Efficient Use of Bio-Inspired Nanofabrication in Soft Electronics

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UB Faculty Research Day

Introduction

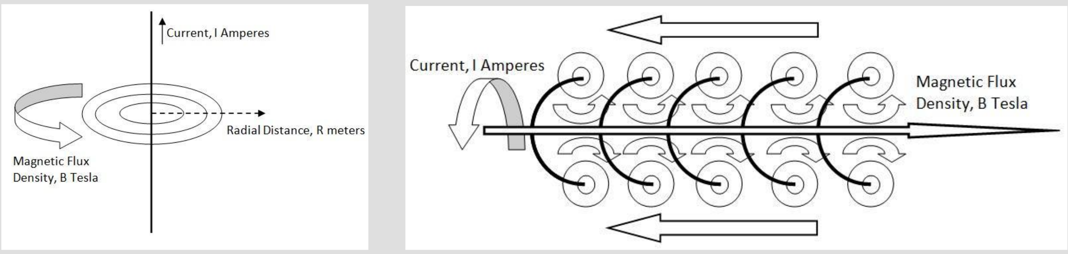
Self-assembly plays an important role in the formation of different nanostructures either organic or inorganic. Controlled assembly of molecules into higher ordered hierarchical structures on the other hand require a thorough insight into the interactive forces that lie behind such an assembly. The interface between organic and inorganic materials is thus of primary significance when it comes to the tasks of selective deposition and assembly of inorganic molecules through organic agents. One of the bacterial species that belong to the class α-proteobacteria called *Magnetospirillum magneticum* (classified as AMB-1) is investigated in this study and it is found that this species is able to fulfill the requirements that are imposed by the complexity of the selective deposition and controlled assembly tasks. AMB-1 contain single-domain crystals of magnetite (Fe_3O_4) called magnetosomes that sense the external magnetic field that is further utilized for cellular displacement (magnetotaxis) through lash-like cellular appendages called flagella. The two flagella located at the proximal and distal ends of the cell consists of a protein monomer flagellin. Individual flagellin in turn that are located on the periphery of each of the flagellum's central channel consists of four sub-domains, two inner domains (D0, D1) made up of alpha helices and two outer domains (D2, D3) made up of beta sheets. However, it is the domain D3 that is exposed to the surrounding micro-environment, thereby interacting with the components to be selectively deposited, in this case, carbon nanotubes (CNT). Based on the electromagnetic and molecular dynamics simulations and the real-time experimental analysis involving optical microscopy utilizing 50 micron diameter conductor (44AWG) magnetic coils as directional magnetic field generation centers to visualize the motion of free as well as loaded AMB-1 as well as electron microscopy (TEM & SEM) to analyze the interactive forces between CNT and AMB-1 flagellum, it is found that once the domain D3 is functionalized with either metallic (m-) or semiconducting (s-) carbon nanotubes (CNT), the AMB-1 cell can be used as an efficient carrier for selective deposition tasks. Two aspects that are of particular interest are the phenomenal control of direction exhibited by AMB-1 using locally generated magnetic field and the efficient interactive forces in the form of short range forces (van der Waals, hydrophobic interactions and hydrogen bonds) and long range forces (electrostatic interactions) between m-CNT or s-CNT and D3. Thus, it is recognized that a compound semiconductor manufacturing technology involving bacterial carriers and carbon-based materials such as carbon nanotubes would be a desirable choice in the future.

