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Printing Holes by a Dewetting Solution Enables Formation of a Transparent Conductive Film

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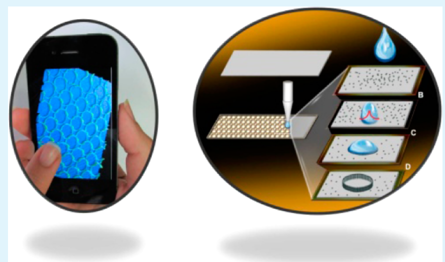
Supporting Information

ABSTRACT: We present hereby a general approach for rapid fabrication of large scale, patterned transparent conductive coatings composed of nanoparticles. The approach is based on direct formation of "2D holes" with controllable diameter onto a thin film composed of metal nanoparticles. The holes are formed by inkjet printing a dewetting aqueous liquid, which pushes away the metal nanoparticles, thus forming a transparent array of interconnected conductive rings.



KEYWORDS: *transparent, conductive, silver, electrodes, holes*

■ INTRODUCTION

The efforts to find an alternative to the most common transparent electrode, indium tin oxide (ITO), are continually growing, and for the past 5 years the number of reports on new materials and methods to fabricate transparent conductive coatings (TCC) have increased dramatically.[1,2] A promising approach to obtain a TCC with a very low sheet resistance is by using metallic nanomaterials. The intrinsic high conductivity of metals such as silver, copper, and gold enables to obtain transparent conductive coatings with sheet resistance as low as 1−10 Ohms per square.[3,4] The most advanced approach is based on coatings composed of metal nanowires.[5,6] For various applications such as touch screens for smart phones, the conductive coating should be patterned.[7] The methods to obtain transparent conductive patterns vary from lithography and self-assembly to printing.[2] Lithography typically requires sophisticated equipment and is considered to be a costly procedure, while self-assembly processes offer a challenge to industrial implementation. In spite of the excellent performance of silver nanowires, which also enables stretching,[8] it is complicated to achieve direct patterning of this material by using digital technologies, such as inkjet printing, due to the large length of the nanowires. Therefore, recently, efforts have been made to utilize metallic nanoparticles (NPs) to obtain the TCC. The NPs can be patterned into a variety of transparent structures such as grids, ring arrays, and honeycombs, provided that the line width is below 5−10 μm.

Ahn et al. reported on the direct patterning of a silver grid by a filamentary printing approach, in which concentrated silver ink is extruded through a single cylindrical nozzle, as small as 1 μm in diameter. For example, patterned arrays (6 × 6 mm) composed of orthogonal silver features (9 μm width) yielded transparency of 77−94% depending on the line spacing.[9] The main drawback of this method is that the lines were printed from a single nozzle at speeds (<2 mm/s) which are not compatible for large scale industrial processes.

Kwon et al. used nanosphere lithography to obtain a transparent honeycomb structure composed of metal nanoparticles. The process is based on three steps: 1. Deposition of polystyrene (PS) spheres on a substrate to form a monolayer or multilayer template by methods such as Langmuir−Blodgett films, spin coating and floating−transferring techniques. 2. The voids in between the PS spheres are filled with a dispersion of silver nanoparticles. 3. The PS sphere template is lifted-off by sonicating in toluene for 3 min, leaving behind a nanostructured pattern on the substrate.[10]

Higashitani et al. used evaporative lithography to self-assemble gold nanoparticles into a transparent grid pattern. After placing a stainless-steel mesh on top of a glass substrate, a droplet containing gold NPs was placed on top of the mesh, instantaneously spreading over the mesh and the glass substrate. During evaporation, the water flowed outward, and the NPs arranged themselves according to the wires of the mesh. After complete evaporation, the mesh was removed from the glass substrate, and a transparent grid composed of the gold NPs was obtained. The lines composing the grids were less than 10 μm in width, and in order to turn the grid into conductive, thermal sintering was conducted (425 °C for 20 min).[11] Layani et al. used a similar approach, which was applied directly on a plastic substrate, polyethylene terphtalate (PET). The sintering was performed at low temperature, by a simple chemical process. This process resulted in a TCC with a sheet resistance of ~9 Ω/□ and ~80% transparency.[12]

