Supporting Information

One-pot synthesis of a stable and cost-effective silver particle-free ink for inkjet-printed flexible electronics

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Section 1. Ink characterization

1) Butanol ink and hexanol ink

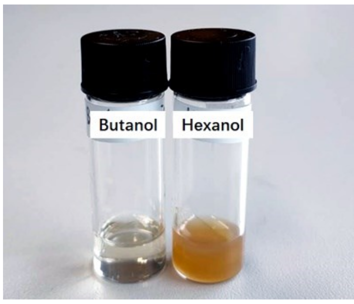

Fig.S1 Optical images of butanol ink and hexanol ink

2) Surface tension and contact angle images of the five silver inks on PI substrates

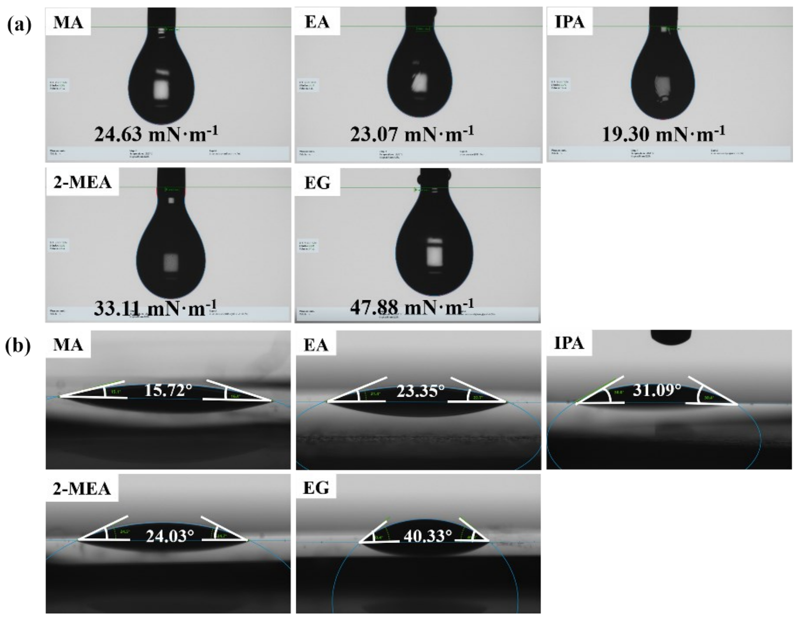

Fig. S2 (a) Surface tension and (b) contact angle images of the as-prepared five silver inks on PI substrates

3) Stability of the as-prepared five silver inks

Stability is also an important aspect of performance. A stable ink is an ink in which all its properties remain constant over time. The stability of the five silver inks was evaluated. The optical images of these inks under different storage periods are given in **Fig. S3a-c**. The freshly prepared MA ink, EA ink, IPA ink and EG ink were transparent without any color. The 2-MEA ink was brown. After storing in a refrigerator at 5°C for one week, the MA ink, EA ink and EG ink had no color change and sediment. The IPA ink turned light yellow. The 2-MEA ink changed into a dull and had some sediments. The color change of these two inks revealed the continuous production and segregation of silver nanoparticles in the inks due to the reducibility of IPA and 2-MEA, suggesting poor stability. After 30 days, the MA ink and EG ink still had no color change, particle precipitation and absorption in the UV-vis spectra (**Fig. S3d and e**), implying good stability and hence long shelf life.

