Journal of Materials Chemistry A



View Article Online

PAPER



Cite this: DOI: 10.1039/c6ta10997g

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nanowires*

wearable heater using a single-step supersonic kinetic spraying technique that deposits silver nanowires (AgNWs) on rollable substrates, facilitating a roll-to-roll process. AgNWs were suspended in an aqueous solution and supersonically sprayed onto a rolling substrate to produce a flexible heater film without use of any binders or additional post-process treatments. Because of the high-speed impact, the intersections of the nanowires were fused, thus creating a junction-free network of nanowires, which significantly reduced the contact and thus the sheet resistance. Cyclic temperature testing confirmed the thermal stability of the AgNW heater. A heater bent to a radius of less than 2 mm was tested for 600 000 cycles; the heater exhibited little change in the sheet resistance. Moreover, it does not experience significant thermal expansion, which would manifest itself in buckling, and thus such heaters do not buckle during operation. AgNWs were sprayed onto a complex surface of a replica of Venus de Milo and Jeju's Dol Hareubang statues, demonstrating the deposition capability onto a 3D surface. Defogging and defrosting tests showed potential applications of this heater in smart mirrors or windows. The highest heating temperature of 160 °C was achieved in a transparent fibrous film having 95% transparency and 15 Ω sq⁻¹ sheet resistance at a supplied voltage of 8 V. Because the film fabrication method is rapid and scalable with the installation of multiple nozzles, the method is commercially viable.

Highly flexible, stretchable, wearable, patternable

and transparent heaters on complex 3D surfaces

formed from supersonically sprayed silver

Received 21st December 2016 Accepted 6th March 2017

DOI: 10.1039/c6ta10997g

rsc.li/materials-a

1. Introduction

Heaters that convert electrical energy into thermal energy *via* Joule heating are useful in various areas, both in household and industrial applications. Household examples include oven ranges, air and water heaters, toasters, heating blankets and films, patio heaters, and defogging and defrosting smart windows.¹⁻¹³ In industrial applications, examples are innumerable, because thermal management of manufacturing of engineered products is frequently required. In general, the temperature requirements to heaters in industry are much more stringent than the requirements to household ones. The

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supplied power (*P*) determines the heating temperature (*T*). Often, power is limited in portable uses because of the low voltage, namely, $P = V^2/R$, where *R* is the resistance of the heating material. The resistance *R* must be minimized in order to maximize *P* to achieve the highest *T*. This requirement narrows the choice of materials, as only low-*R* materials can meet the requirement. In addition, the public demands aesthetically pleasing heaters that are transparent and flexible, which can be installed on complex 3D shapes, so that they can become wearable heating gadgets.

Indium tin oxide (ITO) is the most commonly used material for such heaters, with satisfactorily low *R* and transparency (T_r); however, ITO is brittle and inflexible, and thus cannot be installed on complex 3D surfaces, making it unwearable.¹⁴ Therefore, nanomaterials such as carbon nanotubes (CNTs),¹⁵⁻¹⁸ graphene,¹⁹⁻²¹ and metal nanowires²²⁻²⁸ have been utilized to achieve both heater transparency and flexibility. In general, metal nanowires have much lower resistances than carbon materials (CNTs and graphene); thus, metal nanowires are the preferred materials for portable and wearable heaters that require low electrical resistances. Furthermore, the facile and inexpensive manufacturing process for metal nanowires is more

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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ta10997g

attractive than the complicated and expensive process used for carbon materials. A review by Yao and Zhu discusses various nanomaterials for flexible, stretchable, and transparent electronic applications.²⁹

Silver nanowires (AgNWs) are probably the most popular nanomaterial that guarantees satisfactorily low resistance and can lead to high transparency, and flexibility.30 Because the AgNW thickness is in the range of tens of nanometers, a high rate of light transmission is guaranteed, i.e. light scattering might be low and transmittance high if a few layers of AgNWs would be used. However, despite the relatively low R of AgNWs, there remains room for improvement of heater performance. When AgNWs are overlaid, they form slight tangential contacts with each other, causing a dramatic increase in the contact resistance of the nanowire network. To circumvent this issue, post-treatment processes such as pressing and annealing have been utilized to decrease the contact resistance in the junctions.³¹ However, AgNW films are often damaged by mechanical pressing. Annealing is incompatible with the roll-to-roll process because it melts the polymeric substrates. Rao and Kulkarni used cracked layers as a means to fill in the gold-sputtered junction-free network, which enhanced electrical properties of transparent conducting films. However, their method required multiple steps, including a high-temperature vacuum sputtering process.32 Therefore, there is an urgent need for the development of a simple coating method that can fuse nanowires without post-treatments.

