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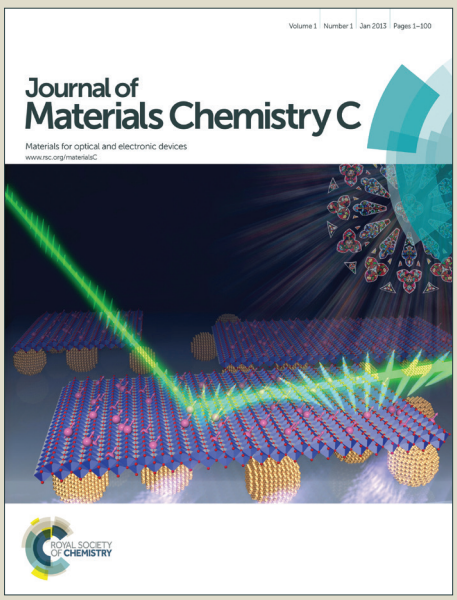

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ARTICLE TYPE

Controllable fabrication of a flexible transparent metallic grids conductor based on the coffee-ring effect

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An effective and facile strategy was developed to fabricate a flexible transparent metallic grids conductor based on coffee-ring effect with inkjet printing technique. In such system, silver nanoparticles (AgNPs) were ink-jet printed to assemble into twin lines directly on flexible poly(ethyleneterephthalate) substrates and subsequently achieved to be sintered at room temperature. Taking advantage of this approach, a highly flexible transparent AgNPs grids-based conductor was successfully fabricated with 5-6 μm line width. The transmittance could achieve up to 93.6% and a sheet resistance was less than 30 Ω /sq. This simple, cost-effective and nonlithographic approach would further enhance current fabrication approaches to create patterned microstructures, and have great potential to be tailored for fabrication of optoelectronics devices.

Flexible transparent electronics has drawn considerable attentions in recent years as it exhibits tremendously applications in various optoelectronics such as LCDs,[1] OLED lighting,[2] solar cells,[3] and touch screen panels devices.[4, 5] To date, wide band gap transparent conductive oxides, especially indium tin oxide (ITO), have been the most widely used conductive materials for transparent electronics due to their low sheet resistance and excellent optical transparency. However, the ITO utility for flexible devices is seriously limited for its high scarcity, fragile nature and huge waste of target material.[6] Therefore, it is very urgent to exploit new conductive materials to meet the growing demands. A great variety of alternatives to ITO, including conductive polymers,[7] carbon nanotubes,[8] graphenes[9, 10] and nanowires[11-16] have been widely investigated for this purpose. Nevertheless, the synthesis procedures of these conductive materials are fairly complicated or time-consuming, and their performances are closely depended on the process of fabrication sample and often can not meet the requirements for the flexible transparent electronics in terms of conductivity, transparency and stability.

Instead, the grids of randomly distributed metallic nanoparticles, especially the grids of silver nanoparticles (AgNPs), are considered as another promising candidate for the next-generation transparent conductive materials due to their theoretically superior electrical and optical properties.[17] Several approaches have been used to fabricate such conductive grids based on the pre-patterning of the substrate surface,[4, 18] laser assisted local sintering[19-26] or with special inkjet printing nozzle.[27] However, these processes involve high-cost equipment and require high energy or complex pre- or post-treatments.[28] As a facile and versatile patterning technique, ink-jet printing has been recognized as the most convenient method to fabricate various patterns on substrates. Compared with aforementioned techniques, this approach can assemble metallic nanoparticles into regular microscopic structures in an energy-conserving and nonlithographic manner.[29, 30] However, the applicability of the printing technology to fabricate a transparent metallic grids conductor is seriously limited by the attainable line width.[31] At present, the minimum width of printed lines is approximately 20 μm in optimized parameters,[32, 33] which is impossible to construct transparent grids-based conductor in such line width.

Recently, we demonstrated a new approach to successfully fabricate a series of conductive patterns with 5-10 μm line widths on hydrophilic glass substrates based on the coffee ring effect.[34] Although this method could be used to construct conductive patters with excellent conductivity and high transparency, it also revealed some inherent limitations. One big problem of this approach was that it needed a higher sintering temperature (200 ℃ for 2 h) to achieve high electrical conductivity, which was incompatible with most heat-sensitive polymer substrates. Obviously, it prevented the possibility for obtaining a flexible transparent grids conductor directly on a plastic substrate, and required an additional complicated transfer process of grids from the glass to a soft film forming material.

