Electrochemical Synthesis of Conducting Polymers on Carbon Nanotube Films and Its Effect on Electrochemical Capacitance

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Abstract

Polyaniline (PANI) and polypyrrole (PPy) were considered as pseudocapacitive coatings for carbon nanotube (CNT) film electrodes. The conducting polymers were deposited electrochemically using cyclic voltammetry (CV). The electrochemical effects of the number of voltage cycles and monomer and electrolyte concentrations on film thickness were studied. The effects of the polymer coating on the capacitance of the CNT electrodes were analyzed as well. The final results were evaluated using CV and scanning electron microscopy (SEM) techniques.

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Introduction

Capacitors, devices designed to store charge, have an extremely broad range of applications in modern electronics. Traditional capacitors are built as two parallel plates separated by a dielectric (insulating) material; they store charge as one plate accumulates an excess of electrons and the other one acquires a deficiency. Although commonplace, these devices have a capacitance, $C = dQ/dV$ in the order of 1 pF to 1 μF. For applications that require greater capacitances, electrostatic capacitors are impractical, since their electrical energy density is very small. In other words, their volume increases rapidly with their ability to store charge. This difficulty has been partly solved by electrochemical capacitors. These are devices that either have a large electrochemically active surface area or exhibit a phenomenon known as pseudocapacitance. For instance, the RuO_2 pseudocapacitance system shows a continuous dependence of the extents of oxidation or reduction on electrode potential; this approximately constant charge-to-potential ratio is equivalent to capacitance, but it is based on a faradaic process (hence 'pseudocapacitance').

Pseudocapacitance is also exhibited by some conducting polymers, including polyaniline (PANI) and polypyrrole (PPy). In sight of this property, the electrodeposition of PANI and PPy by cyclic voltammetry (CV) was studied to establish the optimum growth conditions for the polymers. The effects of the number of voltage cycles and the monomer and electrolyte concentrations on polymer growth were analyzed. Then, CNT electrodes were coated with a conductive polymer film to examine the effects of the coating on the overall capacitance of the composite electrodes. It was expected that the large electrochemically active surface area of the CNTs and the pseudocapacitance of either PANI or PPy would complement each other to produce an electrode material of great capacitance.

Procedure

All electrochemical experiments were conducted using a CH Instruments 700A potentiostat; spectrophotometry measurements were taken with a Stellar-Net EPP2000 UV-vis-near IR spectrometer; all scanning electron microscopy images were taken with a LEO 1530 SEM.

To analyze the effects of the number of cycles on film thickness, three samples (labeled X, Y, and Z) of PANI were grown using cyclic voltammetry on an indium-tin oxide (ITO) working electrode. An Ag|AgCl reference electrode was used for all three samples; a Pt wire was used as a counter electrode. The samples were grown in a 0.1 M aniline, 0.1 M H_2SO_4 solution. The first sample was exposed to 100 sweep segments; the second one, to 150 sweep segments, and the third sample, to 200 sweep segments. For all three samples, the scan rate was 100 mV/s. After PANI had been deposited on the three samples, the thickness of the samples was estimated using visible light spectrophotometry.

To study the effects of solute concentrations on polymer growth, we used six different solutions to deposit a PANI film. The solutions utilized were: 0.1 M aniline, 0.1 M H_2SO_4; 0.1 M aniline, 1 M H_2SO_4; 0.01 M aniline, 0.1 M H_2SO_4; 0.1 M aniline, 0.1 M HCl; 0.1 M aniline, 1 M HCl; 0.01 M aniline, 0.1 M HCl. All six solutions were tested using CV with ITO plates as working electrodes, a Ag|AgCl reference electrode, and a Pt wire counter electrode. Then the structure of the deposited films was analyzed with scanning electron microscopy.

To examine the effects of conducting polymer coatings on the capacitance of CNT films, we prepared three samples in different pyrrole solutions and then tested their capacitance in an electrolyte solution. The three samples were coated with PPy deposited electrochemically through CV experiments that had CNTs as working electrodes, a Ag|AgCl reference electrode, and a Pt mesh counter electrode. The three CNT samples were labeled A, B, C. Sample A was prepared in a 0.1 M pyrrole, 0.1 M KNO_3 solution. Samples B and C were prepared in a 0.1 M pyrrole, 0.1 M K_2SO_4 solution. CV data was recorded to compare the capacitances of the films produced; capacitance was tested in a 0.222 M K_2SO_4 solution. The CNT-PPy composite samples were then studied using SEM.

