Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

Patterning Microporous Paper with Highly Conductive Silver Nanoparticles via PVP-modified Silver-Organic Complex Ink for Development of Electric Valve

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Keywords: electric valve, silver reactive ink, electrowetting, microfluidics, polyvinylpyrrolidone, hydroxyethylcellulose**.**

1. Results and Discussion

1.1. Characterization of PVP-stabilized silver-reactive ink

To study the stabilization effect of PVP on silver cations, Fourier transform infrared spectroscopy analysis method was performed (Fig. S1). The FTIR spectra of the paper on which the PVP and PVP-modified ink, respectively, had been deposited, showed that the resonance peaks of both C–O and C–N were affected, see **Fig. S1 (A)**. The appearance of a shoulder at 1661 cm^{-1} indicates the stabilization of the silver NPs (of which the size ranges from 500–1000 nm) by the carbonyl group of the PVP[1]. Additionally, the redshift exhibited by the C–N bands at 1019 cm^{-1} and 1056 cm^{-1} confirms the stabilization of silver NPs of smaller size. The formation of silver oxide induced by the deposition of a conventional silver-reactive ink on paper was confirmed by the FTIR spectra, as shown in **Fig. S1 (B)**. The resonance peaks that appear at 3162 cm^{-1} and 1050 cm^{-1} on the FTIR spectrum of silver complex ink unmodified by PVP on paper are attributed to the Ag-O-H stretching and O-Ag-O vibration of Ag_2O, respectively. On the other hand, **Fig. S1 (B)** shows the FTIR spectrum of silver patterns on HEC-modified Whatman No.1 paper formed by deposition of PVP-modified silver complex ink and annealing at 60 °C. The intensities of the resonance peaks at 3162 cm^{-1} and 1050 cm^{-1} decreased, confirming the absence of silver oxide.

1.2. Calculation of Conductivity

To calculate the conductivity of formed silver patterns of Whatman No. 1 paper, two-probe methods via conventional multimeter was used. The thickness of the material was calculated from a cross-section Fe-SEM image of patterns, see Fig. S3 (A). It is worthy to note that compared to other work, silver patterns were formed exclusively on the surface of cellulose fiber in our work. Therefore, the thickness of paper was considered as the thickness of conductive material. The conductivity was calculated using equation (1)

$$\sigma = \frac{l}{RA} \qquad (1)$$

Where R is the resistance (0.4Ω), l is the length (0.04 m) and A is the cross-section which is the product of width (0.002 m) and thickness (31.23 x 10^{-6} m)

To show the difference in conductivity of silver tracks formed by conventional AgR-ink and PVP-modified AgR-ink we have investigated the resistance of different silver tracks deposited on Whatman No.1 paper via three methods (**Fig. S3**)

1.3. Conductivity and porosity of silver patterns

To further investigate the conductivity of silver tracks versus porosity of paper, the PVP-modified AgR-ink was deposited on different paper substrates, and resistance of patterns was recorded (**Fig. S4)**. Substrates with lower permeabilities, such as sulfuric paper, showed a higher conductivity due to the accumulation of silver nanoparticles on the surface of the substrate. These results confirm once again that this method enables the formation of highly conductive silver patterns on macroporous paper, simultaneously preserving its porosity. Therefore, wicking properties were investigated via the capillary rise method of rhodamine solution (10^{-3} M). As shown in **Fig. S5** the immersion of 1.5 mm of silver patterns in rhodamine solution resulted in a migration of solution to about 7 mm through capillary pores. In contrast, this solution has migrated to 12 mm on non-patterned paper upon immersion in 1.5 mm deep. Modification of silver organic ink with PVP solution showed a promising result in the development of highly conductive patterns on microporous paper. Therefore, achieved high conductivity and ability to preserve the porosity of silver patterns deposited by novel developed ink makes them suitable in the development of paper-based flexible electronics, to design paper-based electrochemical sensors, and to print radio-frequency identification (RFID) antennas (**Fig. S6**).

