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Synthesis and optimization of PEDOT:PSS based ink for printing nanoarrays using Dip-Pen Nanolithography

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Abstract

Due to the current interest in organic printable electronics, Dip-Pen Nanolithography (DPN) is increasingly being explored as a method to pattern electroactive materials such as conducting polymers (CPs) on the micro- and nanoscale. In general, printing process depends strongly on the ink-substrate properties and fundamental forces required to drive and stabilize the ink transfer to the substrate. Controlling these parameters is especially difficult when operating under the nanometer confinements of the DPN probe. For the printing of CPs, one step towards addressing these challenges is rational ink design, as the use of existing commercial-based inks may not be suitable for the DPN ink transfer process on the nanoscale.

Keywords

ink, printing, optimization, nanoarrays, pedot, dip, pen, nanolithography, synthesis, pss

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Synthesis and optimization of PEDOT:PSS based ink for printing nanoarrays using Dip-Pen Nanolithography

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Due the current interest in organic printable electronics, Dip-Pen Nanolithography (DPN) is increasingly being explored as a method to pattern electromaterials such as conducting polymers (CPs) on the micro- and nanoscale. In general, printing process depends strongly on the ink-substrate properties and

10 fundamental forces required to energetically drive and stabilize the ink transfer to the substrate. Controlling these parameters is especially difficult when operating under the nanometer confinements of the DPN probe. For the printing of CPs, one step toward addressing these challenges is rational ink design, as the use of existing commercial-based inks may not be suitable for the DPN ink transfer process on the nanoscale. In this study, we synthesized and developed a poly(3,4 ethylenedioxythiophene)

15 poly(styrenesulfonate) (PEDOT:PSS)-based ink, to which we could add known constituents for optimizing the printing, adhesive and conductive properties of an aqueous dispersed ink. For silicon and gold surfaces, we demonstrate that the DPN patterning of the ink could achieve PEDOT:PSS (dot) arrays with diameters ranging from the submicron down to ~160 nm. These dimensions represent a dramatic improvement in resolution compared to previous attempts in patterning of CP via physioadsorption

20 process using DPN. This work highlights that rational design of CP inks is critical, especially for DPN where the ink transfer process is governed by fluid physical properties and surface forces in the nanodomain. Knowledge of the constituents and overall ink composition will also lead to a greater understanding of these fundamentals that facilitate the patterning of CP inks on the nanoscale using DPN.

1. Introduction

25 Conducting Polymers (CPs) are increasingly being integrated into microdevices due to their unique properties, including intrinsic ionic-electronic conductivity, mechanical flexibility and biofunctionality. Since CPs merge these attractive properties with “close to metals” electrical conductivities¹, they are being

30 targeted for use as electronic components (e.g. electrode arrays) in bio-related applications such as biosensors, implantable electrodes and organic microelectronics. To gain an advantage, many of these technologies demand that the electronic components be scaled down and patterned in the nanodomain to

35 improve spatial resolution and signal-to-noise ratio. In particular, nanoscale CP sensors for detection of gases and biomolecules can provide relatively higher sensitivity and faster response times than conventional macro- and microsized sensors.²⁻⁵ Thus miniaturization of chemical and biological sensors is desirable

40 and provides further opportunities for lowering detection limits, reducing volumes needed for sensing, enhancing selectivity, increasing portability and in vivo applicability.

Fabrication of CPs at the nanoscale-level can be realized through template synthesis and post-assembly methods^{6,7} as well

45 as with use of photo- and soft lithography.^{8,9} Template synthesis leads to formation of many kinds of discrete CP nanostructures

but precisely controlling their position, for example as part of well-defined electrode array, is challenging. The nanoscale fabrication of CPs using conventional electrochemical deposition

50 is also difficult when applied to submicrometer or nanoscale dimensions due to deviations from simple mass transfer process (i.e., diffusive losses of monomer or reactants from the electrode). Top-down lithography approaches can be used to fabricate precise, high resolution nano-patterned structures from

55 electrochemically prepared macro-sized films; however the use of “single-material” films limits the composition diversity of the patterned structures and areas. Lithography methods have been extensively used for patterning of CPs¹⁰ and especially microcontact printing that can offer versatile, low-cost, surface

60 patterning and submicron accuracy.¹¹ For microcontact printing, an elastomeric stamp is covered with ink and placed in contact against a substrate and in one step it is possible to print a whole series of patterns. Some applications require a process termed “multiplexing” whereby different inks are simultaneously printed.

65 One technique that is able to complement other lithography techniques through multiplexing whilst also patterning with nanoscale resolution is Dip-Pen Nanolithography (DPN). DPN is based on the transfer of ink onto the substrate by a tip with nanoscale dimensions, usually in the form of an atomic force

70 microscopy (AFM) cantilever tip.¹² DPN has been used for the

multiplex printing of different proteins, or protein deposition within existing patterns.^{13,14} DPN has been extensively used for the printing of metal nanoparticle,¹⁵⁻¹⁷ organic compounds^{12,18,19} and more recently applied to patterning of CPs.²⁰⁻²⁴

The DPN deposition process is ascribed by two mechanisms depending of the type of material that is deposited. When patterning relatively small molecules the transport through a liquid meniscus has been proposed.^{12,25} The spontaneous formation of a meniscus between the tip and substrate, which is dependent on the surrounding humidity, facilitates molecular diffusion.²⁶ For liquid-based inks, the deposition is strongly dependent on liquid-surface interactions and generally driven by physio-adsorption processes.²⁷ Liquid inks can importantly act as a “carrier” for different types of particulates or biological molecules.²⁸ In the case of CP dispersions, the ink properties are governed by the CP aggregate-size and related molecular weight and chemistry of the polymer. The major challenges in the application of CP dispersions in DPN printing appear to be connected to dispersion instability, effects of solvent evaporation and adhesion to the substrate.²⁴

