Supporting Information

The Seed-Mediated Growth of Gold Nanoparticles Inside of Carbon Nanotube Fibers for Fabrication of Multifunnctional Nanhybrid Fibers with Simultaneously Enhanced Mechanical and Electrical Properties

*Young-Jin Kim,[a,b] Junbeom Park,[a] Hyeon Su Jeong,[a] Min Park,[a] Seulki Baik,[a,c] Dong Su Lee,[a] Heesuk Rho,[c] Hyungjun Kim,[d] Joong Hee Lee,[b] Seung-Min Kim[a] and Young-Kwan Kim[a]**

[a]Institute of Advanced Composite Materials, Korea Institute of Science and Technology, 92 Chudong-ro, Bongdong-eup, Wanju-gun, Jeonbuk 55324, Republic of Korea

[b]Advanced Materials Institute of BIN Convergence Technology (BK21 Plus Global) & Department of BIN Convergence Technology, Chonbuk National University, Jeonju, Jeonbuk 54896, Republic of Korea.

[c]Department of Physics, Research Institute of Physics and Chemistry, Chonbuk National University, Jeonju 54896, Republic of Korea

[d]Department of Chemistry, Incheon National University, 119 Academy-ro, Yeonsu-gu, Incheon 22012, Republic of Korea

* To whom correspondence should be addressed. E-mail Address: youngkwan@kist.re.kr; Fax: +82-63-219-8239; Tel: +82-63-219-8172

Experimental section

Materials. Hydrogen tetrachloroaurate(III) hydrate was purchased form Kojima Chemicals Co. (Sayama, Saitama, Japan). Hexadecyl-trimethylammonium bromide (CTAB) was purchased form Acros (New jersey, USA). L-(+)-Ascorbic acid was purchased from Alfa Aesar (Massachusetts, USA). 1-Pyrenemethylamine hydrochloride (PMA), acetone, ferrocene and thiophene were purchased from Aldrich Chemical Co. (Milwaukee, WI). Sodium borohydride was purchased from Samchun (Seoul, Korea). Sodium citrate dehydrate, nitric acid and ethanol were purchased from Daejung (Siheung, Korea).

Synthesis of 5 nm-sized Au nanoparticles. 20 mL of 0.25 mM $HAuCl_4$ and 0.25 mM tri-sodium citrate was prepared in a conical tube. 0.6 mL of 0.1 M $NaBH_4$ was added to the solution once with shaking.

Synthesis of 15 nm-sized Au nanoparticles. 50 mL of water was mixed with 50 μL of 250 mM $HAuCl_4$ and the mixture was heated until boiling under stirring. 780 μL of 34 mM tri-sodium citrated solution was added to boiling solution at once and reaction was kept for 15 min.

Synthesis of 40 nm-sized Au nanoparticles. 50 mL of water was mixed with 50 μL of 250 mM $HAuCl_4$ and the mixture was heated until boiling under stirring. 350 μL of 34 mM tri-sodium citrated solution was added to boiling solution at once and reaction was kept for 15 min.

Reference for Q-Chem 5.0

Shao, Y.; Gan, Z.; Epifanovsky, E.; Gilbert, A. T. B.; Wormit, M.; Kussmann, J.; Lange, A. W.; Behn, A.; Deng, J.; Feng, X.; Ghosh, D.; Goldey, M.; Horn, P. R.; Jacobson, L. D.; Kaliman, I.; Khaliullin, R. Z.; Kuś, T.; Landau, A.; Liu, J.; Proynov, E. I.; Rhee, Y. M.; Richard, R. M.; Rohrdanz, M. A.; Steele, Ryan P.; Sundstrom, E. J.; Lee H.; Woodcock III, Zimmerman, P. M.; Zuev, D.; Albrecht, B.; Alguire, E.; Austin, B.; Beran, G. J. O.; Bernard, Y. A.; Berquist, E.; Brandhorst, K.; Bravaya, K. B.; Brown, S. T.; Casanova, D.; Chang, C. –M.; Chen, Y.; Chien, S. H.; Closser, K. D.; Crittenden, D. L.; Diedenhofen, M.; DiStasio Jr., R. A.; Do, H.; Dutoi, A. D.; Edgar, R. G.; Fatehi, S. Fusti-Molnar, L.; Ghysels, A.; Golubeva-Zadorozhnaya, A.; Gomes, J.; Hanson-Heine, M. W. D.; Harbach, P. H. P.; Hauser, A. W.; Hohenstein, E. G.; Holden, Z. C.; Jagau, T. –C.; Ji, H.; Kaduk, B.; Khistyaev, K.; Kim, J.; Kim, J.; King, R. A.; Klunzinger, P.; Kosenkov, D.; Kowalczyk, T.; Krauter, C. M.; Lao, K. U.; Laurent, A. D.; Lawler, K. V.; Levchenko, S. V.; Lin, C. Y. Liu, F.; Livshits, E.; Lochan, R. C.; Luenser, A.; Manohar, P.; Manzer, S. F.; Mao, S. –P.; Mardirossian, N.; Marenich, A. V.; Maurer, S. A.; Mayhall, N. J.; Neuscamman, E.; Oana, C. M.; Olivares-Amaya, R.; O'Neill, D. P.; Parkhill, J. A.; Perrine, T. M.; Peverati, R.; Prociuk, A.; Rehn, D. R.; Rosta, E.; Russ, N. J.; Sharada, S. M.; Sharma, S.; Small, D. W.; Sodt, A.; Stein, T.; Stück, D.; Su, Y. –C.; Thom, A. J. W.; Tsuchimochi, T.; Vanovschi, V.; Vogt, L.; Vydrov, O.; Wang, T.; Watson, M. A.; Wenzel, J.; White, A.; Williams, C. F.; Yang, J.; Yeganeh, S.; Yost, S. R.; You, Z. –Q.; Zhang, I. Y.; Zhang, X.; Zhao, Y.; Brooks, B. R.; Chan, G. K. L.; Chipman, D. M.; Cramer, C. J.; Goddard III, W. A.; Gordon, M. S.; Hehre, W. J.; Klamt, A.; Schaefer III, H. F.; Schmidt, M. W.; Sherrill, C. D.; Truhlar, D. G.; Warshel, A.; Xu, X.; Aspuru-Guzik, A.; Baer, R.; Bell, A. T.; Besley, N. A.; Chai, J. –D.; Dreuw, A.; Dunietz, B. D.; Furlani, T. R.; Gwaltney, S. R.; Hsu, C. –P.; Jung, Y.; Kong, J.; Lambrecht, D. S.; Liang, W. Z.; Ochsenfeld, C.; Rassolov, V. A.; Slipchenko, L. V.; Subotnik, J. E.; Voorhis, T. V.; Herbert, J. M.; Krylov, A. I.; Gill, P. M.W.; Head-Gordon, M. molecular quantum chemistry contained in the Q-Chem 4 program package. *Mol. Phys.,* **2015**, *113*, 184-215.

