Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting information.

Creating Covalent Bonds between Cu and C at the Interface of Metal/Open-Ended Carbon Nanotubes

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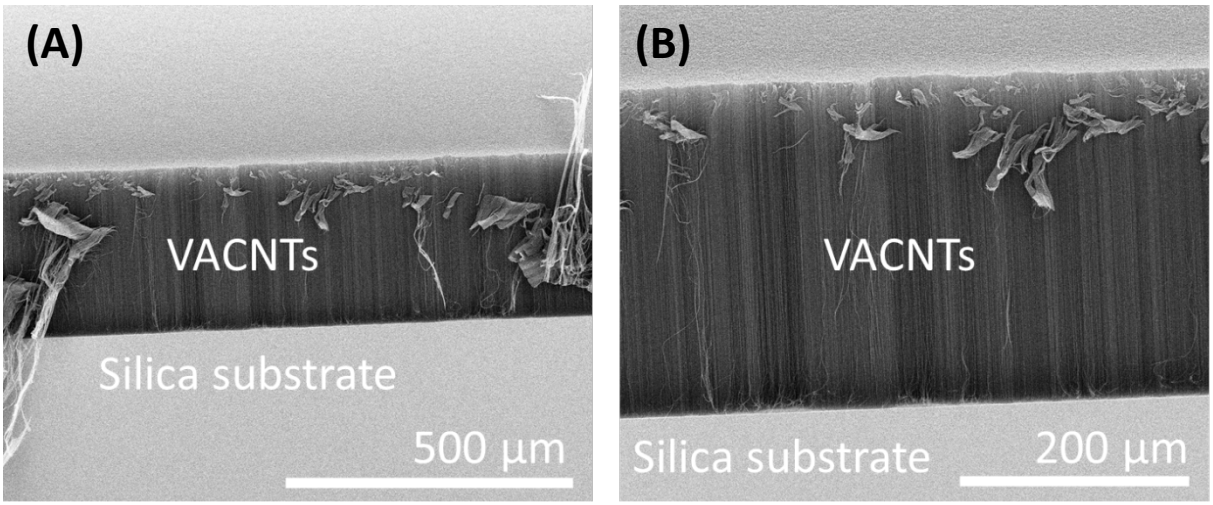

Figure S1. CNT array grown on the silica substrate. (A) low and (B) high magnification.

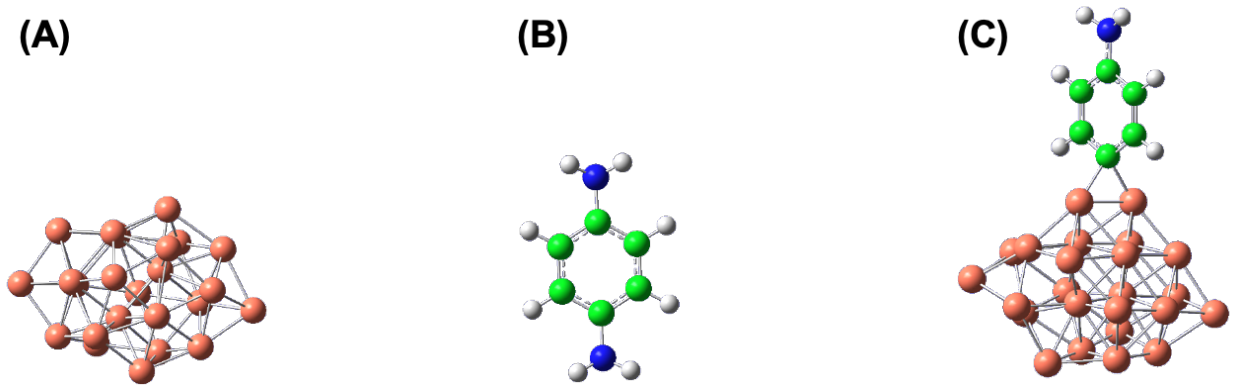

Figure S2. Optimized structures to obtain the IR theoretical spectra (a) bare Cu surface, (b) aminophenyl grafted Cu surface, and (c) solid p-Phenylenediamine, Nitrogen (blue), carbon (green), hydrogen (white) and copper (brown).