Herein we concentrated on printing the conducting poly(3,4 ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS). The patterning of PEDOT is of special interest due to its attractive physical and chemical properties. PEDOT is thermally and electrochemically stable with relatively low redox potentials.^{29,30} When doped with PSS surfactant, it also highly solution processable in comparison with other conducting polymers.³⁰ Importantly, PEDOT:PSS is a favourable material for biological studies due to its biocompatibility.³¹ PEDOT:PSS water dispersions have previously been used as “inks” in DPN studies and deposited as lines²⁰ and dot patterns.²⁴ In the latter approach, commercially available PEDOT:PSS dispersions have been concentrated and used as received. This included an assessment of the DPN printing of a commercial PEDOT:PSS ink on different types of surfaces, including hard and flexible substrates.²⁴ However, these commercial inks are specifically designed for their intended use in spin coating and/or ink-jet printing and may not necessarily be optimized for the transfer mechanisms, or nanometer confined volumes, governing the operation of DPN. For example, solvent evaporation and particulate aggregation is a major issue when relying on the transfer of such small volumes (attolitres), while the nanoscale forces involved in successful transfer of ink are easily influenced (or often adversely affected) by the ink properties, surface chemistry and environmental conditions. We recently found that a commercial PEDOT:PSS could not be reproducibly used for printing as received.²⁴ Stable printing of arrays composed of dots ~1 μm in diameter, with the smallest dimensions of ~700-800 nm, was only achieved through modification of the ink with addition of methanol. Although further optimization of the commercial ink was desired in this study (i.e. to reduce the dot dimension and solvent evaporation effects), it was not possible as the composition of the commercial ink was unknown.

In this study, we aimed to develop a PEDOT:PSS ink starting from raw material synthesised in our labs and then through the incorporation of different additives, such as thickeners, surfactants and ion exchangers. In nanolithography polyalcohols such as glycerol and poly(ethylene glycol) were successfully used

e.g. to improve the mobility of the ink on the polymer pens in mixtures of proteins and buffer solutions³² or to assist photoresist microfabrication.^{33,34} Hence, herein, the main additive to our PEDOT:PSS inks was glycerol that had the added function of improving the conductivity of the bulk PEDOT:PSS. Applied modifications provided a more rational approach toward the development an ink and allowed various ink properties to be systematically varied for optimization of the DPN process.

2. Experimental

2.1 Materials and PEDOT:PSS synthesis

The basic ink additives: glycerol, hexadecyltrimethylammonium bromide (CTAB) and Triton X-100 were purchased from Sigma-Aldrich. Commercial PEDOT:PSS was Orgacon Dry dispersible pellets (Orgacon™ Electronic Materials, AGFA). The custom synthesized PEDOT:PSS was made with the use of catalyst in the following way. NaPSS of 70,000 MW (4.954g, 24.02 mmol of repeating unit, 4.421 g PSS equiv, 2.06 mass ratio) was dissolved in 150 mL of water. Ammonium persulfate (4.455g, 19.52 mmol) was added to the stirred solution which was then deoxygenated with a flow of N₂ bubbles for 5 min. The solution was stirred at 750 rpm then EDOT (1.5 mL, 2.145 g, 15.09 mmol) was added by syringe in one shot. A few crystals of Fe₂(SO₄)₃·9H₂O (1 mg, 2 10⁻⁶ mol) were added as a catalyst. The solution was stirred under nitrogen at room temperature for 20 hours, at which time a thick deep blue colored paste was evident. The mixture was transferred to a centrifuge tube with the aid of 50 mL H₂O and spun at 4500 rpm for 30 min, and the supernatant was decanted. Addition of water (135 mL) centrifugation (4500rpm/30min) and decantation was repeated another 4times. Then 500 mL of water was added and the mixture was placed in an ultrasound bath for 60 min, followed by centrifugation and decantation. Another 500 mL of water was added and the mixture was boiled for 2 hours, cooled and then centrifuged once more. The supernatant was drawn off and the final water was removed by rotary evaporation under reduced pressure. The final estimated yield was 70-80 %. The specific conductivity of the material was 36 ± 2 S cm⁻¹ untreated and 141 ± 7 S cm⁻¹ when the drop-cast film was treated with ethylene glycol and the material heated at 120 °C for 30 min.

2.2 Ink preparation

Both commercial and custom synthesized PEDOT:PSS were dissolved in ultrapure water (~2.5 % solid content). The dispersions were left for 5 minutes in a sonication bath followed by an extensive tip sonication for 10 minutes and finally transferred into a high-speed homogenizer. After plain PEDOT:PSS solutions were obtained, tip sonication was repeated to ensure that the PEDOT:PSS solutions could be passed through a 1.2 μm pore size syringe filter. For preparation of inks ready to print using DPN, 0.2 volume % of Triton X-100 was added to the sonicated and filtered PEDOT:PSS dispersions. CTAB with a concentration of 0.01 M was dissolved in glycerol and assisted with heating. The final ink formulation was prepared by mixing the PEDOT:PSS dispersion containing Triton X-100 with 10 volume % of glycerol (+ 0.01 M CTAB) and then used immediately for DPN printing. Conductivity and viscosity measurements were made using four point probe (Jandel RM3-

AR) and rheometer (TA Instruments AR-G2) respectively.

2.3 DPN deposition and characterization of patterned PEDOT:PSS inks

DPN printing was performed using an Nscriptor system and controlled by InkCAD™ software (both provided by Nanoink Inc.). Twelve pen tip-arrays (Type M, A-frame cantilevers with spring constant of 0.6 N m^{-1} , made of Si_3N_4 , $107 \mu\text{m}$ in length and $22 \mu\text{m}$ in width) were used for printing and silicon inkwell arrays were used for inking. Silicon substrates were also obtained from Nanoink Inc. Gold surfaces were prepared on silicon by evaporation of 4 nm thick layer of chromium and 16 nm layer of gold. The substrates before printing were rinsed with ultrapure water. During the DPN process, the temperature and humidity were kept at $22 \pm 3 \text{ }^\circ\text{C}$ and 65% , respectively. Imaging was conducted using an Asylum Research MFP-3D AFM instrument (Asylum Research, Santa Barbara, CA) and Wyko NT9100 Optical Profilometer (Bruker, Germany). In order to determine an “optimal” volume % of added glycerol in the PEDOT:PSS ink, the glycerol content was adjusted from 3% to $\sim 25 \%$. After the addition of each volume % glycerol, the inks were assessed for DPN printing. For water stability tests, the substrates with printed patterns were annealed at $105 \text{ }^\circ\text{C}$ for 8 h . Glycerol containing 0.01 M of cetrimonium bromide (CTAB) was then drop casted on the patterned areas and left for 24 h . After soaking, the samples were washed with methanol and annealed again using the same conditions as above.

