Highly-facile template-based selective electroless metallization of micro- and nanopatterns for plastic electronics and plasmonics†

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The authors reported a facile, scalable, high-yield, universal fabrication approach for creating micro- and nanoscale metallic patterns for flexible electronic and plasmonic applications through imprint-transfer of catalytic Pd nanoparticles using a reusable imprint mold with selectively adsorbed catalytic nanoparticles and selective electroless deposition of metals. Metallic patterns are mass-produced on flexible plastics according to the predefined micro-/nanofeatures on the imprint mold without any chemical modification on the substrate, which significantly reduces both fabrication costs and environmental pollution, compared to other methods utilizing electroless deposition. The excellent dimensional scalability and material versatility of this method have been confirmed by fabricating metallic micromeshes with a linewidth down to 3 μm, and metallic nanodisk arrays with a pitch of 500 nm. Using this method, flexible transparent electrodes were constructed on Cu micromesh-patterned plastic films with transmittance values higher than 75% and sheet resistance values below 0.4 Ohms sq−1, as well as high figures of merit up to 4 × 103. This method is further demonstrated in the fabrication of flexible thin-film heaters, electroluminescent displays, and flexible printed circuits, as well as plasmonic refractometric sensors.

1. Introduction

Recently, flexible electronics and optoelectronics have been attracting increasing research attention because of their promising applications in many practical fields, such as wearable electronics, medical implants, and portable devices, to name a few.1–5 Novel flexible devices such as solar cells,6 light-emitting diodes,7 touch panels,8 and smart windows,9 rely on the evolution of flexible conductive metallic micro- and nanopatterns.8 Key to such applications is the fabrication of metallic micro- and nanopatterns on flexible substrates. The cost-effective and high-quality fabrication of these flexible and stretchable conductive components, which contain multi-scale features of continuous metals on plastic substrates, is of great importance but still remains challenging. For example, the most commonly used approach in the flexible printed circuit industry is based on the lithography and etching process, which wastes materials, is expensive, causes pollution, and is complicated. New techniques that overcome such limitations have been investigated. One of the most intensively studied methods is inkjet printing using metallic nanoparticle ink.9–12 However, this process is often hindered by the low conductivity of the metallic nanoparticle ink compared with bulk metals and oxidation of the metallic nanoparticles.13,14 Another method for the fabrication of metallic patterns on plastic substrates is based on the combination of three well-developed techniques, i.e., lithography, electroplating and imprint-transfer. Such a technique has been proven to be successful for the fabrication of high-performance micro-mesh transparent electrodes (TEs) and transparent polyaniline mesh chemiresistive ammonia gas sensors.15,16 However, the electroplating process used in this technique requires a patterned intermediate conductive substrate as the electroplating template, which is then transferred to plastic substrates, which inevitably increases production complexity and costs.

Selective electroless deposition (ELD) of metals, which relies on an autocatalytic redox reaction to deposit a thin-layer metal on a catalyst-preloaded substrate, has been explored and has demonstrated its potential to overcome these shortcomings.
The conductivity of the electroless plated metal can reach the same level as that of the bulk metal. However, as an open problem, it is known that untreated flexible plastics cannot well grasp catalyst due to the lack of binding sites, and simple physical adsorption often leads to the diffusion of the catalyst and a poor adhesive strength of the deposited metals. Practically, the modification of bare plastic surfaces to enhance the catalyst adsorption and improve the adhesion of deposited metal is necessary, and numerous efforts have been devoted to the development of selective ELD on flexible plastics. For example, selective ELD on flexible substrates has been demonstrated through polymer grafting, surface silanization, deposition of polyelectrolytes, inkjet printing of ion-adsorption nanoparticles, laser printing of poly(4-vinylpyridine), photopatterning of functionalized polyimide, matrix-assisted catalytic printing, and patterning of a catalyst-adsorption layer. However, all of these methods rely on the chemical modification of plastic surfaces, and the surface modification processes are usually expensive, complicated, and processed in harsh environments (in volatile organic solvents). Microcontact printing (μCP) has been developed and investigated for selective electroless metallization by printing catalytic nanoparticles or functional molecular groups for activation using an inked PDMS stamp. However, an inking process is needed, and the substrates used in μCP often require a chemical modification for catalyst adsorption and metal deposition, which inevitably makes the fabrication process complicated. The durability of the soft PDMS stamp also restricts the further application of μCP in practical manufacturing. Polymer-assisted metal deposition (PAMD) has also been developed as a solution-processed metallization on arbitrary surfaces for the fabrication of multiscale conductors and transparent electrodes. But a copolymer ink coating is needed in the PAMD strategy, and such a coating may change the dielectric properties of the substrate, which is essential for many electronic applications. Therefore, significant progress in the selective ELD technique must be achieved before it can be considered as a potential alternative to the conventional lithography and etching process.