Results and Conclusions

Cyclic voltammograms of the growth of samples X (Appendix A), Y (Appendix B), and Z (Appendix C) are available. Visible wavelength spectrophotometry data for the three samples shows a definite correlation between the absorbance of the film and the number of sweep segments specified for its electrodeposition (Appendix D). This indicates that film thickness increases with the number of voltage cycles, as expected. CV data also suggests that the rate of polymerization increases with the number of cycles; this observation can be accounted for by the gradual increases in current due to the diminishing, caused by an increase in surface area, of the electrode resistance.

CV data is available for the concentration experiments (Appendices E-J). We determined that it was best to utilize a 1:1 monomer-to-electrolyte concentration ratio for electrodeposition of PANI. The best results were obtained with solution 1 (0.1 M aniline, 0.1 M H_2SO_4); a solution of these concentrations produces a cyclic voltammogram similar to some published graphs[1]. In the case of the solutions with a 0.01 M aniline concentration, no significant growth was observed. SEM analysis of the samples showed that the deposited substance has a fibrillar structure, in accordance with expected results if the product of the polymerization was in fact polyaniline (Appendix K). The navy blue color and electrochromic nature of the deposited films provided further confirmation of their identity as PANI.

Cyclic voltammograms of samples A, B, and C show that PPy has a significant effect on the capacitance of CNT electrodes. The CVs of sample B before (Appendix L) and after

(Appendix M) the electrodeposition of PPy were compared, clearly indicating a difference in capacitance of an order of magnitude. Therefore, the experiments were successful in increasing the capacitance of CNT electrode by using a conducting polymer coating. A 0.1 M pyrrole, 0.1 M K_2SO_4 solution seems to be effective for electrochemical production of PPy. SEM images of CNTs coated with PANI were taken (Appendices N-O). Images of CNTs coated with PPy were recorded as well (Appendices P-Q). In both cases, the conducting polymers formed globular clusters around the CNTs. This structure of the composite maintains the high surface area of CNTs while adding the pseudocapacitance of PPy or PANI, allowing for such significant increases in capacitance as the ones reported above.

References

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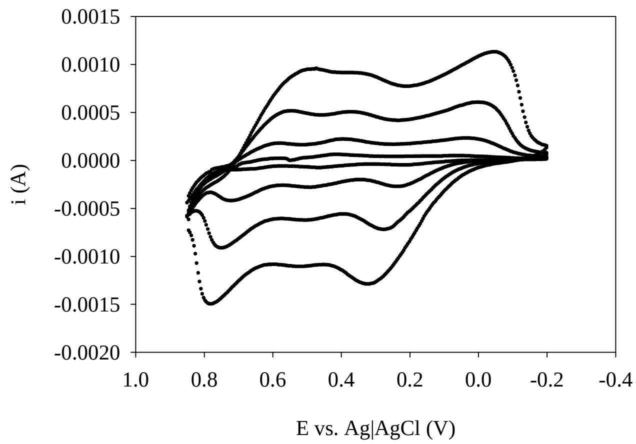
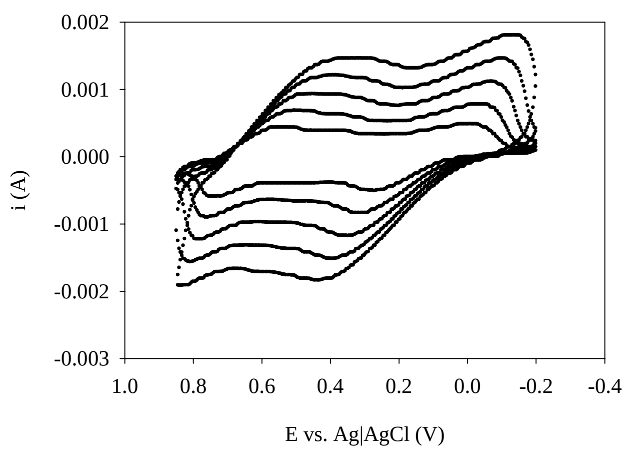
Appendix A