3. Results and discussion

3.1. Preparation of PEDOT:PSS material

PEDOT:PSS starting material was obtained via two different sources. We used a custom synthesized PEDOT:PSS (herein referred to PEDOT:PSS CS, see experimental methods for synthesis) tailored for obtaining relatively high conductivities and, for comparison, a commercially available Orgacon Dry PEDOT:PSS material that was selected because to the best of our knowledge did not contain any surfactant or additives.

After dispersing the two different types of PEDOT:PSS in water through extensive sonication, their physical properties were assessed and are listed in Table 1. PEDOT:PSS CS has both longer PEDOT and PSS chains compared to the commercial material, in addition to a tenfold higher viscosity. In order to deliver as much as possible of CP material to the sample surface we used relatively higher solid content ($\sim 2.5 \%$) of PEDOT:PSS aqueous dispersions when compared to typical commercial dispersions (e.g. up to 1.3% of solid content).

Table 1 shows that conductivity of both PEDOT:PSS inks as drop-casted films increased significantly with the additives (see Table 2) in comparison to PEDOT:PSS without any additives. It is believed that the increase in the electrical conductivity of the PEDOT:PSS is related to an optimal polymer structure, or secondary doping mechanism, when the glycerol is added. This is analogous to previously reported effects on the inclusion of polyalcohols into PEDOT:PSS films that increase their electrical conductivity.³⁵

3.2. Additives and rational ink development

Printing of PEDOT:PSS with DPN directly from a pure aqueous

dispersion is problematic mainly due to dispersion instability and solvent evaporation.²⁴ Thus to develop a suitable ink the additives listed in Table 2 were incorporated into both the custom synthesized and commercial PEDOT:PSS to rationally address the intended properties and functions of the ink. Among the important physical properties of the ink is a low surface tension and vapour pressure. In particular, proper wetting of the tip is essential during the process of sufficiently “inking” the AFM tip when it (the tip) is dipped into microfluidic wells. To lower the surface tension of the aqueous PEDOT:PSS, the surfactant Triton X-100 was added. Another consideration of the ink properties is that the high volatility of water modifies the ink properties over time and subsequent lack of stability may prevent or temporarily limit patterning or upscalability of the printing process. To address this aspect, the addition of glycerol greatly improves ink stability and, as already discussed, also results in an increase in the PEDOT:PSS conductivity. After systematically adjusting the glycerol concentration followed by assessment for DPN patterning, we found that 10% was the minimal concentration required to enable PEDOT:PSS patterns (i.e. no patterns observed below this value). The addition of higher glycerol % showed no apparent improvement in printing since the obtained patterns qualitatively looked the same. The use of these additives follows similar studies that have investigated the use of glycerol and Triton-X in commercial aqueous PEDOT:PSS inks for inkjet printing.³⁶ However, the composition of these commercial PEDOT:PSS ink, which most likely contains other constituents, are unknown. Patterning of PEDOT:PSS from solutions containing only one additive (Triton X-100 or glycerol) did not give any printing results even at higher concentrations.

The addition of the quaternary ammonium salt, cetrimonium bromide (CTAB), was intended to have a twofold function. CTAB is a cation surfactant and acts as a second dispersant in the ink. Its other desired function is related to the improvement of the PEDOT:PSS stability and adhesion to the substrate after the CP patterns had been immersed in water or electrolyte. PEDOT:PSS in water forms particles in which the core consists of PEDOT and the outer-layers of negatively charged PSS groups. The interaction between PEDOT:PSS particles can therefore be stabilized by the addition of cations, which in some case results in the formation of a gel. Multivalent cations such Mg^{2+} , Ca^{2+} or $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ have previously been used to crosslink PEDOT:PSS.³⁷ The addition of ammonium cation also results in crosslinking of PEDOT:PSS particles. For example, CTA^+ exchanges with sodium and hydrogen ions and because the CTA^+ is relatively large the “crosslinking effect” is enhanced.³⁸ The deposition of PEDOT:PSS with this ammonium salt was seen as a means to improve stability through enhanced cross-linking and possible surface adhesion of the deposited PEDOT:PSS patterns after exposure to an aqueous solution, which is required for their electrochemical applications. The concentration of CTAB in glycerol was adjusted to 0.01 M and was generally the highest concentration at which ease of solubility could be achieved. Printing with the inks containing both Triton X-100 and glycerol but without CTAB is possible, though the addition of the ammonium salt greatly prolonged the printing times before needing to re-ink the tips in the silicon inkwell arrays. This was most likely due to the increased stability of the PEDOT:PSS

dispersion.

3.3. DPN patterning of PEDOT:PSS inks

In order to demonstrate the deposition and patterning of the PEDOT:PSS based inks, multi-pen tips (twelve pens) were used in the DPN for printing. For each experiment, the multi-pen tips were dipped into inkwells and then initial contact made with the surface prior to patterning to remove excess ink from the tip. After this initial “bleeding” step, it was possible to stably pattern dots across all 12 pens for well in excess of over an hour, which amounted to 40 μm dot arrays (comprising 9x9 dots) being able to cover an approximate surface area of 2 x 2 mm (each pen is separated by $\sim 60 \mu\text{m}$). Fig. 1 A and B shows optical profilometer images of patterned regions from 3 different pens for the different PEDOT:PSS inks. Some variation in dot dimensions within, and between arrays, were observed, particularly the first dot printed in each array and subsequent dots along the first row (i.e. bottom row of arrays). Non-uniformities in the dot size may largely be a consequence of utilizing a liquid based ink. For example, care must be taken when comparing the results achievable by liquid inks vs molecular inks. The rate of transport of molecular inks (e.g. MHA on gold) can be regarded as constant over a short timeframe. However, in the case of liquid inks accumulation of the ink on the end of the tip can occur with time, resulting in a larger than average dot at the beginning of a grid and subsequently along the first row. Registration of the dots relative to the original array pattern inputted in the InkCAD™ software was not always precise. In contrast to a molecular ink that will adsorb directly on to the substrate at the point of deposition, it is likely that the precise location adopted by a liquid ink droplet, is subject to the phenomenon of contact line pinning (due to, for example, surface energy inhomogeneity, surface roughness, surface defects, the dynamics of deposition etc.) The result is that the deposited liquid feature will sometimes migrate slightly to adopt a lower energy arrangement on the surface.

