Transparent Conductive Coatings by Printing Coffee Ring Arrays Obtained at Room Temperature

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ABSTRACT We report here a concept for utilization of the "coffee ring effect" and inkjet printing to obtain transparent conductive patterns, which can replace the widely used transparent conductive oxides, such as ITO. The transparent conductive coating is achieved by forming a 2-D array of interconnected metallic rings. The rim of the individual rings is less than 10 μm in width and less than 300 nm in height, surrounding a "hole" with a diameter of about 150 μm; therefore the whole array of the interconnected rings is almost invisible to the naked eye. The rims of the rings are composed of self-assembled, closely packed silver nanoparticles, which make the individual rings and the resulting array electrically conductive. The resulting arrays of rings have a transparency of 95%; resistivity of 0.5 cm^2 was 4 ± 0.5 Ω/□, which is better than conventional ITO transparent thin films.The silver rings and arrays are fabricated by a very simple, low cost process, based on inkjet printing of a dispersion of 0.5 wt % silver nanoparticles (∼20 nm diameter) on plastic substrates. The performance of this transparent conductive coating was demonstrated by using it as an electrode for a plastic electroluminescent device, demonstrating the applicability of this concept in plastics electronics. It is expected that such transparent conductive coatings can be used in a wide range of applications such as displays (LCD, plasma, touch screens, e-paper), lighting devices (electroluminescence, OLED), and solar cells.

KEYWORDS: conductive · transparent · inkjet · coffee ring effect · ITO

Transparent conductive coatings are used in a wide range of applications such as displays (LCD, plasma, touch screens, e-paper, *etc*.), lighting devices (electroluminescence, OLED), and solar cells. The markets for these applications are moving toward flexible and printable products ("plastic electronics"), for which the current technology based on transparent conductive oxides (TCO) has many disadvantages, such as complexity of the manufacturing process, high cost, abundance of the precursors, and relatively low conductivity. Consequently, much effort is devoted nowadays to finding alternatives for the most widely used tin-doped indium oxide, ITO, which will bring high conductivity and yet high transparency.

There are several reports on possible alternatives to obtain transparent conductive coatings. Wu *et al*.[1] showed the application of carbon nanotubes as transparent electrodes, exhibiting transmittance properties in the IR range that are superior to ITO. Jiang *et al*. used Al-doped ZnO films for OLED devices,[2] and Wang *et al*.[3] used ultrathin graphene films for solar-cells.

We propose a nonlithographic concept for obtaining transparent conductive coatings, based on self-assembly of metallic nanoparticles in the form of arrays of interconnected micrometric rings. The rim of each ring has a width of a few micrometers and is composed of closely packed nanoparticles, which results in high electrical conductivity. The center of each ring is actually a hole, having a diameter of about 150 μm. Owing to this dimension, the whole array of the interconnected rings is optically transparent and yet conductive.

The conductive arrays are obtained by inkjet printing of picoliter droplets of silver dispersion onto a flexible substrate. After printing, each printed dot is self-assembled into a ring by the well-known "coffee ring effect".

As reported by Deegan *et al*.,[4] once a millimeter-size droplet of liquid containing solid particles is pinned to a substrate, upon drying of the droplet, the solid particles assemble into a ring. Hu and Larson showed that in the case of a mixture of liquids, the Marangoni effect is also very significant.[5] Sommer suggested a model analyzing the five forces that affect the particles within the droplets and concluded that the main forces responsible for the ring formation are the interactions between the particles and the substrate, and the flux that takes the particles to the periphery.[6]

Previously we have shown[7] that in the case of dispersions of metallic nanoparticles, this effect can lead to the formation of conductive, millimeter size rings without the need for sintering at high temperatures