Supporting figure

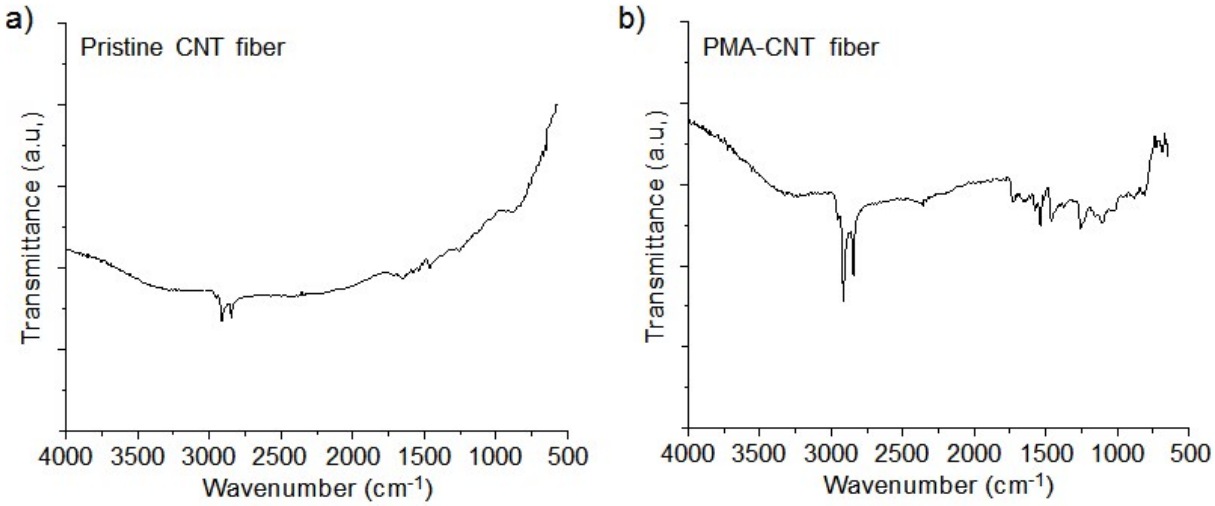

Figure S1. (a) FT-IR spectrum of pristine CNT fiber and (b) PMA@CNT fiber. FT-IR spectrum of pristine CNT fiber showed almost featureless signal. By contrast, the PMA@CNT fiber showed highly increased signal at 2846 and 2915 cm^{-1} from aliphatic C-H stretching and appearance of signal at 1257 cm^{-1} from C-N stretching. This result indicated the surface of CNT fiber was modified with PMA molecules.

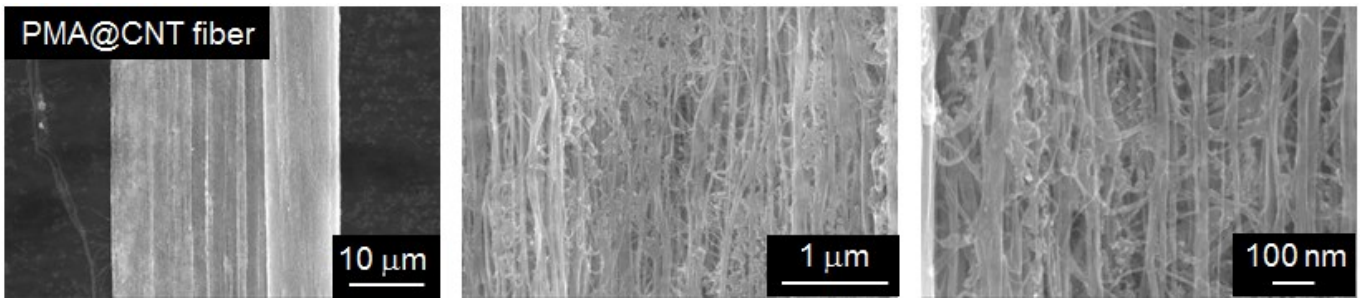

Figure S2. SEM images of PMA@CNT fibers with different magnifications.