In order to overcome these obstacles and performed a similar process directly on flexible substrates, in this work, we introduced an effective and facile strategy to fabricate flexible transparent grids conductors directly on poly(ethyleneterephthalate) (PET) substrates by tuning the characters of AgNPs based on the coffee-ring effect. Taking advantage of this strategy, a series of transparent conductive AgNPs grids with 5-6 μm line width were successfully fabricated and could be sintered at room temperature, exhibiting low sheet resistance and high transparency. This nonlithographic approach could be considered as a universal strategy to construct various flexible transparent microstructures in a simple manner and would have great potential to be tailored for applications in optoelectronics

fields.

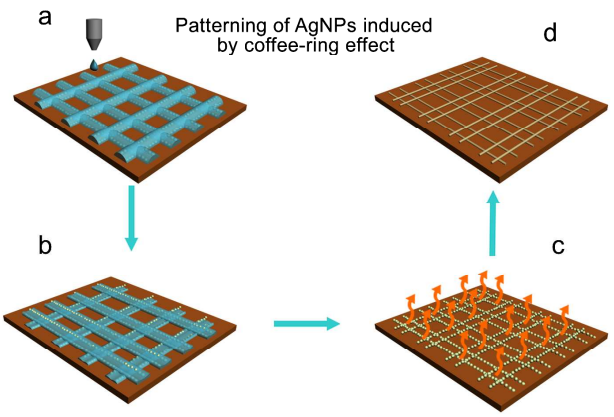

Fig. 1 Schematic illustration of the fabrication process to obtain a flexible transparent grids conductor directly on PET substrate (a)AgNPs were ink-jet printed on PET substrate (b) AgNPs migrated to the TCL during the solvent evaporation (c) AgNPs grids were exposed to HCl vapours (d) the final transparent AgNPs grids pattern

Fig. 1 illustrated our design to fabricate transparent AgNPs grids conductor directly on PET substrate by utilizing the coffee-ring effect with inkjet printing technique. Briefly, the AgNPs were inkjet-printed and form liquid grids on PET substrate (Fig. 1a). Due to enhanced solvent evaporation rates in the vicinity of three-phase contact line (TCL), multitudinous capillary fluid flows were induced to replenish the evaporation loss at TCL with influence of the coffee-ring effect. The dispersed AgNPs in the capillary fluid flows were continuously transported to the TCL, and each printed single line spontaneously splited into twin lines and assembled into an ordered grid (Fig. 1b). Subsequently, the printed PET substrate with formed AgNPs grids pattern was exposed to HCl vapours (Fig. 1c), and the capped elongated macromolecules were effectively detached from the AgNPs surfaces due to the competitive absorption with smaller chlorides. In order to lower the total surface energy and reach a stable state, the AgNPs would spontaneously contact, coalesce, and be sintered at room temperature to achieve a low sheet resistance (Fig. 1d).

The formed grids AgNPs pattern on PET substrate was extremely pivotal to achieve transparent conductor. According to above design, a single flexible AgNPs line was firstly fabricated based on the coffee-ring effect by inkjet printing AgNPs directly on PET substrates, and characterized by surface profiler and scanning electron microscopy (SEM). It was very attractive that the AgNPs of printed single line was induced by coffee ring effect and spontaneously splited into twin lines with an average of 5-6 μm width (Fig. 2a). From the surface profile (Fig. 2b-Fig. 2c), the height of these twin lines was about 0.3-0.4 μm, and the distance between twin lines was 60-80 μm. In Fig. 2d-Fig. 2f, the SEM studies showed that most AgNPs migrated to the TCL and assembled into twin lines, which was ascribed to the coffee ring effect originating from non-uniform evaporation flux loss. In order to further verify the microstructure, atomic force microscope (AFM) was used to investigate the AgNPs distribution in the formed twin lines, and demonstrated in Fig.S2. From the AFM images, most of all the AgNPs migrated to the rims of printed line and assembled into highly regular AgNPs twin lines, and few AgNPs resided between the twin lines, which were in good agreement with the SEM results. Moreover, the line width of AgNPs grids could be tuned by controlling the intensity of coffee-ring effect, which provided an opportunity to construct a transparent conductor directly on PET substrates.