Further imaging of the arrays using AFM for a more detailed analysis was performed on individual 9x9 dot arrays for both PEDOT:PSS inks (commercial and customized PEDOT:PSS ink) on gold and silicon substrates using a dwell time of one second for the DPN process (Fig. 2). The patterned arrays and dimensions of individual dots showed good uniformity, with individual dots diameters having sub-micron dimensions. A statistical analysis of the dot dimensions was performed by measuring the height section profiles of individual dots. For example, from the representative AFM images presented in Fig. 2, 25 dots were arbitrary chosen for analysis. We specifically made the analysis for a region of dots (3x3 = 9 dots) in smaller scan areas of 10 μm to alleviate the effect of tip broadening and confirmed values using smaller scans of 1 μm to image single dots (randomly selected). All measured dimensions were performed from several AFM images and summarized in Table 3. The measured values of both dot dimensions of height and diameter exhibits a very narrow distribution of dimensions for each ink, indicating that the DPN deposition process provided uniform patterning, particularly within arrays. It was found that all inks routinely gave dot widths less than 1 μm , with the customized PEDOT:PSS ink achieving significantly reduced widths down to $\sim 200 \text{ nm}$ in diameter, as shown in Fig. 2F of single dot of the customized PEDOT:PSS ink on silicon. Given

an expected deviation (over-estimation) due to tip broadening effects, these latter dimensions are comparable with DPN printing of poly (ethylene glycol) based block copolymer on silicon³⁹ and mixtures of agarose and tricine on glass substrates.²⁸ The standard deviation of the dot dimensions indicates the degree of uniformity and reproducibility of the patterning, which is also similar to that reported during DPN printing of thiols and acid monolayers deposited on gold.⁴⁰ The dot heights were all lower than 50 nm, indicating a relatively small aspect ratio (dot height/width) of the deposited features. The calculated aspect ratio for dots patterned from the customized PEDOT:PSS ink is around tenfold higher compared to the commercial PEDOT:PSS.

The size of printed dots depends strongly on the contact dwell time of the AFM tip at the surface. To assess this effect and perhaps gain more insight into the ink properties, dwell time calibration patterns were printed using both PEDOT:PSS inks on gold and silicon. For these calibrations, analysis of the dimensions were carried out on 1x1 μm images of single dots totalling 20 dots. Fig. 3 presents an example of AFM images from the dot size calibration and single images of each dot along the same row. The measured dimensions were plotted as a function of the dwell time^{1/2} and showed a linear relationship (Fig. 4), as previously observed for diffusion-controlled processes of ink deposition using DPN. For dot width, the commercial ink showed a stronger dependency (greater slope) on dwell time, indicating an effect from differences in the ink chemistries of the raw PEDOT:PSS material. In contrast, there were no difference in dwell-time dependencies between the different material substrates, gold and silicon, for both inks. For dot height, the dependencies were similar for both inks, with the calibration again confirming previous analysis that the dot heights were clearly greatest for the customized PEDOT:PSS on silicon. These observations confirmed that the dot widths were greater overall for the commercial ink, while the customized PEDOT:PSS ink provided higher aspect ratio dimensions and made it possible to achieve the smallest dimensions of $\sim 160 \text{ nm}$ dot width when applying very fast dwell times of 0.1 s. We do note that in some cases variations in the mean dot dimensions, particularly the width, were observed between arrays or dots produced from different pens. For example, we observed differences in mean dot widths between arrays (Table 3) and those of the calibration patterns (Fig. 4) for the commercial ink on silicon and CS-based ink on gold at 1 s dwell times. These differences may relate to the variation in dot sizes observed in Fig. 1A and B and also correlate with our previous multi-array DPN patterning of a commercial PEDOT:PSS ink that showed a distribution of dot dimensions within an array of a single pen, and also between pens, both of which could vary by $\sim 10\text{-}15 \%$.²⁴

Chemically analysing the components of the final dot printed features is difficult due to the nanoscale dimensions of the dots. Previous studies on AFM-based liquid deposition have shown that the evaporation rate of micron-sized glycerol dots occurs within minutes and is extremely rapid for similar attolitre volumes used in this study⁴¹. With the addition of annealing the patterns at 105°, we expect that the final component will contain little glycerol. Closer inspection of the AFM images, particularly for the gold substrate, show that the printed dots are actually made up of individual particles of $\sim 50\text{-}100 \text{ nm}$, suggesting the

presence of PEDOT:PSS nanoparticles (Fig. 2E). Aqueous dispersions of PEDOT:PSS are known to consist of nanoparticles⁴², and the presence and size of these nanoparticles in our PEDOT:PSS dispersions were confirmed by zetasizer measurements (data not shown).

Similarly, measuring the conductivity of individual dots is difficult due to their nanoscale dimensions. We have previously been able to use conductive AFM imaging and AFM-based I-V spectroscopy to qualitatively show conductive properties of ~ 1 μm commercial PEDOT:PSS dots patterned via DPN²⁴, however, quantifying their conductivity values was not straightforward using these approaches. To overcome this, it is possible to quantify conductivity from lines patterned between two electrodes, as done in our previous work on vapour phase polymerized PEDOT:PSS patterned via DPN²³. Unfortunately, the patterning of lines using the PEDOT:PSS inks in this study was problematic and did not allow for quantifying the conductivity. As the ink is liquid based, deposition occurs upon break of contact between the tip and surface (as opposed to molecular ink transport, where deposition occurs via continuous diffusion). We suggest that the successful drawing of nano- and microscale lines of liquid would require a delicate balance of capillary forces (e.g. liquid surface tension, substrate surface energy), or else the engineering of a chemical affinity between the ink and substrate.