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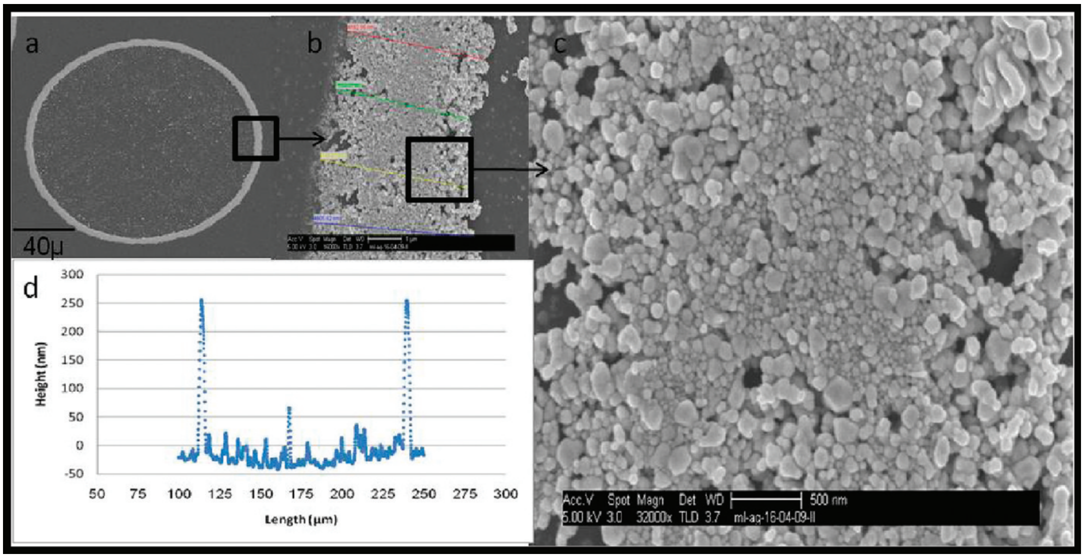

Figure 1. (a) SEM picture of a single ring; (b,c) closer look on the rim of the ring; (d) height profile measurement of a single ring.

due to spontaneous close packing of the silver nanoparticles at the rim of the ring. As shown by Perelaer *et al.*[8] and Kamyshny *et al.*,[9] micrometric individual rings can be obtained by inkjet printing of dispersions of silica particles or microemulsion droplets, respectively.

It should be emphasized that in industrial inkjet printing a uniform pattern is usually required, and the "coffee stain effect" is an undesirable phenomenon.[10,11]

In this paper we show how the coffee ring effect can be utilized to obtain a functional property, namely transparency and conductivity, by forming 2-D arrays composed of interconnected conductive rings. With a low cost process of inkjet printing, the fabrication of the arrays is spontaneous, and the resulting conductivity and transparency are comparable to that of ITO.

Therefore, it is expected that the concept can be utilized in many electronic and electro-optic applications, especially in flexible electronics, for obtaining a replacement for the commonly used TCO.

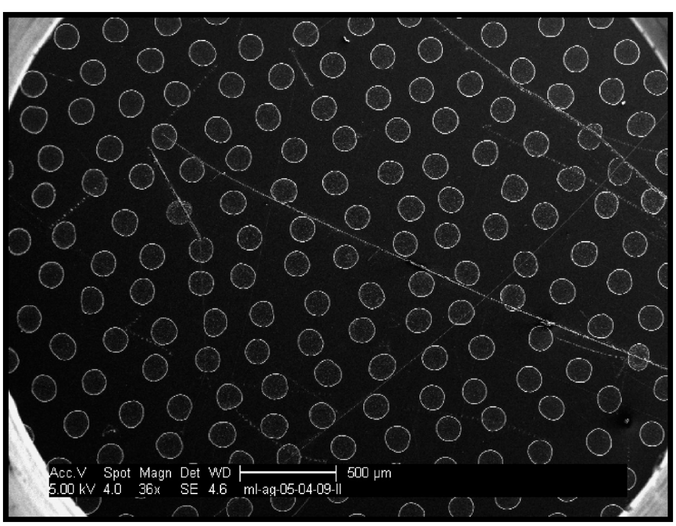

Figure 2. An array of disconnected single rings.

RESULTS AND DISCUSSION

The goal of this research is to obtain a transparent and conductive array composed of connected micrometer-sized rings. To create a 2-D array of rings, it is required first to have a good understanding of the optimal conditions to obtain the building blocks, which are single Ag rings.

After evaluating the conditions for obtaining individual Ag rings, and characterizing their structure and conductivity, the second step, namely printing the individual rings to form a 1-D chain, is conducted, followed by printing of a 2-D array. This array would be conductive only if a sufficient fraction of the rings are electrically connected. Such a ring pattern will remain transparent only if the ring holes are large enough and the ring rim width is less than 10 μm (a width that is almost invisible to the naked eye[12]). Therefore, the formation of the array will be described according to these three steps.