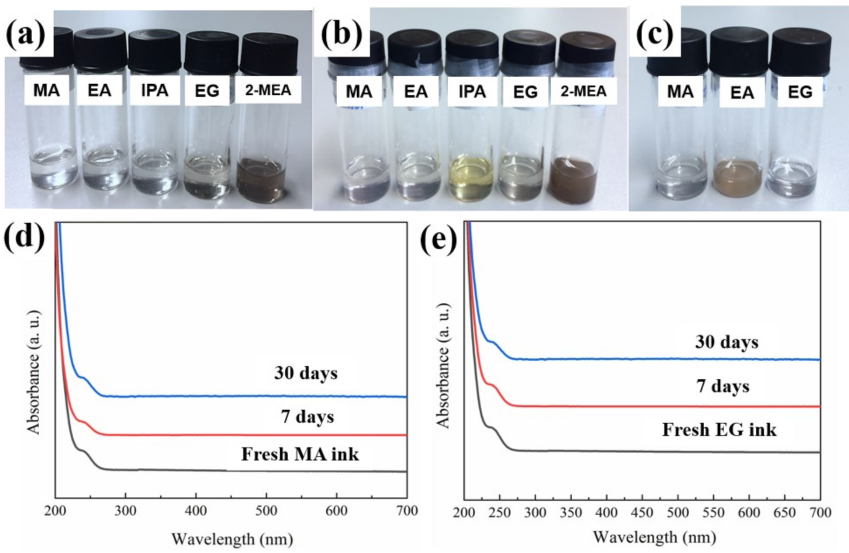

Fig. S3 (a-c) Optical images of the as-prepared five silver inks storing in a refrigerator at 5°C for different times (a. fresh inks, b. 7days, c. 30 days); (d) and (e) UV-Vis spectra of MA and EG inks storing in a refrigerator at 5°C for different times

4) Thermal behavior of the as-prepared five silver inks

The thermal decomposition behavior of the as-prepared five silver complex inks was investigated by DSC and TG-MS analyses, as shown in **Fig. S4**.

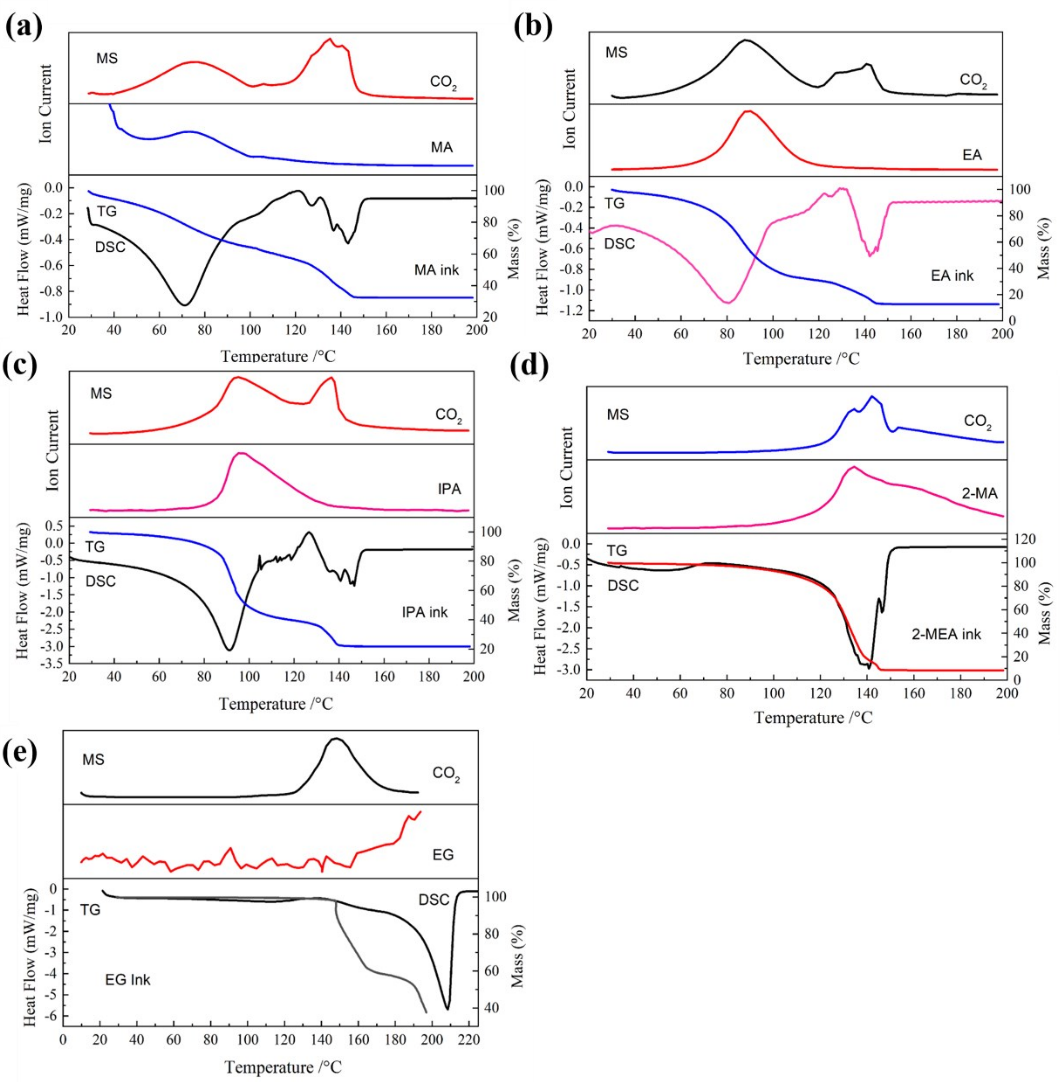

Fig. S4. TG-DSC-MS analysis of the decomposition of the five silver inks prepared using different acohols; (a) MA, (b) EA, (c) IPA, (d) 2-MEA, (e) EG