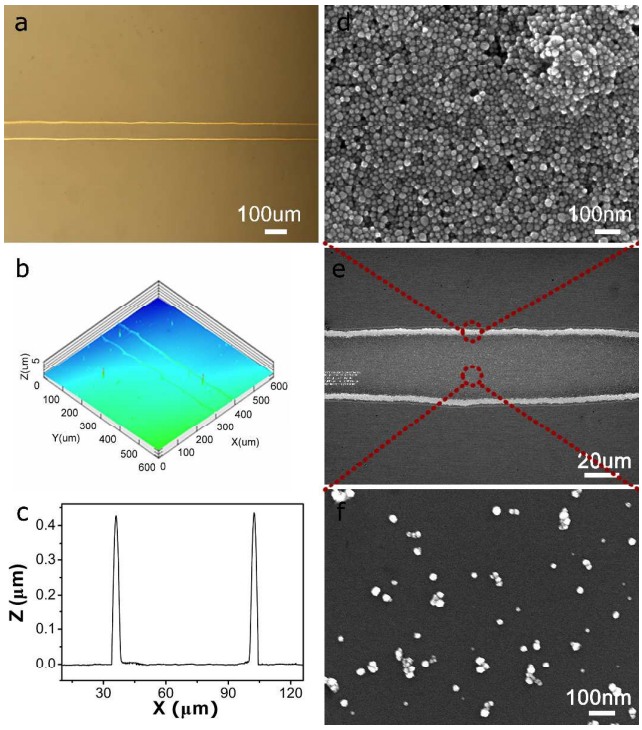

Fig. 2 Structural characterization of AgNPs patterns fabricated by the coffee-ring effect on a PET substrate (a) the optical images of printed AgNPs grids (b) 3D profile of printed AgNPs grids (c) the height profile of printed AgNPs grids (d) SEM images of printed AgNPs grids rim (e) SEM images of printed AgNPs grids (f) SEM images of printed AgNPs grids center

The surface character of the AgNPs was extremely important to the sintering temperature for flexible grids conductor. In order to achieve sintering at room temperature, the AgNPs used throughout the process were synthesized according to the literature with subtle modification.[35] In the case, poly(acrylicacid) (PAA) was chosen as capping molecules to synthesize AgNPs, and the diameters were in the range of 20-30 nm according to UV spectra, transmission electron microscopy (TEM) and SEM images (Fig. S1). Here, AgNPs were chosen as the conductive materials owing to their higher conductivity and oxidation resistance, and could be synthesized in a facile method.

It was confirmed that PAA, as a good capping molecules, could be anchored on AgNPs surfaces and formed proactive layers to efficiently prevent further agglomeration.[5] The main protective effect of PAA molecules was attributed to the Ag-O

interaction between AgNPs surface and carboxylic group, through a bidentate mode probably by ion-dipole interactions.[35] Compared with PAA molecules, chlorides have much smaller stereo-hindrance effect and stronger interactions with the AgNPs surface, and could be fully competent to substitute the PAA molecules.[36] Therefore, the desorption was spontaneously realized by chlorides replacing carboxylic anchored groups on the AgNPs surface, which enabled the AgNPs to contact much closer each other and triggered self-sinter at room temperature. As a result, the morphology of AgNPs grids was bound to show significant changes when the printed substrates were exposed to HCl vapours.[37]

In order to evaluate the role of the chlorides in the sintering process, the morphology of AgNPs before and after exposed to HCl vapour were investigated. From SEM images in Fig. 3, the changes of AgNPs morphology were triggered by the appearance of chloride. Initially, the AgNPs were uniformly deposited on PET substrate, and isolated from each other due to the presence of PAA protective layers around the AgNPs surfaces (Fig. 3a). After exposed to HCl vapours, a fraction of protective layers were detached from the AgNPs surfaces and replaced by chlorides due to their more intensive interaction and smaller steric effect. It should be noted that most AgNPs gradually contact, coalesce each other, and a lot of necks emerged among the AgNPs aggregate. Thus, multiple percolation paths were continuously formed in the formed twin lines (Fig. 3b), which was fairly pivotal to the electron transmission among AgNPs aggregate.[38] All these SEM results prove that this strategy could be explored to enable AgNPs sintered at room temperature and construct transparent conductors directly on flexible substrates.

