## ACS APPLIED MATERIALS & INTERFACES

## Self-Cleaning Anticondensing Glass via Supersonic Spraying of Silver Nanowires, Silica, and Polystyrene Nanoparticles

Jong-Gun Lee,<sup>†,||</sup> Seongpil An,<sup>†,||</sup> Tae-Gun Kim,<sup>†</sup> Min-Woo Kim,<sup>†</sup> Hong-Seok Jo,<sup>†</sup> Mark T. Swihart,<sup>‡</sup>

<sup>†</sup>School of Mechanical Engineering, Korea University, Seoul, 24801, Republic of Korea

<sup>‡</sup>Department of Chemical & Biological Engineering, University at Buffalo, The State University of New York, Buffalo, New York 14260-4200, United States

<sup>§</sup>Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, 842 West Taylor Street, Chicago, Illinois 60607-7022, United States

## Supporting Information



**ABSTRACT:** We have sequentially deposited layers of silver nanowires (AgNWs), silicon dioxide (SiO<sub>2</sub>) nanoparticles, and polystyrene (PS) nanoparticles on uncoated glass by a rapid low-cost supersonic spraying method to create antifrosting, anticondensation, and self-cleaning glass. The conductive silver nanowire network embedded in the coating allows electrical heating of the glass surface. Supersonic spraying is a single-step coating technique that does not require vacuum. The fabricated multifunctional glass was characterized by X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), ultraviolet–visible spectroscopy, and transmission electron microscopy (TEM). The thermal insulation and antifrosting performance were demonstrated using infrared thermal imaging. The reliability of the electrical heating function was tested through extensive cycling. This transparent multifunctional coating holds great promise for use in various smart window designs.

KEYWORDS: supersonic spray, silver nanowires, SiO<sub>2</sub>, polystyrene, anticondensation, defrosting, self-cleaning

## 1. INTRODUCTION

Energy consumption in buildings has increased dramatically in recent decades, as the demand for buildings and the comfort expectations of their occupants have risen sharply with growth in the world population and economy.<sup>1</sup> For instance, the energy consumption of commercial buildings alone in the United States accounts for 40% of the total energy consumed.<sup>2</sup> Similarly, in China, this number has risen to more than 30% in recent years.<sup>3</sup> Accordingly, the European Union recently decided to reduce national budgets for heating costs in buildings by 50% by 2050, in order to encourage people to lower their energy consumption.<sup>4</sup>

However, new avenues and methods being developed for energy saving and conservation repeatedly fall short of the target because of the inevitable energy losses from buildings and, in particular, through building windows. The amount of energy lost through windows has been estimated to be almost 40% of the total energy consumed in the buildings.<sup>5</sup> Various approaches have been proposed for preventing energy loss from building windows. Among them, the use of functional glasses like a heating and insulating glasses has attracted significant attention. Indium tin oxide (ITO) has attracted attention as a transparent electrical heating material, due to its high transmittance, low sheet resistance, and stability.<sup>6</sup> However, large-scale use of ITO in windows was considered prohibitive because of scarcity of indium.<sup>7,8</sup> Recently, graphene,<sup>9–11</sup> carbon nanotubes (CNTs),<sup>12–14</sup> metal nano-

Received:July 11, 2017Accepted:September 11, 2017Published:September 25, 2017

wires,<sup>15,16</sup> and metal meshes<sup>17,18</sup> have been studied as alternative transparent electrical heating materials.

Often, insulating glass windows consist of a double glass with an interpane.<sup>19,20</sup> Insulating performance of multipane windows can be improved by filling the space between panes with a lowthermal-conductivity inert gas, such as  $argon^{21,22}$  or krypton.<sup>23,24</sup> Alternatively, a vacuum-glazed window, in which the interpane volume is under vacuum, has also been developed.<sup>25,26</sup> However, glass of this structure is complex in design and has a limited range of use.

Recently, multifunctional windows, i.e., so-called "smart windows", have attracted significant attention. With advances in electrochemical technologies, novel windows such as chromic windows,<sup>27–36</sup> liquid crystal devices (LCDs),<sup>37–39</sup> and suspended particle devices (SPDs)<sup>40–42</sup> have been developed. Chromic windows can generally be subdivided into electrochromic (EC)<sup>31–33</sup> and thermochromic (TC)<sup>34–36</sup> windows. In particular, EC windows have been studied actively and are being used in buildings. With power applied to an EC window, the transparency of the window can be controlled, thus altering building heat loss or gain. A specific layer in the EC window consisting of metal oxides plays a crucial role in the color-switching process, which is based on the redox reaction of the metal oxides. Tungsten oxide (WO<sub>3</sub>) is primarily used as the metal oxide in EC windows.<sup>27–30</sup>

Unlike EC windows, TC windows change color in response to changes in the atmospheric temperature. Vanadium(IV) oxide (VO<sub>2</sub>) is one of the most widely used thermochromic materials. The underlying mechanism of LCDs and SPDs involves the rearrangement of liquid crystal molecules and suspended nanoparticles, respectively, in a liquid based on the applied voltage. In addition to the development of such colorchanging smart windows, which are essentially smart shades, novel smart windows that also possess anticondensation and antifrosting characteristics are desirable in order to sustain transparency. To address this need, here we demonstrate fabrication of such a multifunctional window with anticondensation, antifrosting, and self-cleaning features, using supersonic cold spraying, which is a rapid and scalable technique suitable for large-scale commercial production.