Sample X



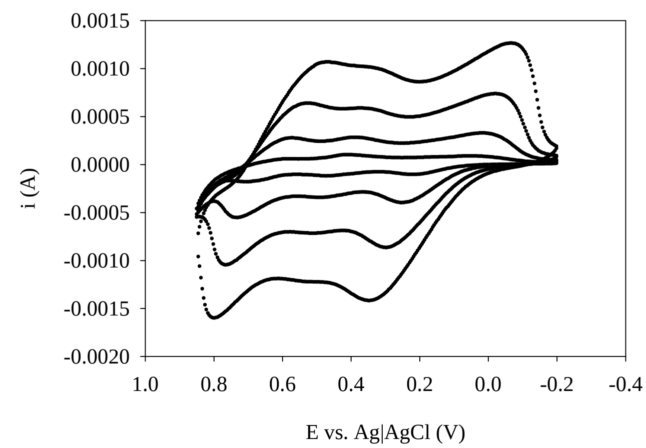
Appendix B

Sample Y



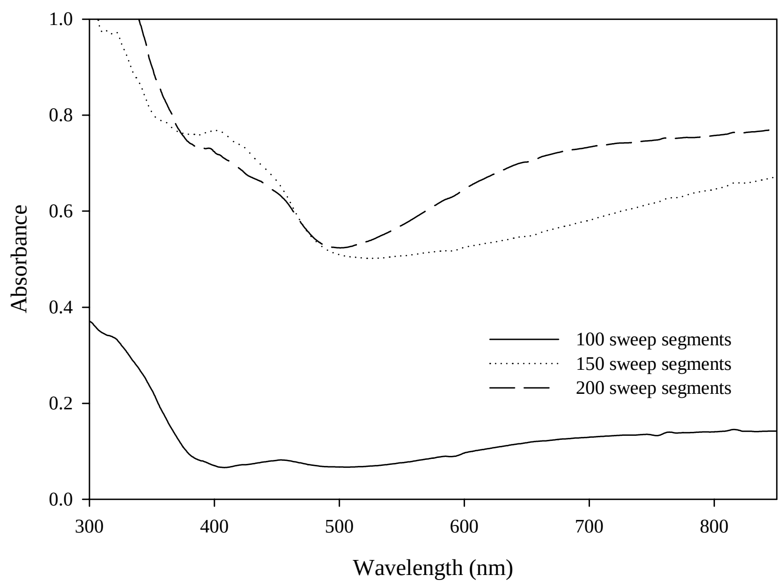
Appendix C

Sample Z



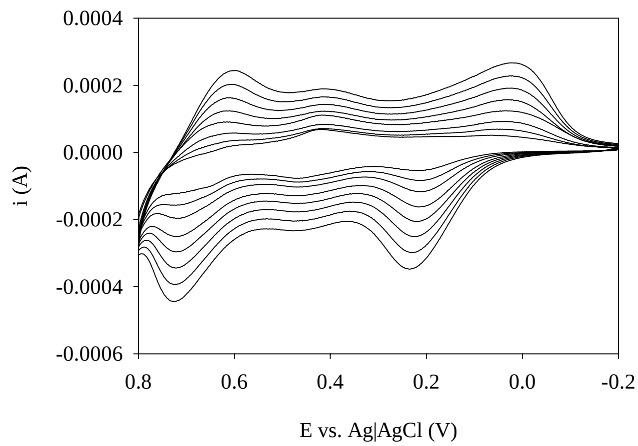
Appendix D

0.1 M aniline, 0.1 M H_2SO_4