Methods

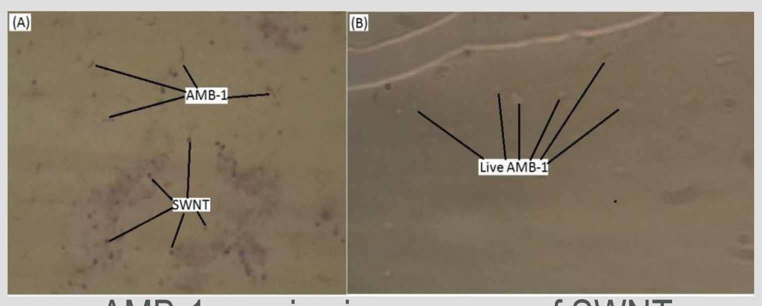
Magnetospirillum *magneticum* (AMB-1) (ATCC - 700264) was purchased and cultivated in-house using the MSGM (magnetospirillum growth medium) protocol given by ATCC. The culture media per 1L of distilled water included: 10ml Wolfe's vitamin solution, 5ml Wolfe's mineral solution, 2ml 0.01M ferric quinate, 0.45ml 0.1% resazurin, 0.68g KH2PO4, 0.12g NaNO3, 0.035g ascorbic acid, 0.37g tartaric acid, 0.37g succinic acid, 0.05g sodium acetate and 1.3g agar (for semi-solid media). After adding the chemicals, the media was checked for the pH of 6.75 and if needed 0.5M NaoH and HCl is used to set the pH. The media is then autoclaved at 121 º C for 15 min and about 1ml of inoculum is injected to a 10ml screw-cap test tube aseptically. The carbon nanotubes for the magnetic experiments were purchased from cheaptubes Inc. Molecular dynamics simulations were prepared and analyzed using VMD (visual molecular dynamics) and were carried out using NAMD. R-type flagellin filament pdb file was obtained from protein data bank and an inbuilt nanotube builder plugin was used to create SWNTs of metallic (12,12) as well semiconducting (5,15) nature with lengths of 1.2nm and 5nm. Domain D3 (97 residues) was isolated from the R-type flagellin monomer for simulation purposes in one set of simulations. The other set consisted of the entire flagellin monomer (494 residues). All simulations used the CHARMM force field along with TIP3 water model. In each simulation, temperature was maintained at 300K by Langevin thermostat and pressure of 1atm was maintained through Nose-Hoover Langevin-piston barostat with a period of 100ps and a decay rate of 50ps; periodic boundary conditions were assumed. Multiple time stepping was employed using an integration timestep of 2fs, with short-range forces evaluated every time step and long range electrostatic forces evaluated every two timesteps. Short range forces were smoothed with a cutoff between 10 and 12 Å, while long range electrostatic forces were calculated using the particle-mesh Ewald algorithm. A salt strength just enough to neutralize the charge of the system was assumed. All-atom simulations of both the interactions between D3 and SWNT and between R-type flagellin monomer and SWNT were performed in a periodic water box. The analysis plugins for root mean square deviation (RMSD) and NAMD energy were utilized to further analyze the nature of interactive forces and associated energies. Dell Studio XPS 9100 system with 8-core Intel i7 CPU and 16-core CUDA acceleration capability was utilized to perform the MD simulations. Optical microscopy was utilized to perform the magnetic experiments involving straight as well as coiled conductors.

Results

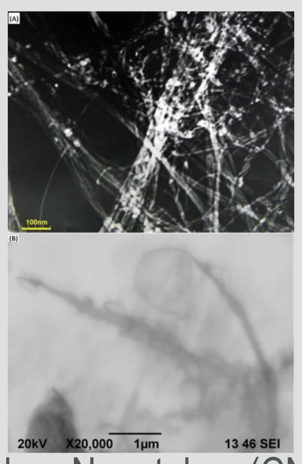
Modeling and Experimental Results:



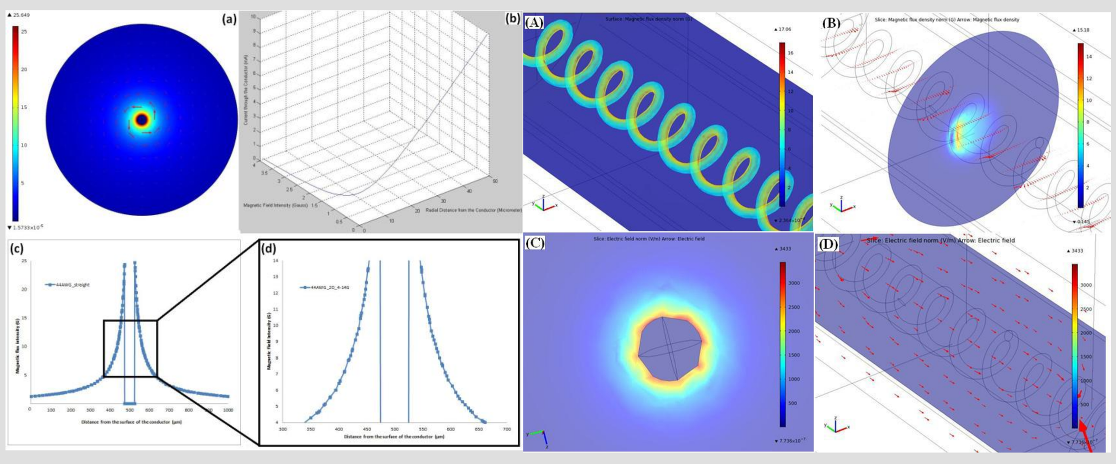
Nature of Magnetic flux around a straight and coiled conductor