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We reported a different approach, which enables fabrication of transparent conductive and direct patterning by inkjet printing of arrays composed of micrometric rings.[13] This approach is based on the "coffee stain effect",[14] in which picoliter droplets of a silver dispersion are printed directly onto a flexible substrate, forming thin rings composed of silver NPs due to the directional movement of the nanoparticles. The printed arrays of interconnected rings are sintered by simple exposure to HCl vapor. Zhang et al. used a similar approach to produce a grid pattern composed of elongated, ellipse-shaped geometry, with nanoparticles accumulating in the narrow lines of the printed ellipse.[15]

However, although ink jet printing is considered a very appealing method for large scale production, obtaining narrow lines, so far, it can only be achieved indirectly, by self-assembly of nanoparticles within the printed droplets, as described above.

We present here a unique and broad approach to rapid production of large scale patterned TCCs. The approach is based on direct printing of "2D holes" with controllable diameters, onto a continuous film composed of metal nanoparticles, by utilizing a dewetting phenomenon.

RESULTS AND DISCUSSION

The fabrication process is performed in the following three steps: 1. A continuous film composed of a dispersion of metal nanoparticles is formed by simple spray or spin coating. After deposition, the film is neither transparent nor conductive, since the NPs are separated from each other and there are no percolation paths. 2. Inkjet printing of picoliter droplets of an aqueous dewetting solution (water and surfactant) onto the film. Upon contact of this solution with the film, dewetting of the film occurs, while the printed solution pushes away the nanoparticles and forms a "2D hole". The size of these holes is easily controlled. After evaporation of all the liquids (coating solvent and droplet solvent), the majority of the particles can be found at the periphery of the hole, resulting in separated rings, as presented schematically in Figure 1. The printing process can be repeated until all the rings are connected together to yield a transparent film. 3. Finally, a thermal, or any other sintering process, is performed converting the transparent film into a TCC.

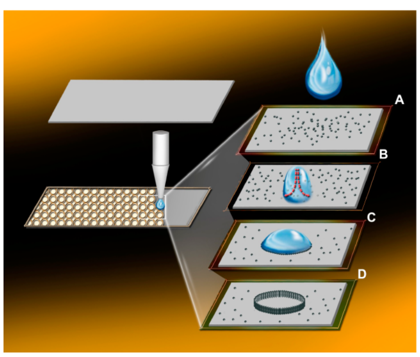

Figure 1. Scheme of the hole formation and transformation of the film into a transparent coating.

It should be noted that making holes in polymeric substrates was reported by the known "breath figures" phenomena[16] which results from condensation of water droplets on the substrate. This is typically obtained under high humidity environment, in which the condensation processes result in a porous 2D or 3D hexagonal array, without specific pattern. To the best of our knowledge, there are two reports[17,18] that present the breath figure method with CNT and ZnO, materials that can potentially be used for transparent electrodes; however, the formation of TCC was not reported. Our approach enables control of placement and size of each droplet, thus permitting fine patterning of the obtained array.

The exact mechanism of the hole formation in our study is not known yet. There are several possibilities for hole formation, as follows:

1. As described by Yarin et al.[19] upon impact of an individual liquid drop with a thin liquid film, splashing occurs and "crowns" are formed and propagate outward.

2. In nonvolatile thin films, under certain conditions, spontaneous dewetting may take place through rupture of the film to form a hole, followed by growth of the holes resulting in a polygonal network.[20] The rupture mechanism may occur due to a heterogeneous nucleation process resulting from defects in the liquid film or due to spinodal dewetting. In our case, it may be that the impact of droplets of the dewetting solution causes local nucleation sites for the rupture of the liquid film.

3. As known, under surface tension gradients, liquids tend to flow toward the higher surface tension region (The Marangoni effect). Upon impact of the dewetting solution with the low surface tension (28 mN/m) with the liquid thin film with the higher surface tension liquid (36 mN/m), the later moves with the silver nanoparticles out of the contact point, thus creating the "hole", in which the silver particles accumulate at the rim of this hole.