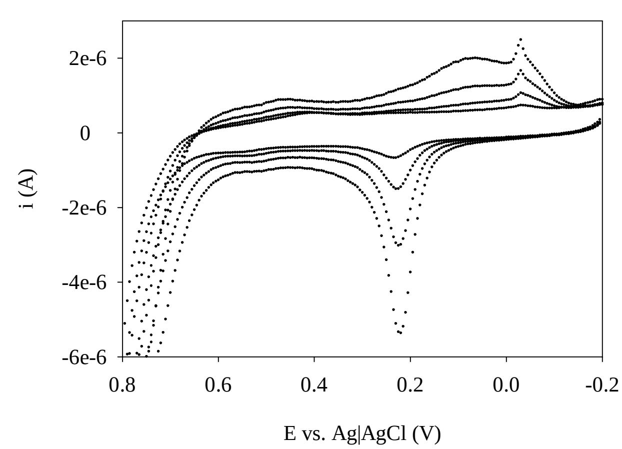
Appendix E

0.1 M aniline, 0.1 M H_2SO_4



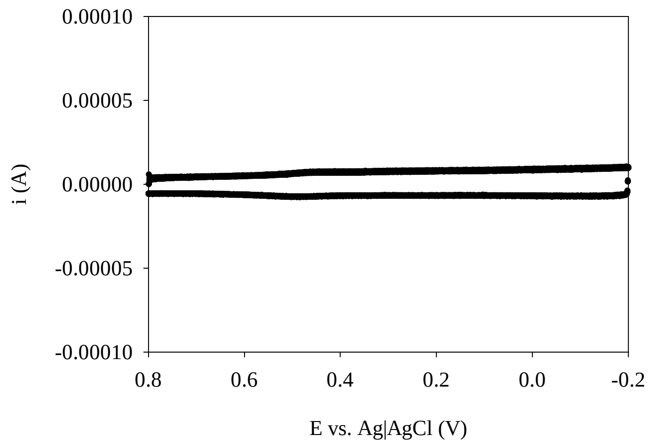
Appendix F

0.1 M aniline, 1 M H_2SO_4



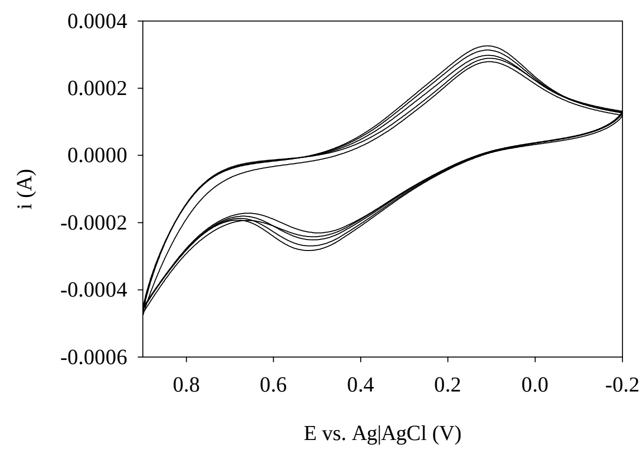
Appendix G