In this research, an environmentally-friendly and cost-effective approach for metallization on thermoplastics by imprint-transfer of catalytic palladium nanoparticles (PdNPs) and electroless plating for mass production of metallic micro-/nanopatterns has been proposed and experimentally demonstrated. An imprint mold consisting of a glass backbone, a PdNP-repellent resin interlayer, a nickel pattern carrying micro-/nanopatterning information, and selectively adsorbed catalytic nanoparticles (SACN), termed a SACN-mold, is employed to synchronously transfer the micro-/nanopattern as well as PdNPs onto thermoplastic substrates with high patterning resolution down to hundreds of nanometers without any pretreatment on the plastic substrates. An electroless deposition process is then employed to selectively deposit metal inside the PdNP-activated imprinted patterns. Because the PdNPs were fully embedded in the plastic substrates, electroless deposited metals were firmly attached to the substrates, which provides excellent mechanical stability for electronic devices based on them. Flexible TEs with Cu micromeshes were fabricated on flexible substrates using this method, demonstrating their excellent optical, electrical, mechanical and chemical performances. Thin-film heaters, flexible electroluminescent displays, and FPCs were constructed on flexible substrates using the proposed method to demonstrate their practical potentiality and versatility in the fabrication of electronic and optoelectronic devices. Moreover, 500 nm-pitch Ag nanodisk arrays were realized on a flexible substrate and investigated as a plasmonic refractometric sensing platform to demonstrate the versatility of the method in patterning metallic structures.

2. Results and discussion

2.1 Imprint-transfer patterning of PdNPs for electroless metallization of micro- and nanoscale structures

The facile and scalable metallization of micro- and nanoscale structures was achieved by a combination of two fabrication processes, including transfer patterning of PdNPs onto thermoplastics adapted from thermal nanoimprint lithography and electroless deposition of metals on the PdNPs-activated area. The fabrication process is schematically shown in Fig. 1a–e. A Ni mold consisting of a glass backbone, a resin interlayer, and a nickel-mesh pattern is employed as the carrier of both the pattern and PdNPs during the SACN process (Fig. 1a). After immersion in a 300 nM PdNP solution (consisting of 13 nm diameter PVP-capsuled PdNPs, see the ESL† for a typical TEM image) at 40 °C for 300 seconds, PdNPs were selectively adsorbed on the nickel-mesh surfaces rather than the resin surfaces because of the hydrophobicity of the resin, which leads to a SACN-mold for the following imprinting process (Fig. 1b). Thereafter, the SACN-mold was used to synchronously transfer both the mesh-pattern and PdNPs onto a thermoplastic film using a thermal imprinting process (Fig. 1c). After cooling down the stack to the demolding temperature, the thermoplastic film was manually peeled off from the SACN-mold, with the mesh-pattern transferred and PdNPs firmly embedded in the trenches of the mesh, which could potentially enhance the adhesive strength of the PdNPs on the substrate (Fig. 1d). Thereafter, metals were selectively deposited on the PdNP-activated trenches to form a uniform metallic pattern by immersing the film in various electroless plating baths (Fig. 1e). Finally, the film was rinsed in deionized water and stored at 60 °C for 30 min to release the internal stress and further enhance the adhesion of the deposited metal layer. A Cu micromesh was fabricated on a 200 μm-thick polyethylene terephthalate (PET) film through this process as a demonstration and it showed excellent uniformity and transparency (Fig. 1f). The entire fabrication process is solution-based, performed in the ambient environment and suitable for large-area fabrication. Additionally, this process can be readily standardized and used during industrial production.