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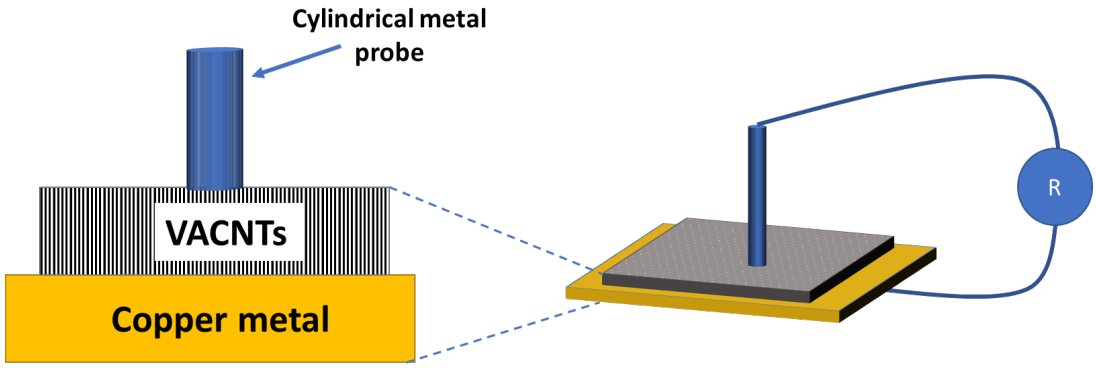
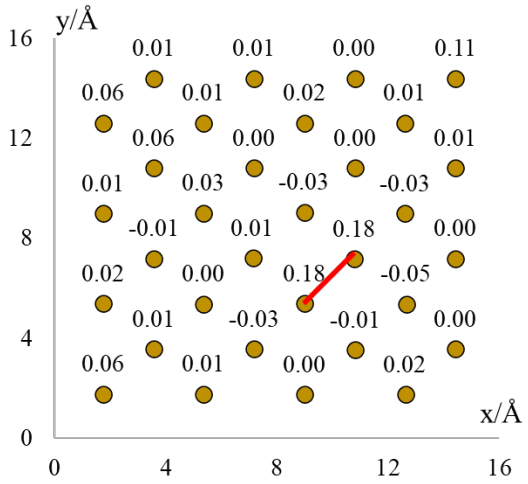
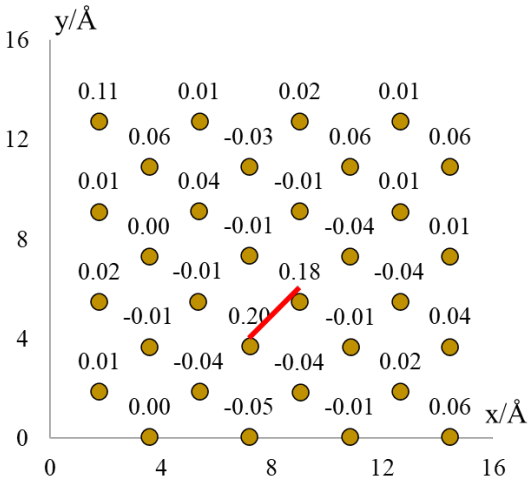


Figure S3. Experimental approach used to measure the interface resistance between VACNTs and Cu metal sheet.(R indicates a multimeter capable of measuring resistance)



Cu (100) – Bridge



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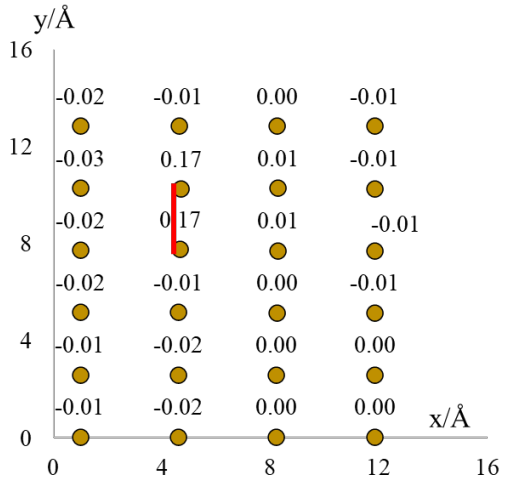
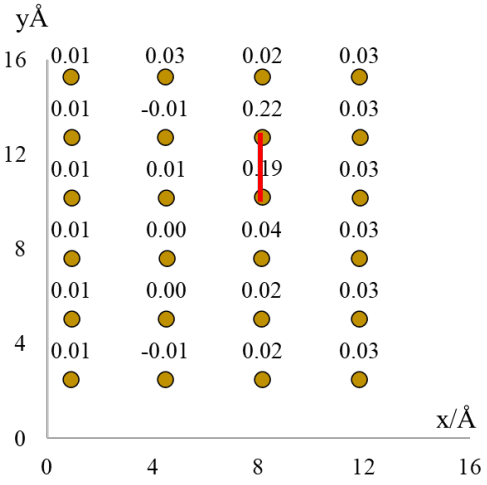
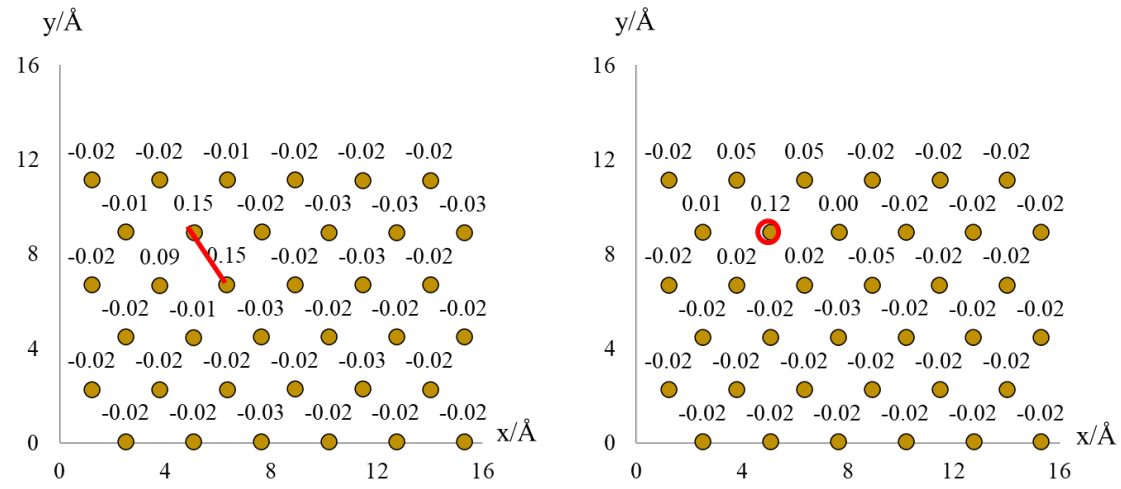


