Supporting Information

Facilitated Embedding of Silver Nanowires into Conformally-Coated iCVD Polymer Films Deposited on Cloths for Robust Wearable Electronics

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Facilitated embedding of AgNWs into copolymer film

Figure S1(a) presents the schematic illustration of initiated chemical vapor deposition (iCVD) process; in iCVD process, polymerization reaction is triggered by radicals from thermally activated initiator. The formed radicals and the vaporized monomers are adsorbed on a target substrate at room temperature (RT) to go through free radical polymerization. Figure S1(b) shows the transmittance of poly((*N*,*N*-dimethylaminomthyl)styrene-*co*-(2-chloroethylacrylate)) (p(DMAMS-*co*-CEA)) copolymer, AgNWs-embedded film on glass, and ITO.

Figure S2 shows the SEM and AFM images of AgNWs on copolymer film (a, c) before and (b, d) after annealing. After annealing, AgNWs were well embedded into copolymer. Moreover, when the annealing time or embedding temperature of the embedding process was changed, sheet resistance of AgNWs-embedded copolymer film was measured. At 70 °C, AgNWs are well embedded in iCVD copolymer film in 20 s (Figure S3(a)). When the annealing time was increased to 30 min, the surface roughness of AgNWs-embedded copolymer film became higher than that in 20 s because longer

annealing time on copolymer film caused a dense packing of copolymer chain, decreasing the thickness of copolymer film (Figure S3(b) and (c)). However, AgNWs were still well embedded in in iCVD copolymer film and the sheet resistance of AgNWs retained the initial value regardless of the annealing time (Figure S3(d)).

As demonstrated in manuscript, next, AgNWs are embedded in copolymer film at 70 °C for 20 s (Figure S3(f)). However, when the embedding temperature was decreased to 50 °C, AgNWs were not perfectly embedded in copolymer film because of the lower chain mobility of the copolymer, exposing the AgNWs on the copolymer film (Figure S3(e)). When the embedding temperature was increased to 100 °C, AgNWs were well embedded in the copolymer film (Figure S3(g)). Sheet resistance of AgNWs retained the initial values regardless of embedding temperature (Figure S3(h)).

The AgNWs-embedded film can be coated any substrates such as PI, PDMS, and nitrile glove (Figure S4).



Figure S1. (a) Schematic illustration of iCVD process. (b) Transmittance of p(DMAMS-*co*-CEA), AgNWs-embedded film on glass ($R_{sh} = 15 \Omega/sq$), and ITO ($R_{sh} = 18 \Omega/sq$).



Figure S2. SEM images of AgNWs on copolymer film (a) before and (b) after annealing. Inset of (b) is cross-sectional SEM image of AgNWs-embedded film. Scale bars for (a) and (b) are 2 μ m. AFM morphology images of AgNWs on copolymer film (c) before and (d) after annealing. The structure is Si wafer / p(DMAMS-*co*-CEA) (300 nm) / AgNWs. Scan size: 10 μ m.



Figure S3. SEM images of AgNWs-embedded copolymer film as a function of annealing times for (a) 20 s, (b) 1 min, and (d) 30 min at 70 °C. (d) Sheet resistance before and after embedding of AgNWs for 20 s, 1 min, and 30 min. SEM images of AgNWs-embedded copolymer film as a function of embedding temperature at (e) 50 °C, (f) 70 °C, and (g) 100 °C for 20 s. (h) Sheet resistance before and after embedding of AgNWs at 50 °C, 70 °C, and 100 °C. Scale bars: 2 μm.



Figure S4. Coating of AgNWs-embedded films on (a) PI, PDMS, and (b) nitrile glove. Scale bar for (a) is 1 cm.

Conformal deposition of AgNWs on cloth

Figure S5 shows the deposition of AgNWs on rough cloth. As-sprayed AgNWs on cloth showed the aggregated network because of non-uniformly spread AgNWs solution on rough, relatively hydrophobic surface of cloth, and rapid evaporation of solvent during spraying. However, water floating-transferred AgNWs showed the conformal and percolated network on cloth.

Figure S5. SEM images of deposition of AgNWs on cloth using (a) spraying and (b) water floating transfer. Scale bars for (a) and (b) are $40 \mu m$.