0.01 M aniline, 0.1 M H_2SO_4



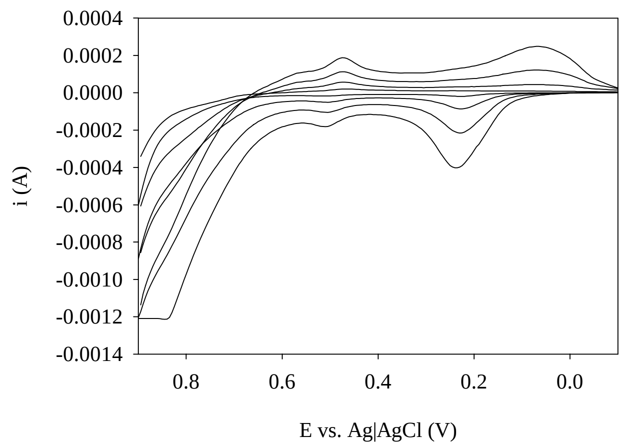
Appendix H

0.1 M aniline, 0.1 M HCl



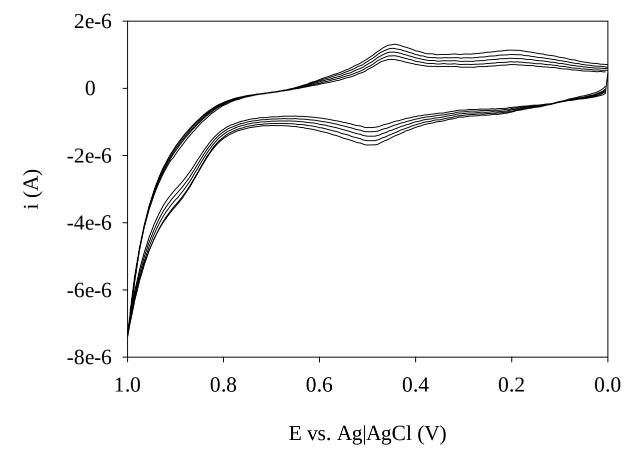
Appendix I

0.1 M aniline, 1 M HCl

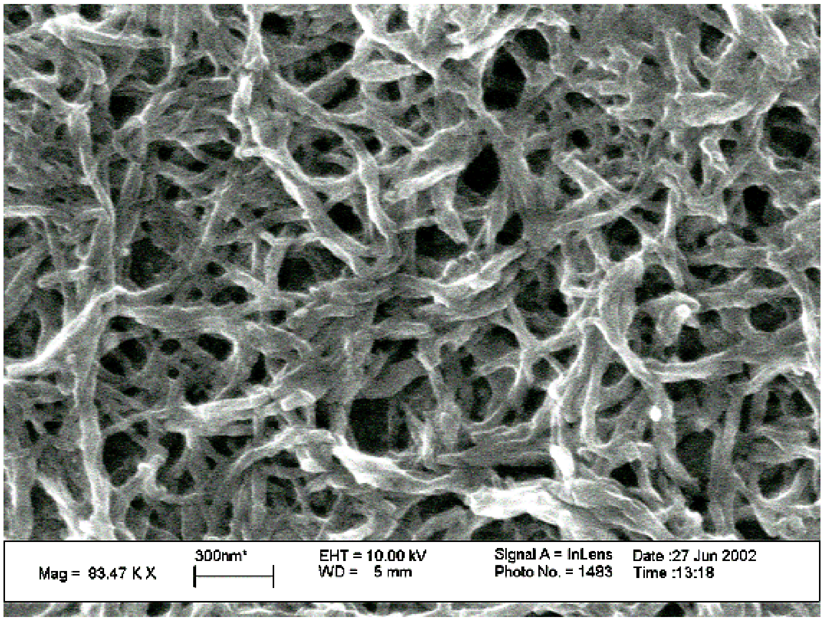