Here we apply a supersonic spraying technique to deposit AgNWs that are self-fused at wire junctions upon impact, which is described in detail elsewhere for transparent conducting electrode applications.³⁰ No heater applications have been explored using the self-fused AgNW heater. In brief, AgNWs are entrained into a supersonic gas stream and move supersonically, and the nanowire junctions are immediately fused upon their collision with the substrate due to a significant kinetic energy converted to heat on impact.30 We demonstrate the fabrication of a roll-to-roll heating film of 10 cm width and meter-scale length. Using the same method, AgNWs were also deposited onto a complex 3D surface and radiated heat under power supply. The heater films were characterized and their flexibility, stretchability, patternability, and wearability were demonstrated. In addition, defogging and defrosting applications were elucidated.

2. Experimental

2.1 Supersonic cold spraying

Fig. 1 is a conceptual depiction of the supersonic cold-spraying deposition process. A liquid AgNW precursor solution is sprayed by the supersonic stream being supplied into it at a flow rate of 1.2 mL min^{-1} using a syringe pump (Legato 210, KDS). The precursor is first atomized by an ultrasonic atomizer (VCX 40 kHz, Sonics & Materials) before atomized drops containing AgNWs are entrained to provide the most monodisperse and finest drops possible. The atomized drops rapidly undergo evaporation, leaving dried airborne AgNWs. Because of the supersonic impact, significant kinetic energy almost



Fig. 1 Schematic of supersonic cold-spray deposition onto a 3D structure. Middle top inset: SEM image of self-fused nanowires. Left bottom inset: a transmission electron microscopy (TEM) image of a self-fused AgNW junction.

instantaneously is dissipated as heat and the wire junctions become fused together (see the SEM and TEM images in the inset in Fig. 1). As a result, the deposited AgNW layer becomes highly conducting and transparent. The supersonic gas velocity is determined by the inlet chamber pressure and temperature of the compressed air, at $1 < P_0 < 4$ bar and $200 \le T_0 \le 300$ °C, respectively (see Table 1), which yields an isentropic air velocity of 690–780 m s⁻¹.^{33,34} In general, coating an area of 30 cm × 20 cm requires ~30 s using this lab-scale, single-nozzle setup. An array of multiple nozzles could allow rapid production of coatings on wider substrates in a roll-to-roll process using a rollable PET substrate, whose thickness is determined based on its transparency as well as durability and hardness. More details on the cold-spraying deposition process can be found in our previous studies.^{35–37}

2.2 Characterization

The surface morphologies and elemental maps of the fabricated films were evaluated using a field-emission scanning electron microscope (FE-SEM, S-5000, Hitachi, Ltd.) and a transmission electron microscope (TEM, JEM 2100F, JEOL Inc.). The currentvoltage curves were measured using a current meter and voltmeter (3288, Digital HiTester 3256, HIOKI). The surface roughness and physical appearance of the films were observed using an atomic force microscope (AFM, XE-100, Park Systems) and an optical microscope (OM, Metaphot, Nikon), respectively. The surface temperature was measured by an IR camera (FLIR-E63900, FLIR, Wilsonvile, OR, USA). The AgNW precursor (Aiden, Korea) had an average diameter and length of 20 nm and 15 μ m, respectively. The precursor used isopropyl alcohol (IPA) as a solvent with 0.15 wt% concentration. The mixing

Pressure [bar]	1-4
Gas preheating temperature [°C]	200-300
Traverse speed [mm s ⁻¹]	40
Nozzle-to-substrate distance [mm]	50

weight ratio was 2:1:6 for the first precursor, second precursor, and newly added IPA, respectively. This mixture is considered to be optimal based on the repeated experimental trials.

