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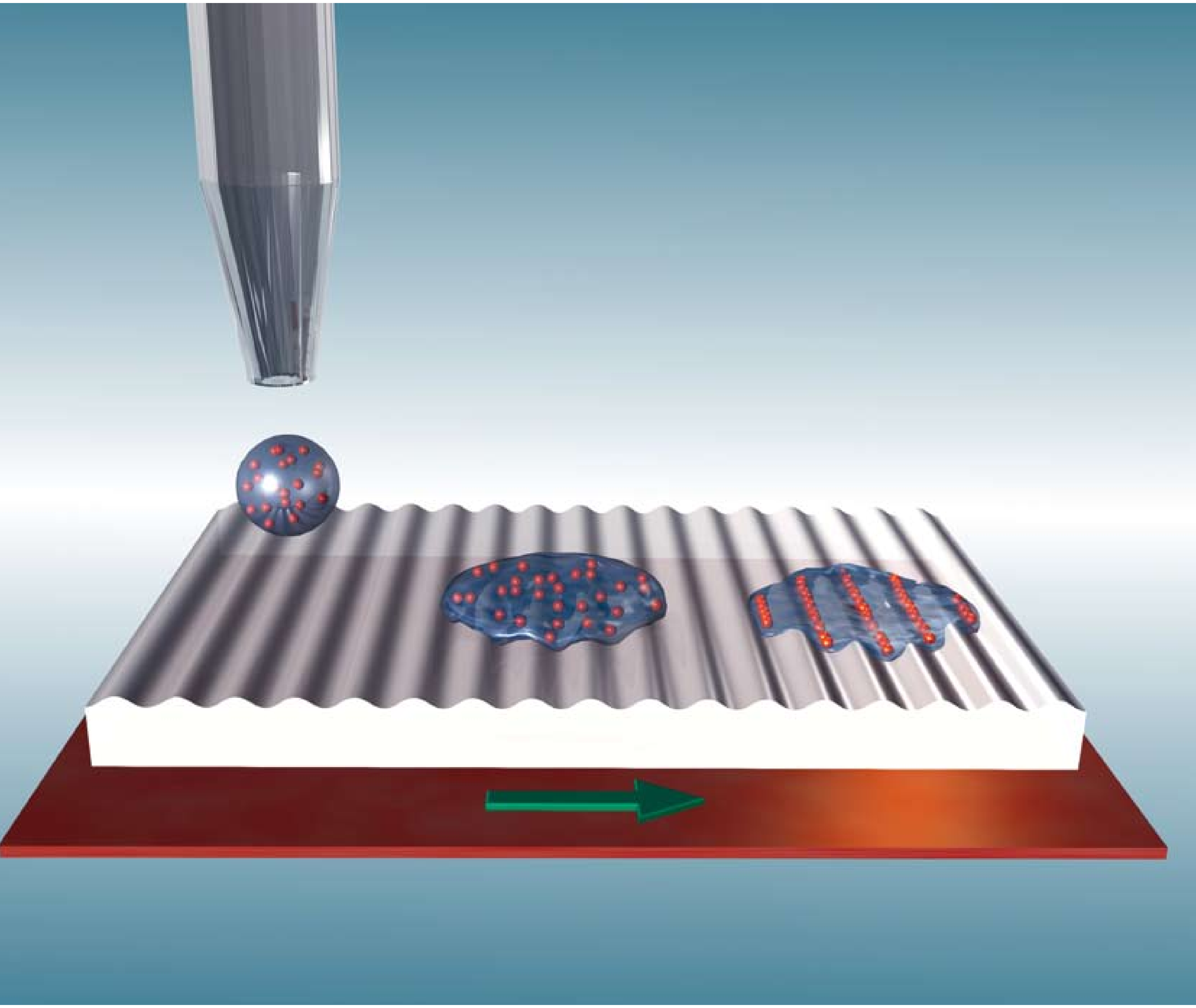

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PAPER
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Printing functional nanostructures: a novel route towards nanostructuring of organic electronic devices