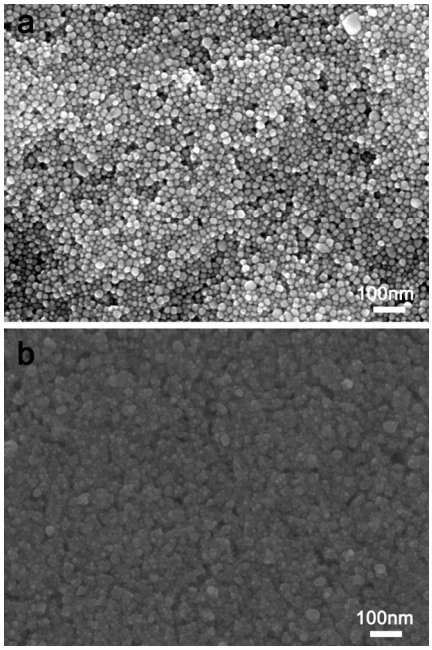

Fig. 3 SEM images of corresponding AgNPs aggregates (a) in initial state and (b) after exposure to HCl vapours

To further verify the sintering mechanism was triggered by the detachment of PAA protective layers from the AgNPs surfaces, X-ray photoelectron spectroscopy (XPS) was used to characterize the AgNPs samples before and after exposed to HCl vapours. The peak signals of C1s spectrum, which mainly originated from carbon atom of alkyl chain in PAA molecules, exhibited a distinct decrease after exposur to HCl vapours (Fig. 4a). Accordingly, the O1s spectrum, attributed to the oxygen atom of carboxylic group in PAA molecules, also demostrated an obvious reduction after exposing to HCl vapours (Fig. 4b), which further confirmed that the PAA proactive layers were effectively detached from the AgNPs surfaces. These XPS analysis proved that PAA molecules on the AgNPs surfaces were effectively replaced by our exposing method, and consequently caused the AgNPs to coalesce and spontaneously be sintered at room temperature.

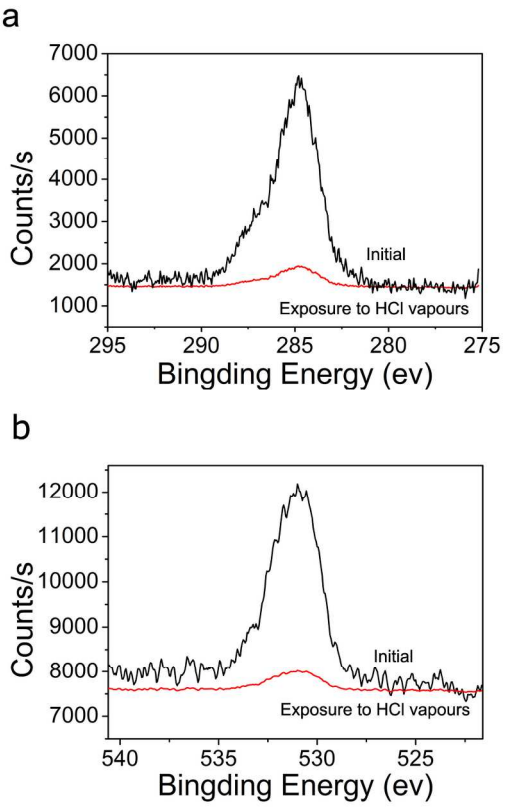

Fig. 4 XPS of the synthesized AgNPs in initial state and after after exposure to HCl vapours (a) C1s spectrum and (b) O1s spectrum

In order to validate the applicability of this fabrication strategy, a series of patterns were designed and fabricated by controlling coffee ring effect with the ink-jet printing technique. An example of a flexible transparent AgNPs grids conductor fabricated by this process was depicted in Fig. 5a. From Fig.5b, almost all AgNPs have been transported to the periphery of TCL and assembled into AgNPs grids with induction of the coffee-ring effect. The junctions between AgNPs grids were not only geometrically continuous, but also have a high density of AgNPs (Fig. S3), and this ensured that the formed AgNPs grids could achieve low sheet resistance.