3. Results and discussion

3.1 Silver nanowires

AgNW-coated on a flexible polyethylene terephthalate (PET) substrate with the compressed air conditions of $P_0 = 4$ bar and $T_0 = 220$ °C yielded the highest transparency and lowest sheet resistance of the fabricated films. The surface roughness or height is in the range of 0-30 nm, even at the junctions of AgNWs, indicating fusion at the two nanowire junctions while a single nanowire has a thickness of 20 nm. The highest point is attributed to multiple overlaid AgNWs, which are fused. The inset in Fig. 1 shows an SEM image that confirms the fused junctions, at which wires are connected to the following nanowire impacting several previously deposited nanowires underneath. An optical image of a coated film demonstrates the uniform distribution of AgNWs over the PET substrate. The crystal structure of AgNWs was also confirmed by TEM. Another inset in Fig. 1 shows the high-resolution TEM (HRTEM) image of two AgNW junctions and the fast Fourier transform (FFT) pattern (as an inset). The observed lattice plane spacing for AgNWs was 2.39 Å, which corresponds to the (111) plane. The FFT pattern (inset) shows a spot on the image corresponding to the (111) plane.

3.2 Heating performance

In Fig. 2a and b the regime above the dashed line is the percolative regime in which 2D nanomaterials suffer from transporting sufficient number of electrons (thus electrical properties degrade). On the other hand, a bulk property in which normal or good electrical properties are retained is observed in the bulk-like regime which is the region below the dashed line.³⁸

Fig. 2a shows the transmittance of the supersonically sprayed AgNW-coated films at each corresponding sheet resistance. Note that the transmittance was measured at $\lambda = 550$ nm with respect to the 100% transmittance of a PET substrate. Because of the self-fused junctions (see the inset SEM image), the films exhibit superior sheet resistance in the range of ~ 101 Ω sq⁻¹, while maintaining high transparency (T > 90%). This low sheet resistance at high transparency is desirable for high performance transparent heaters as the heater temperature is essentially governed by the power (P) which is supplied to the film; $P = V^2/R$, where R is the total resistance of the film. It is noteworthy that two distinct regimes are clearly shown in Fig. 2a; the bulk and the percolation regimes. Fig. 2b is subdivided into two areas: percolation and bulk-like regimes. The bulk regime has persisted up to $T \le 98\%$ without showing any sign of rapid deterioration of the performance. Early bending of the curve, known as the percolation regime, is the indication of a typical performance deterioration of one-dimensional nanomaterials, as extensively investigated by De and Coleman.³⁹ Persistence of this stiff line reaching up to T = 98% reveals the



Fig. 2 (a) AgNW film transparency vs. the sheet resistance. (b) Log-scaled transmittance and sheet resistance of the AgNW films. (c) Timedependent temperature profiles (T_s) of AgNW-based film heaters under the applied voltage of 5 V and different resistances. (d) T_s versus t for various voltages $2 \le V \le 6$ V and a fixed resistance.

superior performance of our supersonically sprayed AgNW transparent conducting films.

Fig. 2c shows the time-dependent surface temperature T_s of the six AgNW films having the sheet resistances of $R_s = 10, 12,$ 15, 20, 30, and 50 Ω sg⁻¹ and the transparencies of $T_r = 88, 92$, 95, 96, 97, and 98%, respectively. The voltage of 5 V is applied for 150 s, after which the power supply is disconnected and the surface temperature decreases, as shown in Fig. 2c. The initial temperature of the testing environment was the room temperature for all tested cases. It is seen that the films with lower sheet resistance yield higher surface temperatures because of the higher power supply at the same voltage ($T_s \propto P = V^2/R$). In Fig. 2d, the link between a higher power supply yielding a higher T_s is also distinguishable. Indeed, as the applied voltage is increased, T_s also increases because $P \propto V^2$ at a fixed *R*. The voltage is increased from 2 to 6 V for the film having $T_r =$ 95% and $R_{\rm s} = 15 \ \Omega \ {\rm sq}^{-1}$. It should be emphasized that the total resistance R is comprised of a contact and a sheet resistance. However, in the present case, the sheet resistance is the dominant part and thus the contact resistance can be safely neglected. Accordingly, in the above discussion it is implied that $R \sim$ $R_{\rm s}$. To confirm whether this assumption is valid, the total resistance of an AgNW film having sheet resistance $R_{\rm s} = 15 \ \Omega$ sq^{-1} and transparency $T_r = 95\%$ was measured. When supplied with the 6 V voltage, the corresponding current was measured to be 0.4 A, which yields the total resistance of $R = V/I = 15 \Omega \text{ sg}^{-1}$, which means that $R \sim R_s$.