2.2 Fabrication of an imprint mold for selective adsorption of catalytic nanoparticles (SACN)

The contrast of selective PdNP adsorption on the SACN-mold is essential in the proposed ELD method. To enhance the contrast
of PdNP adsorption, a Ni pattern was selected as the adsorbing layer and a UV-curable resin was chosen as the interlayer between the Ni pattern and the glass substrate, because Ni has high affinity to the PdNPs but the low-surface-energy nature of the UV-cured resin makes it PdNP-repellent. The fabrication of an imprint mold for the SACN process is schematically illustrated in Fig. 2. In a typical fabrication process, a resist was first spin-coated onto a conductive ITO glass substrate, and a lithographic process was conducted to create a micro-/nanoscale pattern in the resist layer upon ultraviolet (UV) exposure and development or nanoimprinting (Fig. 2a). Then, Ni was deposited inside the lithographically defined exposed trenches and it filled the trenches with a uniform Ni layer (Fig. 2b). Next, a UV-curable resin (NOA-61, Norland Products, USA) was poured onto the Ni-plated ITO substrate (Fig. 2c) and covered with a glass substrate with pressure to form a uniform interlayer of the resin between the resist and the glass substrate (Fig. 2d). After exposure to UV to fully cure the resin (Fig. 2e), the mold was manually separated from the ITO glass, with the nickel pattern transferred by the resin (Fig. 2f). The mold was baked at 130 °C for 5 min before use to further increase the adhesion with Ni and harden the resin.

A 50 μm pitch micromesh patterned SACN-mold was fabricated through this process as a demonstration and further used to fabricate flexible TEs and construct electronic devices. The scanning electron microscopy (SEM) images in Fig. 3a–d show the morphological characterization of the Ni mold and SACN-mold at different stages of the fabrication. Fig. 3a displays the top and cross-sectional view SEM images of the trenches of the photoresist created using photolithography. The photoresist mesh had a 50 μm pitch, and its trench width and depth were 2.6 μm and 650 nm, respectively. Fig. 3b presents the electroplated Ni mesh inside the trenches on the photoresist film under a constant current density (5 mA cm$^{-2}$). As was evident from the image, the thickness of the Ni mesh was approximately 350 nm and could be controlled by the electroplating time. In the presented experiments, the thickness of the Ni ranges from 350 nm to 700 nm for different applications. Fig. 3c shows that the Ni mesh was finally transferred to a glass substrate by the NOA-61 resin. The Ni mesh was supported by an NOA-61 resin backbone and exhibited a protrusion structure corresponding to the original trench pattern on the photoresist film. Energy-dispersive X-ray spectroscopy (EDS) analysis also confirmed the successful transfer of electroplated Ni on the NOA-61 resin (Fig. S2, ESI†). Fig. 3d displays the SEM image of the SACN-mold after adsorption of PdNPs; the cross-sectional view of a single PdNP-coated Ni mesh on the SACN-mold in the inset in Fig. 3d clearly shows that a thin layer (approximately 110 nm) of PdNPs was selectively deposited on the Ni mesh, which is further confirmed by EDS analysis in Fig. S3 (ESI†). Note: the structures on the SACN-mold were slightly distorted and the PdNP layer was separated from the Ni mesh in the cross-sectional SEM images after cutting the sample.