As the first three inks have similar thermal behaviors, the EA ink was chosen as a representative. The first step weight loss from room temperature to 120°C, accompanied by an endothermic peak around 80 °C in the DSC curve, is attributed to the evaporation of EA (boiling point, 78°C) and the partial decomposition of the silver-complex in the ink. This is confirmed by the MS results, where EA and CO_2 gases were detected in this temperature range. The second step weight loss starts from 120 to 150 °C, which is accompanied by an endothermic peak at 142°C in the DSC curve, indicating the total decomposition of the silver-amine complex. The MS detects the production of carbon dioxide. For the 2-MEA ink, the evaporation of 2-MEA (boiling point, 124°C) and the partial decomposition of the silver complex are nearly synchronous, followed by the total decomposition of the silver-amine complex. The decomposition of the silver-amine complex in the EG ink is prior to the evaporation of the solvent EG due to its high boiling point (197.6°C). Here, it should be noted that the silver content deduced from the TG results is not very accurate for all the inks. This is because there is some weight loss due to the evaporation of the solvent when transferring the weighed sample from the balance to the TG analyzer.

From the above analysis, it can be concluded that the difference in solvents has little effect on the thermal decomposition behavior of the MA ink, EA ink, 2-MEA and IPA ink. For EG ink, the decomposition temperature is higher than that of the ink prepared with other alcohols, although EG is more reducible than them. This indicates that the addition of a reducing polyol does not reduce the heat treatment temperature of the ink.

5) Film morphology and resistivity of the five silver inks

According to the DSC results, the temperature of 150°C was chosen to sinter the as-prepared five silver inks to investigate the effect of solvents in the film formation process.

The crystalline structure of the sintered films from the five as-prepared complex inks was detected by XRD, the results were displayed in **Fig. S5a**. Five diffraction peaks at 2θ values of 38.2°, 44.4°, 64.5°, 77.5° and 81.6° appear in all the films. These peaks correspond to the (111), (200), (220), (311) and (222) crystal planes of a face-centered cubic crystal structure of silver, indicating that the films are composed of silver particles. This means that the silver-amine complex in each ink has been transformed into metallic silver. All the five films showed sharp peaks of silver, revealing good crystallinity. The film from EG ink has the highest diffraction intensity, which indicates that ethylene glycol not only plays a role of dissolution but also has a certain reducing effect in the ink. **Fig. S5b** shows the SEM images of the sintered films from the five as-prepared complex inks. It can be seen that the microstructures of the five films were quite different in terms of the particle morphology and size, area of void spaces and the degree of film densification. The silver film from MA ink shows a uniform and dense structure consisting of well-contacted spherical silver nanoparticles and some voids, while the silver film from the EA ink presents a structure consisting of hollow silver nanoparticles. The IPA ink produces a nonuniform film with more voids and the EG ink presents a surface morphology composed of big silver crystals. The film from the 2-MEA ink is the densest and the silver particles have good contact with each other.

