ChemComm

COMMUNICATION

Highly monodisperse conjugated polymer particles synthesized with drop-based microfluidics†

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A facile method for preparing highly monodisperse, sub-micrometre conjugated polymer particles is reported. The particles are prepared through emulsification of a conjugated polymer solution on a microfluidic chip followed by solvent evaporation. The particle size is tuned between 150 nm to 2 μm, by controlling the polymer concentration.

Conjugated polymer particles are a powerful class of materials that can be used for morphology control in optoelectronic devices[1,2] or as tracer beads for fluorescent tagging in biological applications.[3,4] Such particles exceed single dye molecules in their photo-stability, absorption cross-section and emission rates. Moreover, conjugated polymer particles are unlike inorganic quantum dots, as they do not blink and are not cytotoxic.[3] Since conjugated polymer particle dispersions are aqueous, they can be applied in existing ink-jet printing techniques, avoiding costly and non-desirable organic solvents.[5] There are currently two methods for producing particles from conjugated polymers. Conjugated polymer particles can be prepared by miniemulsifying a solution of a conjugated polymer in an aqueous medium, followed by the evaporation of the organic solvent.[6] Alternatively, the conjugated polymer solution can be injected into a liquid, which is miscible with the solvent but not with the polymer. This leads to rapid precipitation of the conjugated polymer, forming particles.[3,4] However, both methods produce highly polydisperse particles; this severely limits their application.

Adaptations of both batch processes can also be performed in microfluidic devices.[7–9] Reprecipitation into particles is performed by injecting a polymer solution at a cross-section leading to small but polydisperse particles and emulsification of a polymer solution into monodisperse droplets and subsequent evaporation of the solvent affords monodisperse particles. However, these processes have not been applied to conjugated polymers due to the incompatibility of non-polar organic solvents with polydimethylsiloxane (PDMS), the most common material for microfluidic devices.

Monodispersity is of paramount importance in organic light emitting diodes[10] and in organic solar cells,[1,2] as morphology control in the active layers is essential for increasing their efficiency. Due to the low entropy of mixing, immiscible acceptor and donor polymers tend to phase separate on a macroscopic scale upon drying of the solvent. By using a mixture of particles of such polymers, the domain size of the individual conjugated polymers can be tailored by tuning the size-distribution of the conjugated polymer particles to fit the exciton diffusion length, leading to increased efficiencies of organic photovoltaic devices.[2] Monodisperse conjugated polymer particles would, therefore, improve the precise control over the domain size in such devices. However, the lack of synthetic methods for monodisperse particles obviates their use in these high-potential applications.

In this communication we report the synthesis of mono-disperse conjugated polymer particles with a wide range of sizes by emulsification of a conjugated polymer solution using a microfluidic drop-making device. We employ polyfluorene (PFO) (M_w = 58 200 Da) as a representative conjugated polymer due to its superior photostability.[11] Monodisperse drops of a solution of PFO are formed in an aqueous phase on chip using poly(vinyl alcohol) (PVA) as a stabilizer. Upon evaporation of the toluene, each droplet produces a single particle, resulting in a highly monodisperse dispersion of conjugated polymer colloids. This method is highly versatile and can be applied to any type of conjugated polymer that can be dissolved in an organic solvent that is immiscible with water.

We use a PDMS microfluidic chip with a cross-junction geometry and a channel height and width of 20×20 μm^2 at the intersection, as shown in Fig. 1a. The microfluidic devices are prepared using soft-lithography.[12] The PDMS can be conveniently bonded to glass, to close the channels; moreover holes can be punched in the PDMS to access the channels. However, non-polar organic solvents swell PDMS, which leads to constriction or full congestion of the channel geometry. To overcome this limitation, we vapour deposit Parylene-C inside the microfluidic channels; this passivates the PDMS against non-polar solvents and prevents swelling.[13] The microfluidic chip is designed with short channels to allow uniform coating inside the channels of the microfluidic chip. Parylene-C is deposited until reaching a thickness of 15 μm on the outside of the device. This results in a thickness of ∼250 nm inside the channels, which is sufficient to act as a barrier towards toluene and to prevent swelling of the PDMS. The Parylene-C coats the glass substrate as well as the PDMS channel walls and smooths

