Thermoelectric temperature sensors by printing with a simple office inkjet printer

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ABSTRACT

We present printing thermoelectric temperature sensors on paper by using a simple office inkjet printer with three different conductive inks based on carbon nanotubes (CNTs), silver nanoparticles hybrid-composited with CNTs silver nanoparticle/CNTs (AgNPs/CNTs) and thermoelectric poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS). Due to novel combination of electrical, mechanical and chemical properties of three distinct materials of carbon, silver metal and organic polymer: e.g., especially high flexible, high conductivity, non-reduction and low temperature curing, they showed superior materials for printable conductive ink especially for flexible paper substrate. Two dimensional temperature sensor printed on paper, showed improved Seebeck coefficients to 20 % than one of the recently published data, indicating enhancement of thermoelectric performance.

Keywords: Thermoelectric, temperature sensor, inkjet printing, conductive ink, printed paper sensor

1 INTRODUCTION

Printing approach for thin film thermoelectric devices has been considerably attractive attention due to their unique advantages, such as high-resolution, large-scale, and low-cost abilities of fabrication so that it considered as an alternative technology to sophisticate but complicate and complex conventional lithography methodology.[1] Among them, printing temperature sensors have been highly demanded in the paper electronics, such as electronic skin for health monitoring, polymer chain reaction for DNA amplification.[2] Paper is composed mostly of cellulose, which is ubiquitous organic polymer in Earth and is best coupled to printing substrate as well as chemical analytical devices such as litmus pH indicator, urine testing strip or pregnancy test. Furthermore, the cellulose fibers of paper strongly absorb a wide range of ink-like materials, enabling various paper-based electronic devices has been realized so far, such as diodes, displays, and batteries. In circumstance that very recently paper electronics has tremendous attention in many research fields especially relaying on printing technology, in this report, the thermoelectric temperature sensor printed on paper has explored to apply to the possible applications, especially the paper-based analytical devices.[3]

Here we, among the conductive inks, selected PEDOT:PSS, which is an organic polymer mixture of two ionomers, for a transducer material used for a temperature sensor because of its novel thermoelectric (TE) property with high Seebeck effect as well as good dispersion in water.[4] Furthermore, a hybrid composite of metal of silver nanoparticles and carbon nanotube, AgNP/CNT ink was used for printed counter electrodes for a thermocouple. Both of two inks was formulated also in water-based dispersive inks, which enable us to use two affordable material and method, such as a paper substrate and an inkjet printer, especially a simple affordable office inkjet printer.

2 RESULTS AND DISCUSSION

On realizing a paper temperature sensor, there are three major factors to be considered as shown in Fig. 1a and b: fabrication of conductive inks including at least one thermoelectric material which takes a role of a transducer converting thermal stimulus to electric energy, a proper printable substrate and printing method. We prepared aqueous PEDOT:PSS ink for the thermoelectric electrode with CNT and AgNP/CNT inks for the counter electrodes, paper and a simple office inkjet printer.[5, 6]

Most widely use of temperature sensor is the thermocouple type. Generally it requires coupling of two metal conductors, such as chromel and alumel, to form two interfaces of electrical junctions, at which the electric motive force generates dependent on their temperature difference, as result of the thermoelectric effect (Fig. 1c). One junction is used for sensing temperature (hot junction, red box in inset) and the other for reference temperature (cold junction).

However, metallic thermocouple is not suitable for printing fabrication method, because it is very hard to obtain the printable non-oxidizing metal inks especially suitable on paper substrate. Even though commercial metallic nano-particle inks of low annealing temperature, cannot be used directly for a simple office inkjet printer, due to their rare water dispersion.[7] Therefore water-dispersive organic conductive PEDOT:PSS composite polymer ink is fairly preferred to paper substrate. Additionally, it is cheap, flexible and high electrical conductive material so that it recently is an emerging material to be alternative material for iodine doped tin oxide (ITO). Since PEDOT:PSS is well known as a p-type doped polymer, if we couple with a n-type polymer it should be best desirable to form a high efficient TE thermocouple, which works by self-power without any external exciting power source. Instead of applying very rare n-type polymer, we choose the carbon nanotube for counter electrode material for a thermocouple. Besides of flexible and durability for oxidation likewise PEDOT:PSS at air ambient environment, due to highly thermoelectric coupling with PEDOT:PSS, the good TE performance was expected. Furthermore, since a good printable water-based CNT ink has developed already in our lab, it is easy way to printing fabrication two inks comprehensively and complementary to form the patterned sensors.[5]