Obviously, printing of the dewetting solution can be achieved at high speed, in any required pattern, just as by other industrial inkjet printing processes, thus enabling fabrication of large TCCs. By proper selection of the type of dispersion and dewetting solution, the process can also be utilized for the alignment of other materials. A major advantage of this new approach is that the printing is conducted with a simple solution that is easy to use, without the usual clogging problems in particle-based inks. It should be emphasized that the yield of the process is exceptionally high, since there is no loss of costly silver nanoparticles.

Figure 2 shows a 3D profile of single and interconnected rings formed by inkjet printing dewetting ink droplets onto a glass substrate which is precoated by silver nanoparticles. The coated film was formed by spin-coating of a 5 wt % silver

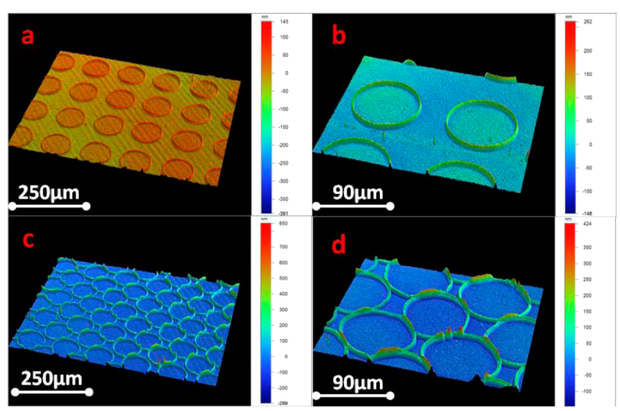

Figure 2. Three-dimensional height profile of single rings (a,b) and connected rings (c,d) formed by printing holes on a 5 wt % silver NP layer spin coated on glass substrate.

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nanoparticles' dispersion. This coating was not conductive even after thermal treatment intended for sintering, and the nanoparticles' concentration was insufficient due to the great distance between the particles, which did not enable any contact between them. After printing the dewetting solution, the particles were pushed away from the area where the droplet came in contact with the substrate, increasing, at the same time, their local concentration (Figure 2 a, 2b). These particles accumulated around the periphery of each droplet at a hole diameter of ~80 μm, line width of ~3 μm, and height of ~200 nm, sufficiently increasing their concentration to enable percolation paths between the particles in the individual rings. Printing the holes at proper distances enables the connections between all rings (Figure 2c), thus converting the whole film into a conductive structure.

It should be noted that in practice, printing is performed in two layers, where the first layer of droplets is printed with gaps left for the second layer. The obtained interconnected rings array formed by the printed holes can be seen in the HRSEM images (Figure 3), in which the connecting lines are composed

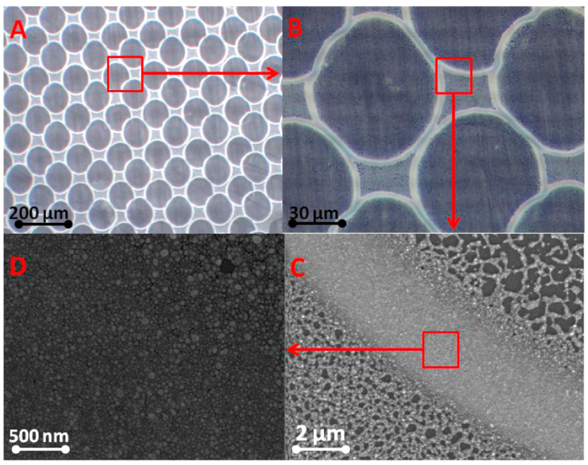

Figure 3. Microscope images (A,B) and HRSEM images (C,D) of connected rings formed by printing holes on a 5 wt % silver NP layer spin coated on glass substrate.

of densely packed and connected silver nanoparticles (image taken after sintering at 250 °C for 20 min). As seen, the obtained film is composed mainly of holes, which should impart transparency, depending on the diameter of the hole and the width of the connecting lines.