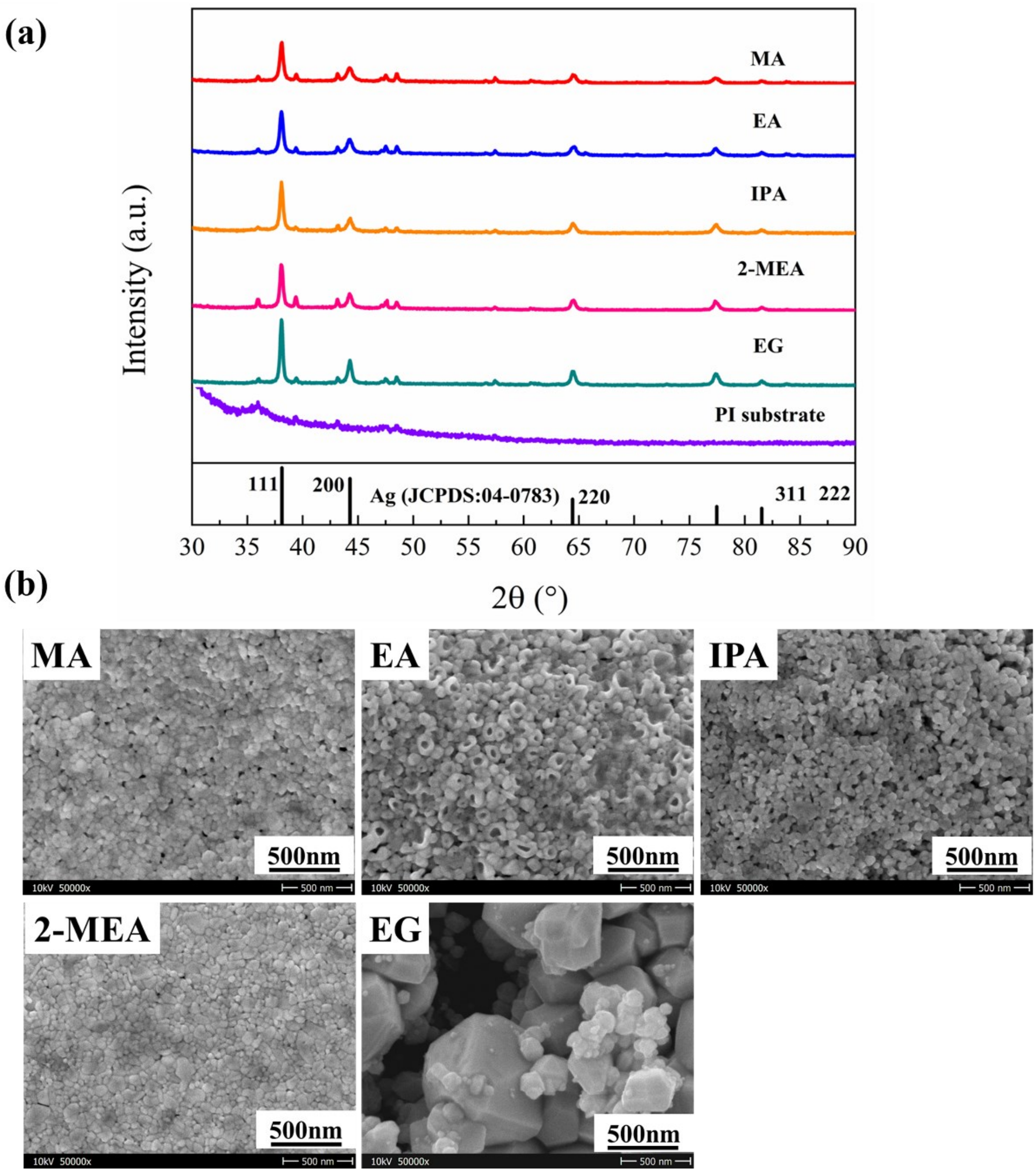

Fig. S5. (a) XRD patterns and (b) SEM images of the sintered silver films on PI substrates from the five silver inks (150°C, 60min)

The resistivity of each spin-coated film is given in **Fig. S6**, where the inset is the corresponding optical images. Here, glass slides were used as the substrates to obtain a relatively accurate sheet resistance. After sintering at 150 °C for 60 minutes, the inks based on MA, EA, IPA and 2-MEA formed conductive films with a metallic luster. Among them, the conductive films formed by the MA ink and EA ink presented obvious coffee-ring effect, while the conductive films formed by IPA were silver-white. The film from 2-MEA ink is relatively uniform. The film from EG ink is covered with a layer of black substance and has no metallic luster. Besides, there was a significant solvent shrink effect and because of this, the formed film does not cover the substrate completely. The film from the MA ink showed the lowest resistivity, with a value of 20.5μΩ·cm, while the film produced from EG ink had a higher value of 234μΩ·cm. The film resistivity from EA ink was slightly higher than that of the 2-MEA ink but had no significant difference with that of IPA ink.