2.3 Fabrication of flexible transparent electrodes (TEs) using the SACN-mold

Our fabrication process allows easy ELD on flexible substrates at microscale patterning resolution. A flexible TE with a Cu micromesh
embedded on a PET film was fabricated through this process using a 50 μm pitch micromesh patterned SACN-mold as a demonstration. As displayed in Fig. 1f, the Cu-mesh electrode prototype shows excellent uniformity and transparency. The SEM and SEM-EDS images in Fig. 4a–c show the morphological characterization of the Cu TEs at different stages of fabrication. Fig. 4a displays the SEM and SEM-EDS images of the SACN-mold with PdNPs selectively adsorbed on the Ni mesh, which is proved by the SEM-EDS analysis (inset in Fig. 4a). A detailed morphology of the adsorbed PdNPs can be found in the ESI† (Fig. S4). The linewidth of the Ni mesh on the SACN-mold was measured to be 2.6 μm from the zoom-in SEM image. After the thermal nanoimprint process, the PdNP mesh was transferred and fully embedded on the PET film from the SACN-mold, as presented in Fig. 4b. No nickel residuals were observed on the imprinted PET substrate and PdNPs were only imprint-transferred on the mesh area as displayed in the EDS images in Fig. S5 (ESI†) as expected, which proves the excellent durability of the SACN-mold. The linewidth of the trenches was 2.6 μm, which also corresponds to the original SACN-mold. Fig. 4c shows the electroless deposited Cu mesh inside the PdNP-activated mesh trenches after immersion in an electroless plating bath for 30 min, and Cu was only deposited in the PdNP-activated trenches as shown in the EDS image in Fig. S6b (ESI†). The EDS signal of PdNPs under Cu was also revealed in the SEM-EDS analysis but the signal was weakened by the deposited Cu layer (Fig. S6c, ESI†). As was evident from the SEM images, the Cu mesh had a linewidth of approximately 3.2 μm, which is slightly wider than the linewidths of both the
Ni meshes on the original imprint mold and imprinted trenches, because of the isotropic nature of the ELD process.

The fabrication process was further investigated by changing the electroless deposition time to fabricate Cu meshes with varying thicknesses, in which the plating temperature (40 °C) and substrate size (3 × 3 cm²) were maintained. Fig. 5a shows the transmittances of typical Cu-mesh electrodes with plating times ranging from 5 min to 30 min in the 450–900 nm wavelength range. No significant differences in the transmittance value among the Cu-mesh electrodes with different plating times were observed, which proves the excellent controllability of the deposition of metals in the lateral dimensions because the ELD process is limited only inside the PdNP-activated trenches. Meanwhile, the sheet resistance of the electrodes can be substantially reduced when the plating time is increased, as displayed in Fig. 5b. A low sheet resistance of 0.38 Ohms sq⁻¹ was observed for the 30 min Cu-mesh electrode, and the transmittance at a wavelength of 550 nm was still above 75%.

To further study how the plating time affects the overall performance of the transparent electrodes, a widely used criterion, the figure of merit (FoM), namely, the ratio of the electrical conductance to the optical conductance ($\sigma_{dc}/\sigma_{opt}$), was calculated for all the electrodes (displayed in Fig. 5b) by using the following expression:\textsuperscript{37–39}

$$\text{FoM} = \frac{\sigma_{dc}}{\sigma_{opt}} = \frac{188.5}{R_s \left( \frac{1}{\sqrt{T}} - 1 \right)}$$  \hspace{1cm} (1)

where $T$ is the optical transmittance at a wavelength of 550 nm and $R_s$ is the sheet resistance of the electrode. Fig. 5b shows the plot of the FoM as a function of plating time. The presented curve indicates that the plating time has a considerable effect on the sheet resistance and hence on the value of the FoM by increasing the thickness of the plated Cu mesh and enhancing its electrical conductivity. Our Cu-mesh electrode achieved a FoM of more than $4 \times 10^3$, which is much better than that of the commercial indium tin oxide (ITO).\textsuperscript{40}

A crucial advantage of the method is that the embedded nature of PdNPs greatly improves the adhesion of the electroless deposited metal with the substrate by providing a mechanically anchored attachment for the deposited Cu with the substrate. The excellent adhesion was investigated by comparing an embedded Cu ‘HK’ word pattern deposited on the imprint-transferred PdNPs on a PET film with the same pattern fabricated using a conventional process with PdNPs directly
deposited on a photolithographically patterned conditioned PET film. Movie S1 (ESI†) shows that Cu deposited by a conventional method suffers easy delamination by a 3M scotch adhesive tape, but the Cu pattern fabricated through this novel process did not change significantly. The optical microscopy characterization in Fig. S7 (ESI†) evidences that a large area of the Cu layer was stripped by the adhesive tape, while only microscale pieces of Cu were observed on the stripped tape for the embedded structure. Moreover, no further delamination of Cu was observed in optical microscopy characterization after an additional 10 cycles of repetitive stripping.

