a coupling agent, aminopropyltriethoxysilane (Fluka, 29 μL). The resulting dapoxyl-silane is then added to a mixture of absolute ethanol (Merck, 17 mL) and 32% (w/w) ammonia in water (Merck, 1 mL), and after subsequent addition of tetraethylorthosilicate (Aldrich, 670 μL), fluorescently tagged silica particles form, as evidenced by an increasing turbidity of the solution. In a typical experiment, the mixture is reacted overnight, and the product particles are purified by sedimentation with subsequent dispersion in pure ethanol (two times) and water (two times) before they are isolated by lyophilization. The average hydrodynamic diameter of these particles is 320 nm, as determined by dynamic light scattering.

The dapoxyl dye exhibits fluorescence that is highly dependent on the solvent, with a Stokes shift of up to 200 nm.[17] A dispersion of the dapoxyl-labeled silica nanoparticles in liquid PDMS

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exhibits a fluorescence excitation maximum located at $\lambda_{max}(ex) =$ 422 nm, which is a good match to the emission maximum of most laboratory UV lamps, as indicated in Fig. 1A. The absorbance of this suspension at a typical UV irradiation wavelength of $\lambda = 365$ nm is $A = 2.6$ per centimetre if the concentration of labeled silica is 1% (w/w); hence, incident UV light of this wavelength is attenuated to less than 5% of its original intensity when passing a distance of 5 mm through the fluorescent silica dispersion. It is this absorption which eliminates the detrimental scattering of the UV light inside the PDMS elastomer. The dapoxyl dye shifts the absorbed light to substantially longer wavelengths with a fluorescence emission maximum at $\lambda_{max}(em) = 522$ nm, as also shown in Fig. 1A.

To incorporate these fluorescent silica particles into microfluidic devices, we use soft lithography and pour PDMS which contains 1% (w/w) of the fluorescent particles along with crosslinker (Sylgard 184 elastomer kit, Dow Corning, base : crosslinker = 10 : 1) onto a silicon wafer patterned with SU-8 photoresist.[15] After solidifying the material for 1 h at 65 °C, devices can be fabricated by oxygen-plasma bonding of the PDMS replicas onto glass slides. To render the channel surfaces hydrophobic, and hence, suitable for water-in-oil emulsification, we treat them with Aquapel® (PPG, Pittsburgh, PA, USA), a commercial windshield treatment.

The resultant microfluidic devices exhibit strong green fluorescence upon UV exposure, as demonstrated in Fig. 1B. This observation confirms that short-wavelength light is efficiently red-shifted inside the device material; it is thus harmless to UV-sensitive compounds in device regions that are not exposed to the primary beam. As a result, these devices show notably less accidental solidification of UV-curable fluids than conventional devices without fluorescent loading.

To illustrate the benefits of this treatment, we compare PDMS devices containing the fluorescently labeled silica nanoparticles to those without and emulsify and photocure semidilute solutions of a photocrosslinkable polymer. This polymer is a thermo-responsive poly(*N*-isopropylacrylamide) which is functionalized with pendant dimethylmaleimide moieties that can be selectively interconnected by UV exposure.[18] We use microfluidic channels that consist of a cross-junction to form pre-microgel emulsion droplets and a wide basin channel to expose these drops to UV excitation to cure them, as shown in Fig. 1C. The cross-junction consists of two rectangular channels that are 50 micrometres wide and intersect at an angle of 90°. The basin channel is patterned right behind the cross-junction, where the horizontal channel dimension widens to a width of 1 cm. All channels have a uniform height of 70 micrometres.

If we inject an aqueous semidilute solution of the photocrosslinkable polymer (50 g L^{-1} polymer, 1 mmol L^{-1} photosensitizer thioxanthone-2,7-disulfonate) and an immiscible paraffin oil into the microchannels at flow rates of 100 μL h^{-1} for the oil and 50 μL h^{-1} for the polymer, we obtain monodisperse droplets of the polymer solution that are dispersed in the oil phase. As these droplets flow downstream the basin channel, they pass through a spot of about 0.5 cm in diameter about 2 cm away from the cross-junction which is exposed to strong UV light (250 mW cm^{-2} at $\lambda = 365$ nm) from the glass backside of the microfluidic chip, thereby photocrosslinking the polymer chains and gelling the droplets, as shown in Fig. 1C. If plain PDMS is used as the elastomeric device material for this experiment, a steady state is only achieved for a time of about 10 min, before undesired photogelation of the aqueous phase sets in at the cross-junction and the polymer inlet channel, as also shown in Fig. 1C. This unwanted reaction occurs due to the stray light which

