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Supplementary Information

Functionalized Nano-silver Particles Assembled on One-dimensional Nanotube Scaffolds for Ultra-highly Conductive Silver/polymer Composites

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Experimental details

A modified procedure published by Yang et al. was used for the synthesis of Ag nano-particles functionalized with phenyl rings [S1, S2]. A solution of $AgNO_3$ (Junsei) in ethanol (0.02 mol/L, 400 mL) was mixed with a solution of benzyl mercaptan (Sigma Aldrich) in ethanol (0.06 mol/L, 800 μL) by strong stirring for 48 hrs. Also, 50 mg of MWNTs (Hanwha Nanotech, Outer diameter: 3~5 nm) were dispersed in 100 mL of ethanol (Deasjung, 95 %) by ultrasonicating at 560 W for 10 minutes. Then the solutions were mixed in a bath sonicator at 200 W for 5 hours. Finally, MWNTs decorated with nano-Ag particles (Ag-MWNTs) were filtered (0.2 μm PTFE membrane), rinsed several times with ethanol and dried in a vacuum chamber.

The Ag-MWNTs were re-dispersed in ethanol by ultrasonicating at 560 W for 5 minutes. Then it was mixed with a solution of glutaric acid ($HO_2C(CH_2)_3CO_2H$, Sigma Aldrich) in ethanol (500ml) by ultrasonicating at 560 W for 20 minutes. The molar ratio of glutaric acid and silver, which is attached on the surface of MWNTs, was 1:1. The solution was additionally sonicated in a bath sonicator at 200 W for 2 hrs. Finally, MWNTs decorated with glutaric-acid functionalized nano-silver particles (g-Ag-MWNTs) were filtered, rinsed several times with ethanol and dried in a vacuum chamber.

The micron-sized silver powders, epoxy and hardener were obtained from Dongbu Fine Chemicals Co. Ltd. The micron-sized silver powders consist of flake and spherical types (3:1 wt ratio) with an average size of 3 and 0.5 μm, respectively. The g-Ag-MWNTs were dispersed in the epoxy by ultrasonication (560 W, 5 min). Then micron-sized silver powders and hardener were introduced into the mixture and stirred at 1800 rpm (MTOP 3040) for 10 minutes.

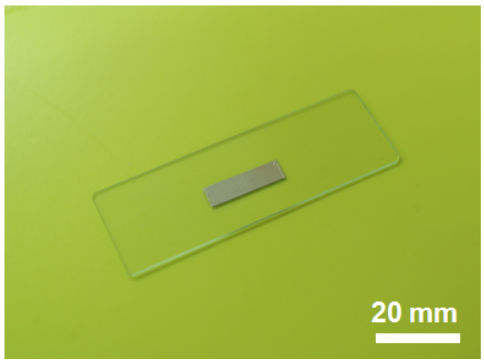

Figure S1.The specimen for the conductivity measurements were screen-printed using the silver/epoxy composite with g-Ag-MWNTs.

The silver/epoxy composite was screen-printed on a glass slide (20 mm × 5 mm × 10 μm) and cured at 185 °C for 1hr as shown in Fig. S1. The electrical conductivity was measured by a four-point in-line method [S3-S5]. An electric current of 2 mA was supplied (Keithely 6221) and a nano voltmeter (Keithely 2182A) was employed. The measurement was carried out 500 times for each sample. The composite was mechanically ground into a thickness of 80 nm using an ultra-microtome (RMC, MT-7000) for high-resolution transmission electron microscopy (HRTEM). Differential scanning calorimeter (Seiko Extra 6000) measurements were carried out in the range of 100 ~ 200 ℃ with a

typical heating rate of 5 °C/min. The bonding state between nano-Ag particles and nanotubes was analyzed with X-ray photoelectron spectroscopy (VG microtech ESCA 2000, ESCA 2000). X-ray diffraction (Bruker AXS, D8 Focus), scanning electron microscopy (JEOL, JEOL-7401F) and 3 dimensional digital microscopy analysis (Hirox, KH-7700) were also performed. Thixotropic index was calculated using the ratio of experimentally measured viscosities at 1 and 10 rpm (Brookfield HBDV-Ⅱ, Viscometer, Spindle # 14, 25 °C).