3.4. Water resistance

Water stability of PEDOT:PSS was improved by introducing 10 volume % of glycerol to which 0.01 M of CTAB was dissolved. After printing, the patterned arrays were annealed at 105 °C for several hours. The patterns were then soaked again in 0.01 M CTAB in glycerol to perform another ion exchange. After washing away excess of glycerol from patterned arrays using methanol, the samples were annealed again at 105 °C. This process offered improved adhesion of PEDOT:PSS to the surface in a water environment. Fig. 5 show an example of commercial PEDOT:PSS patterns printed on silicon after the treatment and after having being exposed to water for up to 2 hours. When tested on the bulk scale (e.g. films with surface area of 0.07 cm²), the deposited ink treated in this way could survive in water for up to one month (data not shown). This treatment process was found to be critical, as annealing itself was not sufficient to provide the enhanced adhesion and stability in water. Furthermore, we could not obtain any water resistance of the patterned arrays, as well as of bulk films of PEDOT:PSS, without addition of CTAB. The exact mechanism of the improved stability and adhesion is unclear though both ion exchange and annealing may be responsible. For ion exchange, exchanging with sodium and hydrogen cation and interacting with PSS chains may limit the solubility of the PEDOT:PSS particles and/or directly crosslink them. However, the annealing and CTAB treatment process did not work for the PEDOT:PSS CS-based ink. This may be due to the PSS chains in PEDOT:PSS CS being longer and thus are more easily dispersed than in the commercial material. To utilize the electrochemical properties of these patterned arrays, their stability in aqueous media is necessary and through the addition

of salt exchangers it is feasible to enhance stability/adhesion; however further studies on the implementation of adhesion promoters are required to optimize the process.

4. Conclusions

By synthesizing and rationalizing designing a new PEDOT:PSS ink, we have been able to achieve pattern dimensions that are much smaller than the limit expected for a liquid ink transferred via physisorption processes, which is typically on the order of ~0.5 to 1 μm . The minimum dot widths down to ~160 nm represent a significant reduction in dimension size for these types of liquid inks. This ability was afforded by the use of additives to enable DPN printing of an aqueous dispersed PEDOT:PSS material, increased adhesion of the ink to the substrate, and enhancement of the conductivity. Furthermore, knowledge of the individual constituents and overall ink composition is critical for enabling systematic studies on the effects of the polymer-dopant mass ratio and different additives – this will lead to a greater understanding of the fluid physical properties that facilitate the patterning of conducting polymer inks on the nanoscale using DPN. The ability to pattern liquid conducting polymers inks on such small scales present interesting possibilities for various applications, including conducting polymer-based sensors, organic and flexible electronics on the nanoscale and bionics applications where biological moieties could conceivably be incorporated into the ink.

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Notes and references

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- 1 A.J. Heeger, *Synth. Met.*, 2001, **125**, 3.
- 2 M.H. Yun, N.V. Myung, R.P. Vasquez, C. Lee, E. Menke and R.M. Penner, *Nano Lett.*, 2004, **4**, 419.
- 3 H.Q. Liu, J. Kameoka, D.A. Czaplowski and H.G. Craighead, *Nano Lett.*, 2004, **4**, 671.
- 4 K. Ramanathan, M.A. Bangar, M.H. Yun, W. Chen, N.V. Myung and A. Mulchandani, *J. Am. Chem. Soc.*, 2005, **127**, 496.
- 5 J.X. Huang, S. Virji, B.H. Weiller and R.B. Kaner, *J. Am. Chem. Soc.*, 2003, **125**, 314.
- 6 L. Pan, H. Qiu, C. Dou, Y. Li, J. Xu and Y. Shi, *Int. J. Mol. Sci.*, 2010, **11**, 2636.
- 7 K. Jackowska, A.T. Bieganski and M. Tagowska, *J. Solid State Electrochem.*, 2008, **12**, 437.
- 8 G.M. Wallraff and W.D. Hinsberg, *Chem. Rev.*, 1999, **99**, 1801.