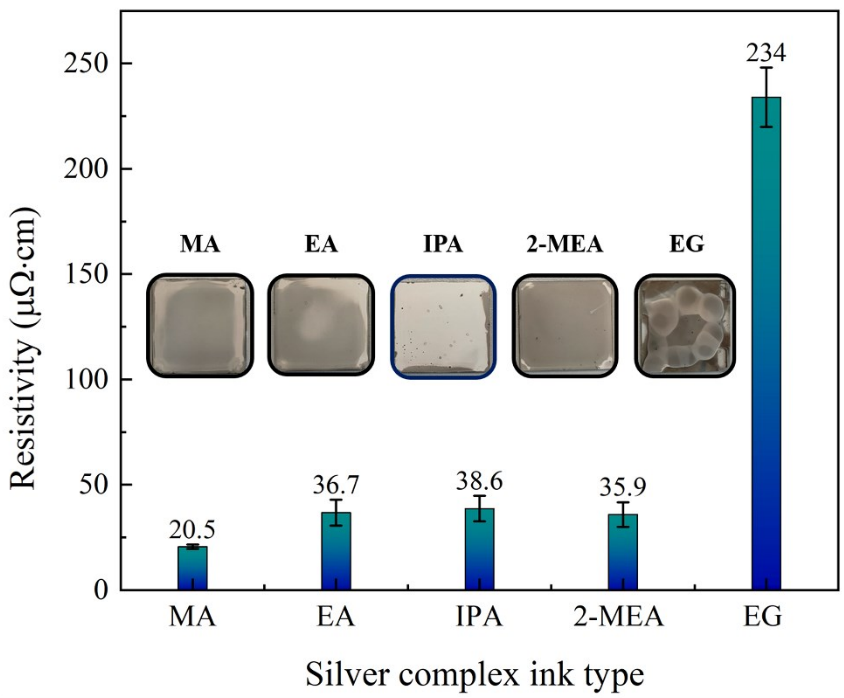

Fig. S6. Resistivity of the silver films prepared at 150°C for 60min from the five silver inks

EDX analysis was performed to investigate the chemical composition of the five films, the results are shown in **Fig. S7**. As expected, three elements (C, O, and Ag) were detected, which further confirmed the presence of silver in all the films and is in accordance with the original chemical composition of the compounds. For the first four films, the silver content has no significant differences and there is only a small amount of organic residue. The film from EG ink has the least silver content and the amount of organic residue is up to 26%, which agrees with the previous analysis.

From these results, it can be deduced that the type of solvent mainly affects the microstructure of the produced film and have little effect to the conductivity when the boiling point of the solvent is below 150°C.

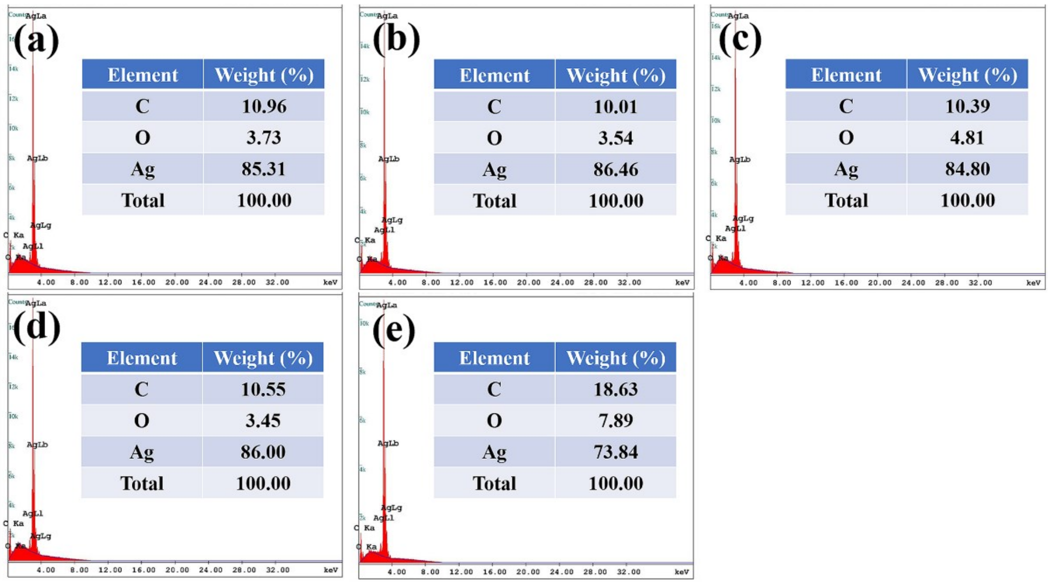

Fig. S7 EDS results of the sintered silver films on PI substrates from the five silver inks (150°C, 60min); (a) MA, (b) EA, (c) IPA, (d) 2-MEA and (e) EG