As shown in Fig. 1a schematically, the thermocouples were successfully printed by using an office inkjet printer, after filling three conductive inks into the separated ink cartridges (PEDOT:PSS in cyan and CNTs in yellow and AgNP/CNT in black), after fabrication of three inks properly to satisfy the specific ink condition, such as viscosity, surface tension, dispersion and particle size as shown in Table 1.

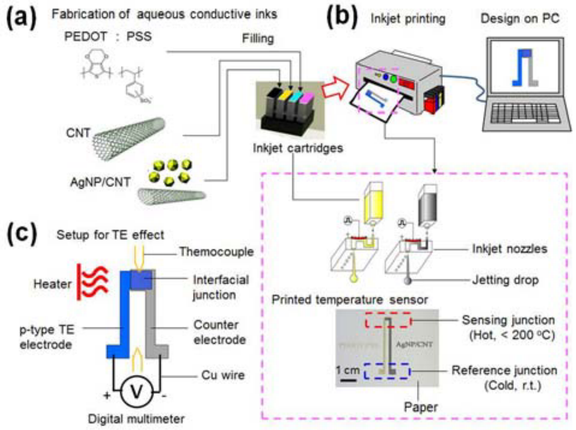

Fig. 1. 1(a) Schematic view of processes of printing thermoelectric temperature sensor on paper: (a) fabrication of aqueous conductive inks and filling of each into separated ink cartridges, (b) printing of thermoelectric temperature sensors, which was designed simply on PC, by using an office inkjet printer, and (c) experimental setup of measurement of TE effect. Inset: Inks filled into multiple cartridges and piezoelectric pressurizing jetting a series of ink drops forming a patterned TE couple on paper.

Table 1. Characterization of conductive inks

Material	Solvent	Viscosity (cP)	Surface tension (mN/m)	Particle size (μm)
PEDOT:PSS	Water	10.0	38	< 0.4
CNT	Water	4.3	22	< 2.0
AgNP/CNT	Water	6.5	40	< 2.5

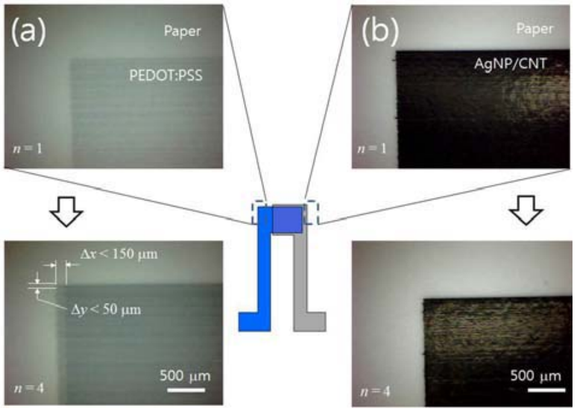

Fig. 2. Morphological images of optical microscopic spectroscope of PEDOT:PSS and AgNP/CNT inks printed on paper as a function of the number of printing times (*n*): (a) PEDOT:PSS and (b) AgNP/CNT for *n* = 1, 4, respectively.

Printed patterned image of PEDOT:PSS electrode by Epson stylus T22, as a function of the number of printing times, has been studied by an optical microscope. Figure 2 showed the detail formation of printed image of the jetting drops of PEDOT:PSS through a piezoelectric pressurized nozzle at first layer. It indicated the homogenous electrodes started to form after at least $n > 3$ with edge resolution of 150 μm and 50 μm in *x*- and *y*-directions, respectively.