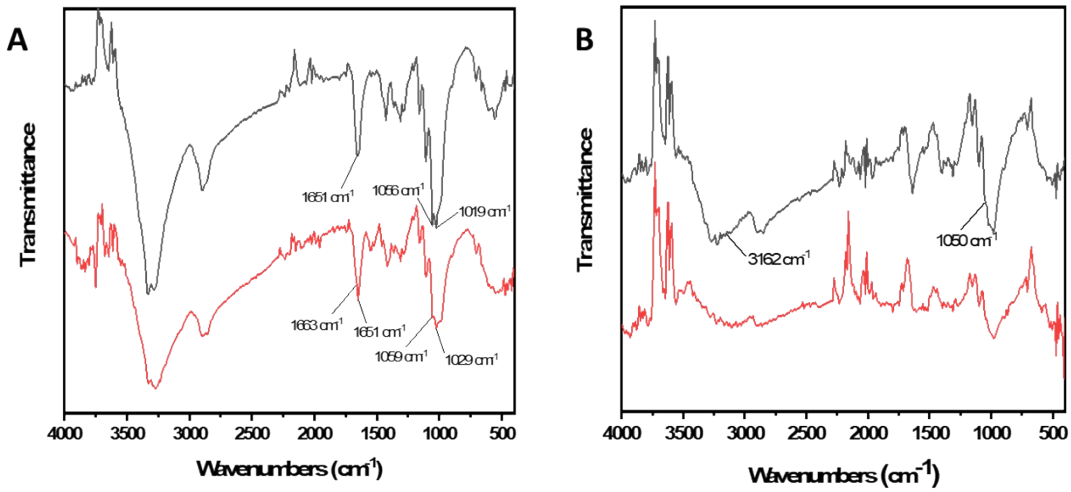

Figure. S1. Characterization of PVP stabilized silver complex ink. (A) FTIR spectra of modified paper: PVP coated Whatman No. 1 paper (black). PVP-stabilized silver-coated Whatman No. 1 paper (red). (B) FTIR spectra of silver coated Whatman No. 1 paper with different methods: Silver-coated paper without PVP on unmodified paper annealed at 60 ° C (black). PVP-stabilized silver coating on HEC-modified Whatman No1 paper annealed at 60 °C (red).