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† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/c1cc14251h
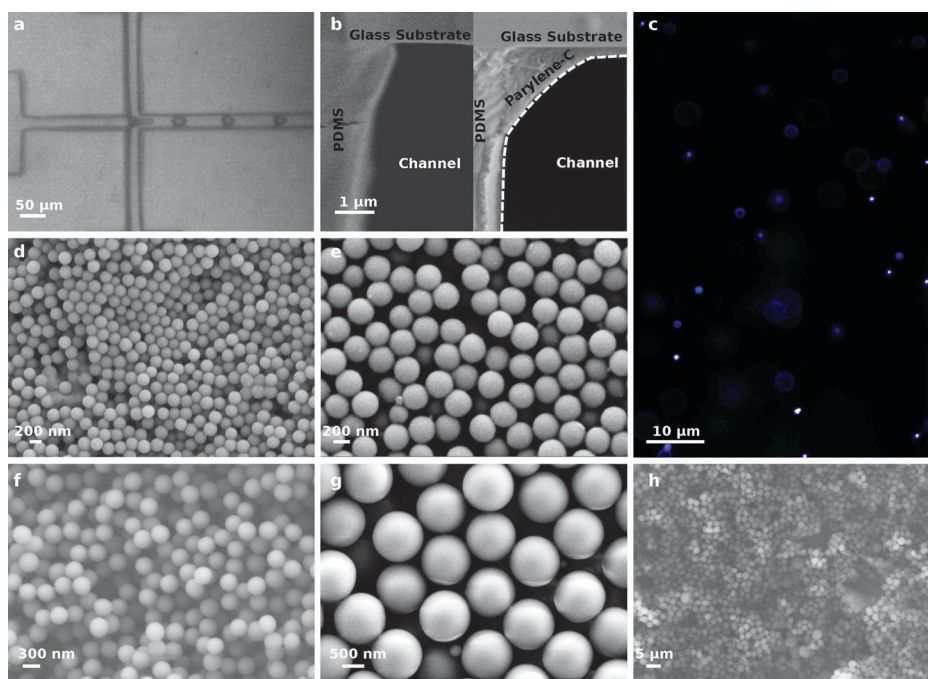
Fig. 1 (a) Optical micrograph of a microfluidic drop-maker, producing PFO in toluene droplets of *ca.* 20 μm. (b) SEM images of (left) a channel corner, where PDMS is bonded to glass, (right) the corner of a channel, which was coated with Parylene-C, as indicated by the dashed line. (c) Fluorescence micrograph of a dispersion of 1.1 μm PFO particles in water. SEM images of PFO particles with diameters: (d) 150 nm, (e) 200 nm, (f) 330 nm, (g) 1.1 μm, and (h) 2.0 μm.

the corners of the channel, as shown in Fig. 1b. Parylene-C is hydrophobic, which leads to wetting of the toluene phase. However, to produce droplets of the organic PFO solution in a continuous aqueous phase, the Parylene-C must be rendered hydrophilic. To accomplish this, the microfluidic chip is exposed to an oxygen plasma just before the device is connected to the fluid reservoirs.[14] The fluids are delivered by pressurizing the fluid-reservoirs with air, driving the fluids through chemically inert polyether ether ketone (PEEK) tubing to the microfluidic drop maker. The droplets are formed in the dripping regime with a pressure ratio of $\sim 1:5$ between the inner organic and the continuous aqueous phase. The PVA is added to the continuous phase to stabilize the resulting dispersion of conjugated polymer droplets. To adjust the droplet size to 20 μm, we observe the creation of droplets through a microscope and vary the pressures. Once the pressures are adjusted, the size of the droplets generated does not vary over time, allowing them to be produced at a rate of ~ 8000 droplets per second while being collected over several days. We use an excess of the continuous phase, to facilitate slow evaporation of the toluene without drying of the continuous phase. After collection, the emulsion is further stirred, to completely remove the toluene, thereby producing a dispersion of highly monodisperse PFO particles. To remove excess PVA, the particles are centrifuged and redispersed in an aqueous solution of an ionic surfactant.