Glutaric Acid Functionalization

Figure S2 compares the color of nano-Ag particles, annealed at 185□ for 1 hr, before and after the glutaric acid functionaliztion. For reasons of clear imaging, binder and MWNTs were not incorporated. The SEM imaging was carried out using the identical condition. The silver particles look more white in SEM images when they are oxidized [S6]. As shown in Fig. S2, the color of coalesced silver particles was darker for the functionalized Ag particles proving that the surface oxidation was effectively prevented.

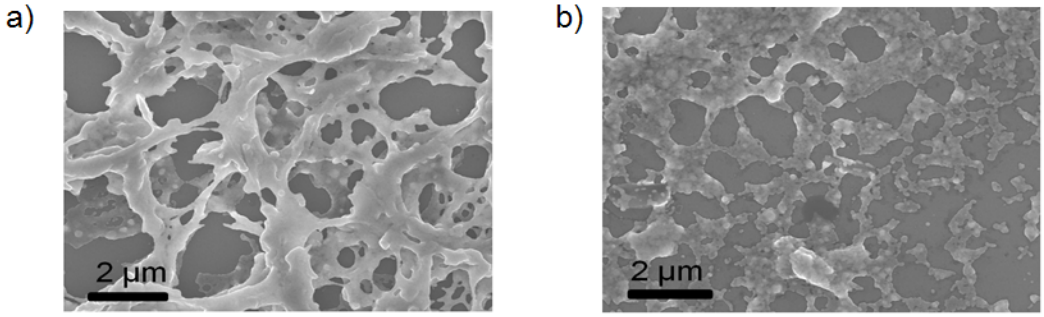

Figure S2. SEM images of coalesced nano-Ag particles annealed at 185 °C for 1 hr. (a) Before glutaric-acid functionalization (b) After functionalization.

Figure S3 compares XRD patterns before and after the annealing process. The structural change of nano-particles can be characterized by the powder XRD since the full width at half the maximum peak (FWMP) is reduced when particles are coalesced [S7]. Figure S3 shows the reduction of FWMP of Ag (111) after the annealing process demonstrating the successful coalescence of nano-Ag particles. The

reduction in FWMP of g-Ag-MWNTs (1:0.63) is greater than that of Ag-MWNTs, (1:0.82). This indicates that the effective coalescence was achieved by the glutaric acid fucntionalization.

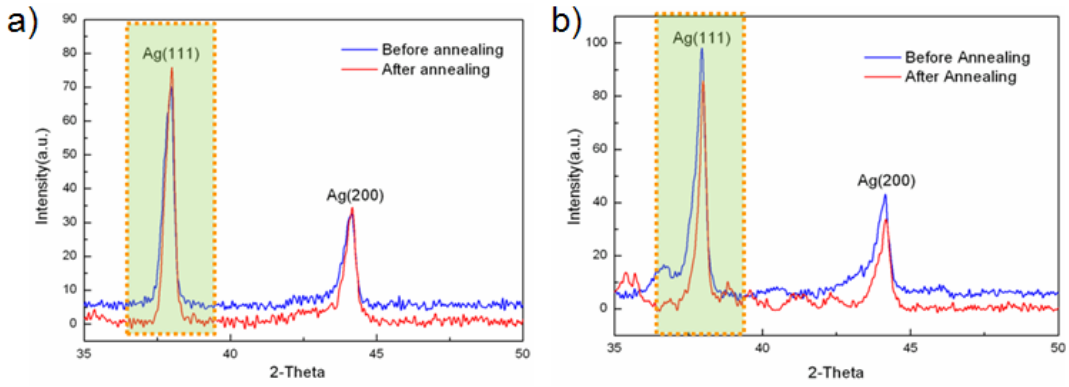

Figure S3. XRD patterns before and after the annealing process at 185 °C for 1 hr. (a) Ag-MWNTs (b) g-Ag-MWNTs.