Fig. 3 shows the heating performance of the AgNW film with the sheet resistance $R_s = 15 \Omega \text{ sq}^{-1}$ and the transparency $T_r =$ 95%. In Fig. 3a and b, the voltage level is gradually increased from 1 to 8 V. The power, calculated as P = IV, can be estimated using the applied voltage and the measured current using the

data for it presented on the right-hand vertical axis in Fig. 3a. As the power is increased, the surface temperature is increased as well, eventually reaching a maximum recorded temperature of 160 °C at 8 V, beyond which the AgNW network breaks down due to melting. Note that the substrate used herein is alumina, so it could sustain high temperatures. A PET substrate would have melted or at least been severely damaged in this hightemperature range, and thus was not used. Fig. 3c and d reveal the long-term cyclic thermal stability of the AgNW film at variable voltage levels of 5 V and 6 V. When the voltage level was applied, the AgNW heater immediately responded with the maximum temperature of 83 and 98 °C for 5 V and 6 V, respectively. For a given period of 3000 s, 18 cycles of ascending and descending temperature are steadily observed, indicating sufficient thermal stability of the film. Overall, up to 200 cycles no degradation of the heating performance was revealed. The maximum temperature of 83 °C and ~98 °C observed in the 5 V and 6 V cases is consistent with the temperatures observed in Fig. 3a and b, indicating the sufficient repeatability of the films' heating performance. Note that the power levels supplied to the 5 V and 6 V cases can be computed with measured current values of I = 0.33 A and 0.40 A, respectively. The corresponding power was P = IV = 1.67 W and 2.4 W, indicating that the higher surface temperature resulted from the higher power supplied.

Fig. 4a shows the defogging performance of the AgNW film. On the left-hand side in this figure, a non-coated bare glass film is held, while on the right-hand side, an AgNW-coated film supplied with the voltage of 5 V is held. Below these two films, a container with boiling water was located, which released vapor toward the films. The bare film is visibly covered with precipitated vapor, while the heated AgNW film prevents vapor condensation due to the heat it releases. In Fig. 4b, a defrosting



Fig. 3 Performance of the AgNW film having the sheet resistance $R_s = 15 \Omega \text{ sq}^{-1}$ and transparency $T_r = 95\%$. (a) Variation of the surface temperature T_s with varying voltage (and thus current). (b) T_s variation in time *t* for varying voltage *V*. (c) Cyclic thermal stability test for cyclic or repeating voltage level of V = 5 V, and (d) 6 V.



Fig. 4 (a) Defogging experiment. Comparison between a non-coated glass (on the left) and an AgNW-coated glass (on the right) exposed to "Vapor" arising from heated water below. (b) An infrared (IR)-image showing the non-heated (left) and heated (right) glasses. (c) Defrosting experiment; three photographs of the AgNW-coated film with $R_s = 15 \Omega$ sq⁻¹ and transparency $T_r = 95\%$ over a 2 min period.

experiment is conducted with a flexible AgNW-coated PET substrate. Because the film is flexible, light reflection is observed in all the three photographs. The left-hand side image shows the initial (t = 0) ice domains on the PET substrate. At t = 1 min (the middle image), all the ice has melted and the remaining water drops are visible. At t = 2 min (the right-hand side image), all water drops have already evaporated, suggesting the potential use of the AgNW heating films as defrosters for smart flexible windows. The film was supplied with 5 V and the temperature was maintained at ~80 °C.