From the typical surface profile (Fig. 5c), the average heights of twin lines in the formed AgNPs grids was 0.3-0.4 μm. The average width at the base of twin lines was 5-6 μm, and these narrow lines led to a high transparency. We evaluated the transmittance performance of the formed AgNPs grids as conductive materials, and Fig. 5d was the transmittance spectrum measured from 350 to 950 nm. It showed that the transmittance of a metallic grid fabricated by this method could achieve up to 93.6%, and be higher than an ITO-based transparent conductor from the visible to near infrared region. Moreover, due to the direct writing nature of the method, the dimensions and distances of AgNPs grids could be easily regulated by controlling the coffee ring effect, which was very favorable to construct multifarious functional patterns.[39]

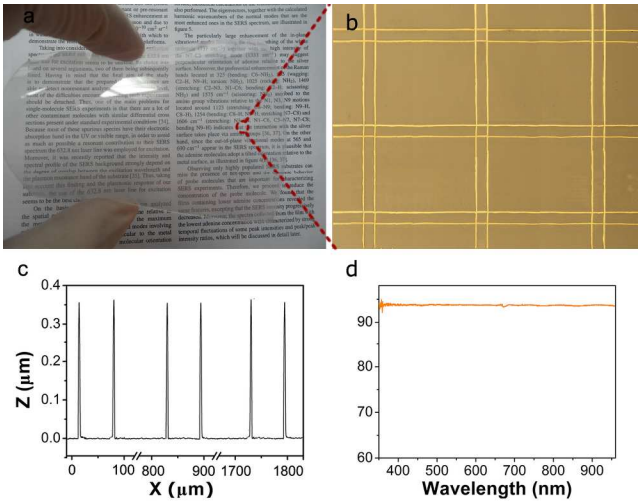

Fig. 5 (a) Optical image of the transparent AgNPs grids printed on PET substrate (b) the higher magnification optical image of transparent AgNPs grids (c) The height profile of AgNPs grids (d)the transmittance of the PET substrate with the AgNPs grids pattern.

In addition to high transmittance, the sheet resistance was another key factor for use of AgNPs grids as transparent conductive materials. To verify the conductivity of the AgNPs grids, the average sheet resistance was measured from randomly selected five distinct spots on the substrate and approximately 26.5 Ω/sq for a 3 cm×3 cm sample. Notably, these values were comparable or even superior to that reported for TCO film.[27, 40] A usual adhesive tape test was performed on a square shaped grid to evaluate the adhesion. A small fraction of AgNPs grid conductors were removed from the substrate after two consecutive attach-detach process. Moreover, the sheet resistance and transparency had no obvious change after storage of the AgNPs grid for 6 months under ambient conditions, revealing the high stability of the AgNPs grid conductor fabricated by our strategy.

In conclusion, a facile strategy was developed to construct a transparent AgNPs grid-based conductor based on coffee ring effect with inkjet printing technique. Multifarious patterns with an average line width of 5-6 μm have been successfully fabricated directly on PET substrates and achieved self-sintering at room temperature. Their performance was comparable to ITO, yielding a transmittance higher than 93.6% and a sheet resistance of less than 30 Ω/sq. This simple method can be directly extended to a large-area flexible substrate, as confirmed by the AgNPs grid fabricated on a PET substrate over a 3 cm×3 cm area. This method would offer promising opportunities to fabricate a flexible transparent metallic nanoparticle-based functional electronic device for real applications in various fields.

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Notes and references

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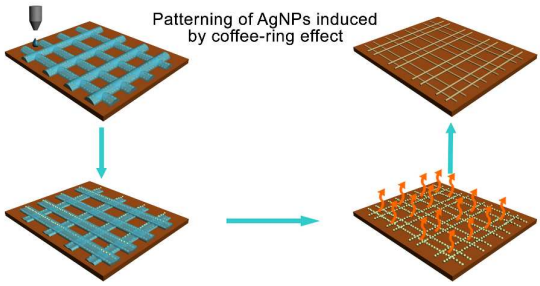

Flexible transparent metallic grids-based conductors were successfully fabricated and sintered at room temperature based on coffee-ring effect.