Patterning of Organic Nanoparticles by Ink-jet Printing of Microemulsions

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Direct ink-jet printing of water-insoluble organic materials may provide a new route for low-cost fabrication of various products that require fine patterning of functional molecules. However, printing by water-based, environmentally friendly inks requires significant research and development efforts aimed at achieving a dispersion of nanoparticles of the specific molecule in water. We demonstrate a concept for direct patterning of water-insoluble organic molecules in the form of nanoparticles, which can be easily adapted to a large variety of molecules such as conducting polymers and organic light-emitting diodes. The method is based on formation of a thermodynamically stable oil-in-water microemulsion in which volatile "oil" droplets contain the dissolved organic molecules. The microemulsion droplets are converted into organic nanoparticles upon impact with the substrate surface due to evaporation of the volatile solvent.

Introduction

Direct ink-jet printing has been successfully demonstrated in the past decade for various applications, such as integrated circuits,[1,2] ceramics,[3,4] biotechnology,[5−7] organic light-emitting diodes,[8] and polymers,[9] in addition to the conventional graphic applications.

Patterning of organic molecules by ink-jet printing can be achieved either by printing a solution of the molecule (in organic solvent) or by printing dispersions of the molecule in water or organic solvent.

The ink-jet technology is based on ejection of ink droplets from a micrometer-size nozzle, and therefore, the particle size of the dispersion should be in the submicrometer size range. Conventional pigments in ink-jet inks contain particles in the size range of 100−400 nm. Formation of nanosized organic particles by methods such as grinding or controlled crystallization brings many technological difficulties and requires tailoring of the formation process and stabilization mechanism for each molecule of interest.

We suggest a concept that would allow formation of various organic nanoparticles, by using oil-in-water microemulsions in which the organic functional molecules will be converted into nanoparticles while the required pattern is formed by piezoelectric ink-jet printing. Figure 1 schematically presents the concept: the functional organic molecule is dissolved in the internal droplets of an oil-in-water microemulsion, in which the droplets are
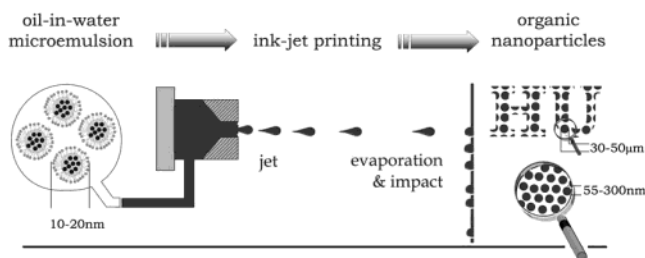
Figure 1. Schematic presentation of microemulsion conversion into nanoparticles by ink-jet printing.
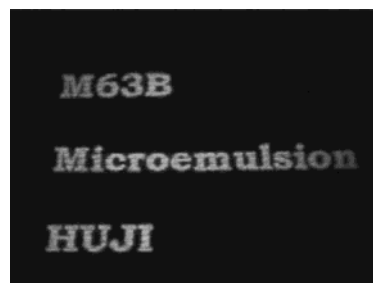
Figure 2. Photograph of fluorescent water-insoluble molecule printed pattern, taken through a red viewing filter (max wavelength of 593 nm), while a polylight lamp, equipped with a 503−587 nm filter, was used for excitation of the fluorescent printed text.

composed of a volatile water-insoluble solvent, such as toluene or butyl acetate. By use of the proper surfactant, solvent, and cosolvent, the microemulsion is spontaneously formed. After printing, the droplets of the microemulsion that are printed on the surface of the substrate (glass, ceramic, etc.) are rapidly evaporated, leaving patterns of the organic functional molecules, in the form of nanoparticles. The initial microemulsion is thermodynamically stable, with droplet size of about 10−20 nm, which is excellent for storage stability and prevention of printhead malfunctions. After printing, nanoparticles with an average size of 55 nm can be achieved, depending on microemulsion composition and printing conditions. Obviously, this method can be adopted easily for many organic, water-insoluble molecules.