REVIEW
Klaus Kroy
Dynamics of wormlike and glassy wormlike chains

Printing functional nanostructures: a novel route towards nanostructuring of organic electronic devices *via* soft embossing, inkjet printing and colloidal self assembly of semiconducting polymer nanospheres

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A new method for nanostructure formation from conjugated polymers is presented: an aqueous dispersion of semiconducting polymer nanospheres (SPNs) is deposited by inkjet printing onto a polymer surface patterned by soft embossing. By interaction between the spheres and the undulated surface a self assembly process is triggered, resulting in the formation of SPN nanostructures determined by the template. Both template layer and assembled SPNs can be incorporated into a device structure. We demonstrate a light emitting structure for use in polymer light emitting devices including analyses by atomic force microscopy and Kelvin probe force microscopy.

Introduction

Today conjugated polymers are utilized as active media in a multitude of devices, like polymer light emitting diodes (PLEDs),[1] light emitting electrochemical cells (LECs),[2] lasers,[3] solar cells,[4] photo detectors,[5] and field effect transistors.[6] But despite the fact that these materials offer the opportunity to produce cheap and flexible devices and that novel organic semiconductors now feature satisfactory stability, there is still demand for deposition and structuring techniques allowing easy and high throughput device fabrication with structures on the micro- and even nanoscales. Recently, nanostructure formation by printing techniques has received particular attention[7] since it could supersede small-scale prototyping processes, and finally lead to large-area production with high throughput capacity. Applicability of these novel fabrication processes is of great concern, because only functional structures that can smoothly be incorporated into devices are of interest for practical applications. Furthermore, of particular concern are environmentally friendly solvents, and deposition processes that combine reasonable throughput speed with low material consumption.

Colloid science offers a novel route to fabrication of nanosized particles from conjugated polymers: by utilizing a miniemulsification process polymers that are commonly only soluble in organic solvents can be dispersed in water.[8] Basically, such a miniemulsion is a system of two immiscible liquids where small droplets with high stability in a continuous phase are created by using high shear. In our case droplets of a polymer solution are stabilized in water with the aid of a suitable surfactant. After subsequent evaporation of the organic solvent a stable aqueous dispersion with spherical polymer particles is obtained. The size of the particles can be controlled by proper choice of surfactants and production process parameters resulting in particles sizes in the 50 to 500 nm range.

The obtained semiconducting polymer nanospheres (SPNs)[9] feature the properties of both semiconducting polymers and spherical nanoparticles. Therefore the self assembly techniques that have already been successfully demonstrated *e.g.* for polystyrene beads[10,11] and metallic nanoparticles[12] can be applied.

SPN dispersions are solution-processable by all kinds of conventional solution based deposition methods (like spin casting or inkjet printing). Since this is an aqueous polymer dispersion it provides the opportunity to fabricate solution-processed polymer multilayer structures by using orthogonal solvents for the individual layers.

A critical point and a main precondition for the practical application of SPNs in organic electronics is that the complex fabrication process must not degrade their conjugated structure. This has been extensively studied by Piok *et al.*, and it was shown that the miniemulsification process neither impairs the photophysical[13] nor the electroluminescent[14] properties of the conjugated polymer. Consequently, SPNs are an excellent alternative to common polymers as active materials in organic electronic devices, as reported for monolayer PLEDs,[14] multilayer PLEDs,[15] LECs[16] and solar cells.[17]

As will be shown in the following, they can be also processed by various assembly techniques. Colloidal particles with diameters in the micro- and nanometre range have been successfully assembled in a multitude of patterns with the aid of templates formed on photoresist layers,[11,12] poly(dimethylsiloxane) films[18] or etched silicon surfaces.[19] Another possibility for assembling nanoparticles is the directed adsorption of charged polymeric colloids *via* electrostatic forces on patterned oppositely charged self assembled monolayers (SAMs)[20] or on patterned polyelectrolyte multilayer surfaces.[21]

However, all assembly methods mentioned above feature several drawbacks when trying to adopt them for the fabrication of organic electronic devices. They use intermediate layers that

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are difficult to incorporate into a device structure, and they all rely on slow sedimentation processes for the deposition of the colloidal dispersion. Quite contrary to these methods there is demand for approaches with high production speed and as little difference to conventional device production processes as possible.