#### 2. EXPERIMENTAL METHODS

**2.1. Materials.** The silver nanowires (AgNWs) used in this study, which had an average diameter and length of 20 nm and 15  $\mu$ m, respectively, were obtained from Aiden. Isopropyl alcohol (IPA) and *N*,*N*-dimethylformamide (DMF, 99.8%) were purchased from Duksan Pure Chemicals. Silicon dioxide (SiO<sub>2</sub>) particles with an average diameter of 15 nm, polyacrylonitrile (PAN,  $M_w = 150$  kDa), and polystyrene (PS,  $M_w = 192$  kDa) were purchased from Sigma-Aldrich.

First, the 0.15 wt % AgNW precursor was prepared by dispersing the AgNWs in IPA and magnetically stirring the dispersion for a few hours. For preparation of the SiO<sub>2</sub> precursor, first an 8 wt % PAN solution was prepared by dissolving PAN in DMF and magnetically stirring the solution for 1 day. The SiO<sub>2</sub> precursor was obtained by subsequently blending 5 g of SiO<sub>2</sub>, 40 mL of DMF, and 0.3 mL of the 8 wt % PAN solution. Similarly, the 0.11 wt % PS precursor was prepared by dissolving 0.5 g of PS in 44.5 mL of DMF and magnetically stirring the solution for 1 day. Soda-lime glass ( $76 \times 26 \times$ 1 mm<sup>3</sup>) was used as a substrate. The substrate had a roughness of  $R_a =$ 0.1 nm based on AFM measurements.

**2.2. Fabrication of AgNW/SiO<sub>2</sub>/PS-Coated Glass.** Figure 1 illustrates the process of fabricating the AgNW/SiO<sub>2</sub>/PS-coated glass samples. The coatings were formed using a supersonic spraying apparatus with an atomizer. The supersonic spraying apparatus consisted of a compressor, a supersonic spraying nozzle, and a gas



**Research Article** 



Atomizer

Я

**Figure 1.** (a) Schematic of supersonic spraying process for fabricating the  $AgNW/SiO_2/PS$ -coated glass sample. Illustrations of the (b) self-cleaning and anticondensing multifunction, (c) transparency, (d) superhydrophobicity, (e) thermal insulation, and (f) heating capability of the AgNW/SiO<sub>2</sub>/PS-coated glass sample.

heater. Highly compressed and heated air was supersonically sprayed through the nozzle, resulting in the conversion of the thermal energy of the heated air into kinetic energy. The details of the supersonic spraying process can be found in our previous works.<sup>43–45</sup>

During the supersonic spraying process, the AgNW dispersion, which was supplied to the atomizer at a flow rate of 1.2 mL/min by a syringe pump (Legato 210, KD Scientific Inc.), was atomized at the exit of the nozzle, as depicted in Figure 1. The atomized droplets of the AgNW suspension were driven into the supersonic air stream, resulting in their uniform spraying and deposition on the glass substrate. Next, the SiO<sub>2</sub> and PS precursors, which were supplied at flow rates of 1.5 and 1.2 mL/min, respectively, were atomized and sprayed in this order in a similar manner. The fabrication conditions are listed in Table 1. It is noted that the motorized stage, on which the

Table 1. Conditions of the Supersonic Spraying Process

	layer		
parameter	AgNW	SiO <sub>2</sub>	PS
pressure [bar]	4	4	3
gas preheating temperature [°C]	220	250	350
nozzle-to-substrate distance [mm]	200	200	200
number of sweeps	1	2	1

uncoated glass substrate was fixed, allowed for the fabrication of largearea samples, of up to 30 cm  $\times$  20 cm. Glass slides cleaned in an ultrasonic bath with deionized water for 5 min were used as substrates in this work.

2.3. Characterization. The surface morphologies and elemental compositions of the samples were analyzed using a scanning electron microscopy (FE-SEM) system (S-5000, Hitachi) and transmission electron microscopy (TEM) system (JEM 2100F, JEOL Inc.). The sample for TEM was prepared by focused ion beam milling to produce a thin lamella (FIB, LYRA3 XMH, TESCAN). The transmittances of the deposited films were measured using an ultraviolet-visible spectrophotometer (Optizen POP, Mecasys). The crystallinities of the coated glass samples were characterized by X-ray diffraction (XRD) analysis (SmartLab, Rigaku), while their surface roughness was measured using an atomic force microscopy (AFM) system (Park systems, XE-100). Finally, the water contact angles of the samples were measured from images obtained with a high-resolution CCD camera (Phantom 9.1, Vision Research, Inc.). A hot plate (PC-420D, CORNING Inc.) and DC power supply (SPS-1820, GW Instek) were used for the thermal property test, with an FLIR-E63900 thermal camera for thermal imaging of the samples.

#### 3. RESULTS AND DISCUSSION

**3.1.** Properties of AgNW, AgNW/SiO<sub>2</sub>, and AgNW/SiO<sub>2</sub>/PS Layers. Figure 2a shows the XRD patterns of the AgNW, SiO<sub>2</sub>, and AgNW/SiO<sub>2</sub>/PS layers for 2θ values of 10–



Figure 2. (a) XRD patterns of different layers. (b) Transmittance spectra of AgNW-, AgNW/SiO<sub>2</sub>-, and AgNW/SiO<sub>2</sub>/PS-coated glass substrates. SEM and AFM images of (c) AgNW-, (d) AgNW/SiO<sub>2</sub>-, and (e) AgNW/SiO<sub>2</sub>/PS-coated glass substrates.