Cu (110) – Bridge



Cu (110) – Bridge



Cu (111) – Bridge Cu (111) – Top

Figure S4. Charges of the Cu atoms located at the surface. Red line indicates the position of the aminophenyl and the Cu atoms that are bonded to the C for the different configurations.

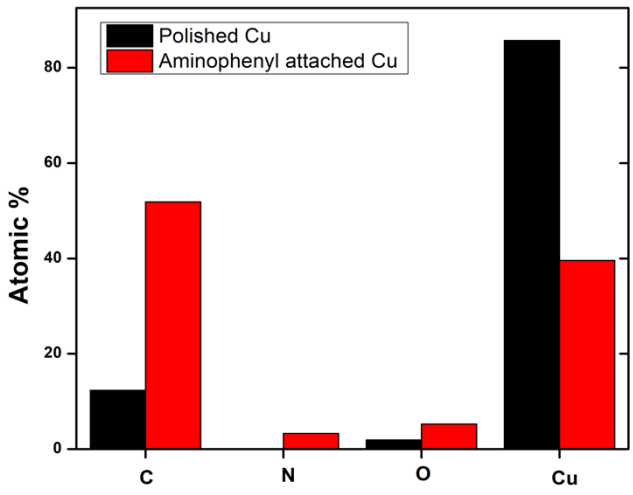


Figure S5. Percent elemental abundance on the grafted surface before (polished Cu) and after (Aminophenyl attached Cu) as determined by EDAX.

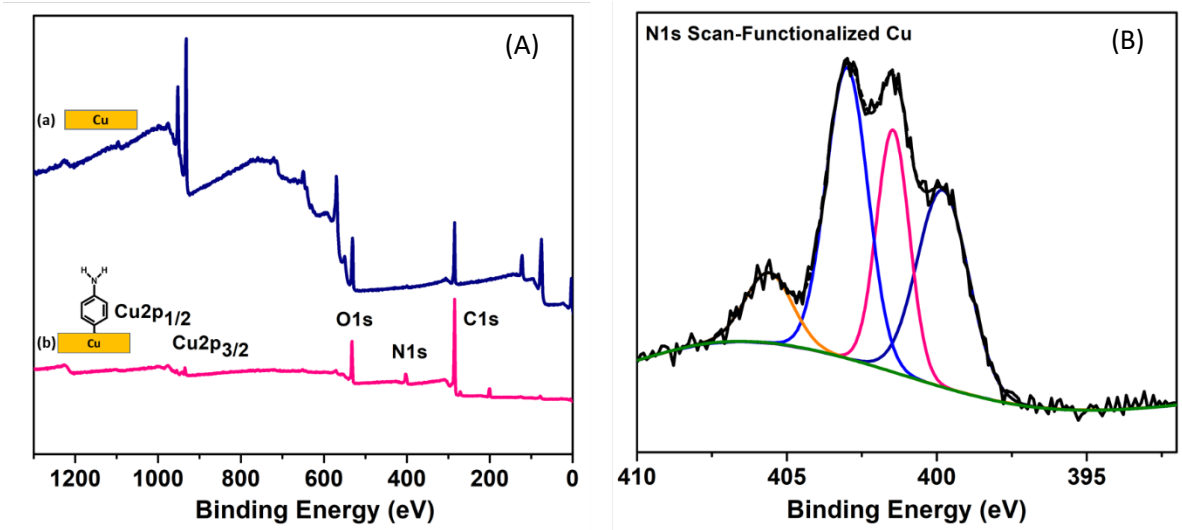


Figure S6. XPS survey spectra of bare Cu metal surface and organic group grafted Cu metal surface. (Blue-XPS survey spectra for bare Cu surface, Pink-XPS survey spectra for organic grafted Cu surface, 5 min reaction time).