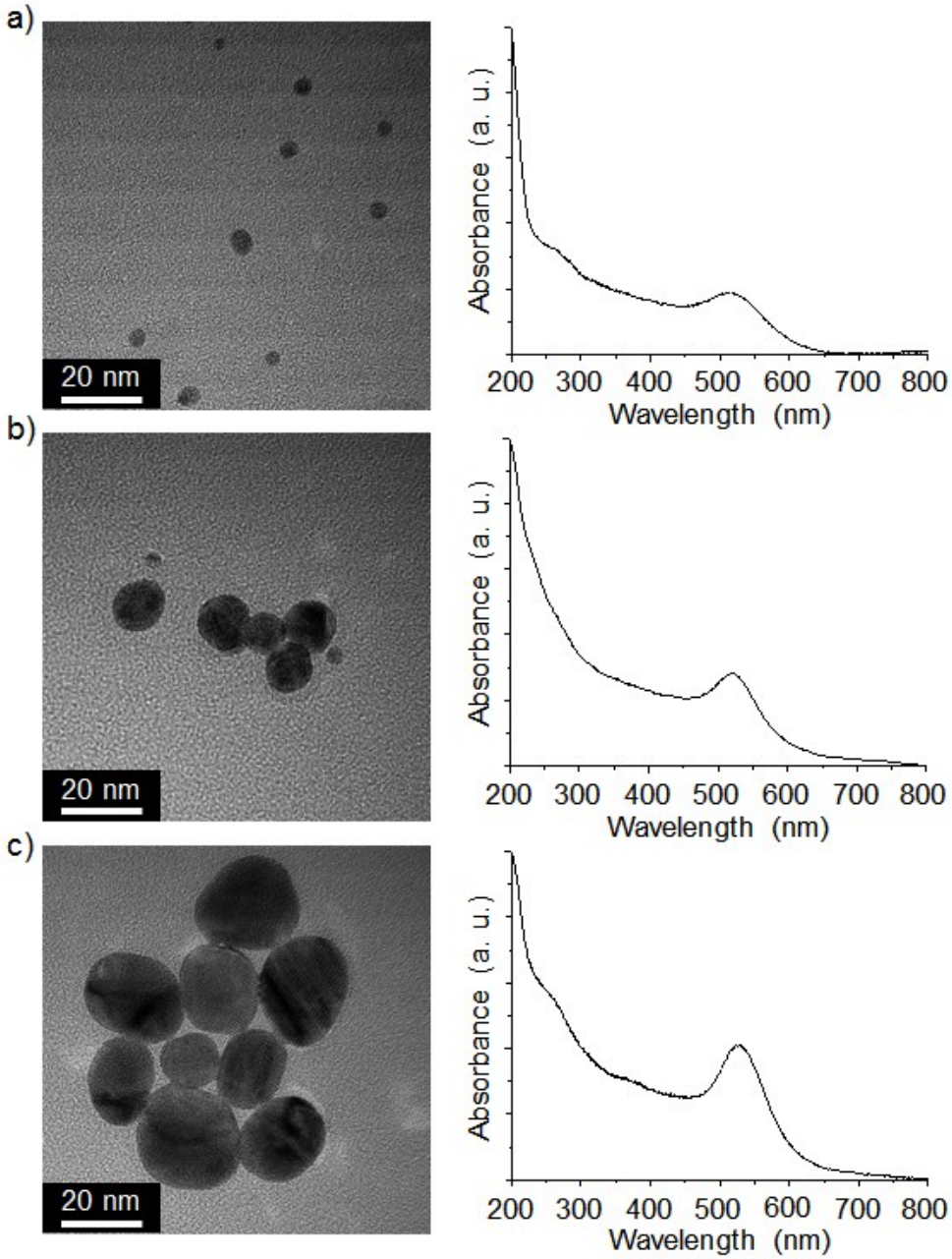

Figure S3. TEM images (left column) and UV-Vis spectra (light column) of 5 (a), 15 (b) and 40 nm (c) sized Au seeds.