80°. The two main diffraction peaks at  $2\theta$  values of  $38.2^{\circ}$  and  $64.9^{\circ}$  in the cases of the AgNW and AgNW/SiO<sub>2</sub>/PS layers, respectively, correspond to the (111) and (220) planes of Ag (JCPDS 870597). The weak and wide peak at  $2\theta$  of 22.5° seen in the case of the SiO<sub>2</sub> layer is attributable to amorphous SiO<sub>2</sub>. This peak was not observed in the case of the AgNW/SiO<sub>2</sub>/PS layer, but an even weaker broad feature was visible at a slightly higher diffraction angle. This may be due to the presence of the PS layer above the SiO<sub>2</sub> layer.

Figure 2b shows the transmittance (Tr) spectra of the AgNW-, AgNW/SiO<sub>2</sub>-, and AgNW/SiO<sub>2</sub>/PS-coated glass substrates across the visible spectrum ( $\lambda = 400-800$  nm). An uncoated glass substrate was used as the reference (or background) for the transmittance measurements (the Tr value of the uncoated glass was taken to be 100%). The AgNWcoated glass substrate exhibited a high Tr value, of 93.4%, at  $\lambda$  = 550 nm (black line in Figure 2b) and a low sheet resistance ( $R_s$ ; 10  $\Omega/sq$ ). The R<sub>s</sub> value was determined by averaging data acquired at 10 different points. As the SiO<sub>2</sub> and PS layers were added, the transmittance value of the glass decreased to Tr = 88% and 74%, respectively. The high-transparency AgNW/ SiO<sub>2</sub>/PS-coated glass sample was fabricated by optimizing the deposition conditions (see Table 1). That optimization showed that films with Tr value greater than 90% exhibited unsatisfactory insulating and hydrophobic properties (data not shown here). Therefore, we tested the coated glass substrate with Tr = 74% instead.

The AgNW layer is underneath the insulating  $SiO_2$  layer for the following reasons. First, AgNWs must be protected from water or ice because AgNWs can be easily scratched or damaged if exposed to an open-air environment. Second, the insulating  $SiO_2$  layer should be placed on top to facilitate hydrophobicity for the self-cleaning features. Third, this multifunctional glass is designed for both deicing and anticondensation purposes. In the case of deicing, it would be desirable to have the AgNW layer (heater) as close as possible to the surface. Thus, the AgNW layer located between the substrate and the  $SiO_2$  layer is most desirable. In the anticondensation case, the exposure of the AgNW layer to water is not desirable, and thus it must be located below the surface.

Figure 2c shows the overall surface morphologies of the AgNW, AgNW/SiO<sub>2</sub>, and AgNW/SiO<sub>2</sub>/PS layers. The twodimensional single-layered AgNWs (see SEM and AFM images in Figure 2c) were self-fused at their junctions, because of the high-energy mutual impact of the wires entrained by the supersonic air flow. As a result, the maximum thickness (or diameter) of the fused AgNWs (30 nm) was smaller than the sum of the diameters of two individual AgNWs (40 nm). Thus, there was no need for postsynthesis treatments such as pressing and annealing, which are typically performed after nanowire coating deposition. Self-fusion of AgNWs resulted in a layer with high electrical conductivity, owing to the decrease in the electrical contact resistance at the wire junctions (this was confirmed through the sheet resistance measurements).<sup>43</sup> Thus, the AgNW layer improved the heating performance, as described in Section 3.2, and can be used in various antifrosting applications.

The supersonically sprayed  $SiO_2$  nanoparticles deposited on the AgNW layer are shown in Figure 2d. Not only were the  $SiO_2$  clusters naturally formed, but also the fine pores between the  $SiO_2$  particles allowed micro- and nanoscale air pockets to be formed within the layer. Thus, because of the insulating properties of  $SiO_2$  and air, the layer possessed good thermal insulation properties, as described in Section 3.2.

Further, even though the AgNW/SiO<sub>2</sub> layer had a rough surface, the supersonically sprayed PS layer deposited on top of it exhibited a smooth surface, as shown in Figure 2e. The hydrophobic layer used in multifunctional glasses should be transparent. In general, a material possesses superhydrophobic properties when its surface roughness is very high. However, this lowers the transparency because of light scattering. Thus, superhydrophobicity and transparency can be determined by a trade-off between the roughness of a material surface and the chemical properties of the surface.<sup>46</sup> The surface roughness of AgNW/SiO<sub>2</sub>/PS glass was  $R_a = 36$  nm, as determined by AFM.

Figure 3 shows cross-sectional TEM images of a AgNW/ SiO<sub>2</sub>/PS-coated glass substrate. The sample was prepared for imaging by focused ion beam (FIB) milling to produce a lamella.<sup>47,48</sup> A 200 nm layer of Pt was coated on top of the sample to prevent damage from FIB milling. The observed



Figure 3. (a, b) High-magnification TEM images and elemental maps of the FIB-treated  $AgNW/SiO_2/PS$ -coated glass substrate.

thicknesses of the individual SiO<sub>2</sub> and PS layers were 1.1 and 0.5  $\mu$ m, respectively. The porous SiO<sub>2</sub> layer with air pockets and the highly dense PS layer can be seen clearly in the TEM images. We note that the single layer of AgNWs was not degraded (or detached) by the supersonically sprayed SiO<sub>2</sub> nanoparticles, as can be seen in Figure 3b. This allows the coatings to exhibit stable heating performance, as described in Section 3.3. The elemental maps at the bottom of Figure 3 confirm that all the coated materials, namely, SiO<sub>2</sub>, PS (as made evident by the presence of carbon), and AgNWs, are present on the coated glass substrate and in the expected locations.