XPS spectra of copolymer film before and after thermal post-curing as a function of temperature

The p(DMAMS-*co*-CEA) copolymer consists of three parts, which correspond to ionic crosslinking, tert-amine containing, and alkyl chloride containing part. Among them, the crosslinking degree can be expressed by quaternary ammonium (N⁺) contents that can be calculated by N⁺_{atom} % / (N_{atom} + Cl_{atom} + N⁺_{atom}) % derived from high resolution XPS spectra. In order to confirm whether the ionic salt (-NR₃⁺Cl⁻) linkage was formed or not, the XPS analysis was conducted. Figure S6 represents high resolution XPS spectra about N_{1s} and Cl_{2p} atoms. Generally, in XPS spectra, the N⁺ ion peak is observed at 402 eV binding energy region and the Cl⁻ ion peaks are observed at 196, 197 eV binding energy regions.¹⁻³ Figure S6 clearly shows that N⁺ and Cl⁻ peaks are increased after thermal postcuring process. The crosslinking degree of copolymer can be changed by thermal post-curing temperature. Below 90 °C, crosslinking reaction does not occur. Therefore, embedding process of AgNWs can be possible because this region is near the *T*_g of copolymer. At above 120 °C, N⁺ and Cl⁻ peaks are increased, which means that crosslinking degree is increased. Figure S7 shows the AgNWsembedded cloth after thermal post-curing. The morphology remained without any pores and defects.

Finally, the crosslinked copolymer showed high T_g compared to that of non-crosslinked copolymer (90 °C). (Figure S8)

Figure S6. High resolution XPS data [(a) N_{1s} and (b) Cl_{2p}] of p(DMAMS-*co*-CEA) copolymer with respect to thermal post-curing temperature.

Figure S7. SEM images of embedded-AgNWs cloth after annealing and thermal post-curing. Scale bar is 40 μm.

Figure S8. Differential scanning calorimetry (DSC) before and after thermal post-curing of copolymer

Principle of spontaneous embedding of AgNWs into copolymer film

Figure S9 shows the embedding the AgNWs on (a-d) non-crosslinked and (e-h) crosslinked copolymer. The surface energies of AgNWs and copolymer were measured by contact angles of AgNWs and copolymer by dropping water and glycerol droplets on them.⁴ Interfacial energy between AgNWs and copolymer is calculated by an equation (1).⁴ The sample structure is Si wafer / AgNWs or copolymer (300 nm).

$$\gamma_{inter} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p}$$
(1)

Figure S9. Schematic illustration and SEM images of AgNWs transferred non-crosslinked (before thermal post-curing) (a, b) before and (c, d) after annealing, and crosslinked polymer film (after thermal post-curing) (e, f) before and (g, h) after annealing. The structure is Si wafer / p(DMAMS-*co*-CEA) (300 nm) / AgNWs. Scale bars are 2 μm.

Adhesion of bare copolymer on various substrates

Adhesion of bare copolymer on various substrates was measured by a 90° peel test (Figure S10). The 90° peel test was performed using a high precision mechanical testing machine with two linear stages in Y-axis and Z-axis. A 12 mm wide tape (3M 810D) was attached and detached atop the sample at a 90° angle with a peeling speed of 1 mm/s. The sample moved along the Y-axis while the tape was detached along the Z-axis at the same speed.

Figure S10. Image of 90° peel test.

Charge interaction between AgNWs and copolymer after thermal post-curing.

Figure S11 shows the high resolution Ag_{3d} XPS data of AgNWs embedded-film. The corresponding peaks of the pristine AgNWs are 367.3 and 373.3 eV, respectively. In AgNWs embedded film, the peaks were shifted largely toward low binding energy region by 0.5 and 0.43 eV, respectively. This observation indicates that AgNWs interact strongly with crosslinked p(DMAMS-co-CEA).

Figure S11. XPS data of AgNWs-embedded film and bare AgNWs film. The phenomena of the binding energy peak shift is related with charge interaction between crosslinked p(DMAMS-*co*-CEA) and AgNWs. Peak shift is related to charge interaction between crosslinked p(DMAMS-*co*-CEA) and AgNWs.

AgNWs-embedded film on polyimide substrates.

When we conducted the folding test of AgNWs-embedded copolymer film on a polyimide (PI) substrate that has smooth and flat surface, the sheet resistance showed a mere 2-fold increase of initial resistance ($12 \Omega/sq$) even after 1000 cycles as shown in Figure S12. The radius of curvature during the folding cycle was approximately 400 µm. However, when the folding test was conducted to AgNWs-embedded copolymer film on cloth, the folding imposes the large deformation and gap between fibers on surface of cloth that consists of many strands of fibers. Therefore, AgNWs-embedded film on cloth has higher physical damage and deformation compared to that on PI, hence limiting the number of folding cycles to 300.