3.3 Flexibility, stretchability, and patternability

In order to demonstrate the heater flexibility, an AgNW-coated PET substrate was gripped on both ends by holders with 30 mm in between (as shown in Fig. 5a on the left). The film underwent a cyclic bending down to the radius of curvature of $R_{\rm b}$ = 2 mm for 600 000 cycles (not shown, because the resistance change over time was immaterial). During these bending cycles the film was powered and permanently continued to release heat, with the maximum surface temperature approaching 80 °C, as shown in the infrared (IR) photographs in Fig. 5a. The bending strain was $\varepsilon = d/2R_{\rm b} = 0.00325$, where *d* is the substrate thickness (d = 0.013 mm).⁴⁰ The change in the sheet resistance $(\Delta R_{\rm s})$ was measured after the bending cycle, with $\Delta R_{\rm s} = (R_{\rm s} - R_{\rm s})^2$ R_{s0} / R_{s0} , where R_{s0} is the initial resistance and R_{s} is the resistance after the bending experiment. The value of ΔR_s remained below 0.1% after the bending experiment. Such a negligible change in the sheet resistance indicates an excellent mechanical robustness of the AgNW film fabricated by supersonic cold-spraying.

Fig. 5b shows the stretching of an AgNW sample coated on an eco-flex substrate. The AgNW film had the sheet resistance of $R_s = 15 \ \Omega \ \text{sq}^{-1}$ and the transparency of $T_r = 95\%$. Both ends of the film were tightly held during stretching. Initially, the film was L = 10 mm in length and then stretched up to 400%, while heating took place simultaneously, with the maximum temperature being about 47 °C under 4 V of the applied voltage. Beyond the 400% stretching, the film network was broken and thus heating stopped. The film could have been stretched longer if a sufficient amount of AgNWs were coated. However, the transparency of this AgNW film was purposely set high at $T_r = 95\%$ and thus only a limited amount of AgNWs was present in the film, which prevented the heater from stretching beyond 400%.

Fig. 5c shows a stainless steel mask used for spraying through a mask. The patterned characters should still be interconnected to be able to carry the electric current. The mask resembled the character sequence "SCAL", which was reproduced on an AgNW-coated flexible PET heater. The highest temperature of the patterned substrate approaches 72 °C. This is lower than the typically observed maximum of 80 °C because of an increased resistance of a meandering patterned structure compared to the un-patterned one. Nevertheless, the patterned AgNW structure was capable of releasing heat uniformly over the characters. This is encouraging because heaters in certain applications require patterned shapes, some of which can only be achieved by complex multiple-step lithographic procedures. The supersonic spraying of AgNWs can achieve the same goal *via* simply spraying through a mask.

3.4 Complex surfaces and roll-to-roll processing

Fig. 6a shows an AgNW-coated glove heater juxtaposed with a bare non-coated glove; this demonstrates the heater mode in active heating when electric power is supplied. Namely, on the left, two electrodes are attached to the glove top to supply voltage for Joule heating. In Fig. 6b, human hands were inserted into the AgNW-coated glove on the left and non-coated (bare) glove on the right. Note that no power was supplied in this case. The AgNW-coated glove exhibits a lower temperature because the AgNW layer acted as a thermal insulator, preserving body heat inside the glove by efficiently entrapping air. On the right in the bare case, however, the body heat is readily removed from the glove. The emissivity of Ag is relatively low, about $\epsilon = 0.02$,⁴¹



Fig. 5 (a) Photographs and infrared (IR) images of an AgNW film during bending tests at (left) the initial conformation and (right) the final conformation. The AgNW film used had $R_s = 15 \Omega$ sq⁻¹ and $T_r = 95\%$ and was supplied with a voltage of 5 V. It should be emphasized that in the panel (left) a slight elevation difference of the two grips causes a small bending of the sample, which is clearly different from the heating-related buckling (absent here). (b) Photographs and IR images of the AgNW films during the stretching experiment at (left) the initial state (L = 10 mm), (middle) the intermediate stages of stretching with the strain values in percentage shown in the panels, and (right) the final state (L = 50 mm) for the film having $R_s = 15 \Omega$ sq⁻¹ and $T_r = 95\%$. The substrate used was a stretchable eco-flex. (c) A photograph of a stainless steel mask and an IR image of the character patterning reading "SCAL" on an AgNW-coated PET substrate. The AgNW film used had $R_s = 15 \Omega$ sq⁻¹ and $T_r = 95\%$ and was subjected to a voltage of 5 V.

which was calibrated at the surrounding temperature in the range of $19 \le T \le 200$ °C.⁴² This indicates that an object covered with Ag emits little heat and therefore, in turn, traps the body heat by entrapping the air. For the situation shown in Fig. 6b, human body heat is trapped and not lost to the relatively cold