Single Rings. Single rings with a diameter of ~150 μm were obtained by inkjetting the Ag dispersion on polyethylene terphthalate (PET) substrate with the single nozzle print-head. Preliminary printing tests performed by varying the waveform, surface tension, and metal load of the dispersion indicated that during the evaporation of individual droplets circular rings were formed. As presented in Figure 1a, the ring diameter is about 150 μm, while most of the metallic particles are concentrated at the rim of the ring. SEM evaluation (Figure 1b,c) shows that the rim is composed of closely packed silver nanoparticles. Profilometer measurement (Figure 1d) reveals that the height of this layer of nanoparticles is about 250 nm. As shown in Figure 2, the ring formation process can be repeated for a large number of droplets, while the formed rings are very similar in size and shape. This is due to the inkjet printing process, which enables (within the same printing parameters) obtaining a uniform size of droplets and consequently uniform dots, as shown by Perelaer *et al.*[13]

To obtain a conductive array composed of rings, each ring should be conductive. Therefore, at the first stage, resistivity measurements of individual rings were performed by connecting the ring to microelectrodes obtained by vapor deposition of Au/Cr bilayer through a suitable mask.

To achieve low resistivity of the rings without heating the plastic substrate, we applied a recently developed method that causes close packing of the particles due to surface charge neutralization of the nanoparticles[14] upon exposure to HCl vapors. The resistivity of such individual rings (calculated from the measured resistance and the ring cross-section area and length), was 4.3 ($\pm$0.7) $\times$ 10^{-7} Ωm, which is only 7 times greater than that for bulk silver. This is quite remarkable, considering the granularity of the ring. It should be noted that such low resistivities were reported until now only after a prolonged heating process. This value remained constant for at least 3 months.

Further insight into the structural conductance properties of the silver ring is provided by the C-AFM data presented in Figure 3. The topographic 3-D (Figure 3a) image shows a continuous line having maximal height of 400 nm and width of about 7 μm. The corresponding 2-D current map (Figure 3c) and image (Figure 3b) show that the line is indeed conductive. It should be emphasized that even though a small area of the ring is scanned, the fact that this area of the ring is conductive proves electrical continuity over a much larger range, at least as far as the distance to the Au/Cr counter-electrode.

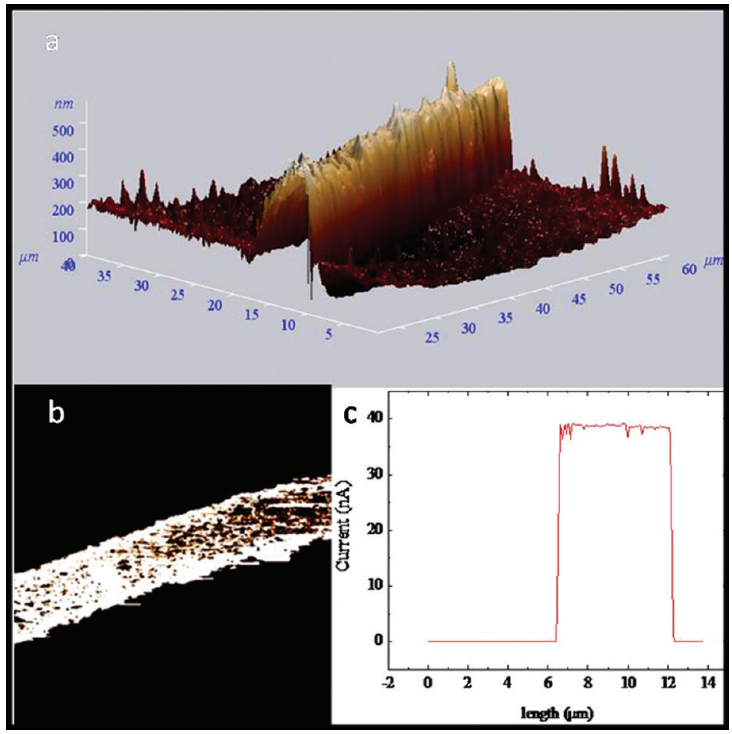

Figure 3. Conductive AFM measurement of the rim of a single Ag ring. (a) Topographic image. The corresponding current image, acquired at tip bias of 0.5 V, is presented in panel b. The current range in the cross section of the silver line (c) is 0−40 nA (the saturation current in the measurement was 40 nA).