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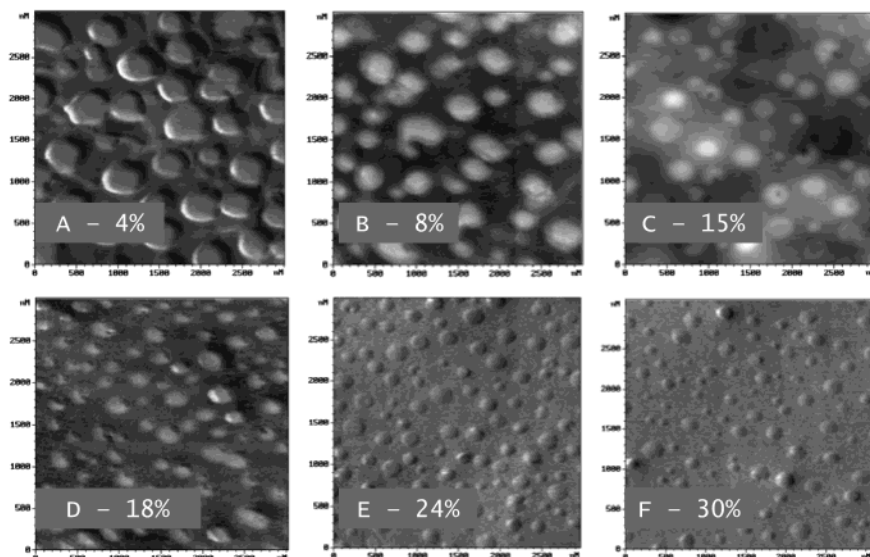
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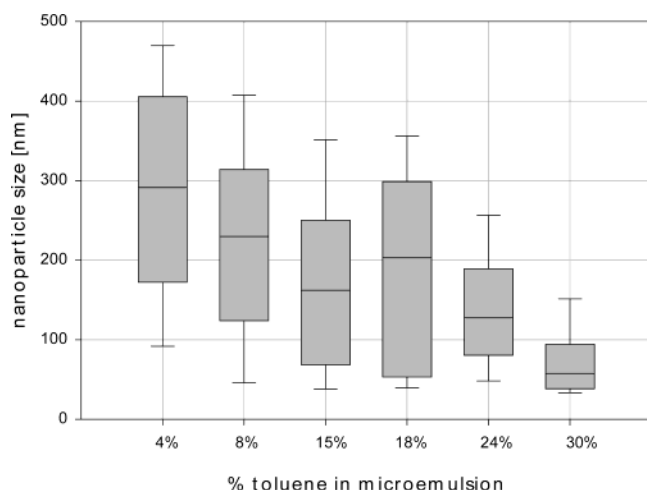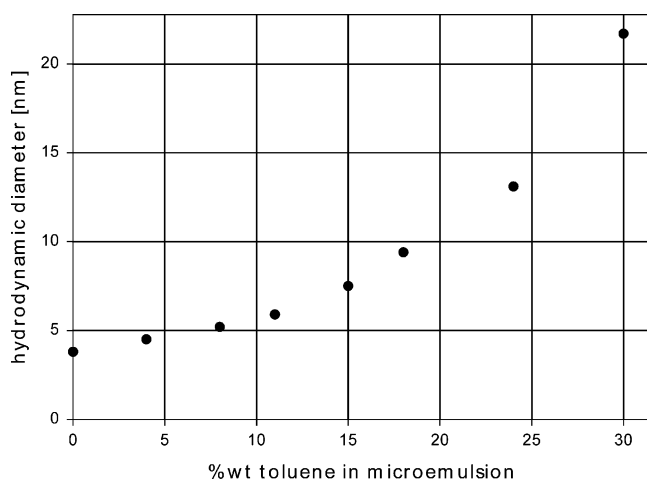
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Figure 3. AFM images of organic nanoparticles at various toluene concentrations in the microemulsion.

Figure 4. Nanoparticle size analysis of AFM images in Figure 3.

Figure 5. Average size of microemulsion droplets at various toluene concentrations as measured by dynamic light scattering.