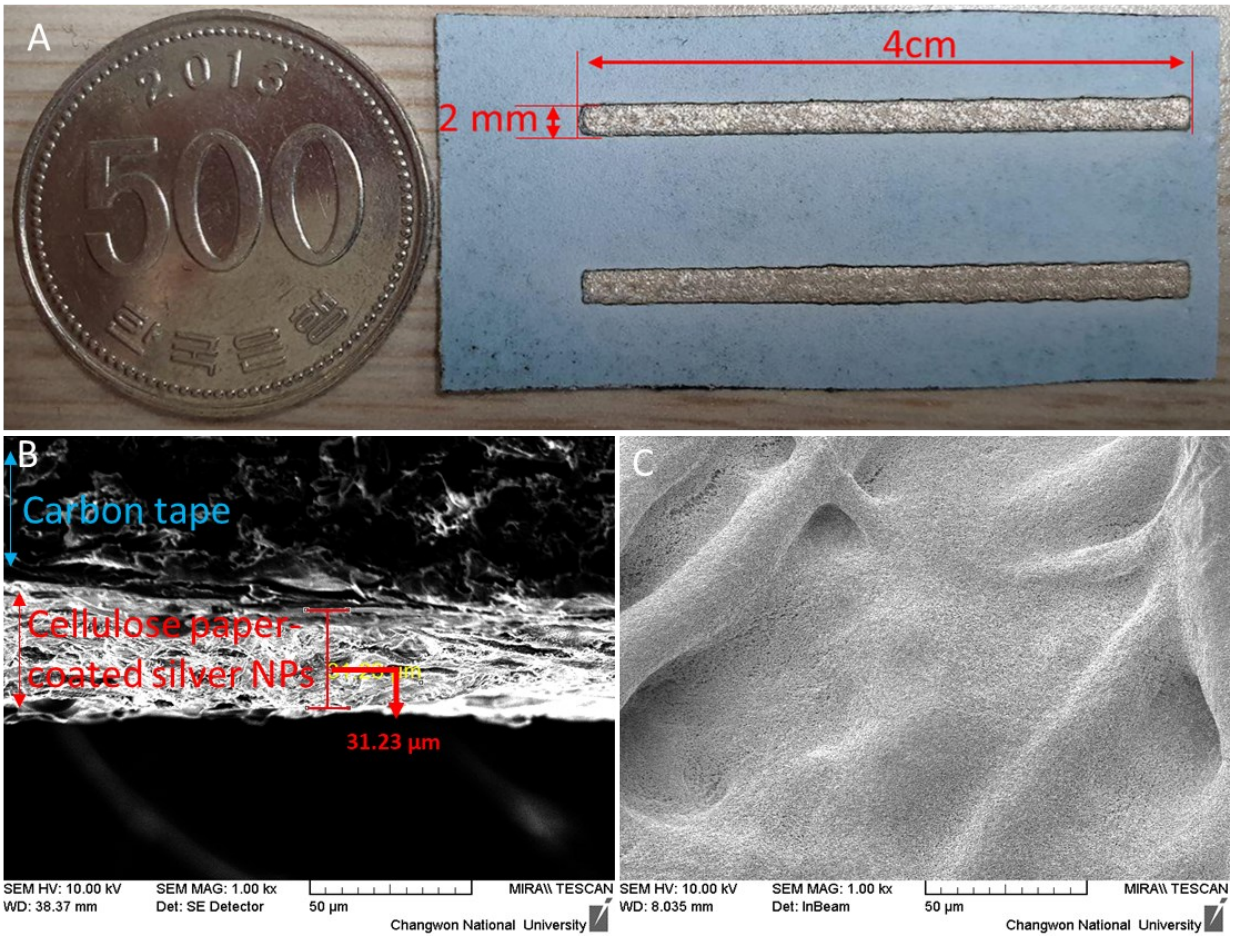

Figure. S2. Photographic image and FE-SEM images of silver patterns on Whatman No. 1 paper (A). Cross-section of the paper-coated silver annealed at 60 °C (B). FE-SEM image of paper-coated silver NPs in lower magnification (C).