Chains of Connected Rings. Chains composed of overlapping printed rings were obtained by printing a first forward line of rings with predetermined spaces between the rings, followed by printing a backward, second line of rings, with a proper distance adjustment between the two lines. Optimization of the chain formation process was achieved by adjusting the jetting frequency (35 Hz) and the substrate movement (10000 μm/s). Part of such a chain is shown in Figure 4.

It should be noted that the deposition of one ring on top of another was previously reported to lead to the destruction of the first ring due to its redispersion (Deegan *et al.*[4]). However, by adjusting various ink and printing parameters such as concentration of silver nanoparticles in the ink, delay between line printing, and substrate temperature, the close packing of the silver particles, while dried, was achieved, enabling us to overcome the possible redispersion of the predeposited rings. By controlling the positioning of the rings, continuous chains

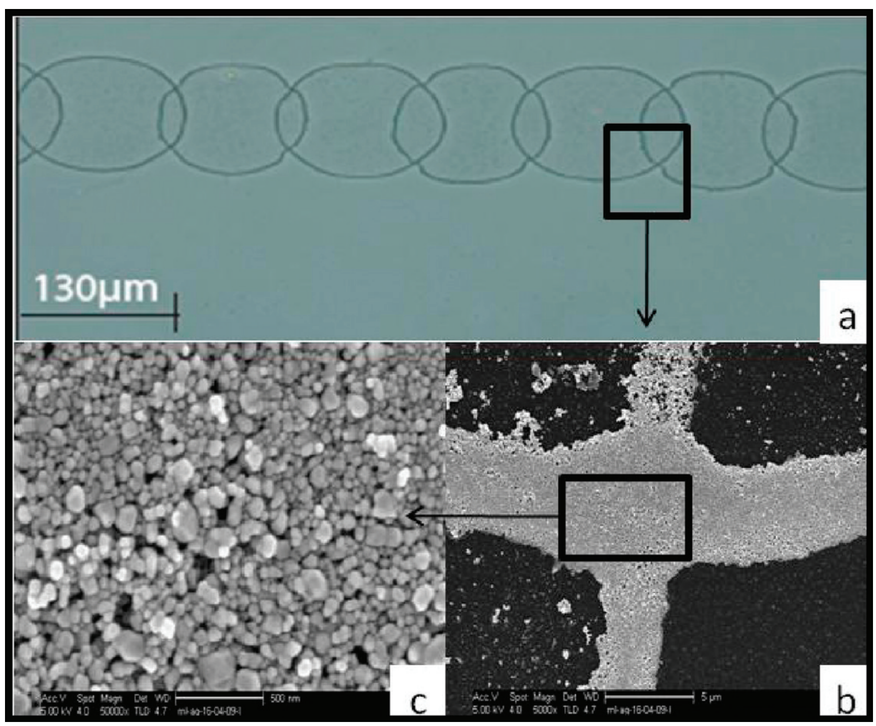

Figure 4. (a) Light microscope image of a chain of rings. (b,c) SEM images showing a closer look on the junction between two rings. It is clearly seen that close-packing of the particles is not damaged by the new junction.

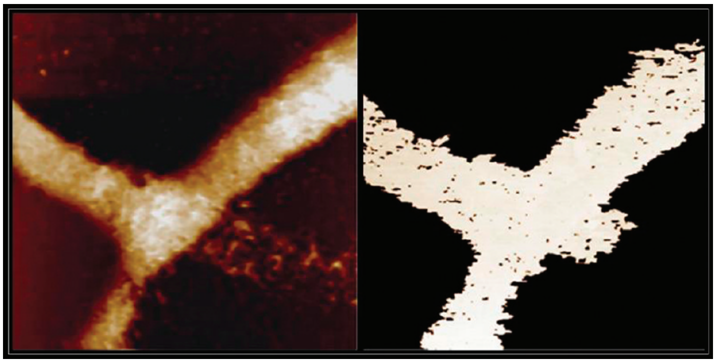

Figure 5. A 40 × 40 μm² topographic image (left) and corresponding current image measured with tip bias of 1 V (right). The current image range is 0−40 nA (the saturation current in the measurement was 40 nA).

with fine contact between the rings were formed (Figure 4b,c). Indeed, comparison between the topographic AFM image (Figure 5a) and the current map image (Figure 5b) of the same area (by C-AFM) reveals that the junction between the rings is not only geometrically continuous, but also has high electrical connectivity.