The formation mechanism of the organic nanoparticles due to solvent evaporation on the printed substrate is probably similar to the mechanism of formation of micro- and nanoparticles, in bulk, by solvent evaporation from oil in water emulsions.[10] In general, oil-in-water emulsion is prepared, in which the oil phase is a volatile organic

solvent such as methylene chloride or chloroform, and an organic material is dissolved within the oil droplets. The dispersed droplets, which are composed of the volatile solvent and the dissolved material, are evaporated at proper temperature−pressure conditions, thus leading to precipitation of the dissolved organic materials. Obviously, utilization of this method for production of micro- and nanoparticles is based on the high evaporation rate of the dispersed droplets relative to the continuous aqueous phase. This method was demonstrated for the preparation of various organic drug carriers such as polylactide.[10] It is generally found that the size of the resulting particles is similar to that of the initial emulsion droplet size. Thus, nanoparticles were obtained by using submicrometer emulsions prepared under high shear forces by a Microfluidizer.[11] We expected, therefore, that it would be possible to conduct the solvent evaporation process not only in the bulk of the emulsion but also on the substrate onto which the emulsion droplets are placed by the printing process.

It should be mentioned that preparation of inorganic nanoparticles, as bulk materials, by reverse microemulsions (water-in-oil) is well-known, such as the formation of silver bromide nanoparticles with AOT/*n*-heptane/water microemulsions.[12] However, there is only a limited number of reports on formation of organic nanoparticles in microemulsions. Examples are the preparation of cholesterol nanoparticles from reverse microemulsions,[13] preparation of solid-lipid nanoparticles by dilution of oil-in-water microemulsions in water,[14] and preparation of latex nanoparticles via microemulsion polymerization.[15] We also found that the emulsion−solvent evaporation method can be applied to oil-in-water microemulsions, from which organic nanoparticles were obtained in bulk.[16]

The use of microemulsions in ink-jet printing for graphic art has been described, aimed at overcoming problems

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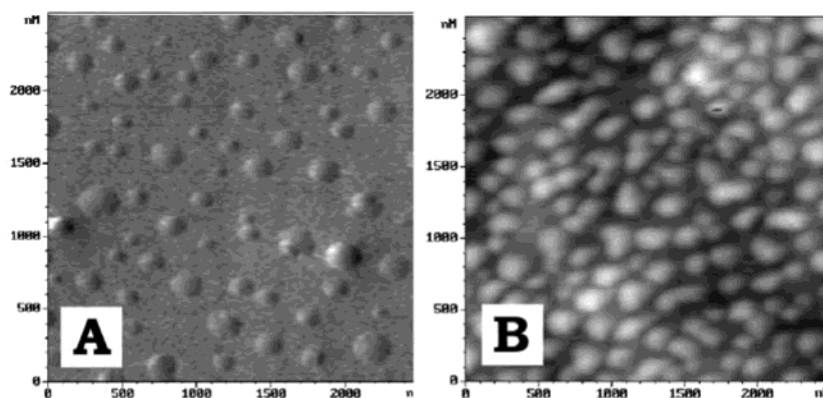(12) MonnoYer, P.; Fonseca, A.; Nagy, J. B. *Colloids Surf. A—Physicochem. Eng. Aspects* **1995**, *100*, 233−243.
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Figure 6. AFM images of organic nanoparticles formed by coating of microemulsions at two temperatures; (A) 22 °C; (B) 2 °C.

related to ink stability and image quality such as feathering, bleeding, and wicking. The reported micro-emulsions were utilized due to their inherent stability and in some cases due to phase transition from liquid into liquid-crystalline phase at specific temperatures.[17−28] These patents are mostly applicable for thermal ink-jet printing. However, the formation of patterns of organic nanoparticles by use of microemulsions is not described, probably due to the inapplicability of the concept described in the present paper for thermal ink-jet printing.

In this work, oil-in-water microemulsions were prepared, as described recently by Magdassi et al.,[29] with the gemini-type surfactant didodecyldiphenyl ether disulfonate (C12-DADS).

Experimental Section

Materials. All materials used for sample preparation were used as described in ref 29. Muscovite mica films were obtained from Pelco International and freshly cleaved prior to spin coating.

Spin Coating. A custom-made spinner was used for all the spin coating experiments, which were carried out at room temperature. Samples were filtered through a 200 nm filter and dispensed onto the central portion of the spinning mica film, which was accelerated to the process speed of 3100 rpm. In each case, the total spin time was kept fixed (60 s). Upon cessation of spinning, coated substrates were let dry horizontally at room temperature for 15 min before the AFM imaging was carried out.