**3.2. Wettability.** For measurement of the water contact angle (WCA,  $\theta_w$ ) of each layer, a single water droplet was placed on the AgNW-, AgNW/SiO<sub>2</sub>-, and AgNW/SiO<sub>2</sub>/PS-coated glass substrates, and the equilibrium WCA was measured, as shown in Figure 4. The WCA of the uncoated



Figure 4. CCD camera photographs of a single water droplet on the following: (a) uncoated, and (b) AgNW-, (c) AgNW/SiO<sub>2</sub>-, and (d) AgNW/SiO<sub>2</sub>/PS-coated glass substrates. The images were used for WCA measurements.

glass was  $\theta_w = 35^{\circ}$  (Figure 4a), indicating that it was hydrophilic. In the cases of the AgNW- and AgNW/SiO<sub>2</sub>coated glass substrates, however, the WCA was very low ( $\theta_w \approx$ 0°; Figure 4b,c), indicating that they were superhydrophilic and had high surface energies. In contrast, the AgNW/SiO<sub>2</sub>/PScoated glass substrate was hydrophobic, exhibiting a high WCA of  $\theta_w = 120^{\circ}$  (Figure 4d); this was attributable not only to the intrinsic hydrophobicity of PS but also to the slightly nanotextured surface of the final layer.<sup>49</sup>

Contaminants on superhydrophobic surfaces can be removed readily through the so-called "self-cleaning effect", wherein water droplets falling on such surfaces remove the contaminants as they roll off the surface.<sup>50,51</sup> Figure 5a,b shows the uncoated and AgNW/SiO<sub>2</sub>/PS-coated glass substrates with (insets) and without contaminants. A reduced graphene oxide (rGO) powder was used as the contaminant in this study. In



Figure 5. Photographs of (a) uncoated and (b)  $AgNW/SiO_2/PS$ coated glass substrates. A few (dyed) water droplets were placed on the substrates to demonstrate the self-cleaning capability.

contrast to the case of the uncoated substrate (Figure 5a), when a few water droplets were placed onto the AgNW/SiO<sub>2</sub>/PS-coated glass substrate, the contaminant particles formed clusters and were entrained by the rolling water droplets. This phenomenon confirmed the self-cleaning ability of the layer, with the glass surface becoming clean once the substrate was tilted (see Movie S1).

**3.3.** Anticondensation and Antifrosting Performance. When relatively warm, humid air comes in contact with a cold solid substrate, water vapor in the air condenses rapidly into water droplets on the surface of the cold substrate. If the substrate is a transparent window, these tiny water droplets lower the transparency of the window by inducing light scattering. For a practical solution for this issue, easy-toimplement anticondensation and antifrosting techniques that result in minimal transparency loss need to be developed, so that commercially viable efficient multifunctional glasses can be realized. Figures 6 and 7 show schematics illustrating the



Figure 6. Schematic of the (a) condensation and (b) evaporation process on a material surface. (c) Schematic cross-sectional view of the  $AgNW/SiO_2/PS$ -coated glass substrate.

anticondensation and antifrosting properties of the AgNW/  $SiO_2/PS$ -coated glass substrate and the results of the measurements of these properties.

First, to test the anticondensation effect of the AgNW/SiO<sub>2</sub>/ PS-coated glass substrate and to compare its anticondensation properties with those of the uncoated glass (Figure 7a), both the uncoated glass substrate and the AgNW/SiO<sub>2</sub>/PS-coated glass substrate were placed on ice (Figure 7a). The water vapor in the air began to condense on the uncoated glass substrate, and tiny water droplets formed on it gradually. After 10 min, water droplets could be seen clearly on the substrate (left in Figure 7b). In contrast, no water droplets formed on the AgNW/SiO<sub>2</sub>/PS-coated glass substrate (right in Figure 7b) because of the thermal insulation effect of the SiO<sub>2</sub> layer which increases the temperature of the surface in contact with vapor, while ice is underneath the substrate (Figure 7c). With time, however, condensation occurred on both glass substrates (Figure 7c). For removal of the condensed droplets on the AgNW/SiO<sub>2</sub>/PS-coated glass substrate, a voltage was applied to the AgNW layer. This heated the glass and induced evaporation. The glass temperature increased rapidly to 40 °C, and the water droplets evaporated within a few seconds (Figure 7d).

In addition to the excellent insulation properties under cold conditions, the  $AgNW/SiO_2/PS$  layer also demonstrated good thermal insulation characteristics under hot conditions, as shown in Figure 8. As can be seen from the figure, pieces of chocolate were placed on both the uncoated substrate and the



Figure 7. IR images and photographs of (left) uncoated and (right) AgNW/SiO<sub>2</sub>/PS-coated glass substrates during (a-c) thermal insulation and (d) heating tests.



Figure 8. Photographs of the thermal insulation test performed with uncoated and  $AgNW/SiO_2/PS$ -coated glass substrates on a hot plate using chocolate pieces: (a) start of the test and (b) after a few minutes.

AgNW/SiO<sub>2</sub>/PS-coated glass substrate, which, in turn, were placed on a hot plate, and the difference in the melting process of the chocolate pieces was observed. The temperature of the hot plate was set to 200 °C. The chocolate piece on the AgNW/SiO<sub>2</sub>/PS-coated glass substrate melted slowly, while the one on the uncoated glass melted immediately within a few seconds (see Movie S2). This confirmed that the AgNW/SiO<sub>2</sub>/PS layer holds great promise for use in multifunctional glasses.