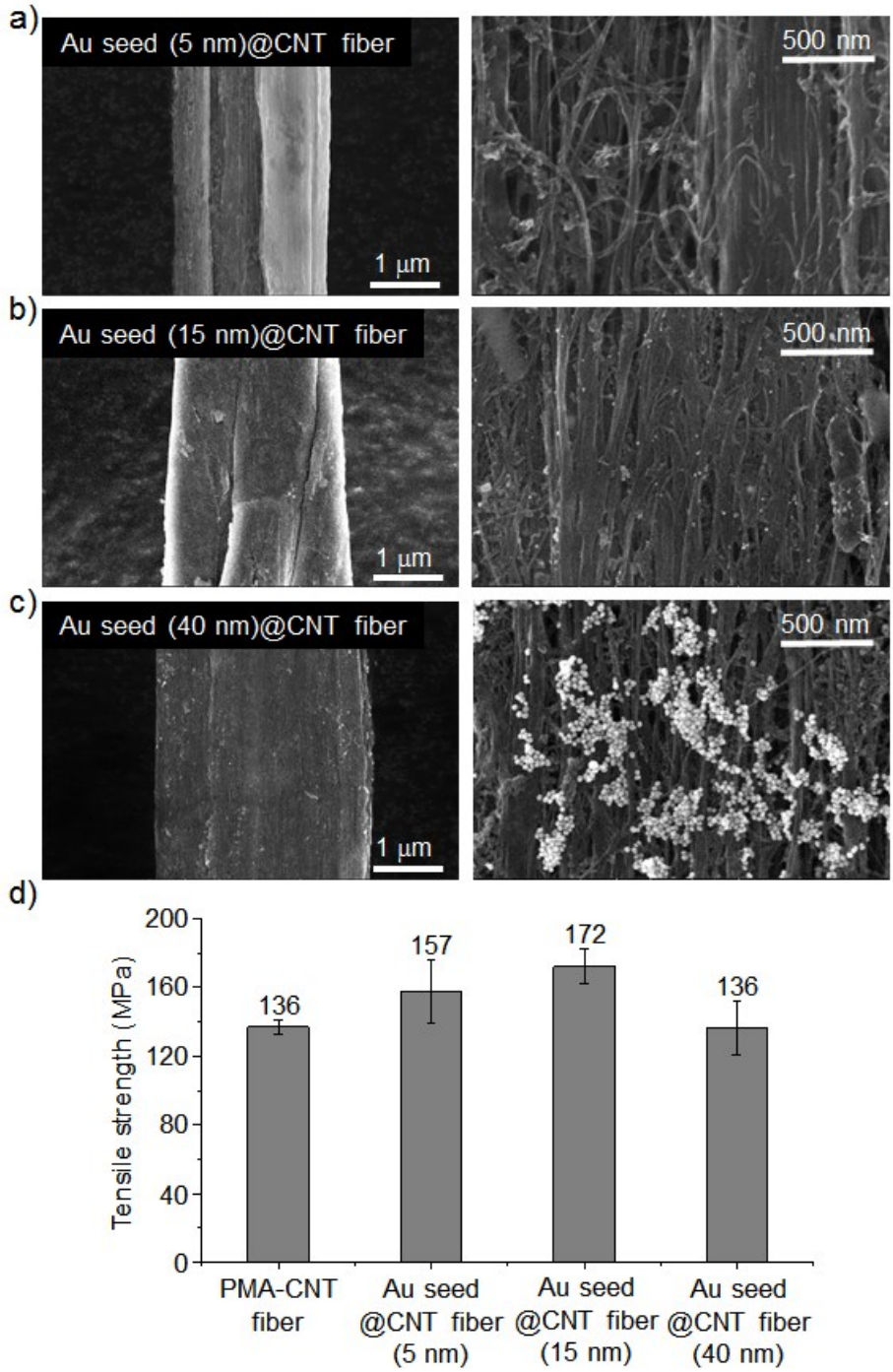

Figure S4. SEM images of Au seed@CNT fibers prepared by using 5 (a), 15 (b) and 40 nm (c) sized Au seeds. d) Tensile strength of PMA-CNT and Au seed@CNT fibers prepared with 5, 15 and 40 nm sized Au seeds. The tensile strength of PMA-CNT fibers (136 MPa) increased to 157 and 172 MPa with 5 nm- and 15 nm-sized Au seeds, respectively (Figure S4d), but 40 nm-sized Au seeds did not affect the tensile strength of PMA-CNT fibers. These result indicated that 15 nm-sized Au seeds provided efficient penetration into porous structure of PMA-CNT fibers and acted as a bridge to inter-connect PMA-CNT fibers. 5 nm-sized Au seeds might be too small to inter-connect PMA-CNT fibers and 40 nm-sized Au seeds cannot efficiently penetrate into the porous structure of CNT fibers