Section 2. Film structure from inks based on mixed alcohol solvents

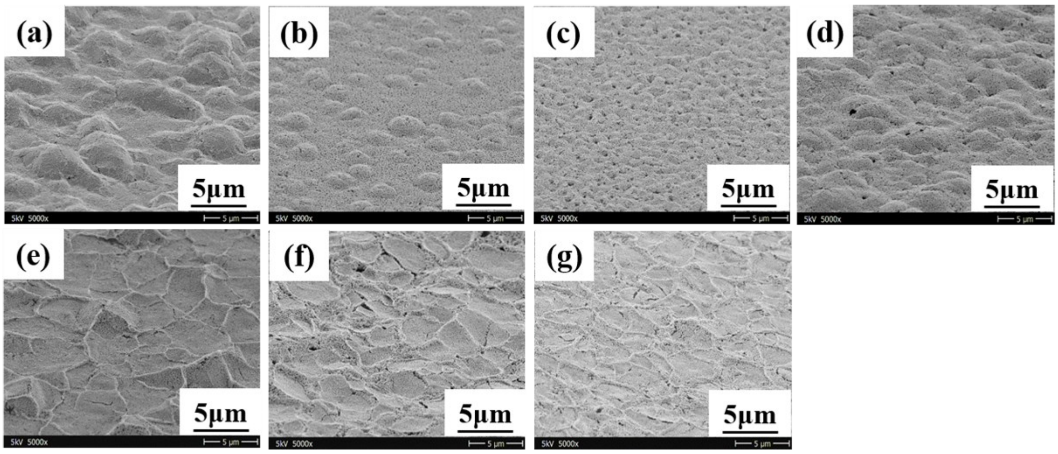

Fig. S8. SEM images of silver films on glass substrates sintered at 150°C for 60min from silver oxalate inks prepared using a mixture of MA and EG in different ratios (MA/EG), (a) 5:0, (b) 4:1, (c) 3:2, (d) 1:1, (e) 2:3, (f) 1:4, (g) 0:5

Section 3. Printability of the optimal silver ink

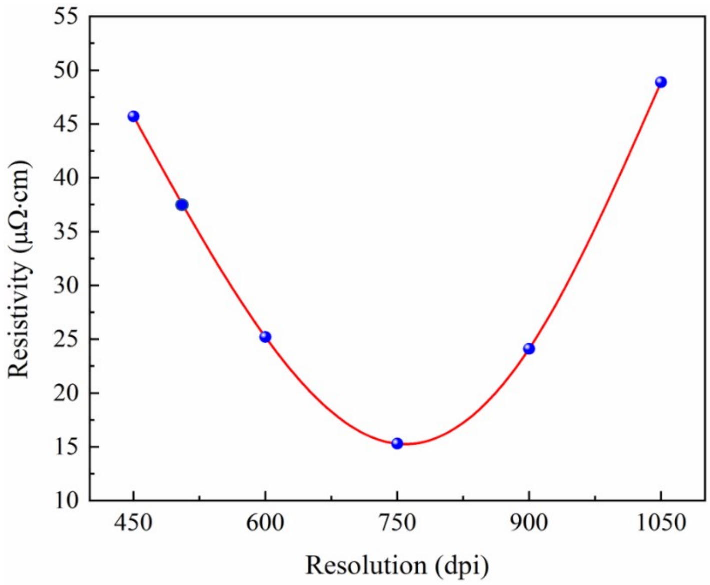

Fig. S10. Resistivity of the silver films on glass substrates printed with different resolution and sintered at 200°C for 60 minutes, (a) 300 dpi, (b) 450 dpi, (c) 500 dpi, (d) 600 dpi, (e) 750 dpi, (f) 900 dpi, (g) 1050 dpi

Fig. S10 shows the electrical resistivity of the printed square films on glass substrates sintered at 200 °C for 60 minutes. As the resolution was increased to 750dpi, the resistivity decreased to a minimum of 15.28μΩ·cm. This value is acceptable and comparable to other researchers and it may result from the lower silver content of the ink.