Several thermal tests were conducted with the uncoated (glass) and coated (glass/AgNW/SiO<sub>2</sub>/PS) samples. The purpose of these tests was to quantify the thermal response of the coated sample as compared to the uncoated one. It should be emphasized that the thickness of the coating layers comprises only 0.15% of the entire sample thickness. For example, the glass substrate is  $1 \times 10^{-3}$  m thick while the thickness of the AgNW/SiO<sub>2</sub>/PS coating is about  $1.5 \times 10^{-6}$  m. Nevertheless, this 0.15% increase in thickness (accompanied by the addition of different materials) is large enough to cause notable delay in the thermal response, albeit the steady-state

temperatures for both uncoated and coated samples should eventually be identical.

In the thermal response test, the samples were placed on a hot plate. Both bottom  $(T_b)$  and top surface  $(T_s)$  temperatures were measured using thermocouples located at those locations. Figure 9a shows that the temperature increases at these locations, starting from the initial temperature of  $T_{\infty} = 28$  °C. It is seen that the rate at which temperature increases is slowed down in the presence of the coating for both bottom and top surfaces, indicating the increased thermal inertia due to the coating. Eventually, both  $T_b$  and  $T_s$  reach the steady-state values. Because both coated and uncoated samples are subjected to the same power supply of  $q_{\text{uncoated}}'' = q_{\text{coated}}'' = q'' = h(T_s - T_{\infty}) = 0.52 \text{ kW/m}^2$ , they reach the same steady-state temperatures. For example, the steady-state temperature  $T_s = 80$  °C has been reached at the top surface of the uncoated sample.

In Figure 9b, the results for four different heat flux levels (q''= 0.27, 0.52, 0.7, and 0.81 kW/m<sup>2</sup>) are presented for the uncoated sample. They revealed four different steady-state surface temperatures  $(T_s; \text{ or } \Delta T = T_s - T_{\infty})$ . The case of Figure 9a (with  $q'' = 0.52 \text{ W/m}^2$ ) according to Figure 9b yields  $T_s = \Delta T + T_{\infty} = 52 \ ^{\circ}\text{C} + 28 \ ^{\circ}\text{C} = 80 \ ^{\circ}\text{C}$ , which is consistent with the steady value of  $T_s$  presented in Figure 9a. This calculation is conducted using the fact that  $q'' = h(T_s - T_{\infty}) =$  $h\Delta T$ , where the heat transfer coefficient  $h = 10 \text{ W}/(\text{m}^2 \text{ K})$  (for natural convection from the upper face of a horizontal plate<sup>52</sup> and the ambient air temperature of  $T_{\infty}$  = 28 °C). It is noted that slight distinctions between the steady-state temperatures of the uncoated and coated samples visible in Figure 9a can be attributed to the uncontrollable effect of different surface roughnesses. This uncertainty level increases as the heat flux increases, as is hinted by the results in Figure 9b. It is noted that q'' = Q/A, where Q is the power supplied to the substrate area of  $A = 0.002 \text{ m}^2$ , with  $Q = (A/A_t)Q_t$ , where the hot plate area  $A_t$ = 0.11 m<sup>2</sup>, and the total power supply  $Q_t$  varied from 30 to 77.5 W.

In steady state, the heat flux can be expressed as<sup>52</sup>

$$q'' = k_{g} \left( \frac{T_{b1} - T_{s1}}{\Delta x_{g}} \right) \equiv \frac{T_{b2} - T_{s2}}{\frac{\Delta x_{g}}{k_{g}} + \frac{\Delta x_{AgNW}}{k_{AgNW}} + \frac{\Delta x_{SiO_{2}}}{k_{SiO_{2}}} + \frac{\Delta x_{pS}}{k_{PS}}}$$
(1)

where subscripts 1 and 2 correspond to the uncoated and coated samples, respectively, and k is the thermal conductivity of each material. As mentioned earlier, the thicknesses  $\Delta x$  of the AgNW, SiO<sub>2</sub>, and PS layers are relatively small (in total, they comprise a 0.15% increase in the thickness). Therefore, the heat-conduction process is still dominated by glass in the coated sample, resulting in approximately the same factor for  $(T_b - T_s)$  on both sides in eq 1. Since  $T_s$  is the same for coated and uncoated samples as explained above,  $T_b$  should also be the same in both these cases, as corroborated by the experimental data in Figure 9a. It is noted that Table 2 summarizes the values k and  $\Delta x$  for all the materials used.

Figure 9c illustrates the resilience of the heaters which underwent 30 cycles over the time span of 275 min at three different power levels. Both "uncoated" and "coated" heaters were coated with AgNW so that they could be heated via Jouleheating. The "uncoated" heater did not have either an SiO<sub>2</sub> or a PS layer. Though slight differences in the peak temperature are seen, the heaters are repeatable and reliable for many hours.