Resistance measurements performed for various chains composed of 4−20 connected rings revealed that the (average) resistivity is 5.1 (±0.5) 10^{-7} Ωm, which is close to the resistivity of an individual ring (described in the previous section), further demonstrating the high quality of the junctions between the rings. This resistivity was constant for at least 3 months at room temperature. It should be noted that this resistivity is much lower than that obtained by ITO, which is typically in the range of 10^{-6} Ωm.[15]

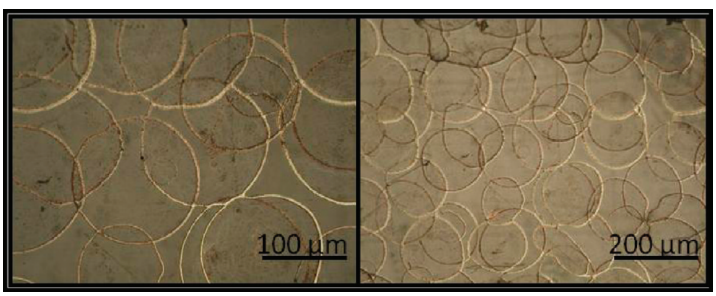

Figure 6. Array of interconnected rings.

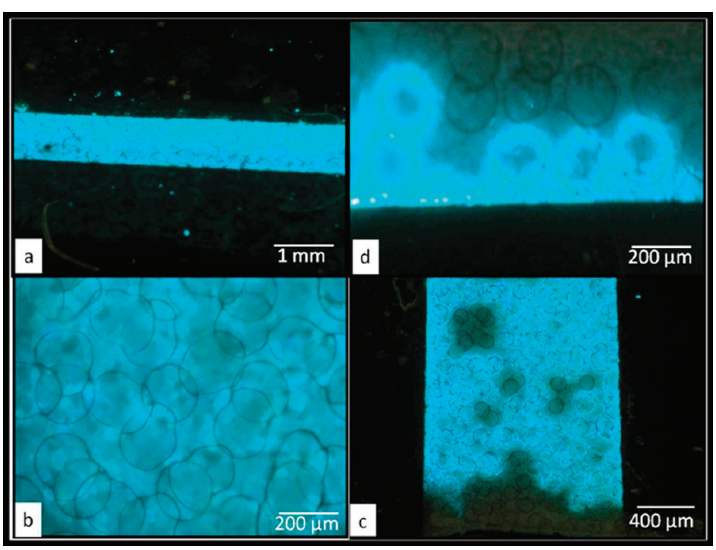

Figure 7. Electro-luminescent glow from the rings: (a,b) 2 mm × 1 cm device at different magnifications, (c) defects in the pattern in which some rings are not connected to the whole array, (d) glow from a few or a single ring.

2-D Arrays. Two-dimensional (2-D) arrays of such rings were formed by repeating the chain formation procedure for a large number of lines, while keeping a constant distance between the lines. As shown in Figure 6, 2-D arrays composed of connected chains could be obtained. The array is actually composed mainly of holes (the inner part of each ring), ~150 μm in diameter, which are connected by narrow lines, about 5 μm in width, located around each hole. The sheet resistance of such a 2-D array (sample area of 0.5 cm²) was very low, 4 ± 0.5 Ω/□. It should be noted that qualitative bending experiments show that these values remained constant even after bending the substrate at angles below about 20°, showing that the arrays may be suitable for applications in which flexibility is required. For comparison, the typical sheet resistance of ITO thin films that have more than 80% transparency is much greater, in the range of 20−100Ω/□.[16,17]

Obviously, the 5 μm lines are almost invisible to the naked eye, thus the 2-D pattern is almost transparent. Quantitatively, the transmittance measured by a spectrophotometer at 400−800 nm was as great as 95(±3) % T. In the graphic table of contents associated with this paper, the transparency of the conductive array is demonstrated by placing it on top of text, which can be easily read.

To further test these ring patterns as a TCO replacement, these conductive arrays were evaluated as the transparent electrode in an electroluminescent device. The device was fabricated on top of the transparent ring array by depositing layers of ZnS and $BaTiO_3$ by conventional screen printing, followed by deposition of a second silver electrode. As demonstrated in Figure 7a, for a 2 mm × 1 cm device, the printed ring array is indeed conductive and transparent. As shown in Figure 7b, in the areas in which the rings are connected there is a uniform light emission by the device (the decay length for emission was estimated to be about 20 μm). In Figure 7c it can be seen that when there are defects in the pattern, namely some rings are not connected to the whole array, black islands are formed. It should be noted that the glow can be limited to just a few rings or even to a single ring (Figure 7d), thus enabling formation of a miniature electroluminescent device.