Appendix J

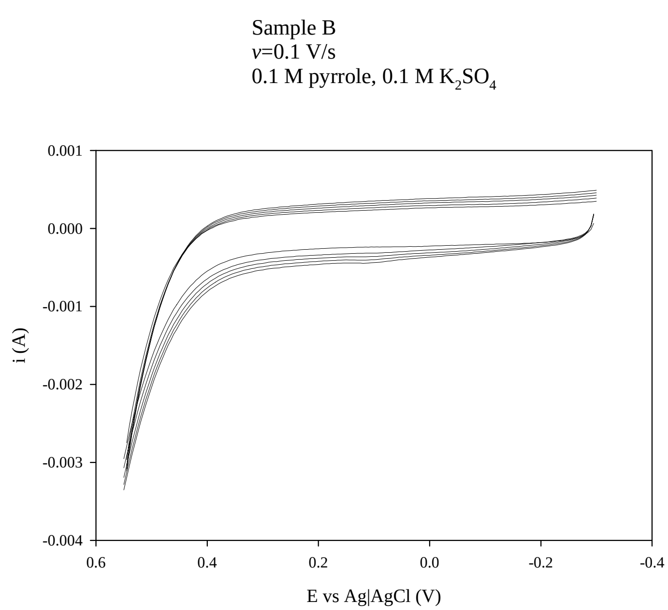
0.01 M aniline, 0.1 M HCl



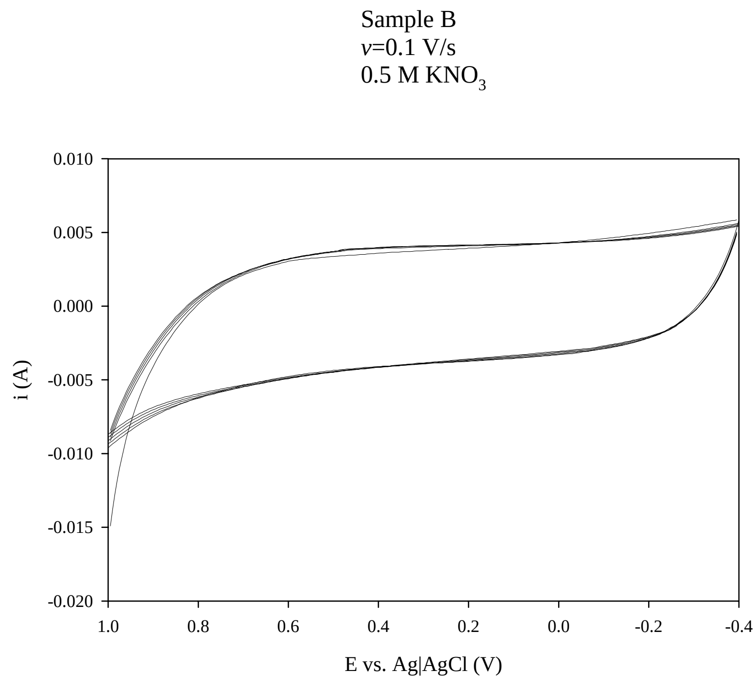
Appendix K



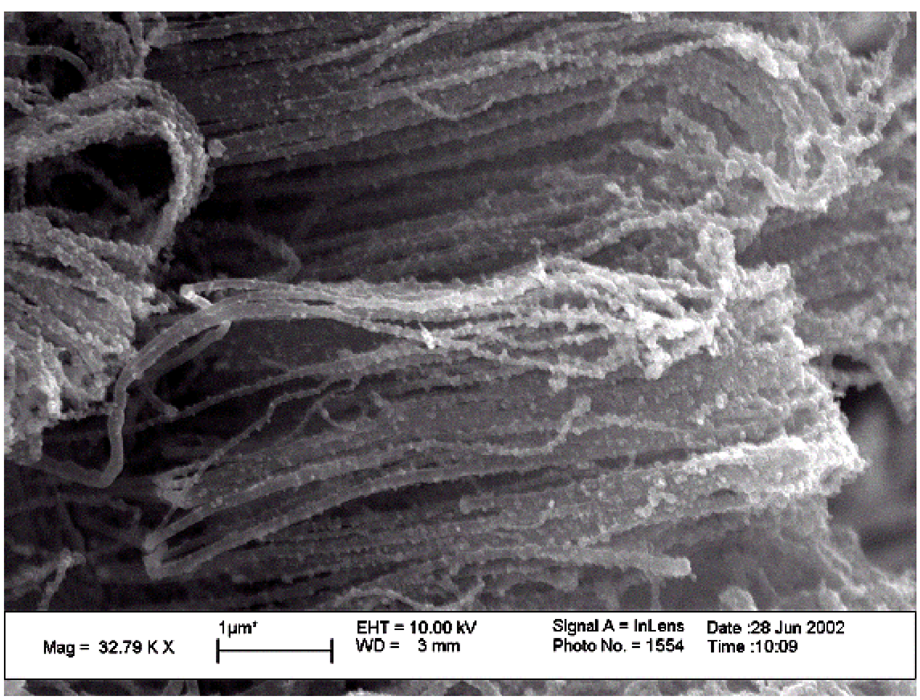
Appendix L