The PFO particles exhibit photoluminescence (PL) in the blue spectrum, as shown in the fluorescence micrograph of a dilute PFO particle dispersion (see Fig. 1c). The particles are monodisperse with smooth surfaces, as observed by scanning electron microscopy (SEM) shown in Fig. 1d–h. By using concentrations between 0.005 and 0.5 g L^{-1}, particle sizes
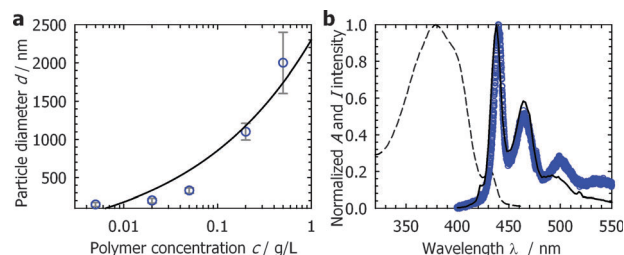

Fig. 2 (a) The influence of the polymer concentration on the particle diameter. The black line represents $d \approx \sqrt[3]{c}$. (b) Normalized absorption A (dashed line) and photoluminescence spectrum I (solid line) of a spin-coated PFO film and a dried glassy film of 330 nm PFO particles (circles).

between 150 nm and 2 μm can be produced (see Fig. 2a). The size varies with the cube root of the PFO concentration $d \approx \sqrt[3]{c}$, indicating that the emulsions are stable with no coalescence during drying. Sets of at least 300 particles are analysed by SEM to determine size distributions. The particles are monodisperse with standard deviations of less than 10%, as represented by the error bars in Fig. 2a. The 2 μm-diameter-particles have a larger standard deviation in size; this is due to their non-spherical shape. These particles are slightly oval, which is a result of the slow drying process. The toluene droplets with PFO are less dense than the aqueous phase, which leads to creaming of the droplets at the water–air interface after collection from the microfluidic device. These more concentrated droplets are squeezed by their own buoyancy leading to non-spherical particle shapes after drying.

To analyse the PL characteristics of the particles, dispersions are dried on a substrate by blowing air over the dispersion; this

results in a colloidal glass of PFO particles. The particles are excited at 380 nm and their PL spectrum shows well resolved emission peaks with a maximum at 440 nm; both characteristics are indicative of the β-phase in PFO (see Fig. 2b). For comparison the absorption and emission spectra of a spincoated PFO film in the β-phase is measured, represented by the black lines in Fig. 2b. The PL spectrum of the particles overlaps well with that of the film. Unfortunately, the absorption profile of the dried particles could not be accurately determined due to significant scattering of the particles. The β-phase is a meta-stable morphology in PFO, characterized by an extended rigid-chain conformation in the conjugated polymer backbone. Interestingly, the morphology of the polymer changes to the β-phase formation upon evaporation of the toluene and the slow drying of the particles.[11] The size of the particles does not alter the PL emission profile as expected for conjugated polymer particles.[4]

This method of producing monodisperse conjugated polymer particles is highly versatile, and can be applied to other polymers, provided they are miscible in non-polar organic solvents and can be emulsified in an aqueous phase. These monodisperse conjugated polymer particles represent a novel class of photonic materials with a wide spectrum for applications. For example, applications of monodisperse conjugated polymer particles can be envisioned in coatings, where they create physical colour by diffraction,[15] or in photonic crystals as photonic band-gap materials for wavelength conversion[16] or as colloidal laser resonators.[17] Such devices are currently only created in inverse opal structures, where monodisperse colloids are backfilled with a conjugated polymer solution. Creating a direct photonic crystal from conjugated polymer particles should lead to greater efficiencies of such devices as the volume fraction of the active material is increased; this should lead to lower onset-thresholds and improved performance.

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