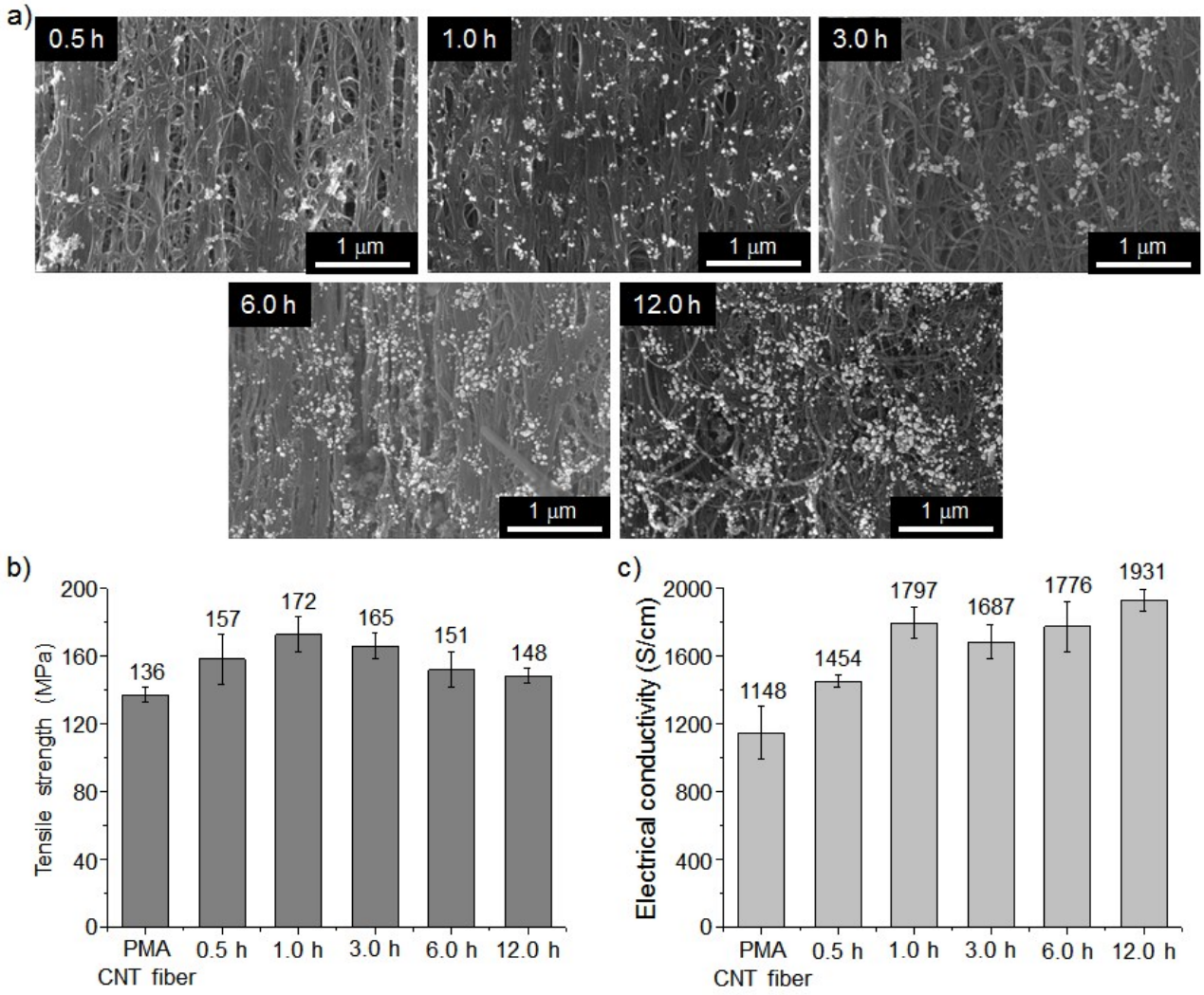

Figure S5. a) SEM images, tensile strength (b) and electrical conductivity (c) of Au seed@CNT fibers prepared by using 15 nm sized Au seeds with different incubation time (0.5, 1.0, 3.0, 6.0 and 12.0 h). It was found that the Au seeds tended to form aggregated structures on PMA-CNT fibers with incubation time (Figure S5a), and thus the enhancement of tensile strength and electrical conductivity of PMA-CNT fibers reached to plateau (172 MPa and 1797 S cm^{-1}) after 1 h incubation. Further incubation lead to slight decrease of tensile strength and electrical conductivity of Au seed@CNT fibers. These results indicated that the formation of aggregated structures of Au seeds diminished the reinforcement effect of Au seeds for PMA-CNT fibers.

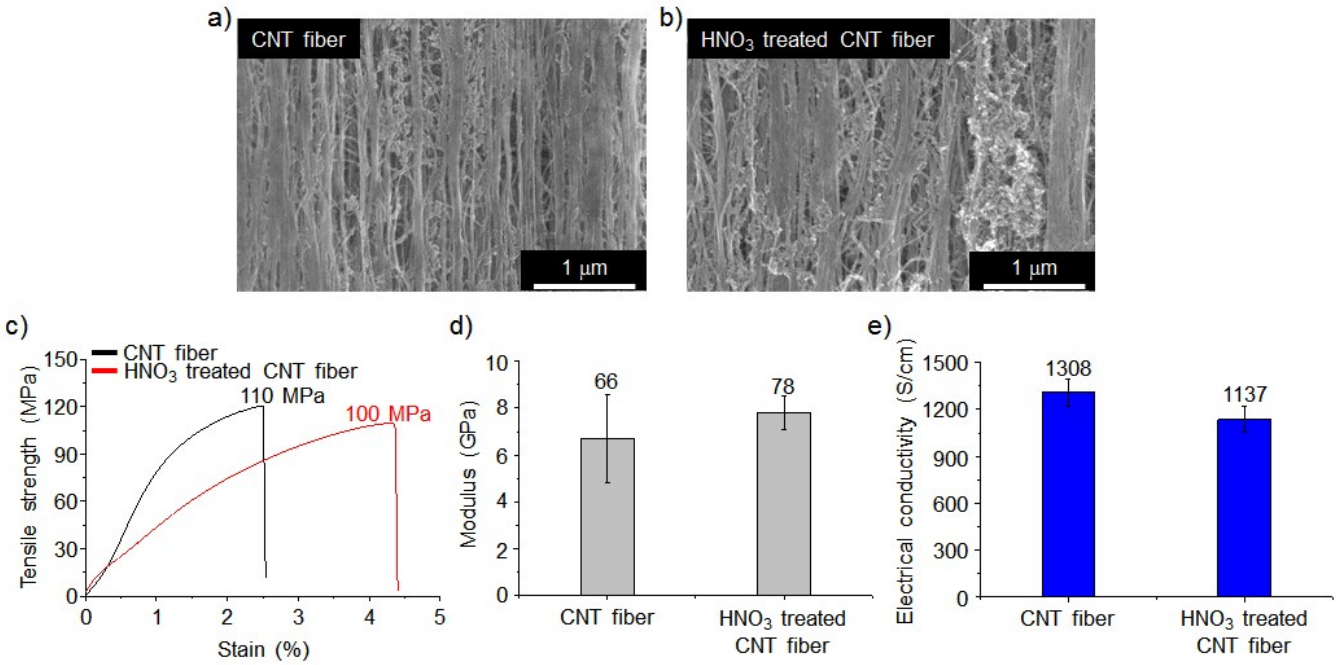

Figure S6. SEM images of pristine CNT (a) and nitric acid treated CNT fibers (b). (c) stress strain curves, (d) tensile modulus and (e) electrical conductivity of pristine and nitric acid treated CNT fibers.