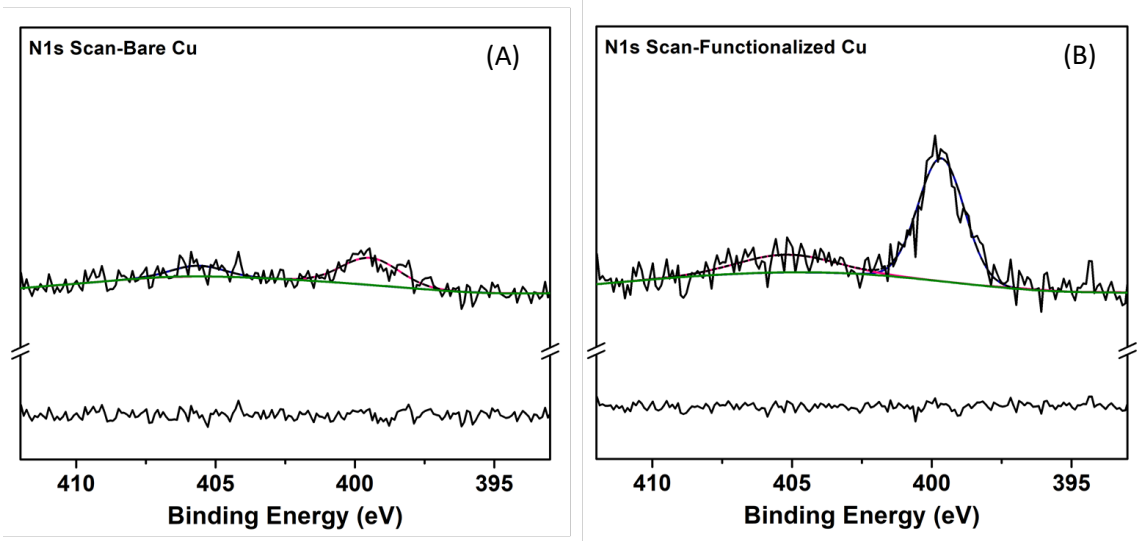
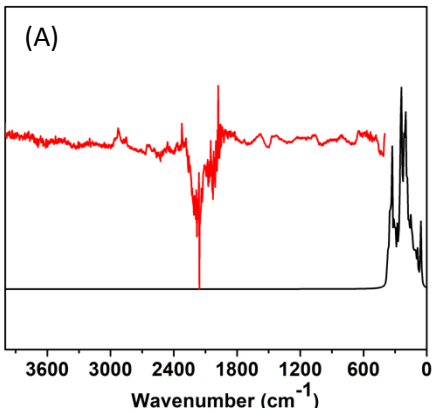
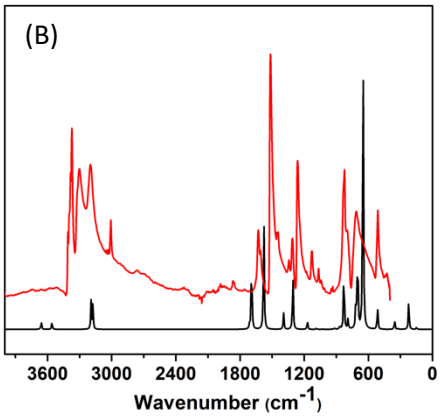


Figure S7. N1s core level XPS spectra of: (A) bare Cu surface and (B) organic grafted aminophenyl surface.





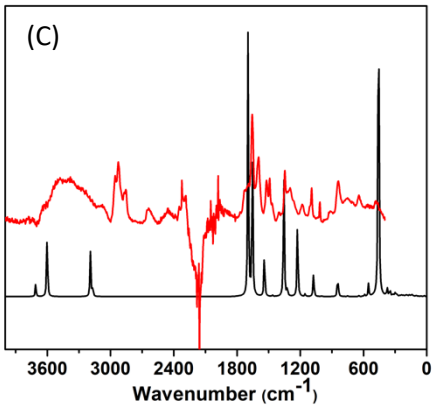


Figure S8. Comparison of experimental observed normalized and baseline corrected IR spectra of: (A) Cu metal, (B) Phenylenediamine, (C) aminophenyl grafted Cu surface with theoretically predicted IR spectra.

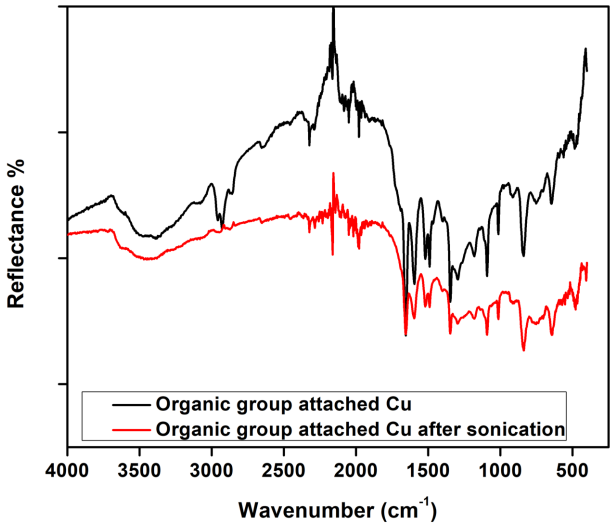


Figure S9. IR spectra for organic grafted Cu surface before and after ultrasonication.