The Cu-mesh electrode also shows great enhancement in its stability upon bending, heating, and chemical attack because of the embedded nature of the imprint-transferred PdNPs. Fig. 6a shows the variation in the sheet resistance of the Cu-mesh electrode prototype as a function of the number of cycles for repeated tensile bending to a radius of 4 mm in comparison with a commercial ITO/PET film. The curves show a lack of significant changes that occur up to 1000 bending cycles, while, as a comparison, the variation in the ITO/PET is larger than 600 times after 400 bending cycles. The environmental stability of the as-fabricated flexible Cu-mesh electrode was evaluated by exposing the electrodes to high-temperature conditions (40 °C and 80 °C) and dipping them in ethanol, methanol, and toluene. Fig. 6b shows that after heating at 40 °C and 80 °C for 6 h, the sheet resistances of the electrode remained unchanged. Fig. 6c shows the variation in the sheet resistances of the electrode after dipping in ethanol, methanol, and toluene for 30 min. The results clearly indicate that no obvious changes in the sheet resistances of the electrode were observed, which also proves the superior stability of our flexible TEs upon chemical attack.

2.4 Flexible thin-film heaters, electroluminescent displays, and flexible printed circuits

Thin-film heaters have various applications such as defrosting, defogging, thermal-based sensing, and thermal therapy.41–50 The key requirements for a high-performance thin-film heater include homogeneous and steady temperature distribution over large area, fast heating and cooling rates, as well as low power consumption. Therefore, the low sheet-resistance, large-area, and facile fabrication nature makes our TE a good candidate. A flexible thin-film heater was then constructed on an electroless deposited Ni TE for practical application, as schematically illustrated in Fig. 7a. A DC voltage was supplied to the thin-film heater through Cu electrodes at the two ends of the film, and the Joule heating performance of the film was characterized using an infrared thermal imaging camera. Fig. 7b displays the time-dependent temperature changes of the heater experimentally measured under different applied DC voltages of 3.70 V, 2.80 V and 1.90 V. The temperature was generated and saturated to a desired value within 20 s under the applied voltage. The environmental temperature was maintained at 23 °C in the presented experiments. Movie S2 (ESI†) displays the temperature distribution of the heater when a voltage of 3.70 V was supplied. The relationship between the center temperature of the heater and the applied DC voltage is shown in Fig. 7c. A 100 μm-thick thermochromic ink (color to clear at 43 °C) was then blade-coated on the heater to visualize the heat generation process. Fig. 7d presents (1) a photograph of the ink-coated heater before applying the voltage and (2) a photograph and (3) an infrared image after being supplied with an external voltage of 3.70 V. The vanished color indicates the generation of heat on the film and Movie S3 (ESI†) shows the rapid response of the thermochromic ink due to the high efficiency of our heating device. (Note: cyclic olefin copolymer
(COC, grade 5013) was used as the substrate material and Ni TEs were chosen in thin-film heaters for better performances.

A flexible electroluminescent display was also constructed as another application of our selective ELD method; the configuration of the display is schematically illustrated in Fig. 7e. The flexible electroluminescent display consists of three layers: one transparent electrode layer (Cu TE), one light emitting layer (Cu doped Zn sulfide particles), and one conductive Cu layer with the desired pattern. These layers are stacked to form a sandwich structure, and when an AC voltage is supplied across the electrodes, ZnS:Cu particles will be excited and emit light. The SACN-mold used for fabricating a patterned Cu layer is shown in Fig. 7f. Fig. 7g displays a representative image of the electroluminescent display fabricated on a 3/C2/cm2 PET film. As displayed in the figure, the light emitted from the display is bright and uniform because of the low sheet resistance of our TEs.

We also fabricated an FPC to demonstrate the scalability and versatility of our method in the field of electronic device manufacturing. Fig. 7h shows a photograph of an FPC on the PET film. Compared with the commonly used methods in the FPC industry, the high-throughput, low-cost, etching-free, environmentally-friendly, and facile fabrication makes our selective electroless plating method a unique approach for the FPC industry.