The overlaid printing method also offered an increase of conductivity to enhance percolation of conductive particles into cellulose in paper pulp. The measured surface resistance for printed PEDOT:PSS and CNT electrodes by using four-point probe method was investigated as a function of the number of printing times (Fig. 3). The power curve revealed that the printing aqueous PEDOT:PSS ink is well coincident to a typical percolated adsorption.

However, since the conductivity of printed CNTs is relatively low, improvement of the conductivity was required. Hence, we introduced composition with AgNPs, which was hybridized with metal particles and carbon nanotubes, at which mixture the composited ink kept printability without loss properties of aqueous ink, such as viscosity and surface tension (Table 1). Furthermore, surprisingly the enhanced conductivity increased in three orders of power by low temperature thermal annealing of 150 °C, so much as it reached to the conductivity when

AgNP printed alone as shown in Fig. 3. Therefore, we selected this hybrid composited AgNP/CNT ink for printing the counter electrode of PEDOT:PSS TE sensing electrode with thermal curing at 150 °C after printing, at which temperature paper is thermal resistant sufficiently because of its limit is about 200 °C. On the other hand, AgNP/CNT ink showed a somewhat eccentric behaviour of decreasing of conductivity for $n > 4$. This decreasing was attributed to an increase of irregularity and formation of non-uniform of paper surface after swelling of pulp in paper. It is because the newly created swelled pulps crevasse is too longer and deeper for the aqueous colloidal AgNPs to interconnect each other.

Meanwhile, it is well known that the conductivity of organic conductive PEDOT:PSS polymer is strongly dependent on dopants due to its p-type doped via oxidation, addition of cosolvent with water and fractional amount of composited PSS. In this study we did only focused improving the interface between printed PEDOT:PSS and AgNP/CNT electrodes to enhance the thermoelectric efficiency. Instead of reduction of PEDOT:PSS, we increased the counter electrode as mentioned above, such that it overcame significantly certain benefit that could be obtained from increasing of conductivity via oxidation of PEDOT:PSS.

According to the Seebeck effect, the properties of thermoelectric materials is providing a electro motive force (emf), ΔV, under the temperature gradient, ΔT,

$$\Delta V = S\Delta T \tag{1}$$

where S is the Seebeck coefficient depended on the material, which represents the thermoelectricity of a specific material.

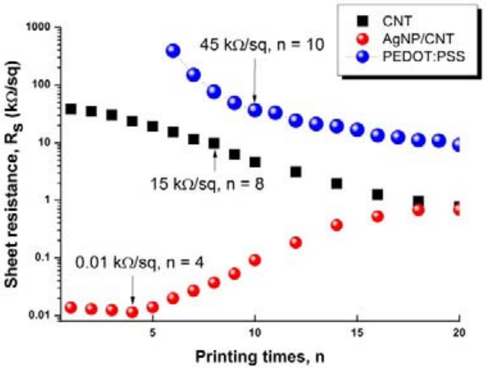

Fig. 3. Sheet resistance of PEDOT:PSS, CNT and AgNP/CNT hybrid composited inks as a function of the number of printing times. Remarks were selected n and $R_s(n)$ used for a thermocouple.

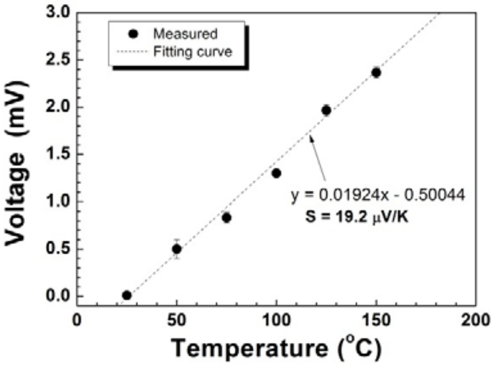

Fig. 4. Measurement of Seebeck effect for three different conductive electrodes which printed on paper