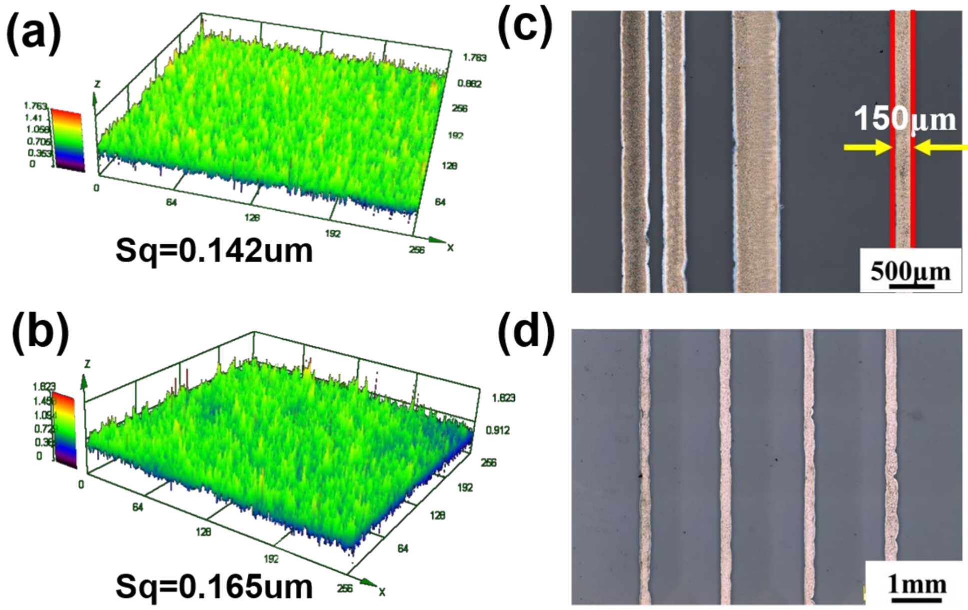

Fig. S11. Surface profile of the silver films on glass substrates printed with 750dpi (a) and 900 dpi (b) and sintered at 200°C for 60 minutes, (c-d) the printed silver lines with different widths

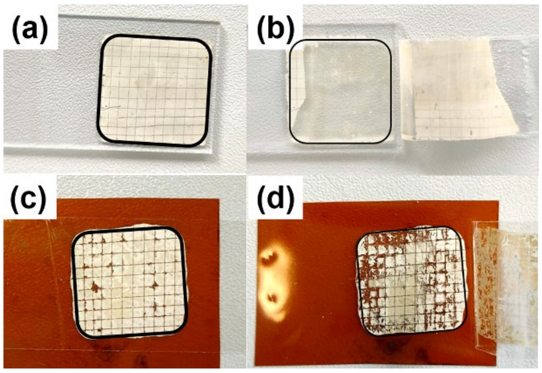

Fig. S12. The adhesion test of the printed films on glass (a-b, before and after ripping) and PI substrates (c-d)

Section 4. Cost and performance assessment

Table S1. Comparison of the reported silver particle-free inks

Ink types	Ag wt%	Price	Ink Composition			Fluid properties	Patterning Method		Resistivity (μΩ•cm)	Key advantages	Disadvantages
			Silver precursor	Complexing agent	Solvent		Deposition	Sintering conditions			
Silver citrate ink[1]	10%	18.87€/25ml	Silver citrate	1,2-diaminopropane	Methanol and isopropanol	Viscosity 3.7 mPa·s (25°C), surface tension 23 mN/m	Ink-jet printing	150°C for 50 min	17	Excellent stability, Good adhesion (5B)	No detailed information about printing parameters such as the smallest line width, the printer is not industrial-grade.
Silver carbonate ink[2]	25%	46.52€/25ml	Silver carbonate	Isopropyl amine	Glycol and DI water	Viscosity 13.8 mPa·s (20°C), surface tension 36.9 mN/m	Handwriting	150°C for 60 min	18	Simple synthetic route	less stable, easily degrades at room temperature
Silver acetate ink[3]	22%	52.78€/25ml	Silver acetate	Ammonium hydroxide, formic acid (reducing agent)	Aqueous containing butanediol	Viscosity 2mPa·s (20°C)	Ink-jet printing, direct-writing and airbrush-spraying	90°C for 15 min	1.6	Good stability, Excellent conductivity at low sintering temperature, suitable for a wide range of patterning techniques	12h aging time and need to filter the produced silver particles, may not good for a long-term inkjet printing process because it may lead to the formation of silver particles in the nozzle and clog it due to the low decomposition temperature[4]
Silver	17%	42.42€/25ml	Silver	Ethylamine,	DI water containing	Viscosity 4.95	Ink-jet printing	150 °C for 30 min	4.71 (PEN	Good jetting and	12h aging time and need