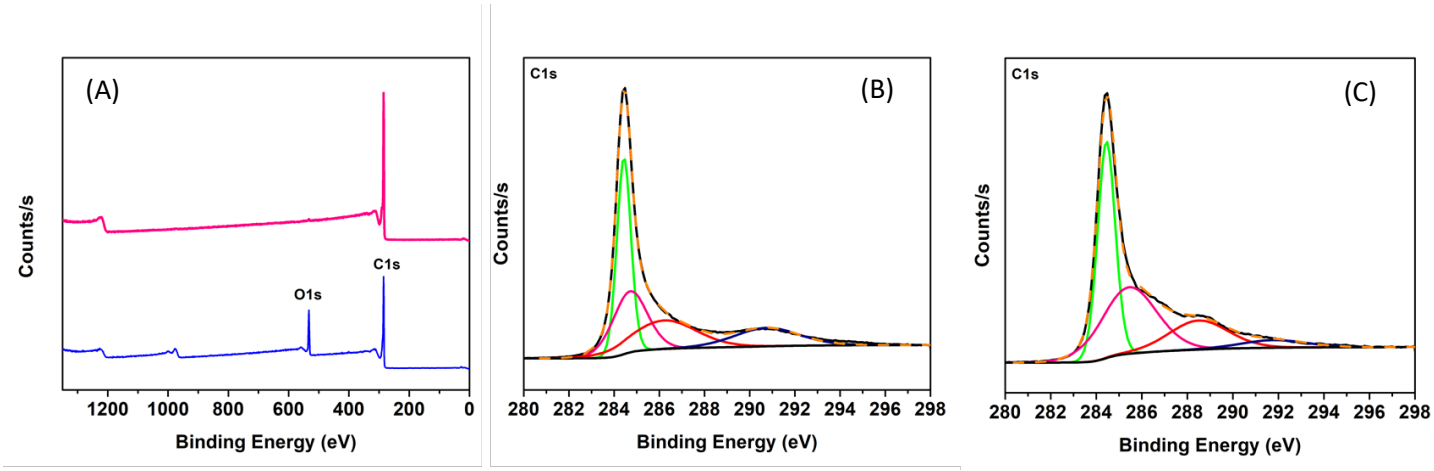


Figure S10. (A) Survey spectra of plain CNT array (pink) and plasma functionalized CNT array (blue). (B) Core level C spectrum of plain CNT array. (C) Core level C spectrum of plasma functionalized CNT array.