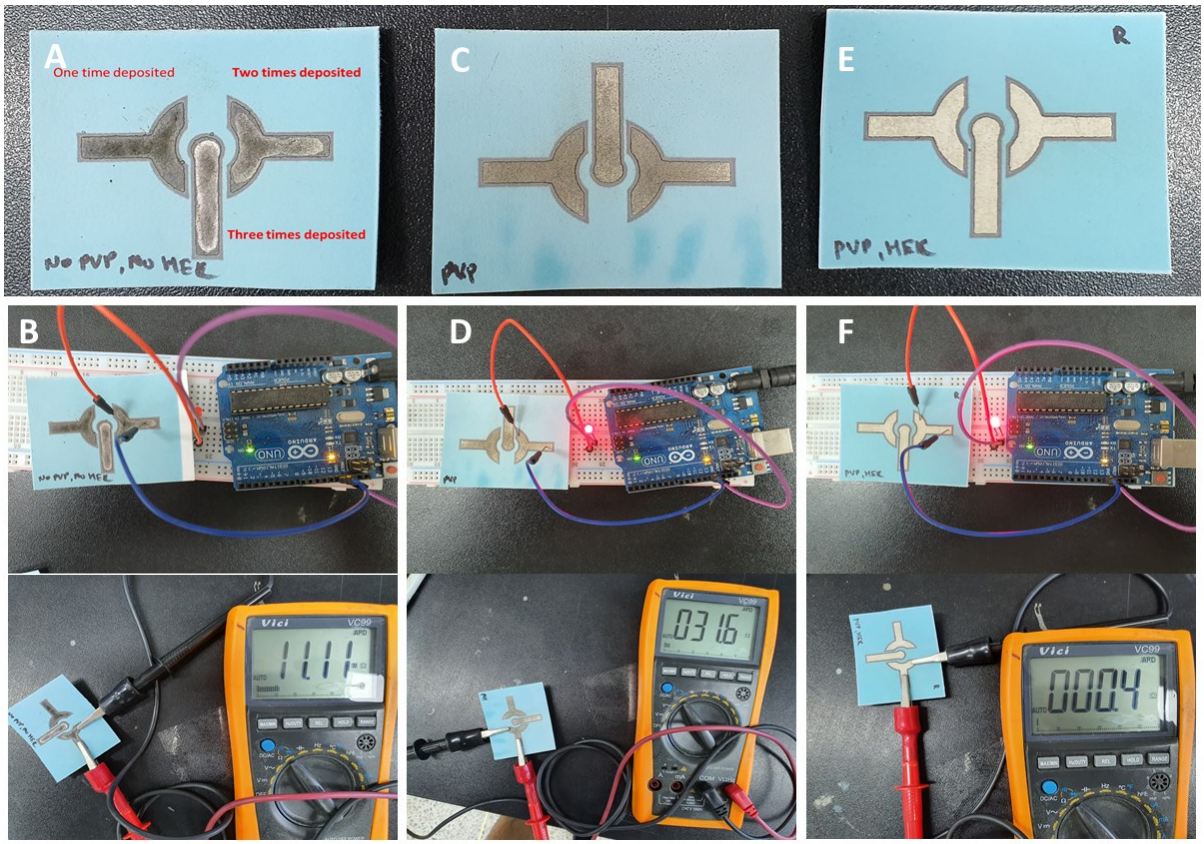

Figure. S3. Photographic image of Whatman No. 1 paper deposited with silver inks. silver-reactive ink on Whatman No. 1 paper and its resistance (A, B). silver-reactive ink modified with PVP on Whatman No. 1 paper and its resistance (C, D). silver-reactive ink deposited on HEC@Whatman No. 1 paper and its resistance (E, F).