Atomic Force Microscopy. Tapping mode imaging was carried out on a Solver P47 (NT-MDT, Moscow, Russia) scanning probe microscope. Two different tips of 90 μm and 110 μm long Ultrasharp silicon tips, with a radius of curvature of less than 35 nm (SC-12 series, NT-MDT), were used. These tips have typical resonance frequencies of 105 and 155 kHz and typical spring constants of 0.95 and 1.75 N/m, respectively. Height mode images were collected along with either amplitude or phase images. A scan rate of 2−2.5 Hz was typically sufficient to maintain good signal-to-noise ratio. Imaging was repeated with the two tips. Only features that were reproducible from tip to tip are reported. Multiple scans were imaged in each case, with a variety of areas examined for consistent sample morphology.

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(23) U.S. Patent US5342440.
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Particle Size Measurements. The average particle size of the samples was measured at 25 °C by dynamic light scattering with the Zetasizer-3000, Malvern Instruments, U.K. (70 mW Ar laser, wavelength 488 nm, detector angle 90°, dispersant viscosity 0.89 cP, dispersant refractive index 1.33, sample refractive index 1.50). The particle size (according to the particle number distribution) was taken as a mean value of three measurements. Samples were filtered prior to measurements through a 0.2 μm filter.

Results and Discussion

To demonstrate the basic concept, we performed a direct printing (piezoelectric office printer, Epson Stylus 680) of water-insoluble fluorescent molecule (Nile Red) on a paper, using the microemulsion composition described in ref 29, with 24 wt % toluene and 2 wt % Nile Red. The photograph of the fluorescent water-insoluble molecule printed pattern (Figure 2) was viewed through a red viewing filter (max wavelength of 593 nm), while a polylight lamp, equipped with a 503−587 nm filter, was used for excitation of the fluorescent printed text. The resulting microemulsion with the Nile Red was stable, having an average droplet size of 12 nm. The printed pattern could not be rinsed off from the paper, an indication that the Nile Red is present in the form of hydrophobic particles attached to the paper surface.

The process of conversion of the microemulsion droplets into nanoparticles was studied by atomic force microscopy after printing or spin coating of the microemulsion on muscovite mica slides.

In general, we found that nanoparticles were indeed formed on the mica surface, as shown in Figure 3. It is clear that the size of the nanoparticles decreases with increasing initial toluene concentration (internal phase of the microemulsion), from an average size of 300 nm to 55 nm for microemulsions with 4 wt % and 30 wt % toluene, respectively.

The AFM images were analyzed by a grain analysis algorithm (NT-MDT software), and the box plot of the calculated particle sizes (Figure 4) shows that with the decrease in average size a narrower size distribution is obtained. In most samples, small particles in the range of 40−60 nm are present.

To understand the decrease in particle size upon increasing the toluene concentration, we measured the initial microemulsion droplet size by dynamic light scattering (Malvern, Zetasizer 3000 HS$_A$) at various toluene concentrations. As shown in Figure 5, the average diameter of microemulsion droplets with 4 wt % toluene is 4 nm, compared to 22 nm with 30 wt % toluene. Obviously, the size of the nanoparticles after evaporation is larger than that of the initial microemulsion droplet.

It is most probably due to the rapid increase of the microemulsion droplet during spreading on the mica surface and composition changes during the evaporation process.

Size measurements of microemulsion droplets during evaporation in a beaker indicated that the droplet's size increases with evaporation time. For example, when a microemulsion containing 18 wt % toluene was evaporated in a beaker, the droplets' average size increased from 9.4 nm to 19, 25, and 490 nm, after evaporation of 4%, 9%, and 14% of the total weight of the microemulsion, respectively.

To evaluate the effect of toluene evaporation on the nanoparticle size, we performed the spin coating with microemulsions stored at 22 and 2 °C. As shown in Figure 6, the nanoparticles formed by coating of microemulsion stored at room temperature (average size of 55 nm) is much smaller than that stored at 2 °C (average size of 125 nm). This indicates that the nanoparticles' growth is mainly controlled by the evaporation rate during the coating and printing process. The higher temperature of the microemulsion allows faster evaporation of the solvent, and therefore it is expected that the size of the nanoparticles will be close to that of the initial microemulsion droplets.

Conclusions

In conclusion, we demonstrated that organic nanoparticles could be patterned, by printing of an oil-in-water microemulsion, in which the organic functional molecules are initially dissolved within the internal phase of the microemulsion. It is expected that the concept can be applied to a variety of organic molecules, including polymers, without the need for complex preparation processes prior to pattern printing by ink-jet printers.