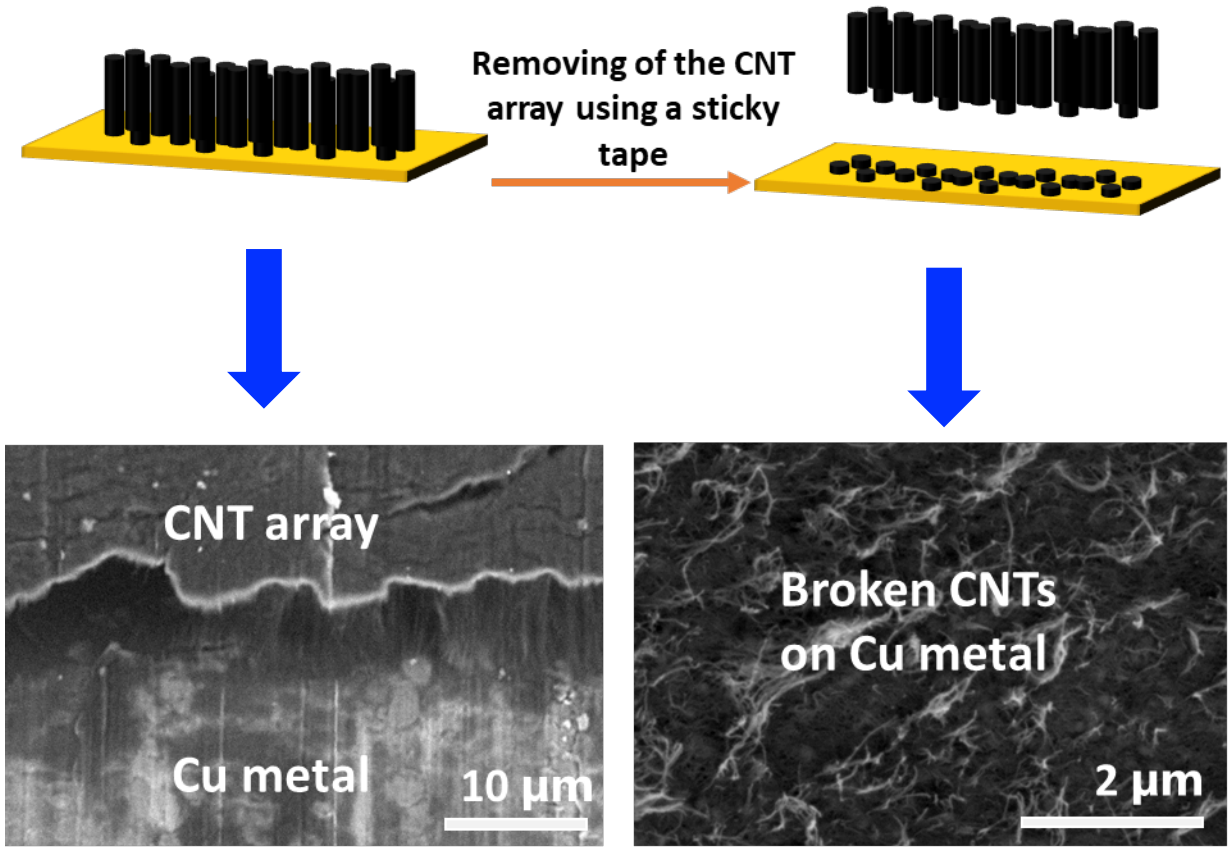


Figure S11. CNT array attached Cu surface (left), and broken CNTs after removing CNT array with adhesive (right).

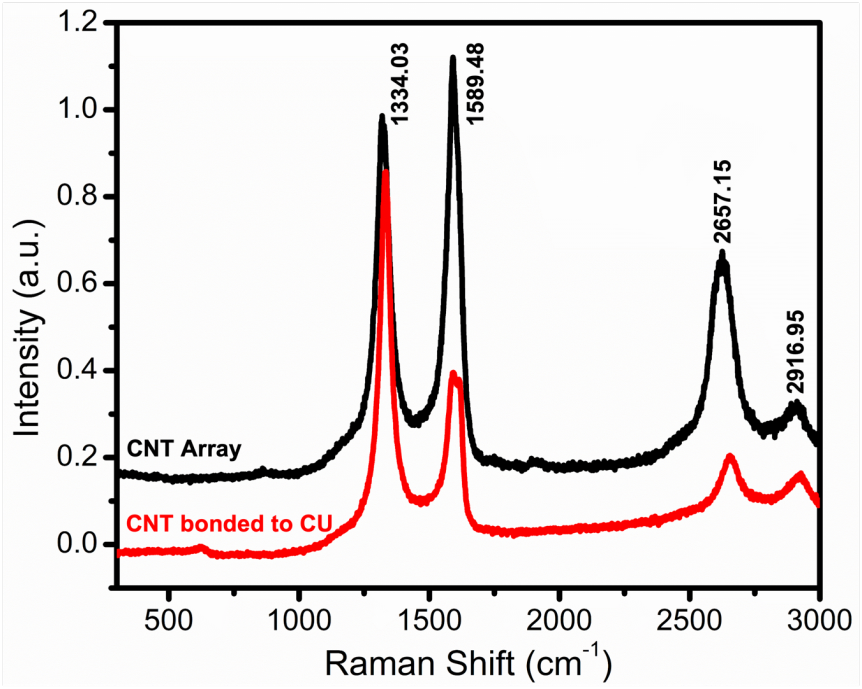


Figure S12. Raman spectrum of the Cu metal surface after removing CNT array using adhesive tape.