Fig. 6 (a) The comparison of the heating (the AgNW-coated) and nonheating gloves on the left and right, respectively. (b) The comparison of the insulating AgNW-coated and IR-radiating gloves with human hands inside on the left and right, respectively. (c) A heater mode when power is supplied. Without power supply, the AgNW film can function as a thermal insulator because of the entrapped air.

surroundings, as evidenced by the "cold" IR image of the AgNWcoated glove on the left, juxtaposed to the non-coated glove radiating body heat on the right. Fig. 6c summarizes both functionalities of the heating and insulating modes of the AgNW-coated surface when voltage is and is not supplied, respectively.

Fig. 7 shows a clay-pressed replica of the Venus de Milo statue and Jeju's Dol Hareubang coated with AgNWs. The spraying conditions remained as stated before, but a sufficient $(t_{\rm spray} \sim 60 \text{ s})$ amount of AgNWs was sprayed over the complex 3D surface to carry the electric current. Spraying this amount of AgNWs changes the statue color from white to grey, as shown in Fig. 7a. Unlike the previous cases, herein, the relatively high voltage of 20 V is supplied, because the larger 3D curved surface is subjected to greater thermal losses. Nevertheless, the Venus statue radiates heat with a surface temperature of 85 °C, as shown in Fig. 7b. Notably, no pre- or post-treatment (such as cleaning or any buffer layer) is required to produce this 3D complex-surface heater. A simple sweeping of the nozzle over the 3D surface produces the heat-radiating structure. An AgNWcoated replica of Jeju's Dol Hareubang and the corresponding IR image are shown in Fig. 7c and d, respectively. Fig. 7e shows a roll-to-roll PET substrate that could extend to an arbitrary



Fig. 7 (a) AgNW-coated replica of Venus de Milo statue (plaster) and (b) the corresponding IR image. (c) AgNW-coated replica of Jeju's Dol Hareubang (basalt) and (d) the corresponding IR image. (e and f) AgNW film deposited on a roll-to-roll PET substrate with 10 cm width and meter-scaled length.

length with a width of 10 cm. The spraying conditions are the same as stated before. First, the electrical conductivity of the AgNW-coated roll-to-roll film is confirmed through a strip of LEDs forming a circuit, as in Fig. 7e (see movie S1†). This confirms that a sufficient current is carried by the film to light the LEDs. Fig. 7f also shows an AgNW-coated roll-to-roll film connected at both ends to a power supply to provide Joule heating. Fig. 7f shows an IR image, confirming that the film releases heat at a surface temperature of 62 °C for the applied voltage of 12 V. The heat release of the film at 12 V is encouraging, because it demonstrates that the film could be installed on automobile windows as a transparent heater.^{15,16,43} In general, automobile window heaters require the voltage level of $V \leq 13$ V, in addition to other stringent optical requirements

such as a haze level $h \leq 1\%$ and transparency $T_r \geq 90\%$. As mentioned previously, the sheet resistance (R_s) of the transparent heater film should be low enough to result in a significant power ($P \geq 100$ W) at lower voltages ($V \leq 13$ V) and lower haze levels ($h \leq 1\%$) for automobile windows. The challenges lie in achieving a low R_s using fewer AgNWs to reach a higher transparency and lower haze, which is considered to be impossible with existing AgNW heaters. However, the present AgNW network, self-fused *via* supersonic spraying, demonstrates a sufficiently low sheet resistance ($R_s < 10 \Omega \text{ sq}^{-1}$), high transparency ($T_r > 95\%$), and low haze h < 1%. This network performance demonstrates that the commercialization of such defogging/defroster smart windows for automobile applications is plausible and holds great promise.