Figure 4 shows a glass slide, in which the holes are printed in an area of an inner square. Immediately after the spin coating of the silver NP dispersion, a semitransparent, reddish, continuous layer is obtained (Figure 4a). The transparency of the coating is very low (<40%), and it is not conductive. After printing of the

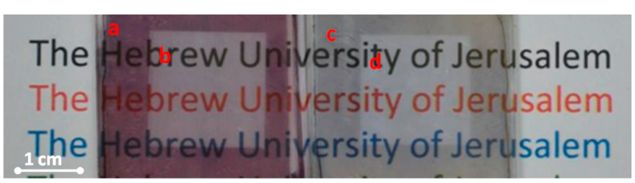

Figure 4. Optical image of two glass slides with printed holes in the inner square, before (a,b) and after (c,d) sintering. The inner squares (b,d) are more transparent compared to the outer area (a,c) due to the presence of holes.

dewetting droplets, a transparent array of interconnected holes is obtained at the inner, printed square (Figure 4b). It should be noted that the inner part of the holes is not completely free of material. It contains some silver nanoparticles, in a random structure, while some of the particles are forming a short network and some are disconnected particles, as shown in Figure S3. Upon heating the slide (250 °C for 20 min), sintering of the nanoparticles occurs, the color changes to grayish, and the transparency is further increased (Figure 4d). The sintering is performed at high temperature, 250 °C, and at that temperature both complete evaporation of the solvent (boiling point 230 °C) and the merging of the particles should occur. Both processes should cause a closer packing of the nanoparticles, and this must be accompanied by higher transparency. Of course, this can happen only if the particles are not strongly bound to the glass substrate.

This glass slide has a sheet resistance of <60 Ohm per square and a transparency of ~70%. The increase in transparency results from the narrowing of the connecting silver lines due to the sintering of the nanoparticles.

Both transparency and conductivity can be controlled by changing printing parameters and silver and dewetting inks composition. For example, in Figure 5a we present the effect of metal loading in the silver ink on the sheet resistance of the obtained structure after printing the holes. Figure 5b presents the correlation between the transparency and resistivity, as expected; the higher the sheet resistance, the higher the transparency. It should be noted that we found that the same

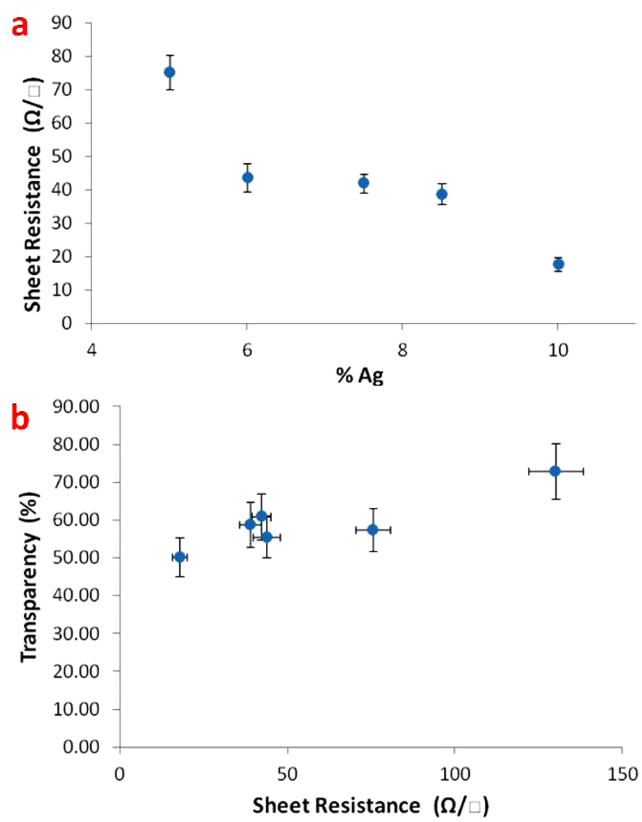

Figure 5. a) The dependence of the sheet resistance on silver ink metal loading, after printing holes with the dewetting ink followed by sintering. b) The correlation between the transparency and the sheet resistance for transparent conductive films made of silver ink at various concentrations presented in part a.

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phenomena of hole formation occurs also on plastic substrates such as PET, indicating the general validity of the process. However, since the plastic substrate has many surface inhomogeneities, the resulting holes had various diameters, and therefore connecting the holes became technically challenging and required more tailoring of the dewetting ink and printing parameters and using a high quality PET.