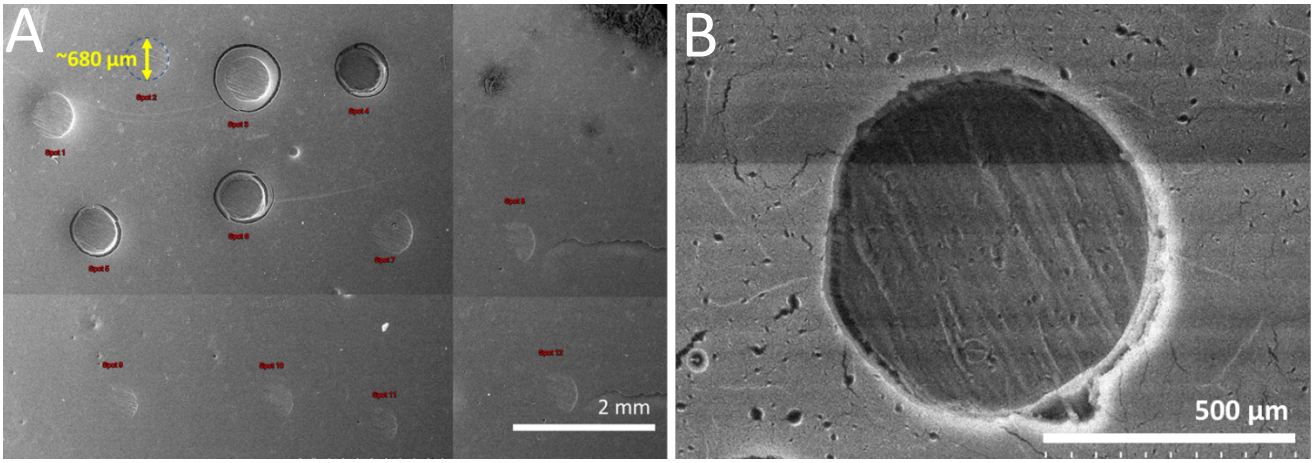
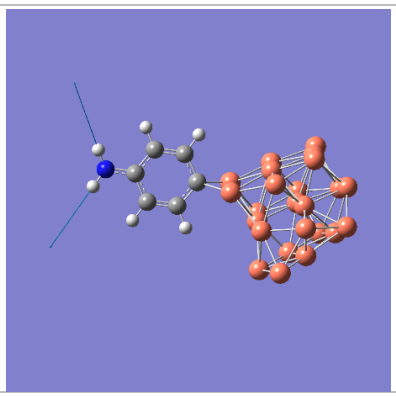
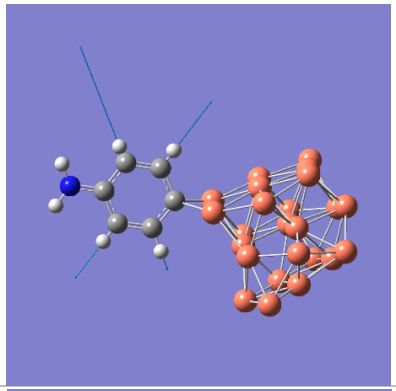
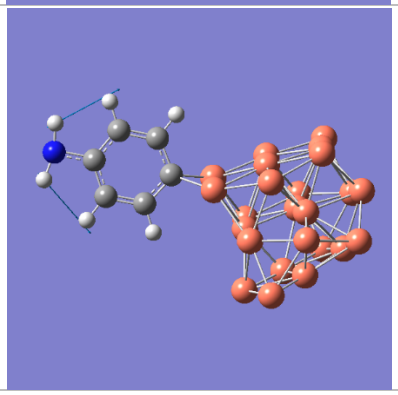
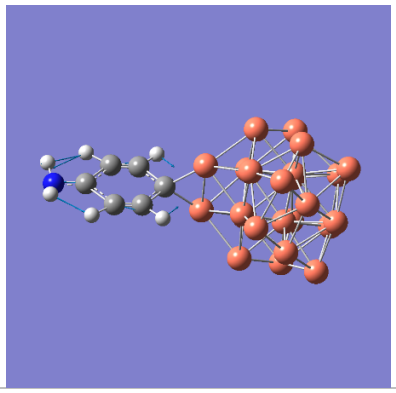
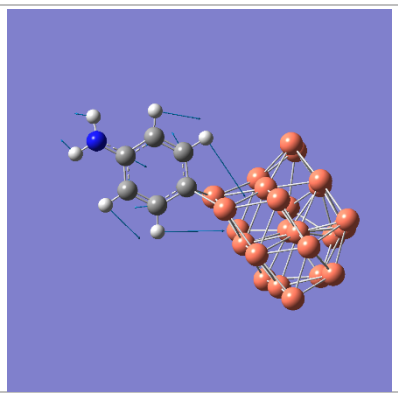
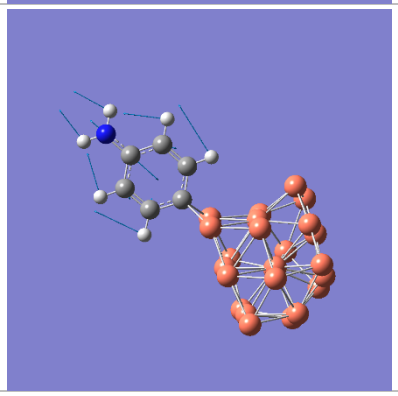
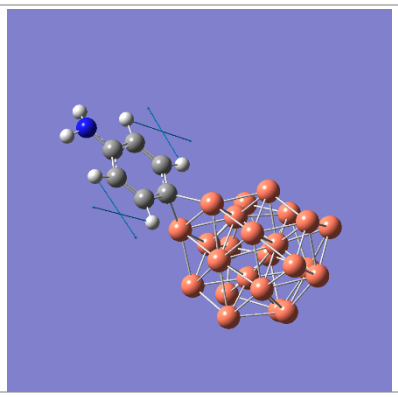
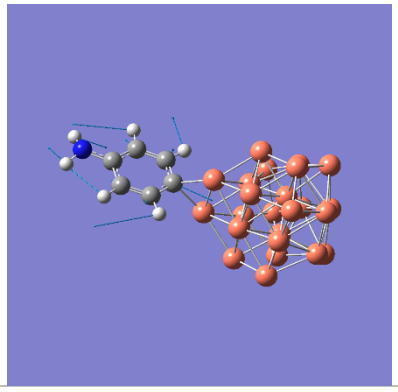
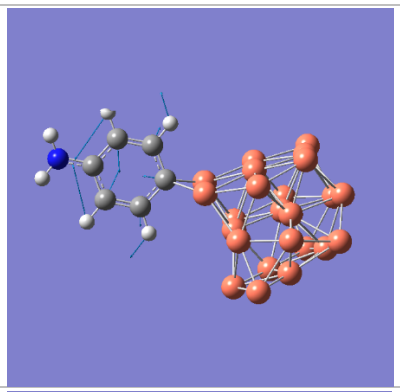
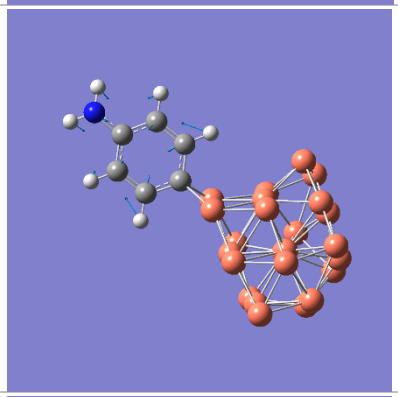
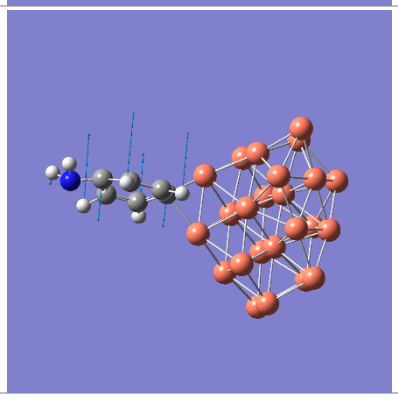
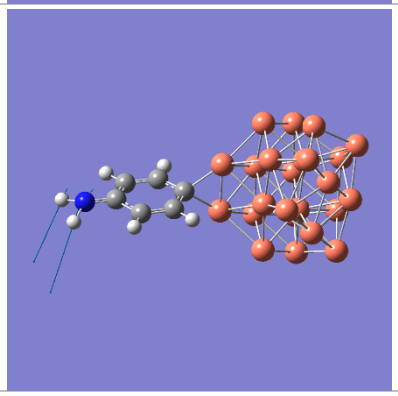