4. Conclusion

Supersonically sprayed AgNWs were deposited on 3D complex surfaces, as well as on both plane rigid and flexible substrates. Defogging performance was demonstrated on a rigid glass substrate, while defrosting was tested on a flexible PET substrate. The flexible and transparent AgNW films underwent rigorous bending tests with the bending radius of 2 mm for 600 000 cycles, revealing practically no change in performance. The AgNW film was also sprayed on an ecoflex substrate; the heater could be operated at stretching levels of 400% and greater. Also, an AgNW-coated glove was heated with Joule heating. Without a supplied voltage, the glove behaved as a thermal insulator, preventing the removal of body heat from the glove. A replica of the Venus de Milo and Jeju's Dol Hareubang statues also released heat being coated with AgNWs and subjected to power supply. A roll-to-roll PET substrate was coated with AgNWs and the film so produced released heat at a surface temperature reaching 62 $\,^\circ\mathrm{C}$ with a supplied voltage of 15 V. The present results also revealed the potential usefulness of supersonically cold-sprayed AgNWs as flexible smart window coatings for mobile applications in which high voltages are impossible.

Acknowledgements

This research was supported by the Global Frontier Program through the Global Frontier Hybrid Interface Materials (GFHIM) of the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (2013M3A6B1078879) and the Technology Development Program to Solve Climate Changes of the National Research Foundation (NRF-2016M1A2A2936760). S. S. Yoon expresses his appreciation to the Vice Deanship of Scientific Research Chairs at King Saud University.

References

- 1 S. Thiriat, US 6341554 B2 Pat., 2002.
- 2 T. Itoh and M. Sakamoto, US 4455479 A Pat., 1984.
- 3 J. C. Fan and F. J. Bachner, Appl. Opt., 1976, 15, 1012-1017.
- 4 K. Nishio, T. Sei and T. Tsuchiya, *J. Mater. Sci.*, 1996, **31**, 1761–1766.
- 5 M. Alam and D. Cameron, *Thin Solid Films*, 2000, 377, 455-459.
- 6 D. M. Mattox, Thin Solid Films, 1991, 204, 25-32.
- 7 I. Hamberg and C. G. Granqvist, J. Appl. Phys., 1986, 60, R123-R160.
- 8 S.-S. Kim, S.-Y. Choi, C.-G. Park and H.-W. Jin, *Thin Solid Films*, 1999, **347**, 155–160.
- 9 G. Leftheriotis, S. Papaefthimiou and P. Yianoulis, *Solid State Ionics*, 2000, **136**, 655–661.
- 10 M. Smyth, P. Eames and B. Norton, *Sol. Energ.*, 2001, **70**, 391–401.
- 11 A. Du Pasquier, H. E. Unalan, A. Kanwal, S. Miller and M. Chhowalla, *Appl. Phys. Lett.*, 2005, **87**, 203511.