- 9 Y. Xia and G.M. Whitesides, *Angew. Chem. Int. Ed.*, 1998, **37**, 550.
- 10 C. Luo, *Microsyst. Technol.*, 2009, **15**, 1605.
- 11 A. Perl, D.N. Reinhoudt and J. Huskens, *Adv. Mater.*, 2009, **21**, 2257.
- 12 R.D. Piner, J. Zhu, F. Xu, S. Hong and C.A. Mirkin, *Science*, 1999, **283**, 661.
- 13 K.-B. Lee, J.-H. Lim and C.A. Mirkin, *J. Am. Chem. Soc.*, 2003, **125**, 5588.
- 14 J.-H. Lim, D.S. Ginger, K.-B. Lee, J. Heo, J.-M. Nam and C.A. Mirkin, *Angew. Chem. Int. Ed.*, 2003, **42**, 2309.
- 15 W.K. Lee, Z. Dai, W.P. King and P.E. Sheehan, *Nano Lett.*, 2010, **10**, 129.
- 16 S.-C. Hung, O.A. Nafday, J.R. Haaheim, F. Ren, G.C. Chi and S.J. Pearton, *J. Phys. Chem. C*, 2010, **114**, 9672.
- 17 B. Wu, A. Ho, N. Moldovan and H.D. Espinosa, *Langmuir*, 2007, **23**, 9120.
- 18 K. Salaita, Y. Wang, J. Fragala, R.A. Vega, C. Liu and C.A. Mirkin, *Angew. Chem. Int. Ed.*, 2006, **45**, 7220.
- 19 J.-W. Jang, A. Smetana and P. Stiles, *Scanning*, 2010, **32**, 24.
- 20 H.-H. Lu, C.-Y. Lin, T.-C. Hsiao, Y.-Y. Fang, K.-C. Ho, D. Yang, C.-K. Lee, S.-M. Hsu and C.-W. Lin, *Anal. Chim. Acta*, 2009, **640**, 68.
- 21 J.-H. Lim and C.A. Mirkin, *Adv. Mater.*, 2002, **14**, 1474.
- 22 M. Yang, P.E. Sheehan, W.P. King and L.J. Whitman, *J. Am. Chem. Soc.*, 2006, **128**, 6774.
- 23 C. O'Connell, M.J. Higgins, H. Nakashima, S.E. Moulton and G.G. Wallace, "Vapor phase polymerization of EDOT from submicron scale oxidant patterned by dip-pen nanolithography" (submitted, under review)
- 24 H. Nakashima, M.J. Higgins, C. O'Connell, K. Torimitsu and G.G. Wallace, *Langmuir*, 2012, **28**, 804.
- 25 J. Haaheim, R. Eby, M. Nelson, J. Fragala, B. Rosner, H. Zhang and G. Athas, *Ultramicroscopy*, 2005, **103**, 117.
- 26 B.L. Weeks, M.W. Vaughn and J.J. DeYoreo, *Langmuir*, 2005, **21**, 8096.
- 27 H.-T. Wang, O.A. Nafday, J.R. Haaheim, E. Tevaarwerk, N.A. Amro, R.G. Sanedrin, C.-Y. Chang, F. Ren and S.J. Pearton, *Appl. Phys. Lett.*, 2008, **93**, 143105.
- 28 A.J. Senesi, D.I. Rozkiewicz, D.N. Reinhoudt and C.A. Mirkin, *ACS Nano*, 2009, **3**, 2394.
- 29 J.W. Schultze and H. Karabulut, *Electrochim. Acta*, 2005, **50**, 1739.
- 30 L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik and J.R. Reynolds, *Adv. Mater.*, 2000, **12**, 481.
- 31 M. Berggren and A. Richter-Dahlfors, *Adv. Mater.*, 2007, **19**, 3201.
- 32 Z. Zheng, W.L. Daniel, L.R. Giam, F. Huo, A.J. Senesi, G. Zheng, and C.A. Mirkin, *Angew. Chem. Int. Ed.*, 2009, **48**, 7626.
- 33 J.-W. Jang, R.G. Sanedrin, A.J. Senesi, Z. Zheng, X. Chen, S. Hwang, L. Huang, and C.A. Mirkin, *Small*, 2009, **5**, 1850.
- 34 J.-W. Jang, Z. Zheng, O.-S. Lee, W. Shim, G. Zheng, G.C. Schatz and C.A. Mirkin, *Nano Lett.*, 2010, **10**, 4399.
- 35 A.M. Nardes, R.A.J. Janssen and M. Kemerink, *Adv. Funct. Mater.*, 2008, **18**, 865.
- 36 F. Ely, C.O. Avellanenda, P. Paredez, V.C. Nogueira, T.E.A. Santos, V.P. Mammanna, C. Molina, J. Burg, G. Gibson and L. Zhao, *Synth. Met.*, 2011, **161**, 2129.
- 37 M. Vázquez, P. Danielsson, J. Bobacka, A. Lewenstam and A. Ivaska, *Sens. Actuators B*, 2004, **97**, 182.
- 38 M. Döbbelin, R. Marcilla, C. Tollan, J.A. Pomposo, J.-R. Sarasua and D. Mecerreyes, *J. Mater. Chem.*, 2008, **18**, 5354.
- 39 J. Chai, F. Huo, Z. Zheng, L.R. Giam, W. Shim and C.A. Mirkin, *Proc. Natl. Acad. Sci. U.S.A.*, 2010, **107**, 47.
- 40 S. Rozhok, R. Piner and C.A. Mirkin, *J. Phys. Chem. B*, 2003, **107**, 751.
- 41 T. Ondarcuhu, J. Arcamone, A. Fang, H. Durou, E. Dujardin, G. Ruis, and F. Perez-Murano, *Eur. Phys. J. Special Topics*, 2009, **166**, 15-20.
- 42 J. Pecher and S. Mecking, *Chem Rev.* 2010, **110**, 6260-6279.

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Table 1 Physical properties of studied PEDOT:PSS based inks and their deposits.

Ink type	Solid content/%	Viscosity/Pa s	Conductivity ^a /S cm ⁻¹ (additives)	Conductivity ^a /S cm ⁻¹ (without additives)
Commercial PEDOT:PSS based ink (Orgacon Dry)	~2.5	~0.017	142 ± 30	13.0 ± 0.7
PEDOT:PSS CS based ink (custom synthesized)	~2.5	~0.178	114 ± 58	1.4 ± 0.2

^a The samples were annealed for 8 h at 105 °C.

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25 **Table 2** List of ink additives.

Ink constituents	Concentration	Function of additive	
Triton X-100	0.2 volume %	Improve wetting	65
Glycerol	10 volume %	Ink stability, conductivity increase	
CTAB	0.01 M	Dispersibility, cation exchange (adhesion)	70