2.5 Ag nanodisk array for plasmonic refractometric sensing

Benefiting from the well-developed NIL process, our proposed fabrication is also capable of patterning nanoscale metallic structures, and such structures have been widely used in plasmonic refractometric sensing applications. To demonstrate the dimensional versatility of our method, a Ag nanodisk array was fabricated on a PET film through this process and employed as a plasmonic refractive index sensor. A SACN-mold with an approximately 50 nm-thick, 500 nm-pitch Ni nanodisk array on NOA-61 resin was used in the nanoimprint lithography process. As was evident from Fig. 8a, a 500 nm-pitch Ag nanodisk array was successfully deposited on a PET film. To examine the performance of the Ag nanodisk array as a refractometric sensor, we measured the transmittance spectra of the film at normal incidence when covered with liquids with varying refractive indices. In the experiments, 10 μL of standard liquids (Cargille Labs, USA) with refractive indexes of 1.30–1.44 in steps of 0.02 were dropped on the front side of the film. As displayed in Fig. 8b, redshifts of P1 and D1 with increasing refractive indices were observed. The spectral shift of P1 and D1 versus refractive index is plotted and linearly fitted in Fig. 8c. A high refractive index sensitivity of 407.8 nm RIU⁻¹ with a good linear dependence was obtained for P1. On the other hand, the sensitivity of D1 was only 100.1 nm RIU⁻¹. The result implies that our plasmonic refractometric sensor works within the working wavelength range of Si photodiodes (190–1100 nm), which could greatly reduce the cost of the configuration of measurements by employing cheaper Si-photodiode-based spectrometers.

3. Conclusions

In summary, we proposed and demonstrated a universal fabrication process for micro- and nanoscale metallic patterns on flexible substrates using a novel imprint-transfer method to synchronously transfer patterns and PdNPs onto plastic surfaces and an ELD process. A SACN-mold consisting of a PdNP-adsorbing Ni layer, a PdNP-repelling resin interlayer, a rigid glass backbone, and selectively adsorbed PdNPs was fabricated using photolithography, electrodeposition and imprint-transfer processes. Metals were selectively electroless
deposited on thermoplastic films catalyzed by the thermal imprint-transferred PdNPs. Flexible TEs with good electrical conductivity and optic transmittance were fabricated with this method as practical demonstrations. A high FoM value of \( \frac{4}{10^3} \) was demonstrated on the Cu TE prototypes. Excellent mechanical, chemical, and environment stabilities were observed on the prototype electrodes. Flexible electroluminescent displays and FPCs were constructed with TEs fabricated using this method. Moreover, a plasmonic refractometric sensor with excellent performance was constructed on the electroless deposited Ag nanodisk array. The developed fabrication process was solution-processed, etching-free, and environmentally-friendly and could potentially be adapted for the high-throughput and low-cost manufacture of various electronic, optoelectronic, and plasmonic devices.

4. Experimental

4.1 Materials

PET films were purchased from Dongguan Boyuan Plastics (Dongguan, China). COC films (Grade 5013) were bought from TOPAS (Frankfurt, Germany). Silver nitrate, ammonium chloride, and palladium chloride were all of AR grade obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Copper sulfate pentahydrate, nickel sulfate heptahydrate, potassium sodium tartrate, ethylenediaminetetraacetic acid disodium, sodium hydroxide, \( 2,2' \)-bipyridyl, and potassium ferrocyanide were all of AR grade purchased from Acros Organics (New Jersey, USA). Formaldehyde, hydrogen peroxide (30%), sodium hypophosphite, sodium citrate, PVP (M.W. 8000) and ammonium chloride were of AR grade obtained from J&K Chemicals (Shenzhen, China). Zonyl FSN was purchased from DuPont (Wilmington, USA).

4.2 Preparation of PdNPs

The preparation of PdNPs was adapted from our published work. 900 mg ammonium chloride was first dissolved in 50 mL deionized water by magnetic stirring, and then 300 mg palladium chloride was added to the solution until it completely dissolved. Afterwards, 940 mg PVP (M.W. 8000) was added to the solution until a homogenous solution was formed (solution A). 600 mg ascorbic acid was then dissolved in another 50 mL of deionized water (solution B). Finally, solution B was added dropwise into solution A at a rate of 5 mL min\(^{-1}\) under magnetic stirring, and the mixture was stirred for another 4 h.