acetate ink[4]			acetate	ethanolamine, formic acid (reducing agent)	methanol	mPa·s (20°C), surface tension 33.08 mN/m			substrate)	storage stability, Excellent adhesion, Suitable for a wide range of substrates	to filter the produced silver particles
Silver acetate ink[5]	/	61.10€/25ml	Silver acetate	Ethylamine, ammonia, formic acid (reducing agent)	HEC (viscosifier and stabilizer), ethanolamine (anticlogging additive)	Viscosity 54 mPa s at lower shear stress and 92 mPa s at higher shear stress	Spin-coating or nozzle-jet printing	90°C for 24h (Spin-coating, Glass substrate); 75°C for 60 min (Nozzle-jet printing, PET substrate)	19.8; 36.5	Good stability and excellent adhesive properties on different substrates	12 hours aging, may not good for a long-term inkjet printing process because it may lead to the formation of silver particles in the nozzle and clog it due to the low decomposition temperature
Silver oxide ink[6]	3%	7.71€/25ml	Silver oxide	Ammonium hydroxide, Diethanolamine	DI water	Viscosity 4.4 mPa·s (20°C), surface tension 49.2 mN/m	Ink-jet printing	75°C for 20 min	6	Good conductivity at low sintering temperature, Good adhesion on plastic sheets	Not stable and have sediment over time,
Silver oxalate ink[7]	29.5%	68.06€/25ml	Silver oxalate	Ethylenediamine	DI water	Not given	Ink-jet printing	Thermal-photonic curing: 120°C for 5 min, 3.32 J/cm2	4.28	Good stability and conductivity	A subsequent pulsed photonic sintering method
Our ink	10%	21.16€/25ml	Silver oxalate	1,2-diaminopropane	Methanol and ethylene glycol	Viscosity 8-9 mPa·s (20°C), surface tension 31.09 mN/m	Ink-jet printing	180°C, 5-30min	15.46	Simple synthetic route, Excellent stability and printability	Conductivity and adhesion

Note: the calculations are based on the recipe presented in each reference that gave detailed data. The prices of chemicals used were collected from Sigma Aldrich website.

Reference

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Appendix

The following is the list of chemical prices used for the calculation of ink cost. The data are from Sigma Aldrich website.

	Chemical	Solutions				Powder				
		Order No.	unit size /mL	Price / €	**Price / €/mL**	Order No.	Purity	unit size / g	Price / €	**Price / €/g**
Solvent	Methanol	322415-1L	1000	64.1	**0.064**					
	Ethylene glycol	102466-1L	1000	64.4	**0.064**					
	2-propanol	190764-1L	1000	44.9	**0.045**					
	DI water	8483339200	200000	368	**0.002**					
	Ethanol	1009831011	1000	41.2	**0.041**					
	Formic acid	F0507-1L	1000	45.9	**0.046**					
Complexing agent	Ammonium hydroxide	1054261000	1000	28.3	**0.028**					
	Ethylamine					301264-100G-EU		100	598	**5.980**
	Ethanolamine	15014-1L	1000	41.7	**0.042**					
	Ethylenediamine	E26266-1L	1000	36.2	**0.036**					
	Isopropylamine	471291-1L	1000	37.9	**0.038**					
	1,2-diaminopropane					117498-100G		100	14.2	**0.142**
	Diethanolamine					D8885-500G		500	27.2	**0.054**
Silver source and additives	Silver nitrate					209139-500G	⩾99.0%	500	1250	**2.500**
	Oxalic acid					75688-250G	⩾99.0%	250	46.8	**0.187**
	Sodium hydroxide					655104-2.5KG	97%, powder	2500	195	**0.078**
	Silver oxide					221163-1KG	99%	1000	2000	**2.000**
	Silver acetate					216674-100G	99%	100	562	**5.620**
	Silver carbonate					179647-100G	99%	100	450	**4.500**
	2-hydroxyethylcellulose					8220680500		500	57	**0.114**
	Sodium citrate tribasic dihydrate					C7254-1KG		1000	43.4	**0.043**