Encapsulated AgNWs-embedded film

After the extremely hydrophobic coating on AgNWs-embedded film using (poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate (pPFDMA), transmittance was measured (Figure S13(a)). The encapsulated film showed similar transmittance with AgNWs-embedded film because of transparent pPFDMA polymer at visible wavelength region. Moreover, after the peel test, the AgNWs were not detached from cloth, showing enhanced mechanical durability (Figure S13(b)). The mechanical robustness of encapsulated AgNWs-embedded films was examined by a folding test. The R_{sh} of encapsulated AgNWs-embedded films showed a mere 3-fold increase after 300 cycles, showing similarly enhanced mechanical robustness of AgNWs-embedded films (Figure S14).

Figure S12. $R_{\rm sh}$ change of films with non-embedded and embedded AgNWs on PI substrate after repeated foldings. Initial $R_{\rm sh}$: 12 Ω /sq.

Figure S13. (a) Transmittance of pPFDMA, embedded AgNWs, and encapsulated AgNWsembedded film. Images of sample and tape of (b) encapsulated AgNWs-embedded cloth after peel test.

Figure S14. $R_{\rm sh}$ change of films with non-embedded and encapsulated AgNWs after repeated foldings. Initial $R_{\rm sh}$: 12 $\Omega/{\rm sq}$.

Thermal oxidation stability of encapsulated AgNWs-embedded film

Figure S15 demonstrates the enhanced thermal oxidation stability of encapsulated AgNWsembedded film after 50 days.

Figure S15. SEM images of (a, d) non-embedded, (b, e) embedded AgNWs, and (c, f) encapsulated AgNWs-embedded films before and after thermal oxidation stability test at 90 °C with 98 % relative humidity after 50 days. Scale bar is 2 μm.

Washing of non-embedded AgNWs film

As shown in Figure S16 (a) and (b), the AgNWs network on cloth was fully detached after washing. However, encapsulated AgNWs-embedded film was partially cracked without delamination, showing the enhanced mechanical robustness (Figure S16(c) and (d)).

Figure S16. (a, b) Non-embedded AgNWs and (c, d) encapsulated AgNWs-embedded films before and after washing, respectively. Scale bars: 40 µm.

Waterproof cloth-based heater

For high temperature operation of heater at low applied voltages, we fabricated a heater using high concentration of AgNWs-embedded film. We measured the mechanical robustness of AgNWs-embedded films by a folding test when the concentration of AgNWs was high ($R_{sh} = 1 \Omega/sq$) (Figure S17) and compared the mechanical robustness with that of low concentration AgNWs ($R_{sh} = 12 \Omega/sq$) already measured in Figure 3(c). When the concentration of AgNWs is increased, the R_{sh} of AgNWs-embedded films showed a only 2-fold increase from the initial resistance (1 Ω/sq) even after 300 cycles.

Figure S18(a) shows the waterproof letter-patterned cloth-based heater using encapsulated AgNWs-embedded film. The letter-pattern is fabricated by water floating transfer of patterned AgNWs. After the washing in water, the cloth-based heater was well operated, increasing the temperature to 70 °C at 3 V (Figure S18(b) and (c)).

Figure S17. R_{sh} change of films with non-embedded and embedded AgNWs after repeated foldings. Initial R_{sh} : 1 Ω/sq .

Figure S18. Images of (a) waterproof letter-patterned cloth-based AgNWs-embedded heater and (b) its washing. Scale bar for (a) is 2 cm. (c) Infrared images of heater (i) before and (ii) after washing at bias of 0 V and 3 V voltage.

Tables

Table S1. Surface energies of AgNWs and p(DMAMS-co-CEA) and interfacial energy between

Sample	Surface energy (γ) [mN·m ⁻¹]	Interfacial energy (y _{inter}) with AgNWs [mN·m ⁻¹]	γ _{AgNWs} — γ _{polymer} - γ _{inter}
AgNWs	72.6±0.33		
p(DMAMS- <i>co</i> -CEA) (non-crosslinked)	46.2±1.0	6.1	20.3
p(DMAMS- <i>co</i> -CEA) (non-crosslinked)_90 °C	39.3±0.2	12.3	21.0
p(DMAMS-co-CEA) (crosslinked)	50.1±0.6	4.1	18.4
p(DMAMS- <i>co</i> -CEA) (crosslinked)_90 °C	49.2±0.7	4.6	18.8

AgNWs and p(DMAMS-co-CEA)

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