CONCLUSIONS

A concept for obtaining transparent conductive coating was demonstrated, enabling replacement of conventional TCO, such as ITO. The transparent conductive coating is achieved by forming a 2-D array of interconnected metallic rings. The rim of the ring has a width of less than 10 μm surrounding a "hole" with a diameter of about 150 μm; therefore the whole array is almost invisible to the naked eye. The rims of the rings are composed of self-assembled, closely packed silver nanoparticles and therefore this narrow line is electrically conductive. The resulting arrays of rings have a transparency of 95% and resistivity of 0.5 cm^2 was $4 \pm 0.5\ \Omega/\square$, which is better than conventional ITO transparent thin films.

The array can be fabricated by a simple inkjet printing process, thus making it industrially feasible. It was demonstrated that this 2-D transparent conductive array can be applied as a transparent electroluminescent device. It is expected that because of its superb features (transparency >90%, low sheet resistance, and sustainability to bending) such arrays are suitable to be used as transparent conductive films in applications such as LCDs, electroluminescence devices, solar cells *etc*.

EXPERIMENTAL SECTION

Silver Ink. The aqueous ink contained 0.5 wt % dispersed silver nanoparticles (NP) with a diameter of 5 to 20 nm, stabilized by poly(acrylic acid) (synthesized as described previously[18]). The surface tension of the ink was adjusted to 30 mN/m by the use of Byk 348 (Byk Chemie). The pH was set to 10 using amino methyl propanol.

Printing. The printing of the dispersion was performed by a Microfab JetDrive III printer with a 60 μm wide single nozzle. The applied waveform for all the printing experiments was voltage, 110 V; rise time, 3 μs; echo time, 15 μs; dwell time, 30 μs; and fall time, 5 μs. As expected, as the voltage increased (from the minimal voltage of 20 V), the droplet size increased as well, thus enlarging the rings diameter. Further increase above 110 V was not tested because of device limitation. The dwell time was also increased in steps of 5 μs up to a value of 40 μs (in each change the echo time was double the value of the dwell time), which also caused the droplet volume and rings diameter to increase. Changing the dwell time and the voltage did not effect the edge profile, as it remained in a parabolic shape. The movement of the substrate was performed by a DMC-21x3 XY table (Galil Motion Control, Inc.).

The substrate temperature was set to 30 °C with a Peltier heater/cooler, and the humidity within the printing chamber was 30−40% RH.

Analysis. The cross-sectional profiles of the rings were measured by the use of a Veeco Dektak 150+ Surface Profiler. The surface-tension measurements were carried out by a pendant drop tensiometer (First-Ten-Angstrom 32). The ring patterns were imaged using an optical microscope and a HR-SEM microscope (Philips, Sirion HR-SEM).

Once the patterns were obtained and analyzed, conductivity measurements were performed by attachment of two electrodes on both ends of the pattern (individual ring, a chain composed of several connected rings, 2-D array). The electrodes were fabricated by evaporating a thick gold film on top of a thick Cr adhesion layer, using an Edwards evaporator (base pressure was below 10^{-6} Torr). To avoid sample overheating, the substrate was cooled by anchoring to a nitrogen trap. The temperature was measured with a temperature indicator (3M, 40−50−60 °C) inserted into the chamber. After the electrodes were prepared, the pattern resistance was measured by the use of a Kiethley 2400 multimeter.

The pattern local conductance was mapped by conducive atomic force microscopy (C-AFM, NT-MDT "Solver" AFM system with cantilevers having 0.03 N/m stiffness and Ti−Pt-coated Si tips of radius less than 35 nm).

The four-layer (PET/ring pattern/ZnS/$BaTiO_3$) electroluminescent device was fabricated as follows: Interconnected ring patterns were printed and self-assembled on PET (poly(ethylene terephthalate)), a layer of ZnS particles was screen-printed (MOBIChem Scientific Engineering), and, after drying, a second double layer of BaTitante was screen-printed. On top of the BaTitanat, a continuous conductive layer composed of silver nanoparticles was placed by printing or draw-down.

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