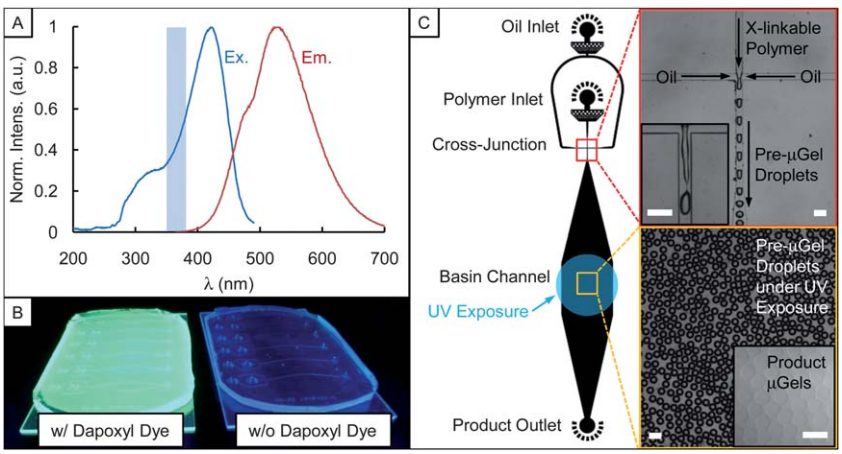

Fig. 1 Complexation of PDMS microfluidic devices with a UV-absorbing, fluorescent dapoxyl dye. (A) Normalized fluorescence excitation (blue line) and emission (red line) of the dapoxyl chromophore bound to silica nanoparticles and suspended in liquid PDMS. The blue bar denotes the light emission of most common laboratory UV lamps, which is effectively absorbed and red-shifted by this dye. (B) Photograph of two UV-irradiated microfluidic chips which are (left device) or are not (right device) loaded with the dapoxyl-functionalized silica nanoparticles. (C) Use of the dapoxyl-loaded device for the production of polymer microgel particles. A cross-junction channel serves to form monodisperse pre-microgel droplets from a semidilute precursor polymer solution, which are exposed to a focused spot of strong UV light as they flow through a basin channel, thereby gelling them. The resultant microgels are isolated from the continuous oil phase and swollen in water, where they swell to a size of about 60 μm, as shown in the lower right inset micrograph. If plain PDMS is used as the elastomeric device material, a steady microgel production is only possible for about 10 min, before uncontrolled, stray-light-induced gelation of the precursor polymer leads to uncontrolled droplet formation and clogs the polymer inlet channel, as shown in the upper left inset micrograph. Only devices which are loaded with the dapoxyl dye guarantee an unperturbed microgel production. All scale bars in panel C denote 100 μm.

crosslinks the polymer prior to its emulsification, thereby clogging the microchannels.

Using a PDMS device that is loaded with fluorescent silica beads solves this problem. Due to the absorption of the stray light inside the PDMS elastomer, the photoreaction is not triggered in unexposed regions of such a device, and photogelation of the aqueous polymer droplets occurs only in the basin channel that is exposed to the primary UV beam from the glass backside of the microfluidic chip. Even after several hours, no perturbation of the steady flow state is observed, and no gel can be detected in the cross-junction of the inlet channels; instead, the device continues to produce monodisperse microgel particles with a composition that is determined by the composition of the precursor polymer.[18]

The method presented in this note provides an easy means to avoid spurious UV irradiation in undesired locations in PDMS microchannels. Since the fluorescence labeling of the silica nanoparticles can be customized, and since different types of labeled silica beads can be mixed in the PDMS elastomer, the spectral characteristics of the device can be chosen at will.

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References

1 T. Nisisako, T. Torii, T. Takahashi and Y. Takizawa, *Adv. Mater.*, 2006, **18**, 1152–1156.
2 R. F. Shepherd, J. C. Conrad, S. K. Rhodes, D. R. Link, M. Marquez, D. A. Weitz and J. A. Lewis, *Langmuir*, 2006, **22**, 8618–8622.
3 Z. Nie, W. Li, M. Seo, S. Xu and E. Kumacheva, *J. Am. Chem. Soc.*, 2006, **128**, 9408–9412.
4 C.-H. Chen, R. K. Shah, A. R. Abate and D. A. Weitz, *Langmuir*, 2009, **25**, 4320–4323.
5 C.-H. Chen, A. R. Abate, D. Lee, E. M. Terentjev and D. A. Weitz, *Adv. Mater.*, 2009, **21**, 3201–3204.
6 A. S. Utada, E. Lorenceau, D. R. Link, P. D. Kaplan, H. A. Stone and D. A. Weitz, *Science*, 2005, **308**, 537–541.
7 M. Seo, C. Paquet, Z. Nie, S. Xu and E. Kumacheva, *Soft Matter*, 2007, **3**, 986–992.
8 R. K. Shah, J. W. Kim, J. J. Agresti, D. A. Weitz and L. Y. Chu, *Soft Matter*, 2008, **4**, 2303–2309.
9 S. Seiffert, J. Thiele, A. R. Abate and D. A. Weitz, *J. Am. Chem. Soc.*, 2010, **132**, 6606–6609.
10 M. Seo, Z. Nie, S. Xu, M. Mok, P. C. Lewis, R. Graham and E. Kumacheva, *Langmuir*, 2005, **21**, 11614–11622.
11 S. Xu, Z. Nie, M. Seo, P. C. Lewis and E. Kumacheva, *Angew. Chem., Int. Ed.*, 2005, **44**, 724–728.
12 Z. Nie, S. Xu, M. Seo, P. C. Lewis and E. Kumacheva, *J. Am. Chem. Soc.*, 2005, **127**, 8058–8063.
13 S. Y. Teh, R. Lin, L. H. Hung and A. P. Lee, *Lab Chip*, 2008, **8**, 198–220.
14 E. Tumarkin and E. Kumacheva, *Chem. Soc. Rev.*, 2009, **38**, 2161–2168.
15 J. C. McDonald, D. C. Duffy, J. R. Anderson, D. T. Chiu, H. K. Wu, O. J. A. Schueller and G. M. Whitesides, *Electrophoresis*, 2000, **21**, 27–40.
16 A. van Blaaderen and A. Vrij, *Langmuir*, 1992, **8**, 2921–2931.
17 Z. Diwu, Y. Lu, C. Zhang, D. Klaubert and R. Haugland, *Photochem. Photobiol.*, 1997, **66**, 424–431.
18 S. Seiffert and D. A. Weitz, *Soft Matter*, 2010, **6**, 3184–3190.