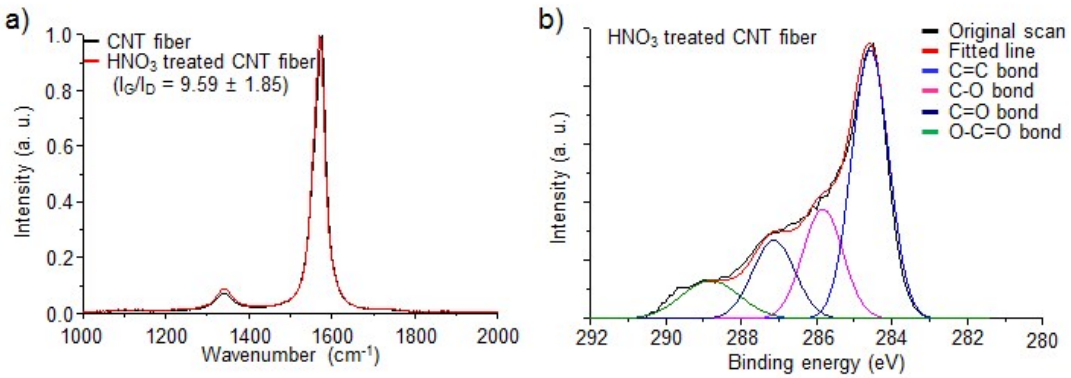

Figure S7. a) Raman spectra of pristine CNT and HNO_3 treated CNT fibers. b) C 1s XPS spectrum of HNO_3 treated CNT fibers. By the HNO_3 treatment, the I_G/I_D of CNT fibers decreased and oxygen-containing functional groups were formed on the surface of CNT fibers.

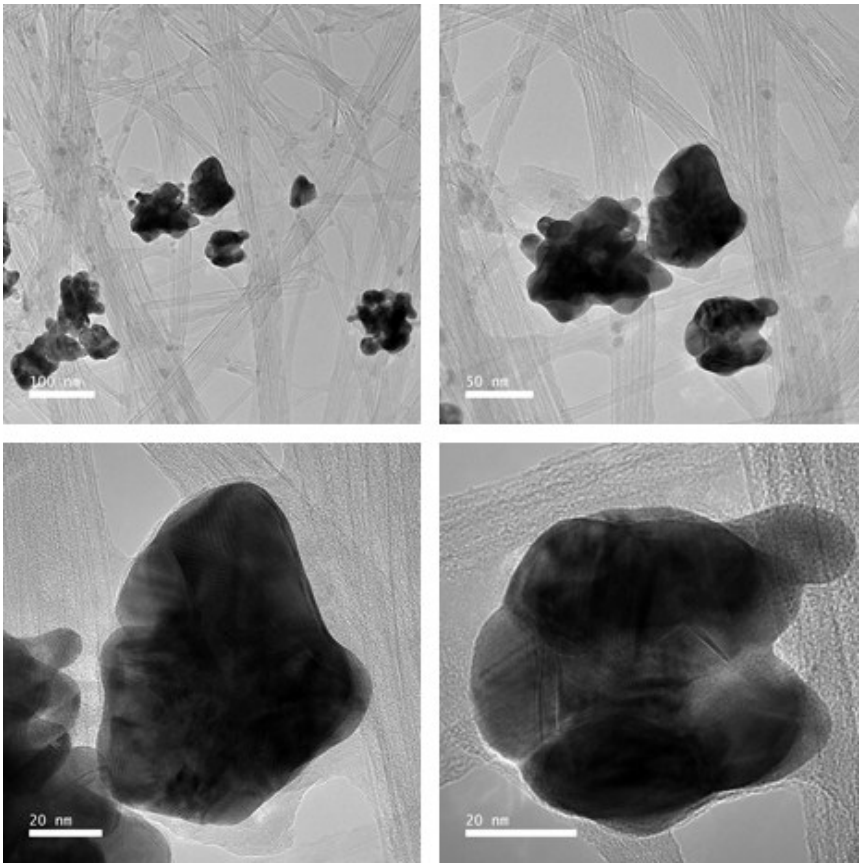

Figure S8. TEM images of Au NP@CNT fiber with different magnifications.