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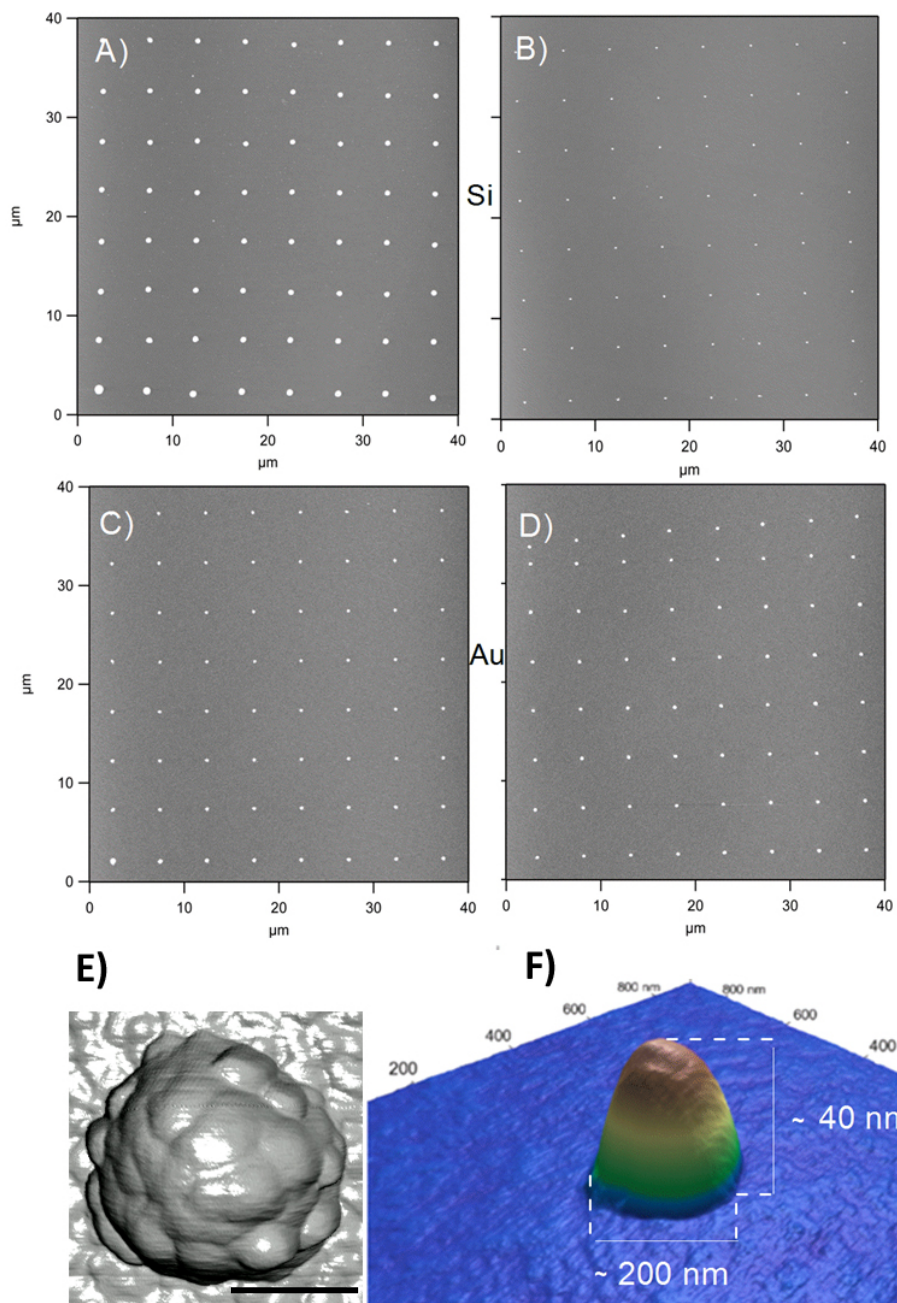
Fig. 1 An example of optical profilometer images of regions of patterned PEDOT:PSS on silicon substrates A) and B) are PEDOT:PSS dot-arrays containing 25 and 81 dots respectively within 40x40 μm.

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5 **Fig. 2** AFM topographic images of PEDOT:PSS 81 dot patterns printed on silicon (A, B) and gold (C, D) from commercial PEDOT:PSS based ink (A, C) and PEDOT:PSS CS based ink (B, D). The dots were patterned by multi-pen with dwell time of one second and spacing between dots is $\sim 5 \mu\text{m}$. High magnification 3-D topographic images of a single dot of customized PEDOT:PSS on gold (E) and (F) silicon. Scale bar in (E) is 190 nm

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Table 3 The dot size of the PEDOT:PSS dots patterned on gold and silicon measured using height section profiles from AFM images.

Ink type	Substrate	Dot width/nm	Dot height/nm	Aspect ratio ^a
commercial PEDOT:PSS based ink	Si	641 ± 10	17 ± 1	0.03
	Au	399 ± 5	16 ± 1	0.04
PEDOT:PSS CS based ink	Si	203 ± 2	28 ± 1	0.14
	Au	400 ± 8	46 ± 3	0.12

^a Dot height to dot width ratio.

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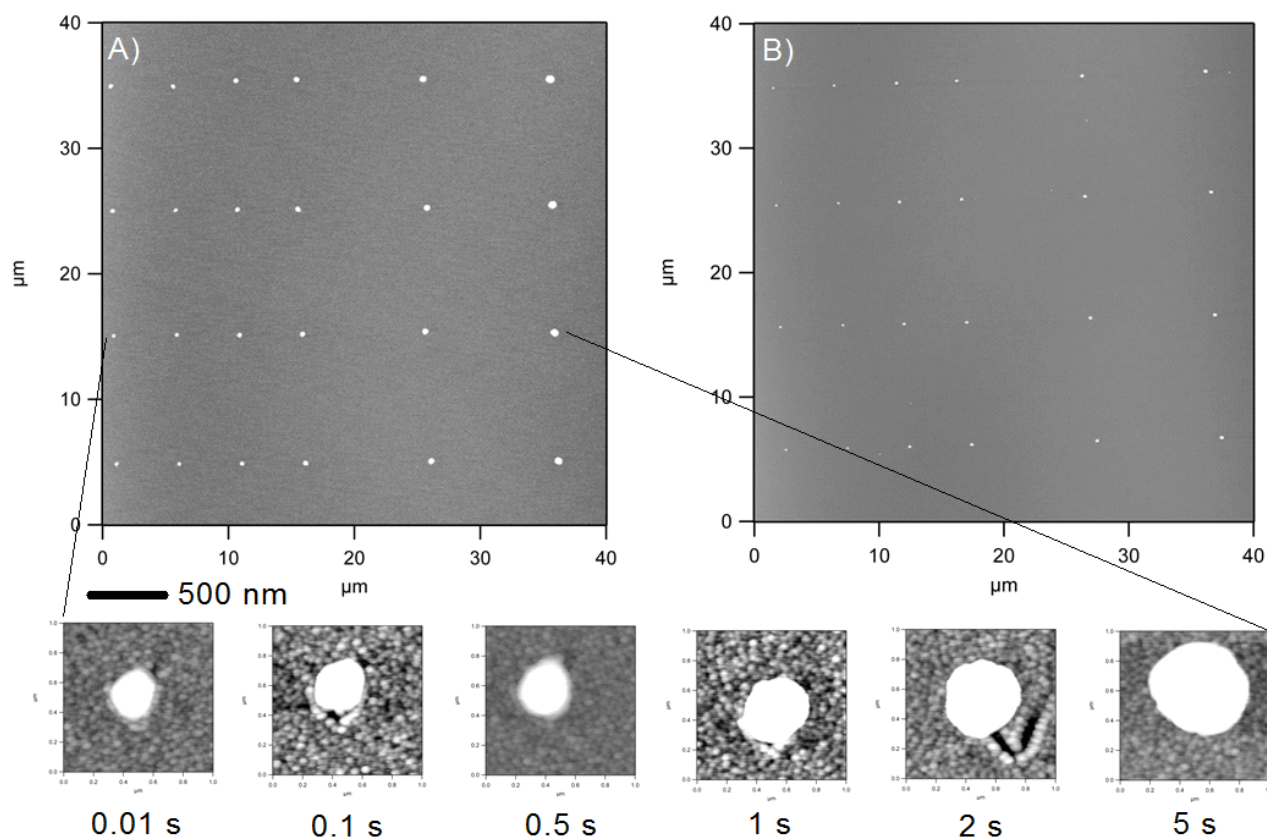
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15 **Fig. 3** AFM topographic images of dot size calibration for pattern printed on gold form commercial PEDOT:PSS based ink (A) and on silicon from PEDOT:PSS CS based ink (B). Insert: an example of AFM topographic images (1x1 μm) of each dot in the calibration pattern.