Based on additional experiments (Figures S1 and S2, Supporting Information), we found that the diameter of the holes can be controlled by simple means such as the surface tension of the dewetting ink and jetting voltage. To show the hole size control, we evaluated the effect of hole size by printing droplets with inkjet printhead of different volumes, 1 and 10 pL. We found that with the 1 pL printhead an array of connected holes was formed, with an average hole diameter of ~40 μm, with a transmittance of only 60%, and a sheet resistance of 37 $\Omega/\square$, whereas with the 10 pL printhead, 60 μm holes were formed, with transparency and sheet resistance of 67% and 50 $\Omega/\square$, respectively. Therefore, conductivity and transparency can be modified according to the required optoelectronic application.

CONCLUSION

To conclude, we have demonstrated a new and simple concept to pattern nanoparticles into a 2D, connected rings array, using inkjet printing and self-assembly of nanoparticles. At present, the resulting transparent conductive coating has a typical sheet resistance of <60 Ohm per square and a transparency of ~70%. We expect that transparency could be increased by increasing droplets diameter, for example, by increasing the wetting agent concentration, voltage of driving pulse, printhead nozzle diameter, etc. We believe that this approach provides a new way to produce transparent and patterned films composed of a variety of functional nanomaterials that can be utilized in various optoelectronic devices. The presented approach has advantages over the reported ones for fabricating TCC, since most reports on making transparent conductors by wet deposition lack the possibility of patterning. In our approach we achieve the patterning by an inkjet printing process, which is simple to perform and suitable for industrial applications. Inkjet printing was previously reported for obtaining TCC made of self-assembled rings. This process is suitable only for materials that can be printed by inkjet and is not suitable, for example, for the widely used silver nanowires[21] and graphene sheets.[22] The new approach of hole printing enables patterning of many types of materials at various sizes and is not limited to metal nanoparticles, since the deposition of the first layer can be performed by a variety of wet deposition methods such as spin coating, flexo, and screen printing.

EXPERIMENTAL SECTION

1. Ag and Dewetting Inks. The silver dispersion containing silver NP was obtained from Xjet (Israel). The dispersion contains 60 wt % silver nanoparticles (average diameter of 10 nm) in Dowanol DB. The dispersion was diluted by Dowanol DB, to yield an ink with desired metal loading.

The dewetting ink was composed of triple distilled water, with dissolved 0.1 wt % wetting agent, Byk 348 (BykChemie,Germany).

2. Holes Printing. In the first stage the precoating was performed by spin-coating (Lourell) 10 droplets of the above ink, at 3000 rpm for 20 s, onto a glass substrate.

The holes were formed by printing the dewetting ink by an Omnijet100 inkjet printer (Unijet, Korea) equipped with Diamatix printhead of 10 and 1 pL, immediately after forming the coating. The fabrication of the transparent electrode was performed in two printing steps. In the first step, droplets were printed so that holes were formed with a gap distance the same as the hole's average diameter. In the next printing step, the droplets were printed in these gaps, as to form a continuous array of rings. It was found that the two step printing is essential in order to form a 2D layer of interconnected rings. If the printing is preformed in one step, the droplets overlap and merge into one large droplet. Furthermore, instead of individual holes surrounded by thin lines composed of densely packed NP, the resulting pattern of holes is without a percolation path. Therefore, the process is performed by printing the first layer of holes, and upon a short drying period, about 1 min, the second layer of holes is printed.

It should be noted that we observed that if the dewetting ink is printed more than 4 h after the formation of the spin coating step, the holes are not formed, probably due to the drying and fixation of the ink layer, thus preventing the dewetting process. The final sintering step was heating the glass slide at 250 °C for 20 min on a hot plate. The sintering of the particles was performed by heat treatment, as reported by various researchers,[23,24] and for which a model was published[25] recently.

3. Characterization Methods. The height profiles of the rings were measured by a Veeco Dektak 150 Surface Profiler. The patterns were imaged using an optical microscope (Contour, Bruker) and a HR-SEM microscope (Philips, Sirion HR-SEM).

The electrical measurements were performed by the use of an Extech Milli Ohmmeter, while attaching two electrodes on both pads. The transparency was measured by a spectrometer VARIAN carry 100 bio.

ASSOCIATED CONTENT

Supporting Information

It was found that the diameter of the holes can be controlled by simple means such as the surface tension of the dewetting ink and jetting voltage. The average hole diameter as a function of the applied voltage and of the surface tension is presented. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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