Results and discussion

The approach presented here is based on the application of a suitable intermediate polymer film which is used as a template layer for the production of the device structure. Basically this intermediate polymer film has two different tasks: on the one hand this polymer layer can be patterned by a soft embossing[22] step, making it a suitable template for self assembly processes of the SPNs, as will be described in the following (see Fig. 1). On the other hand it is necessary, if device formation is desired, to provide an insulating and pinhole-free layer between the anode and cathode to prevent short circuits. The polymer nanospheres are embedded into this layer (which thus acts as a matrix layer for these SPNs) by a heating step to grant contact to both electrodes. Therefore, the layer thickness must be a little less than the diameter of the spheres, and the glass transition temperature (T_g) of the matrix material has to be below the T_g of the SPN material to ensure that the nanoparticles keep their spherical shape.

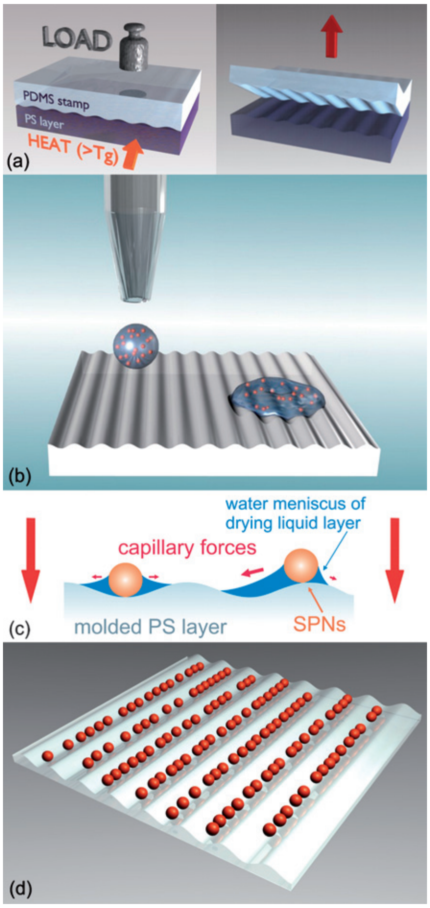

Fig. 1 Schematic of the fabrication process for functional nanostructures from assembled semiconducting polymer nanospheres (SPNs): First a polymeric template is fabricated by soft embossing with a PDMS stamp (a); then the dispersion containing the SPNs is inkjet printed onto this surface (b). Due to capillary forces acting on the spheres (c) they finally assemble in the grooves of the template while the drop dries (d).

In this study we present the substitution of electron-beam lithography-based template structuring processes by a soft lithography technique that employs a re-useable poly(dimethylsiloxane) (PDMS) stamp. This represents a huge step towards large-area patterning with an easy-to-use low-cost technique, since the output of the assembly process is directly applicable in the course of device fabrication. Using the same layer for both templating and embedding therefore greatly simplifies the production process of a nanostructured device.

Please note that all template assisted assembly methods reported earlier use template materials that cannot be incorporated into an organic device like a PLED (*e.g.* photoresist or silicon); however, the intermediate polymer template layer utilized in this study can be integrated without influencing the device characteristics.

The herein described structuring method relies on the advantageous properties of the SPNs when it comes to polymer multilayer formation and self assembly processes. In the following the arrangement of SPNs *via* a template assisted fluidic self assembly process on a molded polymer surface is shown. This technique can be directly used to fabricate organic electronic devices with individual nanospheres as functional spots arranged in a defined pattern. Moreover, inkjet printing is established as a deposition method for the SPNs, which speeds up deposition and expands structuring possibilities to the micro- and millimetre range.

In this manuscript the fabrication of a light emitting nanostructure that is suitable for PLED production is described. Nevertheless this novel approach can also be applied to other types of organic electronic devices by appropriate choice of materials.