**Figure 9.** (a) Steady-state temperature of the bottom and top of the uncoated and coated samples when  $q'' = 0.52 \text{ kW/m}^2$ . (b) Steady-state top surface temperature at various power levels and their comparison against the theoretical predictions. (c) Cyclic test of the heaters at three power levels.  $T_b$  denotes the bottom temperature,  $T_s$  denotes the top surface temperature,  $T_{\infty}$  denotes air temperature far from the surface, and *h* is the heat transfer coefficient for natural convection from the upper face of a horizontal plane.<sup>52</sup>

# Table 2. Thermal Conductivities and Thicknesses of Materials Used<sup>52</sup>

material	k [W/(m K)]	$\Delta x [m]$
glass	0.78	$1 \times 10^{-3}$
AgNW	406	$30 \times 10^{-9}$
SiO <sub>2</sub>	1.4	$1 \times 10^{-6}$
polystyrene	0.023	$0.5 \times 10^{-6}$

## 4. CONCLUSION

We have demonstrated the simple and scalable preparation of a multilayer film on glass that simultaneously exhibited good thermal insulation, antifrosting (electrically heatable), and self-cleaning properties. The scalable supersonic spraying technique employed here did not require any postspraying treatments. A sparse network of AgNWs was used to form the heating layer, for active defrosting and potential combination (in future studies) with thermochromic materials. A porous layer of SiO<sub>2</sub> nanoparticles with embedded air pockets formed the thermally insulating layer, enhancing anticondensation characteristics. Finally, a uniformly deposited smooth superhydrophobic PS layer with a high water contact angle ( $120^{\circ}$ ) was used as the top layer to produce a self-cleaning effect. Such transparent multifunctional coatings hold great promise for use in various smart windows.

#### ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b10013.

Movie S1: comparison of the self-cleaning effect of the (left) noncoated and (right) coated films or windows (AVI)

Movie S2: comparison of the thermal insulation effect of the (left) noncoated and (right) coated films or windows (AVI)

#### AUTHOR INFORMATION

#### **Corresponding Authors**

\*E-mail: ayarin@uic.edu.

\*E-mail: skyoon@korea.ac.kr.

## ORCID <sup>0</sup>

Mark T. Swihart: 0000-0002-9652-687X Alexander L. Yarin: 0000-0001-8032-2525 Sam S. Yoon: 0000-0002-9031-4198

## Author Contributions

<sup>II</sup>J.-G.L. and S.A. have contributed equally.

#### Notes

The authors declare no competing financial interest.

This work was supported by the Industrial Strategic Technology Development Program (10045221) funded by the Ministry of Knowledge Economy (MKE, Korea). This research was supported by the Technology Development Program to Solve Climate Changes of the National Research Foundation (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2016M1A2A2936760), NRF-2017R1A2B4005639, and NRF-2013M3A6B1078879.

## REFERENCES

(1) Ma, H.; Zhou, W.; Lu, X.; Ding, Z.; Cao, Y. Application of Low Cost Active and Passive Energy Saving Technologies in an Ultra-Low Energy Consumption Building. *Energy Procedia* **2016**, *88*, 807–813.

(2) US Department of Energy. *Building Energy Data Book*. http// buildingsdatabook.eren.doe.gov/. (accessed 2013).

(3) Zhang, Y.; He, C.-Q.; Tang, B.-J.; Wei, Y.-M. China's Energy Consumption in the Building Sector: A Life Cycle Approach. *Energy Build* **2015**, *94*, 240–251.

(4) Berge, A.; Johansson, P. Literature Review of High Performance Thermal Insulation; Chalmers University of Technology, 2012.

(5) Grynning, S.; Gustavsen, A.; Time, B.; Jelle, B. P. Windows in the Buildings of Tomorrow: Energy Losers or Energy Gainers? *Energy Build.* **2013**, *61*, 185–192.

(6) Hong, S.-J.; Kim, S.-W.; Han, J. I. Solution-Processed Indium-Tin-Oxide Nanoparticle Transparent Conductors on Flexible Glass Substrate with High Optical Transmittance and High Thermal Stability. *Jpn. J. Appl. Phys.* **2014**, *53* (8S3), 08NF04.

(7) Kumar, A.; Zhou, C. The Race to Replace Tin-Doped Indium Oxide: Which Material Will Win? *ACS Nano* **2010**, *4* (1), 11–14.

(8) Hsu, P.-C.; Wang, S.; Wu, H.; Narasimhan, V. K.; Kong, D.; Lee, H. R.; Cui, Y. Performance Enhancement of Metal Nanowire Transparent Conducting Electrodes by Mesoscale Metal Wires. *Nat. Commun.* **2013**, *4*, 2522.

(9) Sui, D.; Huang, Y.; Huang, L.; Liang, J.; Ma, Y.; Chen, Y. Flexible and Transparent Electrothermal Film Heaters Based on Graphene Materials. *Small* **2011**, *7* (22), 3186–3192.

(10) Lee, B.-J.; Jeong, G.-H. Fabrication of Defrost Films Using Graphenes Grown by Chemical Vapor Deposition. *Curr. Appl. Phys.* **2012**, *12*, S113–S117.

(11) Wang, J.; Fang, Z.; Zhu, H.; Gao, B.; Garner, S.; Cimo, P.; Barcikowski, Z.; Mignerey, A.; Hu, L. Flexible, Transparent, and Conductive Defrosting Glass. *Thin Solid Films* **2014**, *556*, 13–17.

(12) Feng, C.; Liu, K.; Wu, J. S.; Liu, L.; Cheng, J. S.; Zhang, Y.; Sun, Y.; Li, Q.; Fan, S.; Jiang, K. Flexible, Stretchable, Transparent Conducting Films Made from Superaligned Carbon Nanotubes. *Adv. Funct. Mater.* **2010**, *20* (6), 885–891.