4.3 Fabrication of imprint molds for SACN

The indium tin oxide (ITO) glass substrates were first cut into \( 3 \times 3 \) cm\(^2\) pieces. These ITO glass pieces were cleaned with a cotton swab and rinsed thoroughly in deionized water, and then treated with oxygen plasma (Potentlube, China) for 5 min. The samples were then further cleaned by ultrasonication in acetone and isopropanol for 300 s before being dried under nitrogen flow. Then a 945 nm-thick layer of the photoresist (AZ 1500, MicroChemicals, USA) was spin-coated on the ITO substrate and baked at 110 °C for 1 min. Thereafter, the photoresist was exposed using a URE-2000/35 UV mask aligner (Chinese Academy of Sciences, China) for an exposure dose of 55 mJ cm\(^{-2}\) at 365 nm wavelength. The photoresist was then developed using a URE-2000/35 UV mask aligner (Chinese Academy of Sciences, China) for an exposure dose of 55 mJ cm\(^{-2}\) at 365 nm wavelength. The photoresist was then developed using an AZ 351B developer (Clariant, Switzerland) for 1 min. The samples were finally rinsed in deionized water and dried under nitrogen flow. For the imprint mold with a
nanodisk array, a residual-layer-free thermal nanoimprint lithography process was performed on the ITO glass substrate instead.

Ni was deposited on the trenches of lithographically defined patterns on ITO glass substrates through an electrodeposition process. First, the patterned substrate was treated with an anti-sticking agent (perfluorodecytrimchlorosilane, Sigma Aldrich, USA) to reduce the adhesion between electrodeposited Ni and ITO. Then, a Ni electroplating solution (Caswell, USA) was used for the deposition of Ni. A Keithley 2400 SourceMeter was used to supply a current density of 5 mA cm\(^{-2}\) during the electro-deposition process. A two-electrode electrodeposition setup with the ITO glass as the anode and a platinum-coated titanium grid as the cathode was used. Afterward, the sample was thoroughly rinsed with deionized water and dried under nitrogen flow.

0.02 g NOA-61 UV-curable resin was then dropped onto the sample and covered with an oxygen plasma-cleaned glass substrate with an area of 3 × 3 cm\(^2\). A gentle pressure was then applied on the stack to form a uniform interlayer of the resin between the resist and the glass substrate. Thereafter, the stack was exposed to UV light (405 nm, 600 mJ cm\(^{-2}\)) to fully cure the resin. Finally, the imprint mold was separated from the ITO glass manually, with the nickel pattern transferred by the resin.

4.4 Thermal nanoimprint transfer of PdNPs

The imprint mold was first immersed in a 300 mM PdNP colloidal solution at 40 °C for 5 min to adsorb PdNPs for the preparation of the SACN-mold (in the case of fabrication of a nanodisk array, the immersion time was reduced to 20 s). Then the SACN-mold was rinsed in deionized water and dried under nitrogen flow. A thermal nanoimprint process was used to synchronously transfer the pattern and PdNPs onto a 200 μm-thick PET film using a home-built nanoimprint platform consisting of a hydraulic press (Specac Ltd, UK), electrically heated platens with a temperature controller (Specac Ltd, UK), and a chiller (Grant Instruments, UK). The template/substrate stack was heated to 105 °C (150 °C for COC films) for 5 min with an imprinting pressure of approximately 0.5 MPa to press the template and the PET film. Afterward, the heated stack was cooled down to a demolding temperature of 40 °C, and the PET film was peeled off from the glass template after releasing the pressure, leaving PdNPs and the pattern transferred onto the PET film.

4.5 Electroless deposition of Cu, Ni, and Ag

The PET film with imprint-transferred PdNPs was immersed in a Cu electroless plating bath at 40 °C for 5–30 min, a Ni electroless plating bath at 55 °C for 5 min, or an Ag electroless plating bath at room temperature for 30 s to 3 min for metallization. After electroless plating, the samples were rinsed in deionized water and dried under nitrogen flow. The samples were heat-treated at 60 °C for 30 min to relieve the internal stress, leading to better adhesion and stability of the metals.