1. Structuring of the polymeric template layer by soft embossing

As matrix layer, a suitable thermoplastic polymer has to be used. We chose polystyrene (PS) (bulk T_g: 95 °C), which is convenient for both soft embossing and embedding of the SPNs. Furthermore it can easily be solution-processed by spin casting. PS is insulating and non-fluorescent and therefore provides proper contrast in Kelvin probe force microscopy (KPFM)[23] as well as in fluorescence microscopy (FM) analyses and in SPN PLEDs.[24] An 80 nm PS layer was spin cast onto a glass substrate and soft embossed at 120 °C with a PDMS stamp that had been fabricated from a master with a 277 nm wide and 25 nm deep grating, as shown in Fig. 1(a). As depicted in the 3D representation of an atomic force microscopy (AFM) height image in Fig. 2(a), the embossed PS layer nicely features the pattern of the master.

The SPNs used in this study were fabricated from methyl-substituted ladder-type poly(para-phenylene) (Me-LPPP),[25] which is a commonly used, blue–green emitting electroluminescent polymer. The diameter of the SPNs was approximately 100 nm, and they were dispersed in water with the aid of

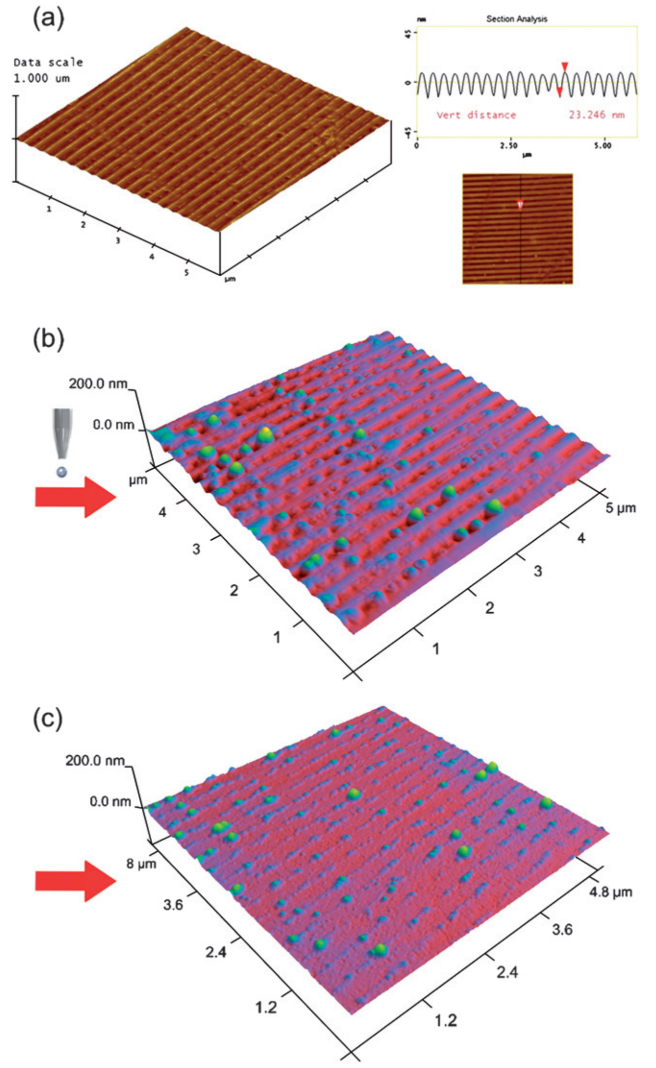

Fig. 2 AFM images of the results of the fabrication steps depicted in Fig. 1, and a subsequent heating step: (a) 3D AFM image and section of the embossed polystyrene layer, (b) 3D AFM image of the SPNs that have assembled in the grooves during inkjet printing. (c) *Via* heating at 140 °C the linearly assembled SPNs (diameter: 100 nm) are embedded deeply into the PS layer (thickness: 80 nm); only the tops of the spheres can be seen protruding from the surface.