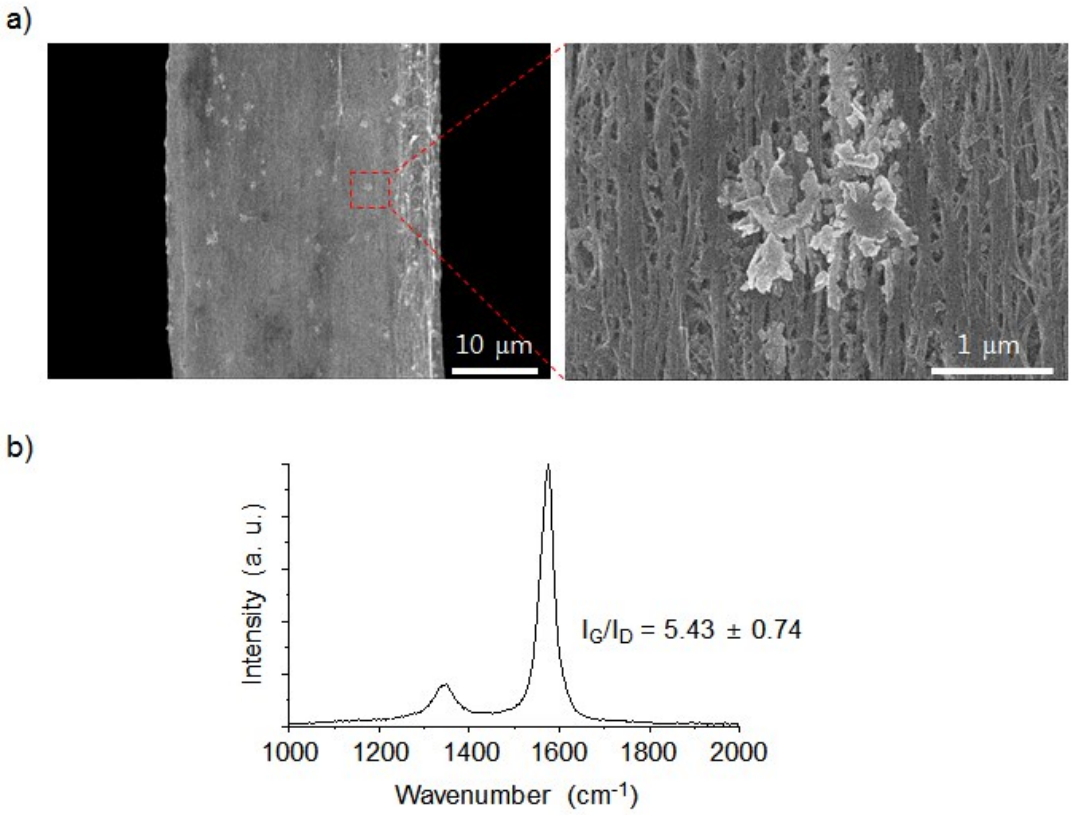

Figure S9. a) SEM images (b) Raman spectrum of CNT fiber incubated in growing solution without PMA modification and Au seed immobilization.

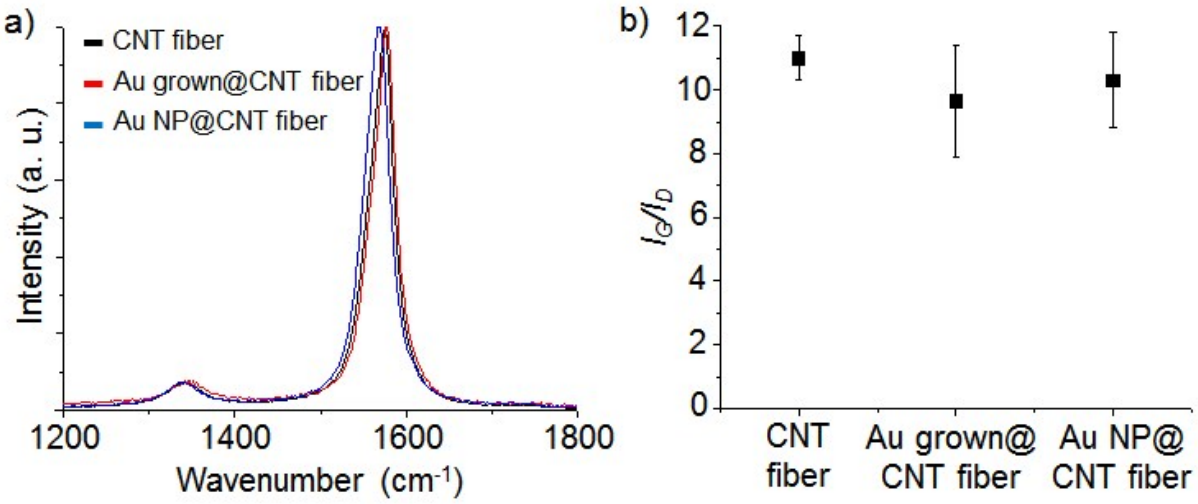

Figure S10. a) Raman spectra and (b) I_G/I_D values of CNT, Au grown@CNT and Au NP@CNT fibers.

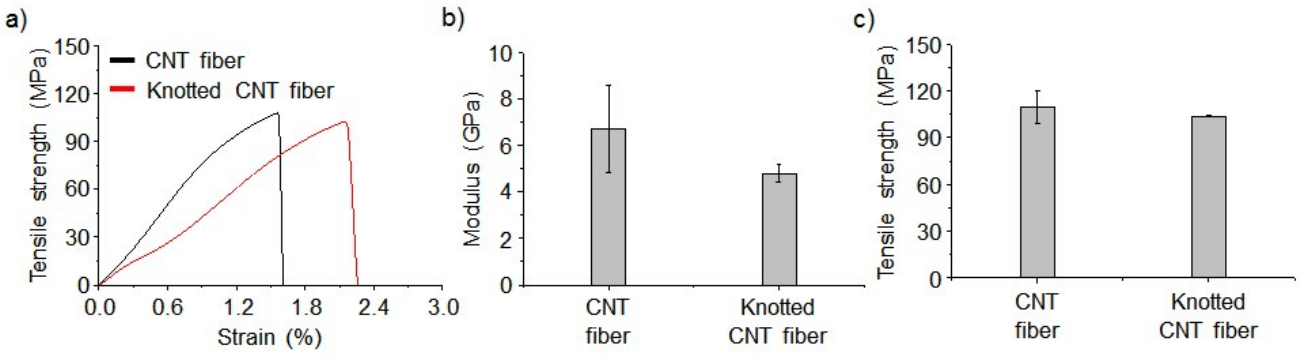

Figure S11. a) Stress-strain curve, (b) tensile modulus and (c) strength of pristine CNT and knotted CNT fibers.

