The spray-assisted layer-by-layer (LbL) technique has been investigated for creating multi-walled carbon nanotube (MWNT) films on porous electrospun fiber mats via LbL assembly of surface-functionalized MWNTs. Negative and positive charges were introduced on outer walls of MWNTs by surface functionalization to enable the assembly of MWNTs into multilayer films without binder via the LbL technique. Conformal coating of MWNT films on individual electrospun fibers was achieved by applying a pressure gradient across the electrospun fiber mat to generate flow throughout the porous membrane during the spray-LbL deposition. The resulting MWNT films were shown to have interpenetrating network of unbundled MWNTs with nanoporous texture, which is well suited as electrode material for numerous applications. These LbL-MWNT/electrospun fiber electrodes were utilized for applications in chemical sensing and energy storage as described below.

First, the LbL-MWNT/electrospun fiber electrodes were employed as flexible chemiresistive sensors for real-time detection of a nerve agent simulant (dimethyl methylphosphonate (DMMP)). Available functional groups (−NH₂ and −COOH) on the MWNT films offer a direct route for covalently attaching a receptor of interest to the MWNTs, in order to tailor the chemical specificity in a modular fashion. Here, a thiourea-based receptor was covalently attached to the −NH₂ functional groups on the MWNT/ES fiber electrodes to enhance sensitivity toward DMMP via hydrogen bonding interaction, resulting in an up to 3-fold increase in sensing response. Chemiresistive sensors based on the engineered textiles displayed reversible responses and detection limits for DMMP as low as 10 ppb in the aqueous phase and 5 ppm in the vapor phase.

Employing the LbL-MWNT/electrospun fiber electrodes described above, we created hierarchical porous (HP) MWNT electrodes by removing the electrospun fiber substrate. The resulting HP-MWNT electrodes, which were self-standing and tens of micron in thickness, contained 3D interconnected macropores and mesoporous network of LbL-MWNT films. HP-MWNT electrodes can deliver a high gravimetric energy of ~100 Wh kg⁻¹ at a gravimetric power of ~25 kW kg⁻¹ in lithium nonaqueous cells. Compared to similar MWNT electrodes without macropores, HP-MWNT electrodes exhibited superior rate capability with an up to 10-fold increase in energy retention when the power was increased from ~100 W kg⁻¹ to ~100 kW kg⁻¹. These HP-MWNT electrodes possess great potential as electrode materials for high-rate electrochemical energy storage applications such as electric vehicles.

In summary, this thesis presents a versatile and easily scalable strategy for depositing functionalized MWNT films on 3D porous substrates to create tailored nanostructured electrodes with various applications, including flexible chemical sensors and energy storage devices.

Thesis Supervisor: Paula T. Hammond, Professor of Chemical Engineering