Lutensol AT50 [hexadecyl-modified poly(ethylene oxide), $(C_{16}H_{33})$ $(EO)_{50}$]. If device fabrication is intended it is necessary to use SPNs with a diameter in the same range as the thickness of thin films that are usually used in PLEDs. Please note that in contrast to commercially available nano- and microbeads fabricated from non-conjugated materials like polystyrene, the Me-LPPP particles are rather polydisperse. This is due to the fact that for conjugated polymers the polymerization has to be performed prior to emulsification, instead of processing the monomer and performing a concluding polymerization step. Consequently, the ultrasonication step of the miniemulsion process has to be performed very carefully to avoid the generation of defects. Further refinement of the fabrication procedure can therefore possibly lead to less variation in particle diameter.

2. Deposition of the aqueous dispersion of semiconducting polymer nanospheres by inkjet printing

After embossing the PS surface with the template pattern the SPN dispersion was deposited. For this purpose inkjet printing was chosen as the deposition method [see Fig. 1(b)]. Inkjet printing polymer solutions from an organic solvent on top of another polymer film is likely to produce holes.[26] By contrast, the use of an aqueous polymer dispersion offers a convenient approach for the formation of polymer multilayer configurations.[15]

Besides, inkjet printing is superior to all other solution-based deposition methods commonly used for PLED production in terms of material wastage, and thus well suited for implementation in industrial scale fabrication processes. It is also by far faster than the sedimentation-based processes usually used for template assisted fluidic self assembly,[11,12,18,19] since the drying time for an inkjet printed droplet of aqueous dispersion is in the range of 1 s.[27] Furthermore, preliminary tests showed that PS is so hydrophobic that spin casting is very inefficient as a deposition method for a water-based dispersion, providing a very unpredictable SPN distribution. However, inkjet printing such an aqueous dispersion results in comparable and reliably reproducible patterns with properties that can be controlled *via* the printing parameters. Moreover, the aqueous SPN dispersion features very good jetting behavior without the undesired bead-on-a-string effect[28] that is caused by dissolved linear polymer chains with high molecular weight and is therefore very well suited for printing processes.[16]

As illustrated in Fig. 1(b) we used a drop-on-demand single-nozzle printer with a heatable, semi-automatic substrate stage. The substrate temperature during the printing process is the governing factor for the drop drying time, and therefore determines the distribution of the SPNs within the printed drop on the structured surface. The procedure of drop formation on the substrate can be described as follows: when the drop hits the substrate it expands first, then contracts again due to the high hydrophobicity of the PS layer (contact angle of water resting on PS is approximately 90°),[29] and finally reaches an equilibrium state with a pinned contact line.[30,31] Simultaneously the evaporation of the solvent causes a flow of the dispersed material within the drop towards the contact line, which results in the formation of a distinctive rim. This characteristic is also known as the "coffee stain effect".[32] The most homogeneous SPN distribution within the dried droplet was found for a substrate temperature of 30 °C, providing an optimized drying behavior. The resulting droplets feature a diameter in the region of 40 µm. The fluorescence microscope images shown in Fig. 3(a) and (e) illustrate different results for unstructured PS surfaces and those structured by soft embossing: on an unstructured surface the printed drop contracts uniformly, resulting in a circular rim shape after drying. Please note that in the interior the SPNs form irregularly distributed clusters. By contrast, when printing onto a structured PS surface, the drop expands circularly first, too, but then the contact line of the drop gets partly unpinned and the drop contracts anisotropically. A comparison of the printed drops shows that the preferred contraction direction is along the embossed channels [see Fig. 3(e) to (h)]. However, the SPNs in the interior are distributed evenly within the dried droplet.