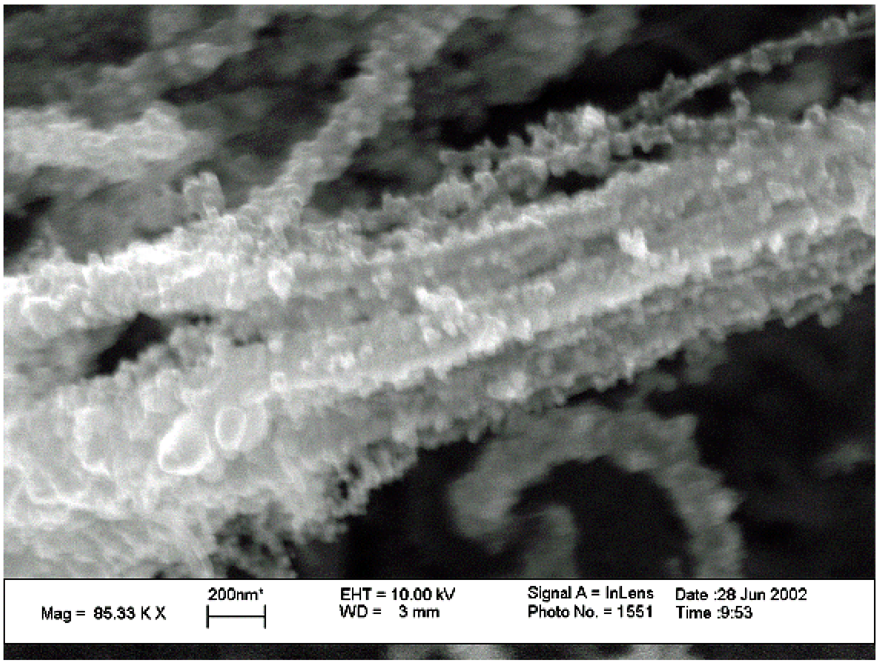
Appendix M



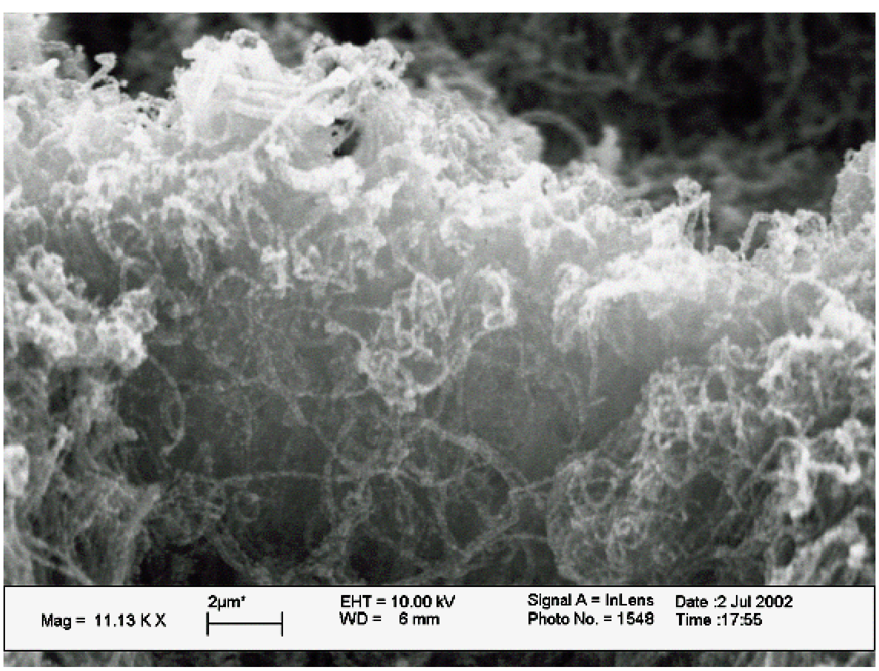
Appendix N



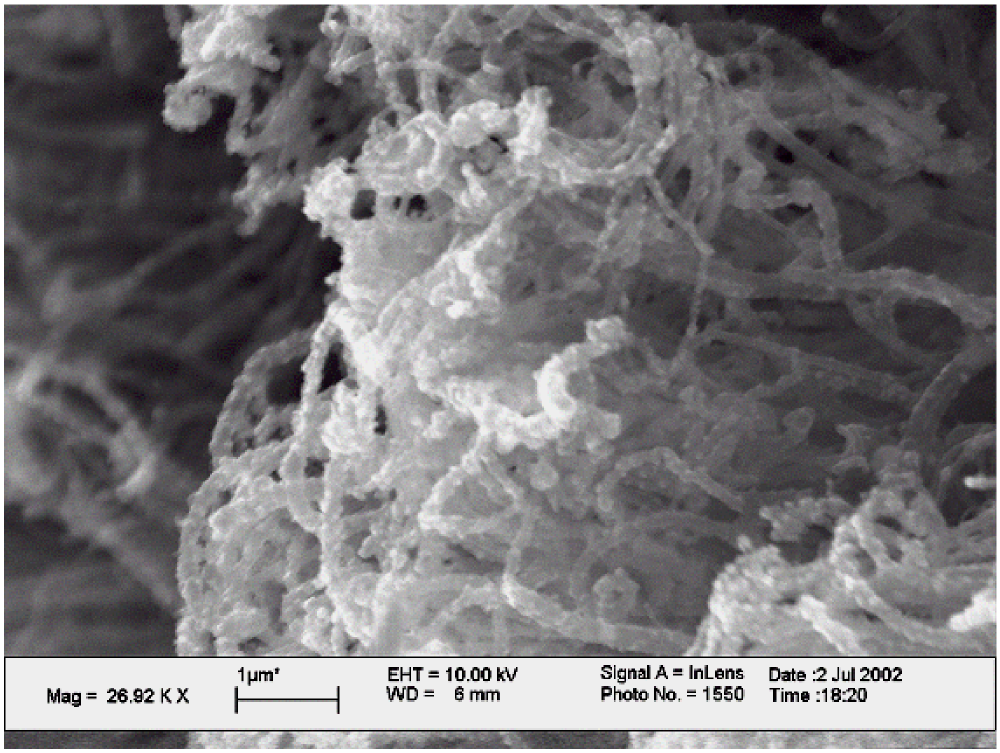
Appendix O



Appendix P



Appendix Q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