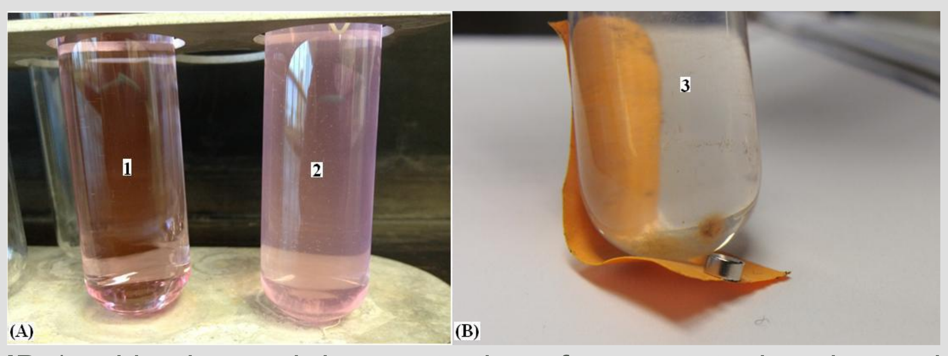
AMB-1 species in presence of SWNTs



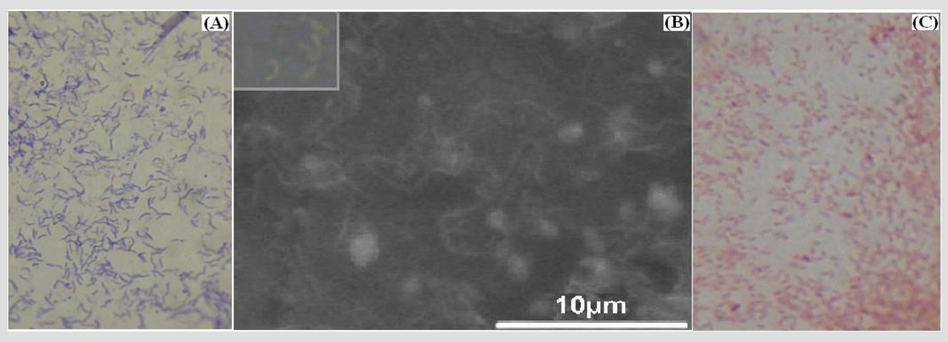
Carbon Nanotubes (CNTs)



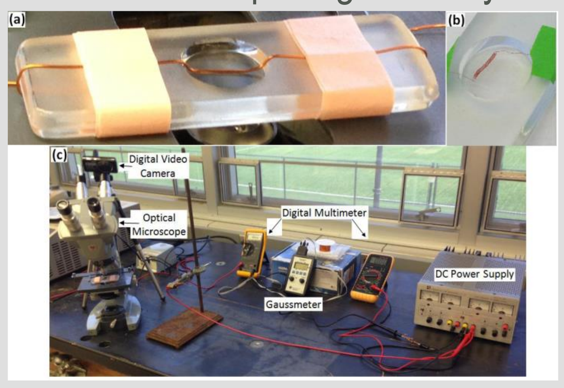
FEM Simulations of the Straight and Coiled Conductors