- 12 C. D. Williams, R. O. Robles, M. Zhang, S. Li, R. H. Baughman and A. A. Zakhidov, *Appl. Phys. Lett.*, 2008, **93**, 183506.
- 13 C. Aguirre, C. Ternon, M. Paillet, P. Desjardins and R. Martel, *Nano Lett.*, 2009, **9**, 1457–1461.
- 14 F. Wong, M. Fung, S. Tong, C. Lee and S. Lee, *Thin Solid Films*, 2004, **466**, 225–230.
- 15 H.-S. Jang, S. K. Jeon and S. H. Nahm, *Carbon*, 2011, **49**, 111–116.
- 16 Y. H. Yoon, J. W. Song, D. Kim, J. Kim, J. K. Park, S. K. Oh and C. S. Han, *Adv. Mater.*, 2007, **19**, 4284–4287.
- 17 D. Jung, D. Kim, K. H. Lee, L. J. Overzet and G. S. Lee, *Sens. Actuators, A*, 2013, **199**, 176–180.
- 18 D. Kim, H.-C. Lee, J. Y. Woo and C.-S. Han, J. Phys. Chem. C, 2010, 114, 5817–5821.
- 19 J. Kang, H. Kim, K. S. Kim, S.-K. Lee, S. Bae, J.-H. Ahn, Y.-J. Kim, J.-B. Choi and B. H. Hong, *Nano Lett.*, 2011, **11**, 5154–5158.
- 20 D. Sui, Y. Huang, L. Huang, J. Liang, Y. Ma and Y. Chen, *Small*, 2011, 7, 3186–3192.
- 21 J. J. Bae, S. C. Lim, G. H. Han, Y. W. Jo, D. L. Doung,
 E. S. Kim, S. J. Chae, T. Q. Huy, N. Van Luan and
 Y. H. Lee, *Adv. Funct. Mater.*, 2012, 22, 4819–4826.
- 22 T. Kim, Y. W. Kim, H. S. Lee, H. Kim, W. S. Yang and K. S. Suh, *Adv. Funct. Mater.*, 2013, 23, 1250–1255.
- 23 R. Gupta, K. Rao, K. Srivastava, A. Kumar, S. Kiruthika and G. U. Kulkarni, ACS Appl. Mater. Interfaces, 2014, 6, 13688– 13696.
- 24 P.-C. Hsu, X. Liu, C. Liu, X. Xie, H. R. Lee, A. J. Welch, T. Zhao and Y. Cui, *Nano Lett.*, 2014, **15**, 365–371.
- 25 S. Sorel, D. Bellet and J. N. Coleman, *ACS Nano*, 2014, 8, 4805–4814.
- 26 H.-G. Cheong, D.-W. Song and J.-W. Park, *Microelectron. Eng.*, 2015, **146**, 11–18.
- 27 S. Hong, H. Lee, J. Lee, J. Kwon, S. Han, Y. D. Suh, H. Cho, J. Shin, J. Yeo and S. H. Ko, *Adv. Mater.*, 2015, 27, 4744– 4751.
- 28 Q. Huang, W. Shen, X. Fang, G. Chen, J. Guo, W. Xu, R. Tan and W. Song, *RSC Adv.*, 2015, 5, 45836–45842.
- 29 S. Yao and Y. Zhu, Adv. Mater., 2015, 27, 1480-1511.
- 30 J. G. Lee, D. Y. Kim, J. H. Lee, S. Sinha-Ray, A. L. Yarin, M. T. Swihart, D. Kim and S. S. Yoon, *Adv. Funct. Mater.*, 2017, 27, 1602548.
- 31 L. Hu, H. S. Kim, J.-Y. Lee, P. Peumans and Y. Cui, ACS Nano, 2010, 4, 2955–2963.
- 32 K. Rao and G. U. Kulkarni, Nanoscale, 2014, 6, 5645-5651.
- 33 M.-W. Lee, J.-J. Park, D.-Y. Kim, S. S. Yoon, H. Y. Kim, D. Kim, S. C. James, S. Chandra, T. Coyle and J. Ryu, *J. Aerosol Sci.*, 2011, 42, 771–780.
- 34 M.-W. Lee, J.-J. Park, D.-Y. Kim, S. S. Yoon, H.-Y. Kim, S. C. James, S. Chandra and T. Coyle, *J. Therm. Spray Technol.*, 2011, 20, 1085–1097.
- 35 J.-G. Lee, D.-Y. Kim, B. Kang, D. Kim, H.-e. Song, J. Kim, W. Jung, D. Lee, S. S. Al-Deyab, S. C. James and S. S. Yoon, *Acta Mater.*, 2015, **93**, 156–163.
- 36 J.-G. Lee, D.-Y. Kim, M. G. Mali, S. S. Al-Deyab, M. T. Swihart and S. S. Yoon, *Nanoscale*, 2015, 7, 19027–19035.

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- 37 D. Y. Kim, S. Sinha-Ray, J. J. Park, J. G. Lee, Y. H. Cha, S. H. Bae, J. H. Ahn, Y. C. Jung, S. M. Kim, A. L. Yarin and S. S. Yoon, *Adv. Funct. Mater.*, 2014, 24, 4986–4995.
- 38 S. De, P. J. King, P. E. Lyons, U. Khan and J. N. Coleman, *ACS Nano*, 2010, **4**, 7064–7072.
- 39 S. De and J. N. Coleman, MRS Bull., 2011, 36, 774-781.
- 40 Q. Huang, W. Shen, X. Fang, G. Chen, J. Guo, W. Xu, R. Tan and W. Song, *RSC Adv.*, 2015, 5, 45836–45842.
- 41 W. M. Haynes, *CRC Handbook of Chemistry and Physics*, CRC press, 2014.
- 42 S. Yao, J. Cui, Z. Cui and Y. Zhu, *Nanoscale*, 2017, DOI: 10.1039/c6nr09270e.
- 43 T. Kim, Y. W. Kim, H. S. Lee, H. Kim, W. S. Yang and K. S. Suh, *Adv. Funct. Mater.*, 2013, **23**, 1250–1255.