Figure S4 compares the Raman spectra of Ag-MWNTs, annealed Ag-MWNTs and g- Ag-MWNTs to investigate the structural defect formation during the glutaric acid treatment and the annealing process at 185 °C for 1 hr. The D peak at 1330 cm^{-1} corresponds to the conversion of sp^2 hybridized carbon to sp^3 hybridized carbon [S8]. Therefore, the increase in the intensity of D peak demonstrates the destruction of nanotube sp^2 structure by physical or chemical treatments [S8]. As shown in Fig. S4, the D peak intensity was not changed proving that MWNTs were not damaged during the glutaric acid treatment and the annealing process. The glutaric acid solution was not strong enough (pH=6.4) to cause structural deformation of nanotubes.

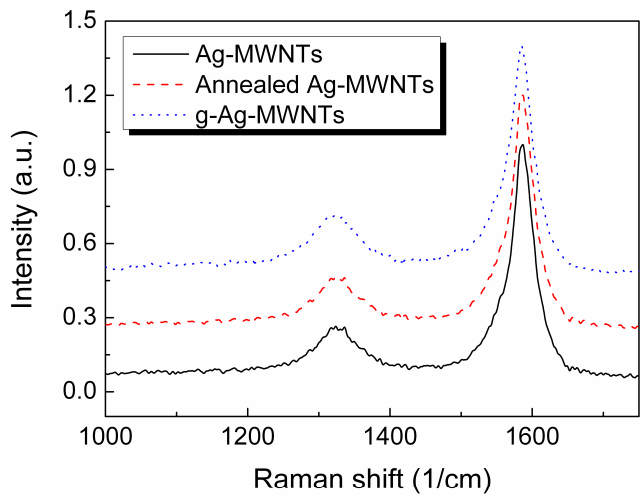

Figure S4. Raman spectra of Ag-MWNTs, annealed Ag-MWNTs and g-Ag-MWNTs. The excitation wavelength was 633 nm (Kaiser Optical, Raman microscope), and the spectra were normalized by the g-peak of nanotubes.

Figure S5 shows the percolation threshold investigation for g-Ag-MWNTs. The total concentration of g-Ag-MWNTs was varied from 0 to 2 wt%, and its effect on conductivity is shown in Fig. S5. The relative ratio between MWNTs and nano-Ag particles was fixed at 65:35 wt%. The concentration of binder was 19 wt% (17.8 wt% epoxy and 1.2 wt% hardener). The rest of the composite was filled using micron-sized silver powders (81~79 wt%). The total concentration of the conductive fillers (g-Ag-MWNTs and micron-sized silver powders) was kept constant at 81 wt%. The maximum conductivity was observed at 1.5 wt% (2.5×10^5 S/cm).

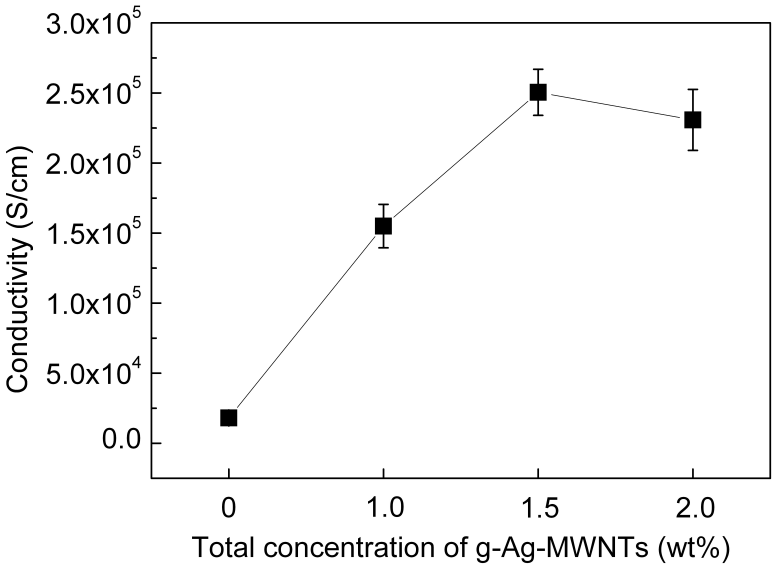

Figure S5. The conductivity of the composite as a function of the total concentration of g-Ag-MWNTs.

References

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