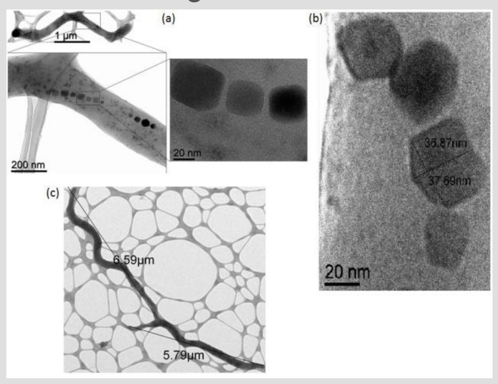
AMB-1 cultivation and demonstration of magnetotaxis using optical microscopy



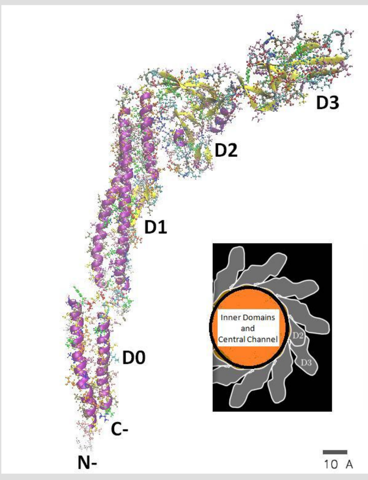
Morphological analysis of AMB-1 using SEM



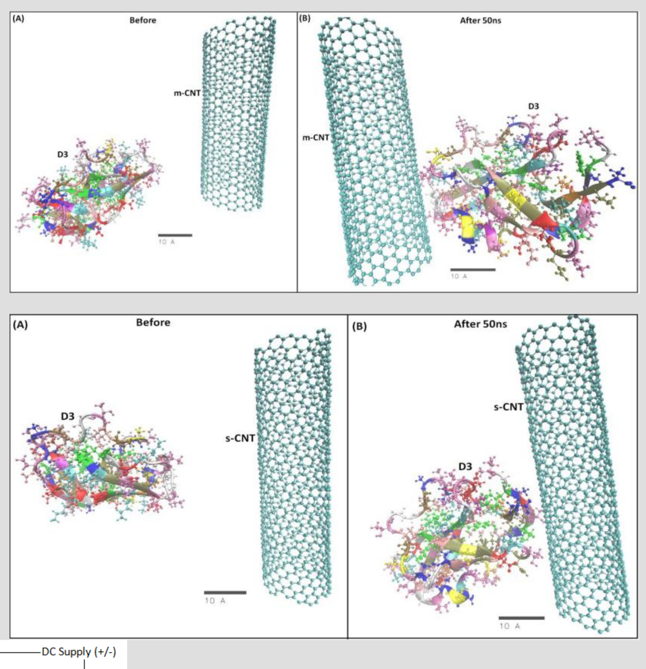
Experimental setup to analyze the motion of AMB-1 through 44AWG straight and coiled conductors generating local magnetic field for precise control.



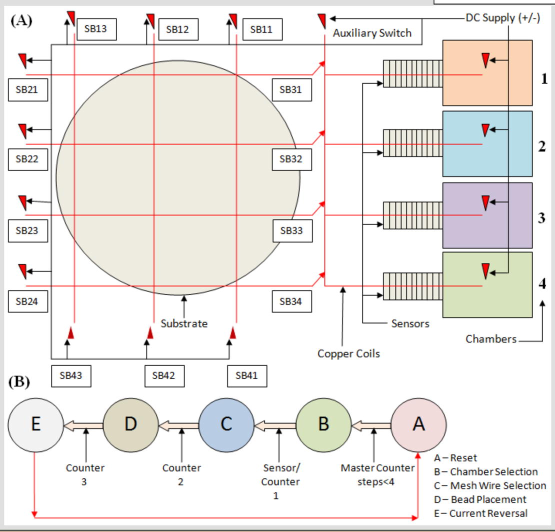
TEM of AMB-1



Flagellin monomer



VMD Simulations of Flagellin domain D3 and Metallic (top) and Semiconducting (Below) SWNT.