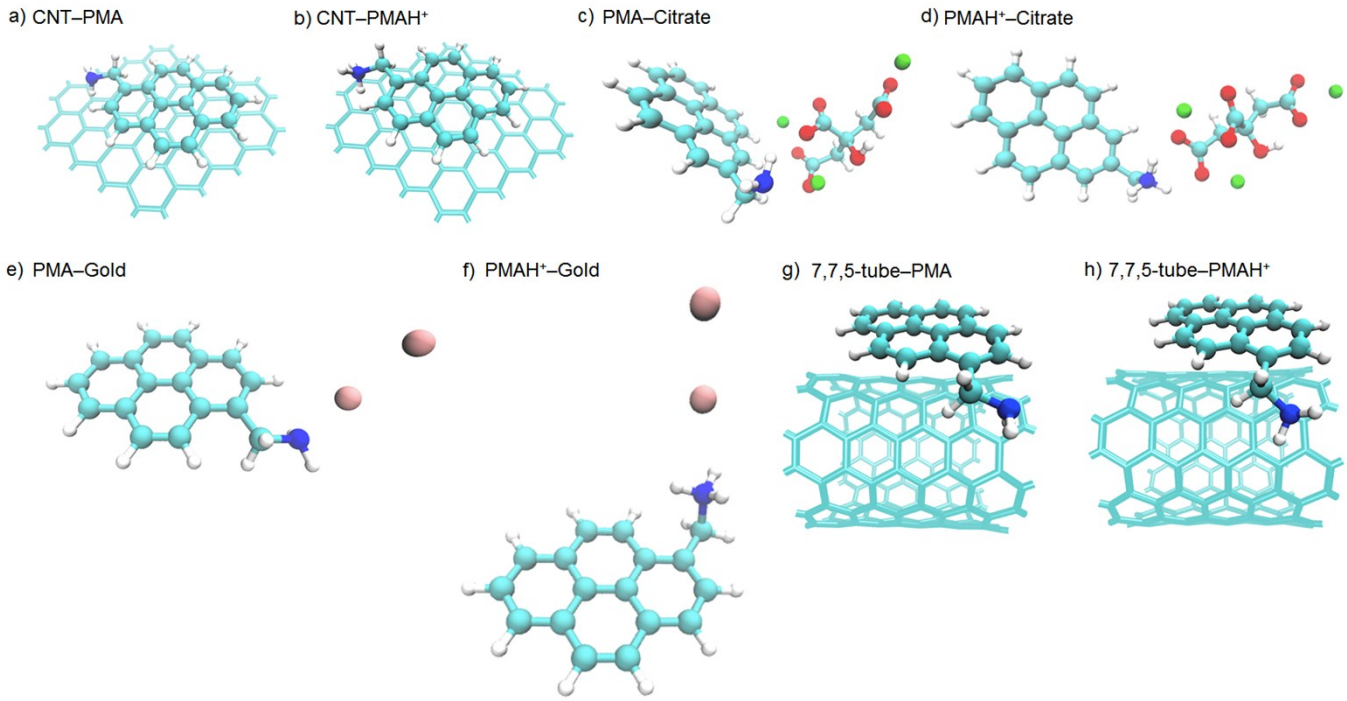

Figure S12. The optimized structures of simulated CNT-PMA (a), CNT-$PMAH^+$ (b), PMA-Citrate (c), $PMAH^+$-Citrate (d), PMA-Gold (e), $PMAH^+$-Gold (f), 7,7,5-tube-PMA (g), and 7,7,5-tube-$PMAH^+$ (h).

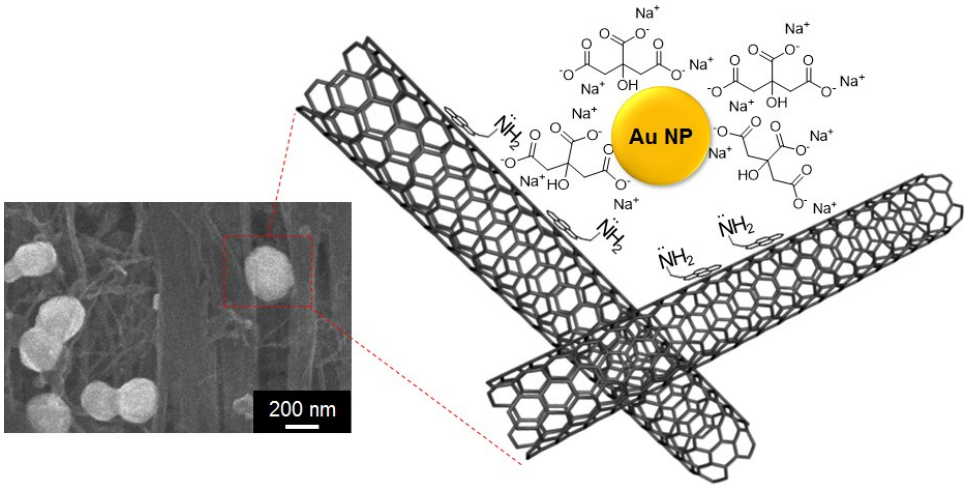

Figure S13. A schematic diagram of the suggested interfacing structure of Au grown@CNT fibers by quantum chemical simulations.