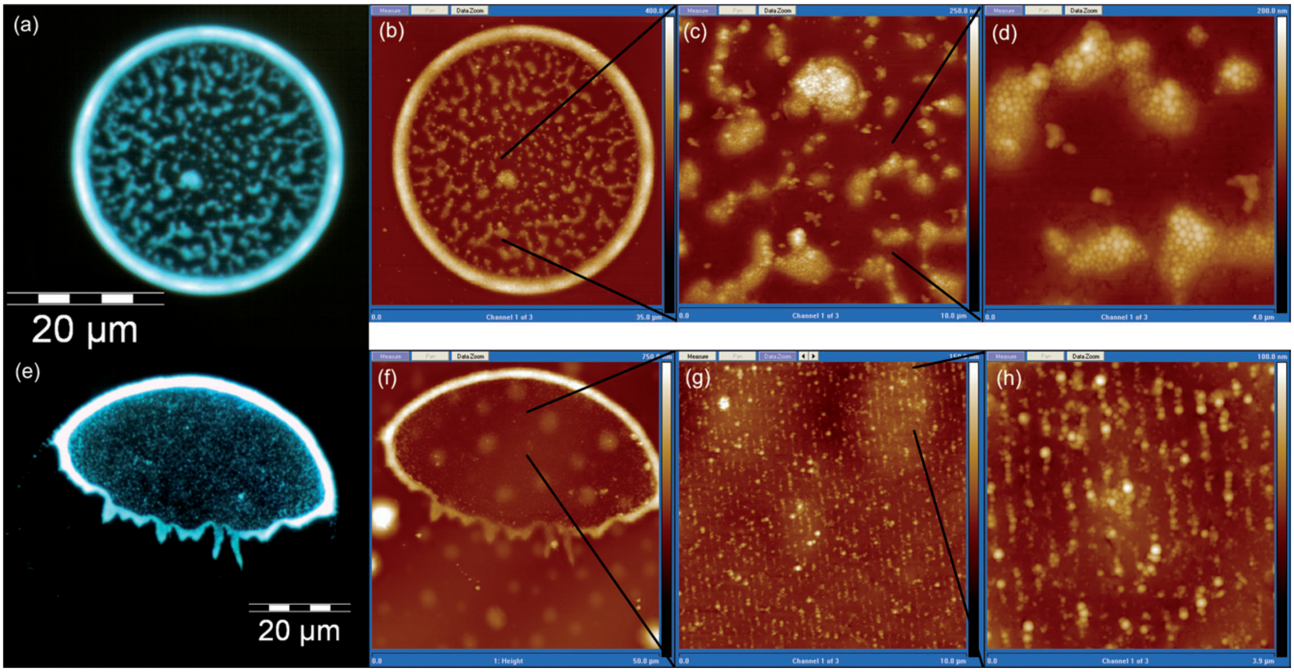

Fig. 3 Comparison of two drops that were both inkjet printed [the same conditions for both printing procedures (temperature, dilution of dispersion)] onto an unstructured polystyrene layer (top) and onto a polystyrene surface that was structured by soft embossing (bottom). Upper row: fluorescence microscopy image (a) and AFM height image [(b) scan size (s.s.): 35 µm, height scale (h.s.): 400 nm] of a drop printed onto a flat polymer surface. The two close-ups [(c) s.s.: 10 µm, h.s.: 250 nm; (d) s.s.: 4 µm, h.s.: 200 nm] show that the SPNs form inhomogeneous, tightly packed clusters. Lower row: fluorescence microscopy image (e) and AFM height image [(f) s.s.: 50 µm, h.s.: 750 nm] of a drop printed onto a structured polymer surface. The two close-ups [(g) s.s.: 10 µm, h.s.: 150 nm; (h) s.s.: 3.9 µm, h.s.: 100 nm] show that the SPNs are assembled according to the embossed structure. Note that the drop is deformed—the short axis is approximately parallel to the grooves of the template pattern, and the rim is frayed. All AFM images were taken after a heating step that flattened the molded polymer surface.

3. Nanostructure formation by template assisted fluidic self assembly of the polymer nanospheres

As already mentioned, the polymer nanospheres get carried along in the evaporating liquid film while the drop spreads and recedes across the molded polymer substrate. As a result a template assisted fluidic self assembly process is triggered, and the SPNs assemble in the grooves of the embossed surface: as soon as the thickness of the liquid film is so low that the SPNs are no longer floating freely, they can get physically confined in the template, and the attractive capillary interaction between the sphere and the substrate rises considerably.[33] As depicted in Fig. 1(c), due to the undulating substrate topography the meniscus of the liquid surrounding a sphere resting on a "hill-side" is deformed, and the force resulting from the varying contact angle[20,34] drags the sphere down into one of the channels. The fact that the SPNs in the "unstructured" droplet [Fig. 3(a) to (d)] do not only form clusters, but are tightly packed [Fig. 3(d)], underlines that these immersion capillary forces are the driving force for the assembly process. Similar behavior has been reported for 2D crystal self assembly processes.[35] Thus, by utilizing capillary forces spherical particles can be assembled in arbitrary patterns, provided a suitable template is used.