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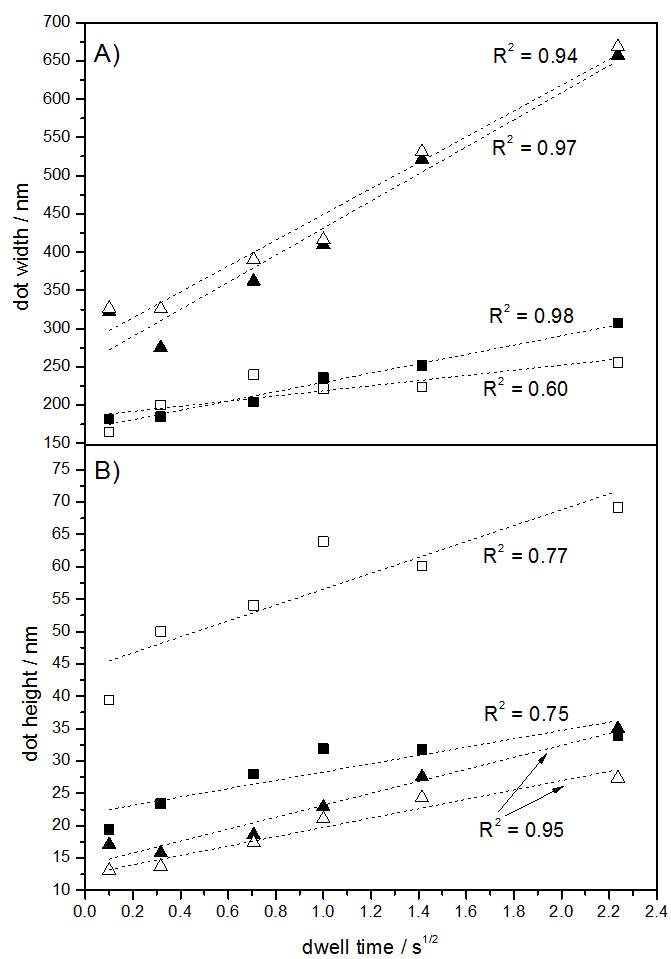


Fig. 4 Dots widths (A) and heights (B) plotted as a function of the dwell time. Representation: PEDOT:PSS CS on Si (■) and Au (□) together with commercial PEDOT:PSS on Si (▲) and Au (△).

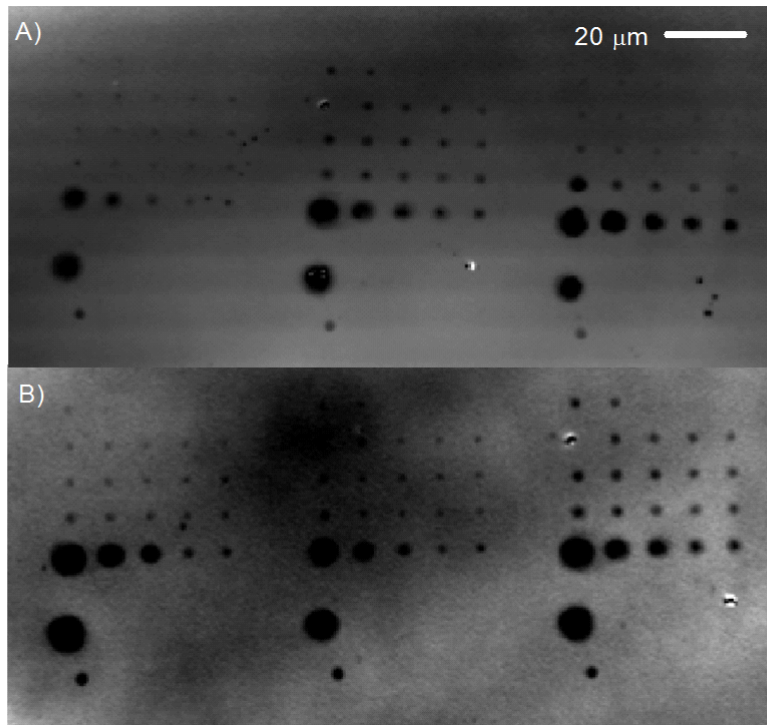
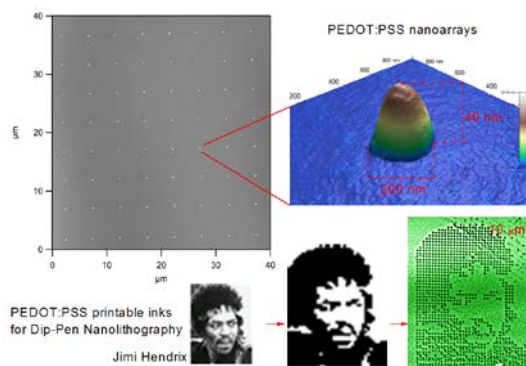


Fig. 5 Optical profilometer images of PEDOT:PSS arrays on silicon after soaking for 24 hours in 0.01 M CTAB in glycerol followed by cleaning in methanol (A) and after exposure to water for 2 hours (B).

Table of content (TOC)

In-house synthesized PEDOT:PSS was used in production of ink which includes several additives making printing process by Dip-Pen Nanolithography suitable for obtaining conducting polymer nanoarrays which can be applied in biology and chemical sensors technology. We report that with our inks one can obtain feature sizes of 160-200 nm.



Picture for table of content entry

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