(13) Yoon, Y. H.; Song, J. W.; Kim, D.; Kim, J.; Park, J. K.; Oh, S. K.; Han, C. S. Transparent Film Heater Using Single–Walled Carbon Nanotubes. *Adv. Mater.* **2007**, *19* (23), 4284–4287.

(14) Kang, T. J.; Kim, T.; Seo, S. M.; Park, Y. J.; Kim, Y. H. Thickness-Dependent Thermal Resistance of a Transparent Glass Heater with a Single-Walled Carbon Nanotube Coating. *Carbon* **2011**, 49 (4), 1087–1093.

(15) Guo, H.; Lin, N.; Chen, Y.; Wang, Z.; Xie, Q.; Zheng, T.; Gao, N.; Li, S.; Kang, J.; Cai, D. Copper Nanowires as Fully Transparent Conductive Electrodes. *Sci. Rep.* **2013**, *3*, 2323.

(16) Lee, J.-G.; Lee, J.-H.; An, S.; Kim, D.-Y.; Kim, T.-G.; Al-Deyab, S. S.; Yarin, A. L.; Yoon, S. S. Highly Flexible, Stretchable, Wearable, Patternable and Transparent Heaters on Complex 3d Surfaces Formed from Supersonically Sprayed Silver Nanowires. *J. Mater. Chem. A* 2017, 5 (14), 6677–6685.

(17) Kiruthika, S.; Gupta, R.; Kulkarni, G. U. Large Area Defrosting Windows Based on Electrothermal Heating of Highly Conducting and Transmitting Ag Wire Mesh. *RSC Adv.* **2014**, *4* (91), 49745–49751.

(18) Kang, M. G.; Guo, L. J. Nanoimprinted Semitransparent Metal Electrodes and Their Application in Organic Light–Emitting Diodes. *Adv. Mater.* **2007**, *19* (10), 1391–1396.

(19) Wolf, A. T. Studies into the Life-Expectancy of Insulating Glass Units. *Build. Environ.* **1992**, *27* (3), 305–319.

(20) Van Den Bergh, S.; Hart, R.; Jelle, B. P.; Gustavsen, A. Window Spacers and Edge Seals in Insulating Glass Units: A State-of-the-Art Review and Future Perspectives. *Energy Build.* **2013**, *58*, 263–280.

(21) Kebabian, P. L.; Romano, R. R.; Freedman, A. Determination of Argon-Filled Insulated Glass Window Seal Failure by Spectroscopic Detection of Oxygen. *Meas. Sci. Technol.* **2003**, *14* (7), 983.

(22) Cuce, E.; Young, C.-H.; Riffat, S. B. Performance Investigation of Heat Insulation Solar Glass for Low-Carbon Buildings. *Energy Convers. Manage.* **2014**, *88*, 834–841.

(23) Reim, M.; Beck, A.; Körner, W.; Petricevic, R.; Glora, M.; Weth, M.; Schliermann, T.; Fricke, J.; Schmidt, C.; Pötter, F. Highly Insulating Aerogel Glazing for Solar Energy Usage. *Sol. Energy* **2002**, 72 (1), 21–29.

(24) Benz, N.; Beikircher, T.; Aghazadeh, B. Aerogel and Krypton Insulated Evacuated Flat-Plate Collector for Process Heat Production. *Sol. Energy* **1996**, *58* (1–3), 45–48.

(25) Fang, Y.; Eames, P. C.; Norton, B.; Hyde, T. J.; Zhao, J.; Wang, J.; Huang, Y. Low Emittance Coatings and the Thermal Performance of Vacuum Glazing. *Sol. Energy* **2007**, *81* (1), 8–12.

(26) Collins, R. E.; Turner, G.; Fischer-Cripps, A.; Tang, J.-Z.; Simko, T.; Dey, C.; Clugston, D.; Zhang, Q.-C.; Garrison, J. Vacuum Glazing—a New Component for Insulating Windows. *Build. Environ.* **1995**, *30* (4), 459–492.

(27) Yin, Y.; Lan, C.; Guo, H.; Li, C. Reactive Sputter Deposition of  $Wo_3/Ag/Wo_3$  Film for Indium Tin Oxide (Ito)-Free Electrochromic Devices. ACS Appl. Mater. Interfaces **2016**, 8 (6), 3861–3867.

(28) Goldner, R.; Chapman, R.; Foley, G.; Goldner, E.; Haas, T.; Norton, P.; Seward, G.; Wong, K. Recent Research Related to the Development of Electrochromic Windows. *Sol. Energy Mater.* **1986**, *14* (3–5), 195–203.

(29) Wang, J.; Khoo, E.; Lee, P. S.; Ma, J. Synthesis, Assembly, and Electrochromic Properties of Uniform Crystalline Wo<sub>3</sub> Nanorods. *J. Phys. Chem. C* **2008**, *112* (37), 14306–14312.

(30) Cronin, J.; Tarico, D.; Tonazzi, J.; Agrawal, A.; Kennedy, S. Microstructure and Properties of Sol-Gel Deposited Wo<sub>3</sub> Coatings for Large Area Electrochromic Windows. *Sol. Energy Mater. Sol. Cells* **1993**, 29 (4), 371–386.

(31) Piccolo, A.; Simone, F. Performance Requirements for Electrochromic Smart Window. J. Build. Eng. 2015, 3, 94–103.

(32) Yeh, M.-H.; Lin, L.; Yang, P.-K.; Wang, Z. L. Motion-Driven Electrochromic Reactions for Self-Powered Smart Window System. *ACS Nano* **2015**, *9* (5), 4757–4765.