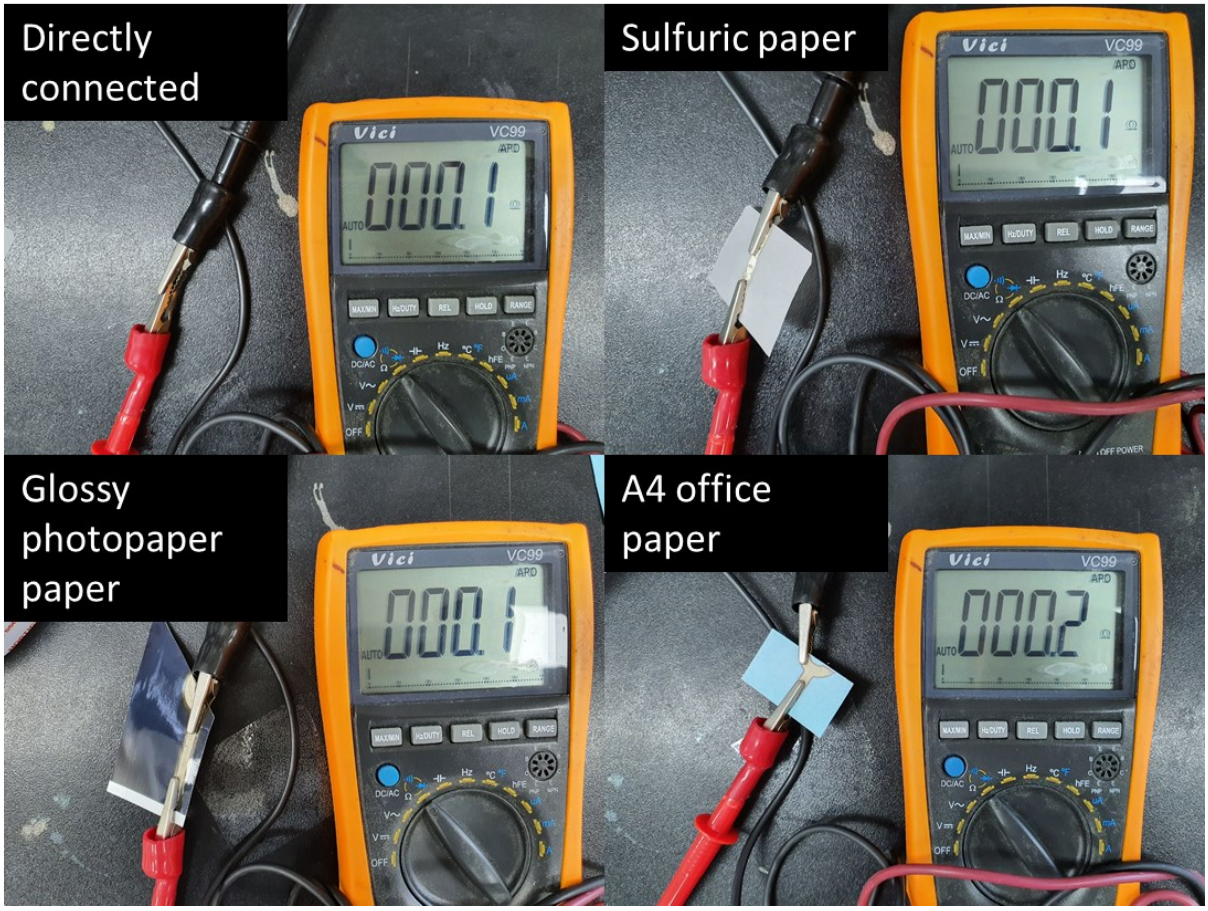

Figure. S4. Photographic image of silver track deposited on different paper substrates and their resistance.

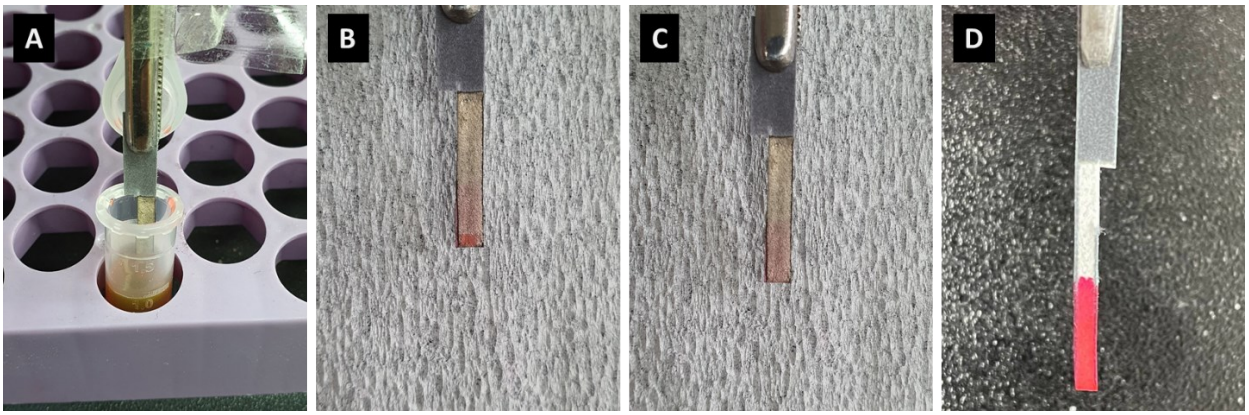

Figure. S5. Photographic image of wicking properties of silver patterns on Whatman No. 1 paper in Rhodamine aqueous solution (10^{-3} M). Immersion of 1.5 mm of silver tracks in Rhodamine aqueous solution(A). Silver track after immersion in Rhodamine solution (B). Silver tracks after drying at room temperature (C). Non-patterned paper immersion in Rhodamine solution (D). §

Notes and references

§ Rhodamine B was used for visualization purpose only

(1) Wang, H.; Qiao, X.; Chen, J.; Wang, X.; Ding, S. Mechanisms of PVP in the preparation of silver nanoparticles. *Mater. Chem. Phys.* **2005,** *94* (2), 449.