Proposed Hybrid Technology involving AMB-1 and CNTs for nanofabrication

Conclusions

Based on the study of *Magnetospirillum magneticum* (AMB-1) through quantitative and qualitative experimental investigation, it is found that AMB-1 can be utilized for selective deposition tasks for controlled assembly of carbon nanotube based nanostructures. Magnetotaxis of the individual AMB-1 cells is found to be controlled by a locally generated magnetic field through localized 44 AWG current carrying magnetic copper coils, whose simulations utilizing finite element analysis techniques in COMSOL multiphysics indicate a reliable and highly potential source of controlled-assembly methodology. Furthermore, MATLAB calculations agree to the hypothesis of controlling the bacterial entities through the magnetic field in terms of both distance and magnitude provided by COMSOL. Similarly, heat analysis using COMSOL provide helpful insights into the potential rise in temperature via heat generated by the current carrying coils and it is found that 0.12 ºC per second of rise in temperature very closely matches the real-time experimental analysis and that beyond 37 ºC, the AMB-1 cells cease to multiply. Electron microscopy studies of the AMB-1 cell confirms the presence of Fe3O4 based magnetosomes having sizes in the range of 35 to 40 nm along with about 500nm width of the spirillum cell having length in the ranges of 5 - 10 microns. Factors governing the attachment phenomenon at nanoscale between the AMB-1 flagellum monomer – flagellin and single-walled carbon nanotubes are investigated and it is found that metallic and semiconducting carbon nanotubes interact in a different manner with flagellin. It is further recognized that electrostatic interactions play a significant role in binding interactions in case of metallic but not in case of semiconducting carbon nanotubes. The short-range forces such as van der Waals, hydrogen bonding and hydrophobic interactions are dominant below the distances of 5Å between flagellin and carbon nanotubes. Glycine plays a dominant role in the interaction mechanism, where metallic carbon nanotubes bind with the flagellin domain D3 in as small as ~4ns placed at an initial distance of ~20Å. On the contrary, semiconducting carbon nanotubes take ~14ns for the onset of adsorption onto the flagellin domain D3 and totally avoid the vicinity of glycine residue indicating that semiconducting nature of the carbon nanotube does require a higher potential voltage for onset of electron conduction and hence interaction on the electrostatic scale as expected. A hybrid alternative technology to the current nanoelectronic fabrication strategy is thus envisioned, where physical phenomena such as locally generated magnetic fields and magnetotactic bacteria can be used to fabricate electronic circuits in the sub-10nm regime.

Future Directions

- Use of Atomic Force Microscopy to study the force patterns between the CNTs and the bacterial flagellum.
- Nanopatterning based strategy using bacterial magnetite through electrospinning.
- Use of micro-controllers to time the current through the coiled conductors and hence the precisely control the motility of AMB-1 cells.
- Use of Circular Dichroism to investigate the nature of binding between the AMB-1 cells and CNTs.
- Influence of AMB-1 cells and magnetite crystals on the morphology of CNTs.
- Understanding the basic mechanisms of iron sequestering and biomineralization of magnetite crystals in vivo through protein matrix.

References

1. Isaac Macwan et al, *Int. J. Hi. Spe. Ele. Syst.* **23**, 1450008 (2014) [16 pages] DOI: 10.1142/S0129156414500086
2. I. Macwan, Z. Zhao, P. K. Patra, "Interaction of Metallic and Semiconducting Single-Walled Carbon Nanotubes with Flagellin," in the *Proceedings of Materials Research Society - Fall 2014 meeting*, Boston, MA.
3. I. Macwan, Z. Zhao, O. Sobh and P. Patra, "Interaction of flagellin with single-walled carbon nanotubes," *Bio-Medical Engineering Society*, Chicago, 2014.
4. I. Macwan, Z. Zhao, O. Sobh, P. Patra, "A flagellum based study of semiconductor nanofabrication through magnetotaxis", *Conf. Proc. IEEE Eng. Med. Biol. Soc.,* 2014.
5. Macwan I, Zhao Z, Aphale A, Rho J, Mahmood A, Patra P. Magnetotaxis as a Means for Nanofabrication. In: *Connecticut Symposium on Microelectronics and Optoelectronics*. New Haven; 2013.

Acknowledgements

- We thank Dr. Jinnque Rho from the Department of Microbiology at the University of Bridgeport for providing access to the labs.
- A special thanks to Jeff Gilarde of Wesleyan University for his help and expertise with the SEM and Kim Kisslinger of Brookhaven National Laboratory for his expertise with the TEM.