(33) Shin, H.; Seo, S.; Park, C.; Na, J.; Han, M.; Kim, E. Energy Saving Electrochromic Windows from Bistable Low-Homo Level Conjugated Polymers. *Energy Environ. Sci.* **2016**, *9* (1), 117–122.

(34) Ye, H.; Long, L.; Zhang, H.; Gao, Y. The Energy Saving Index and the Performance Evaluation of Thermochromic Windows in Passive Buildings. *Renewable Energy* **2014**, *66*, 215–221.

(35) Hoffmann, S.; Lee, E. S.; Clavero, C. Examination of the Technical Potential of near-Infrared Switching Thermochromic Windows for Commercial Building Applications. *Sol. Energy Mater. Sol. Cells* **2014**, *123*, 65–80.

(36) Zhang, H.; Xiao, X.; Lu, X.; Chai, G.; Sun, Y.; Zhan, Y.; Xu, G. A Cost-Effective Method to Fabricate Vo<sub>2</sub>(M) Nanoparticles and Films with Excellent Thermochromic Properties. *J. Alloys Compd.* **2015**, *636*, 106–112.

(37) Hosseinzadeh Khaligh, H.; Liew, K.; Han, Y.; Abukhdeir, N. M.; Goldthorpe, I. A. Silver Nanowire Transparent Electrodes for Liquid Crystal-Based Smart Windows. *Sol. Energy Mater. Sol. Cells* **2015**, *132*, 337–341.

(38) Li, K.; Pivnenko, M.; Chu, D.; Cockburn, A.; O'Neill, W. Uniform and Fast Switching of Window-Size Smectic a Liquid Crystal Panels Utilising the Field Gradient Generated at the Fringes of Patterned Electrodes. *Liq. Cryst.* **2016**, *43* (6), 735–749.

(39) Jung, D.; Choi, W.; Park, J.-Y.; Kim, K. B.; Lee, N.; Seo, Y.; Kim, H. S.; Kong, N. K. Inorganic Gel and Liquid Crystal Based Smart Window Using Silica Sol-Gel Process. *Sol. Energy Mater. Sol. Cells* **2017**, *159*, 488–495.

(40) Ghosh, A.; Norton, B.; Duffy, A. First Outdoor Characterisation of a Pv Powered Suspended Particle Device Switchable Glazing. *Sol. Energy Mater. Sol. Cells* **2016**, *157*, 1–9.

(41) Ghosh, A.; Norton, B.; Duffy, A. Daylighting Performance and Glare Calculation of a Suspended Particle Device Switchable Glazing. *Sol. Energy* **2016**, *132*, 114–128.

(42) Barrios, D.; Vergaz, R.; Sanchez-Pena, J. M.; Granqvist, C. G.; Niklasson, G. A. Toward a Quantitative Model for Suspended Particle Devices: Optical Scattering and Absorption Coefficients. *Sol. Energy Mater. Sol. Cells* **2013**, *111*, 115–122.

(43) Lee, J. G.; Kim, D. Y.; Lee, J. H.; Sinha-Ray, S.; Yarin, A. L.; Swihart, M. T.; Kim, D.; Yoon, S. S. Production of Flexible Transparent Conducting Films of Self–Fused Nanowires Via One– Step Supersonic Spraying. *Adv. Funct. Mater.* **2017**, *27*, 1602548.

(44) Kim, D.-Y.; Joshi, B. N.; Lee, J.-G.; Lee, J.-H.; Lee, J. S.; Hwang, Y. K.; Chang, J.-S.; Al-Deyab, S.; Tan, J.-C.; Yoon, S. S. Supersonic Cold Spraying for Zeolitic Metal–Organic Framework Films. *Chem. Eng. J.* **2016**, *295*, 49–56.

(45) Lee, J.-G.; Kim, D.-Y.; Joshi, B. N.; Lee, J.-H.; Lee, T.-K.; Kim, J.-s.; Yang, D.-h.; Kim, W.-Y.; Al-Deyab, S. S.; Yoon, S. S. Electrically Insulative Performances of Ceramic and Clay Films Deposited Via Supersonic Spraying. *J. Therm. Spray Technol.* **2016**, *25* (4), 763–769.

(46) Yabu, H.; Shimomura, M. Single-Step Fabrication of Transparent Superhydrophobic Porous Polymer Films. *Chem. Mater.* **2005**, *17* (21), 5231–5234.

(47) Melngailis, J. Focused Ion Beam Technology and Applications. J. Vac. Sci. Technol., B: Microelectron. Process. Phenom. **1987**, 5 (2), 469–495.

(48) Giannuzzi, L.; Stevie, F. A Review of Focused Ion Beam Milling Techniques for Tem Specimen Preparation. *Micron* **1999**, 30 (3), 197–204.

(49) Li, Y.; Pham, J. Q.; Johnston, K. P.; Green, P. F. Contact Angle of Water on Polystyrene Thin Films: Effects of  $CO_2$  Environment and Film Thickness. *Langmuir* **2007**, 23 (19), 9785–9793.

(50) Blossey, R. Self-Cleaning Surfaces—Virtual Realities. *Nat. Mater.* **2003**, *2* (5), 301–306.

(51) Fürstner, R.; Barthlott, W.; Neinhuis, C.; Walzel, P. Wetting and Self-Cleaning Properties of Artificial Superhydrophobic Surfaces. *Langmuir* **2005**, *21* (3), 956–961.

(52) Holman, J. Heat Transfer; McGraw-Hill Book Co., 1986.