In our case the SPNs assemble in a pearl necklace-like structure in the grooves of the template. This is on the one hand due to the given template, and on the other hand caused by the aforementioned attractive forces between the nanospheres. The resulting structures are depicted in Fig. 2(b) and (c), Fig. 3(g) and (h) and Fig. 4. Fig. 2(b) shows a 3D representation of an AFM height image of SPNs assembled on a patterned surface. Fig. 3(g) and (h) show close-ups of the AFM height image of a drop (printed onto a structured surface) in Fig. 3(f)

Fig. 4 depicts an AFM height image of assembled SPNs (a) with a corresponding Kelvin probe force microscopy (KPFM) image (b). The contrast in the KPFM image is generated by the

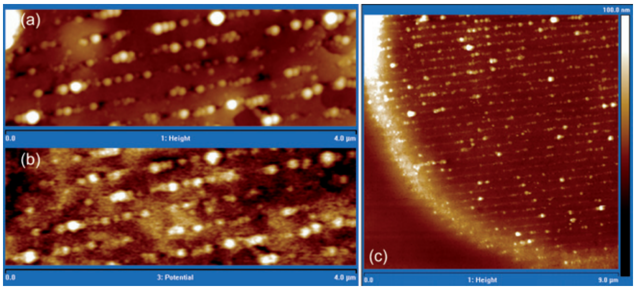

Fig. 4 AFM topography [image (a) and (c); height scale for both images: 100 nm] and KPFM image [(b); scale: 100 mV] of inkjet printed semiconducting polymer nanospheres (diameter: approx. 100 nm) assembled on, and subsequently embedded by annealing into an 80 nm polystyrene layer. The KPFM image visualizes the semiconducting material (Me-LPPP SPNs, bright) enclosed by the insulating PS matrix. Scan sizes are 4 µm [(a) and (b)] and 9 µm (c).

difference in surface potential of the two materials. Therefore, Fig. 4(b) visualizes the semiconducting material (Me-LPPP SPNs, bright) enclosed by the insulating PS matrix. Fig. 4(c) shows about a quarter of a printed drop, including part of the rim. The embossed structure is closely reproduced, almost all particles contribute to the pattern, whereas the surface of the PS layer is flattened again due to the heating procedure necessary for the embedding step (see below). The denseness of particle distribution in the given template can be controlled *via* the printing parameters and the solid content of the dispersion. In PLEDs the ring is non-emitting and does not contribute to the pattern.[24] If the production of large, homogeneous areas that are composed of a huge amount of droplets is intended, some adaptation of the printing process to suppress the formation of a ring (*e.g.* by a suitable interlacing procedure) is necessary.[36]

Since we were aiming for nanosized structures that can easily be incorporated into an organic electronic device a further step was obligatory: it is a prerequisite for successful device formation that the SPNs are fully embedded into the matrix layer in order to establish good contact to the bottom electrode (see Fig. 5). This was done by heating the whole sample at 140 °C, which is well above the T_g of the PS matrix layer, for several hours. Both the decomposition and glass transition temperatures of Me-LPPP are beyond 300 °C,[9] which enables us to process SPNs fabricated from this polymer at elevated temperatures without risking deformation of the nanospheres. Fig. 2(c) shows a 3D representation of an AFM height image of Me-LPPP SPNs with a diameter of 100 nm that are now embedded into an 80 nm PS layer: the surface is flattened due to the heating step, and only the tops of the SPNs that are now embedded in the PS layer can be seen. The flattening of the surface is also important for the deposition of the metallic top electrode, since depositing it on a highly irregular surface would lead to enhanced fields at the spikes formed in the gaps. A further advantage is that the SPNs get firmly fixed in the polymer layer. This would even allow the deposition of inkjet printed water-based top electrode structures (*e.g.* PEDOT:PSS[37]).