Since studying the individual Seebeck coefficient is complicated either theoretically and experimentally, we performed only measurement for the compounded PEDOT:PSS and AgNP/CNT electrodes under an plausible assumption that the Seebeck effects of both AgNP and CNT electrodes is ignorable to that of PEDOT:PSS. Thus, our experimental setup for investigation of thermoelectric effect on a thermocouple is a simply configured as shown in Fig. 1c, which is composed of two heat sinks, hot and cold, to provide the temperature gradient. Plate heater was used to supply the thermal stimulus, and he measured emf was read by a digital multimeter.

Because the thermocouple is a kind of thermal engine its achievable thermal performance is limit to the highest efficiency of the ideal Carnot engine. Actually if the efficiency of any TE-module, such as our thermocouple, is high, it can be used electric power generator. Rather than the efficiency, the measurement of the Seebeck coefficient was formed due to its simple, easy and rapid detection. Varying current supplying to the heater mounted beneath the sensing hot junction, the temperature gradient was provided while keeping the reference junction at room temperature via two long leg connections between two junctions. This point is one of good advantages of paper based substrate utilizing its high thermal resistance, because paper itself is a good thermal insulator.

As shown in Fig. 4, the measured data is clearly linear in rage of room temperature to 150 °C, so that from the slope of the best fitting curve the Seekbeck coefficient was obtained: +19.2 μV/K, which was about 20% improve relative to one published data of 14 μV/K.[8] Positive sign of PEDOT:PSS leg indicated the p-type TE material. To enhance the molecular binding at the interface of junction ultraviolet irradiated at 5W power for 20 min. However, unexpectedly, there was no noticeable observation.

Two current suggesting models are possible to understand our enhancing thermal effect. Firstly, it is possible to assume that the PEDOT:PSS oxidation to help doping to increasing of TE effect took places mostly during the thermal annealing for printed AgNP/CNT electrode. Secondly, according to a model of the hoping type carrier transport between conductive PEDOT segments in grains, in which PEDOT is shelled in a long chain insulating PSS, the enhancement of hoping was caused due to removal of shell by not only thermal annealing. In addition, the AgNPs on CNT help the hoping electrons between interfacial PEDOTs by reducing the energy barrier at their interface. To confirm this hypothesis, the morphological observation of interfacial surface of printed PEDOT:PSS and AgNP/CNT electrodes was performed through SEM images (Fig. 5), revealing the formation of AgNP grains clearly.

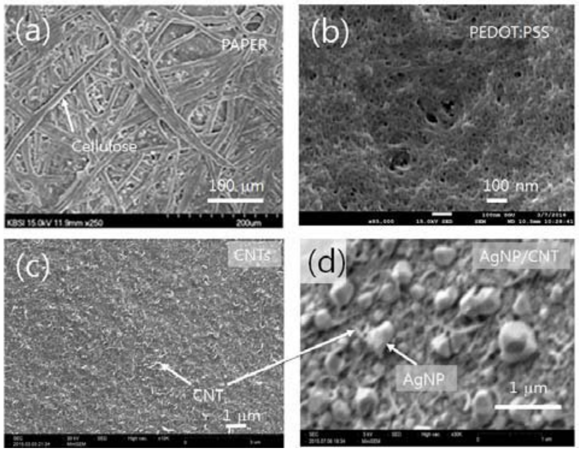

Fig. 5. SEM images for (a) pristine paper, and (b) printing deposited PEDOT:PSS, (c) CNTs, and (d) AgNP/CNT electrodes on paper after thermal annealing.

In conclusion, we successively printed the thermocouple of organic PEDOT:PSS and metal-carbon hybridized AgNP/CNT composited electrodes by using an office inkjet printers after filling the multiple cartridges instead of color pigment inks. The linear Seebeck coefficient by thermocouple effect was clearly achieved such that it can be applicable to a printed paper temperature sensor.

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