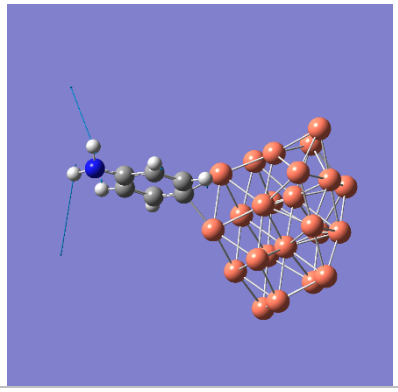
Figure S13. SEM images of CNT arrays bonded to Cu surface where pressure was applied by the cylindrical probe in order to make good contact for electrical measurements. A) lower magnification with multiple probe prints, B) higher magnification with single probe print.

Table S1. Observed and calculated vibrational wavenumbers (cm $^{-1}$) of the optimized structure of aminophenyl attached Cu surface with peak assignment.

Observed/ cm^{-1}	Calculated/ cm^{-1}	Assignment
3200 cm^{-1}-3700	3601	
2925	3191	
1654	1695	
1595	1654	

1519	No peak	
1490	1539	
1346	1356	
1295	No peak	
1181	1225	
1092	1072	

1014	1025		
837	846		
644	552		
485	458		

Out of range	375	

Additional Computational Methods

A fully ab initio DFT with a Green's function approach is used to determine the I-V characteristics of the use of the linker to connect a CNT with a Cu surface. The electronic structure of two models: CNT (8, 0) over Cu surface and the CNT (8, 0) + linker over the Cu surface were obtained using DFT with the hybrid functional B3PW91 [1,2] encoded in the Gaussian-16 program[3]. The density and superposition matrices of these calculations were entered into the Generalized Electron Nano-Interface Program (GENIP) [4,5] program to obtain the I-V characteristics of the bondings reported in this work.

1]Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. The Journal ofChemical Physics 98, 5648-5652, doi:10.1063/1.464913 (1993).

2]Perdew, J. P. & Wang, Y. Accurate and Simple Analytic Representation of the Electron-Gas Correlation-Energy. Phys Rev B 45, 13244-13249, doi:DOI 10.1103/PhysRevB.45.13244 (1992).

3] Gaussian 16 Rev. C.01 (Wallingford, CT, 2016).

4] Benitez, L. & Seminario, J. M. Electron Transport and Electrolyte Reduction in the Solid-Electrolyte Interphase of Rechargeable Lithium Ion Batteries with Silicon Anodes. J Phys Chem C 120, 17978-17988, doi:10.1021/acs.jpcc.6b06446 (2016).

5] Derosa, P. A. & Seminario, J. M. Electron transport through single molecules: Scattering treatment using density functional and green function theories. J Phys Chem B 105, 471-481, doi:10.1021/jp003033 (2001)"