As already reported[24] a direct implementation of Me-LPPP SPNs into inkjet printed PLEDs by embedding them into the template layer could be shown. The combination with a template assisted fluidic assembly process now allows the fabrication of nanostructured PLEDs from aqueous dispersions.

However, in order to optimize the production process for nanostructured devices fabricated from SPNs a significant reduction in processing time will be necessary. This can, for example, be realized by further optimization of the embossing process, as demonstrated recently for nanostructures in polystyrene that were produced by a soft embossing process that lasted for merely 200 s.[38] Careful adjustment of the process parameters of the SPN embedding procedure might lead to shorter device fabrication times, too.[39]

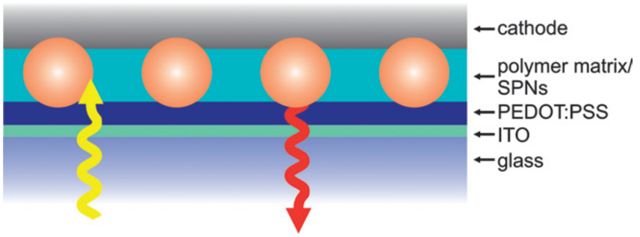

Fig. 5 Schematic of the structure of a device fabricated from SPNs that are inkjet printed onto an organic embedding layer: depending on the choice of material the device can be utilized as a light emitting device (red arrow) or solar cell (yellow arrow).

In order to boost functional nanostructures beyond purely academic use, potential applications have to be introduced. A possible utilization that requires controlled arrangement of different components on a nanoscale, combined with fast and cheap large-scale production methods are organic solar cells: the production and patterning technique for devices presented here is a further step towards controlled structuring of two-phase systems. The possibility to apply SPNs in solar cells has been proven lately.[17,40] The choice of appropriate combinations of organic materials for the embedding layer and the SPNs is merely limited by the necessity of compatible T_g.

Fig. 5 shows a schematic of an organic electronic device fabricated from SPNs: depending on the favored mode of operation the materials can be chosen to form either an organic solar cell or a PLED.[24]

Experimental

A poly(dimethylsiloxane) (PDMS; Sylgard 184 from Dow Corning) stamp fabricated from a suitable master (channel width 277 nm, channel depth 25 nm) was used for the embossing procedure. The size of the stamp was about 1 cm^2. Polystyrene (PS) (purchased from Sigma Aldrich, $M_w \sim 350\,000$, bulk T_g: 95 °C) was dissolved in chloroform (solid content 10 g l^{-1}) and deposited onto cleaned glass substrates by spin casting, resulting in a layer thickness of 80 nm. Then the PDMS stamp was deposited on the PS film and weighed down with a small weight (80 g), and both were put in an oven at 120 °C for 2 h. After cooling down the stamp was carefully peeled off the PS, and the SPN dispersion (0.07 wt% of Me-LPPP dispersed in water, diameter of particles: ~100 nm) was deposited at a substrate temperature of 30 °C. A drop-on-demand single-nozzle printer (from MicroFab) with a nozzle orifice of 50 μm and a heatable, semi-automatic substrate stage was used. The resulting droplets had a diameter of approximately 40 μm.

AFM and KPFM images were recorded with a Veeco Dimensions 3100 (Nanoscope 4a controller with Hybrid Scanner) in tapping mode.

Conclusion

Concluding, we succeeded in assembling semiconducting polymer nanospheres by using a polymer template layer that was patterned by soft embossing. The deposition of the polymer dispersion was accomplished by inkjet printing with a single-nozzle printer at a substrate temperature of 30 °C.

In contrast to methods that suggest the combination of a self assembly process in a re-useable template with a subsequent transfer printing step to shift the structure to another substrate,[18] the method presented here relies on the application of a polymer template layer, so that the structure that is formed with the SPNs can be incorporated into a device. This "dual-use" polymer matrix layer and the application of an embossing process in combination with the high throughput rates of inkjet printing offers a convenient route towards arbitrarily patterned polymer light emitting devices and other nanostructured organic electronic devices fabricated from semiconducting polymer nanospheres.

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