The Cu electroless plating bath consisted of copper sulfate pentahydrate (12 g L\(^{-1}\)), nickel sulfate heptahydrate (1.28 g L\(^{-1}\)), potassium sodium tartrate (11.2 g L\(^{-1}\)), ethylenediaminetetraacetic acid disodium (15.6 g L\(^{-1}\)), sodium hydroxide (14 g L\(^{-1}\)), 2,2′-bipyridyl (0.4 mg L\(^{-1}\)), potassium ferrocyanide (0.6 mg L\(^{-1}\)), DuPont Zonyl FSN (0.5 mL L\(^{-1}\)), and formaldehyde (15 mL L\(^{-1}\)). The Ni electroless plating bath consisted of nickel sulfate heptahydrate (30 g L\(^{-1}\)), sodium hypophosphite (28 g L\(^{-1}\)), sodium citrate (35 g L\(^{-1}\)), ammonium chloride (30 g L\(^{-1}\)), and DuPont Zonyl FSN (0.5 mL L\(^{-1}\)), and the pH value of the plating bath was adjusted with ammonia to be approximately 8.0. The Ag electroless plating bath consisted of silver nitrate (2 g L\(^{-1}\)), ethylenediaminetetraacetic acid disodium (0.2 g L\(^{-1}\)), and formaldehyde (1 mL L\(^{-1}\)). Silver nitrate and ethylenediaminetetraacetic acid disodium were first dissolved in a suitable amount of deionized water; then silver nitrate solution was gently poured into ethylenediamine tetraacetic acid disodium solution with stirring. Afterwards, 25 wt% ammonia was added to the mixed solution until it became clear again. Then 1 mL L\(^{-1}\) formaldehyde was added to the solution, and the volume of the solution was adjusted to be 1 L with deionized water. The Ag electroless plating bath was used immediately after preparation.

4.6 Fabrication of electroluminescent displays

An ‘HKU’-letter pattern was created on a PET film imprint using the SACN-mold. Then the patterned sample was immersed in a Cu electroless plating bath for 15 min for metallization. Afterward, electroluminescent ZnS:Cu particles (Shanghai KPT, China) were mixed with a polybutene glue with a mass ratio of 1.5:1. Then the mixture was spin-coated onto the substrate at 500 rpm for 15 s and baked in an oven at 60 °C for 10 min to solidify the emission layer partially. Finally, a Cu TE was attached to the emission layer with pressure and left the assembled stack in an oven at 60 °C for 12 h to complete the fabrication of an electroluminescent display. The electroluminescent display was driven using a DG2-3-T AC voltage driver (Shanghai KPT, China).

4.7 Morphological characterization

The morphologies of the samples were characterized using scanning electron microscopes including an LEO-1530 Gemini (Zeiss, Germany), S-4800N (Hitachi, Japan), and S-3400N (Hitachi, Japan). EDS analysis was performed using S-3400N and S-4800N scanning electron microscopes. A CM-100 tunneling electron microscope (Philips, Netherlands) was used to investigate the morphology of the PdNPs.

4.8 Measurement of the transmission spectra

All spectra were recorded on an ultraviolet/visible/near-infrared spectrometer (HR2000+, Ocean Optics, USA). All transmittance values presented in this paper were normalized to the absolute transmittance through the bare PET film.

4.9 Performance measurements

The sheet resistances of the TEs were measured using a four-probe method to eliminate the contact resistance. During the measurement, four probes were placed on the two silver paste-covered edges of a square sample, and the resistance was recorded with a Keithley 2400 SourceMeter (Keithley, USA),
During the measurement of the repetitive bending or stretching process, the sample was fixed to a home-built moving stage controlled using an Arduino microcontroller. For thin-film heater application, a DC voltage was supplied using the Keithley 2400 as a DC power supply to the heater through two Cu adhesive tapes at the film edge. The temperature of the film was measured using a FLIR ONE infrared thermal imager (FLIR Systems, USA).

4.10 Measurement of refractive index sensitivity

The index sensitivity was determined by dropping 10 μL of standard liquid on the same sample and recording the transmission spectra. The standard liquids (Cargille Labs, USA) had refractive indices of 1.30–1.44 in steps of 0.02. After each measurement, the sample was thoroughly rinsed with isopropanol and dried under nitrogen flow.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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