Biomolecule-Functionalized Carbon Nanotubes: Applications in Nanobioelectronics

Eugenii Katz and Itamar Willner*[a]

Carbon nanotubes (CNTs) revealing metallic or semiconductive properties depending on the folding modes of the nanotube walls represent a novel class of nanowires. Different methods to separate semiconductive CNTs from conductive CNTs have been developed, and synthetic strategies to chemically modify the side walls or tube ends by molecular or biomolecular components have been reported. Tailoring hybrid systems consisting of CNTs and biomolecules (proteins and DNA) has rapidly expanded and attracted substantial research effort. The integration of biomaterials with CNTs enables the use of the hybrid systems as active field-effect transistors or biosensor devices (enzyme electrodes, immunosensors, or DNA sensors). Also, the integration of CNTs with biomolecules has allowed the generation of complex nanostructures and nanocircuitry of controlled properties and functions. The rapid progress in this interdisciplinary field of CNT-based nanobioelectronics and nanobiotechnology is reviewed by summarizing the present scientific accomplishments, and addressing the future goals and perspectives of the area.

ChemPhysChem **2004**, 5, 1084 – 1104

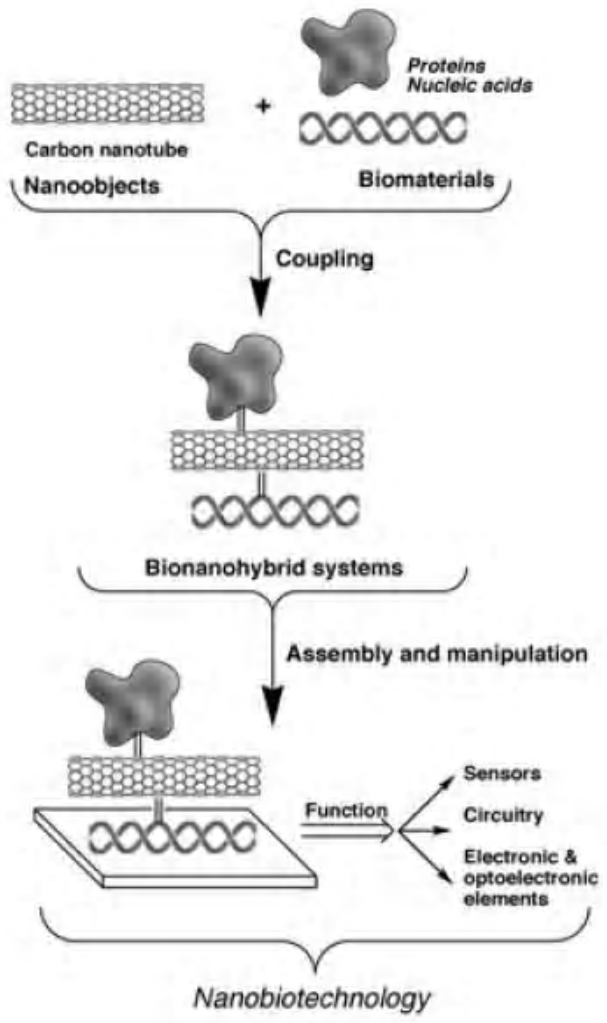
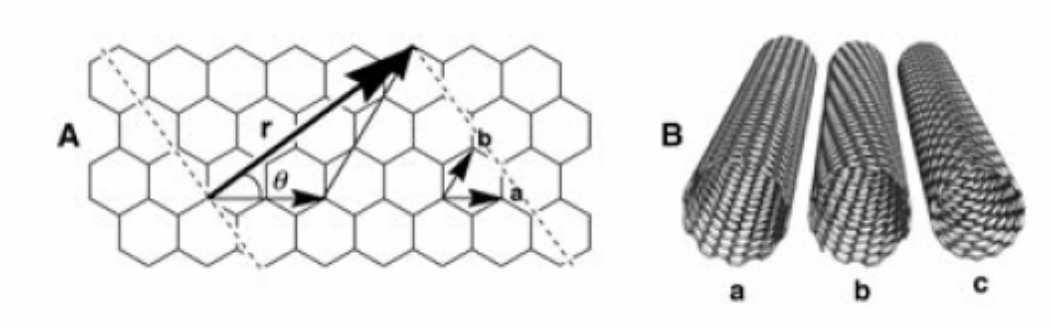


Figure 1. *The conceptual generation of biomolecules–carbon nanotube conjugates, and their assembly to yield functional devices.*

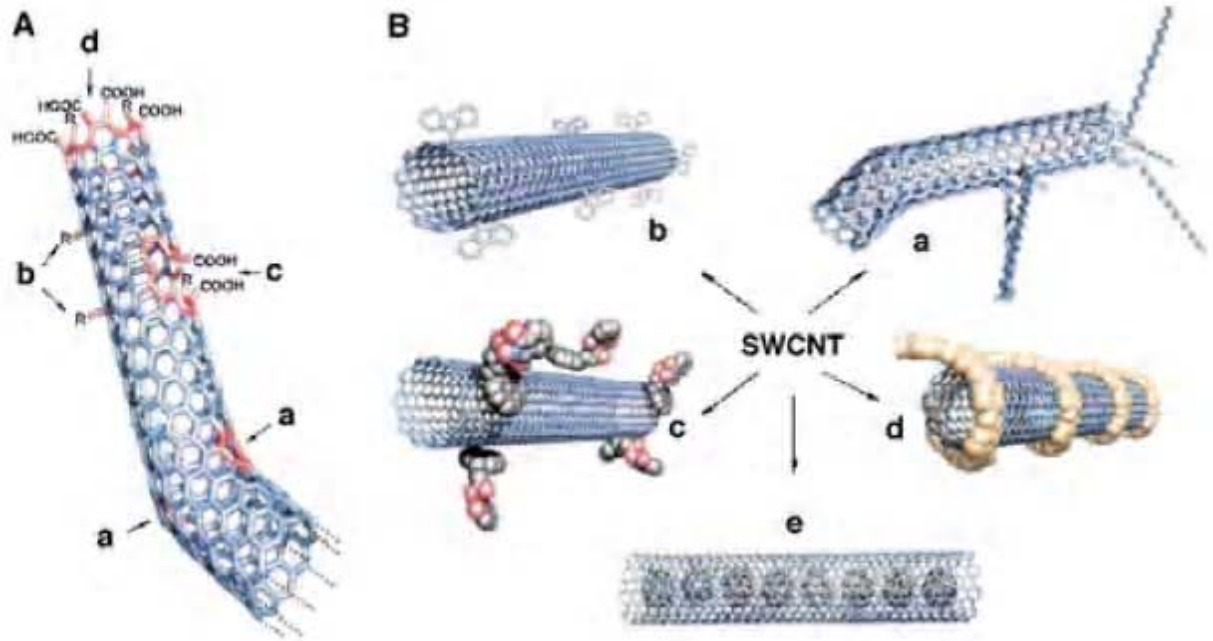
Structure and Electronic Properties of Carbon Nanotubes



$$\mathbf{r} = n\mathbf{a} + m\mathbf{b}$$

metallic (when $n-m=3p$, where p is integer)

semiconducting (all other n and m values).



Typical defects in a SWCNT:

Functionalization of Carbon Nanotubes with Biomolecules

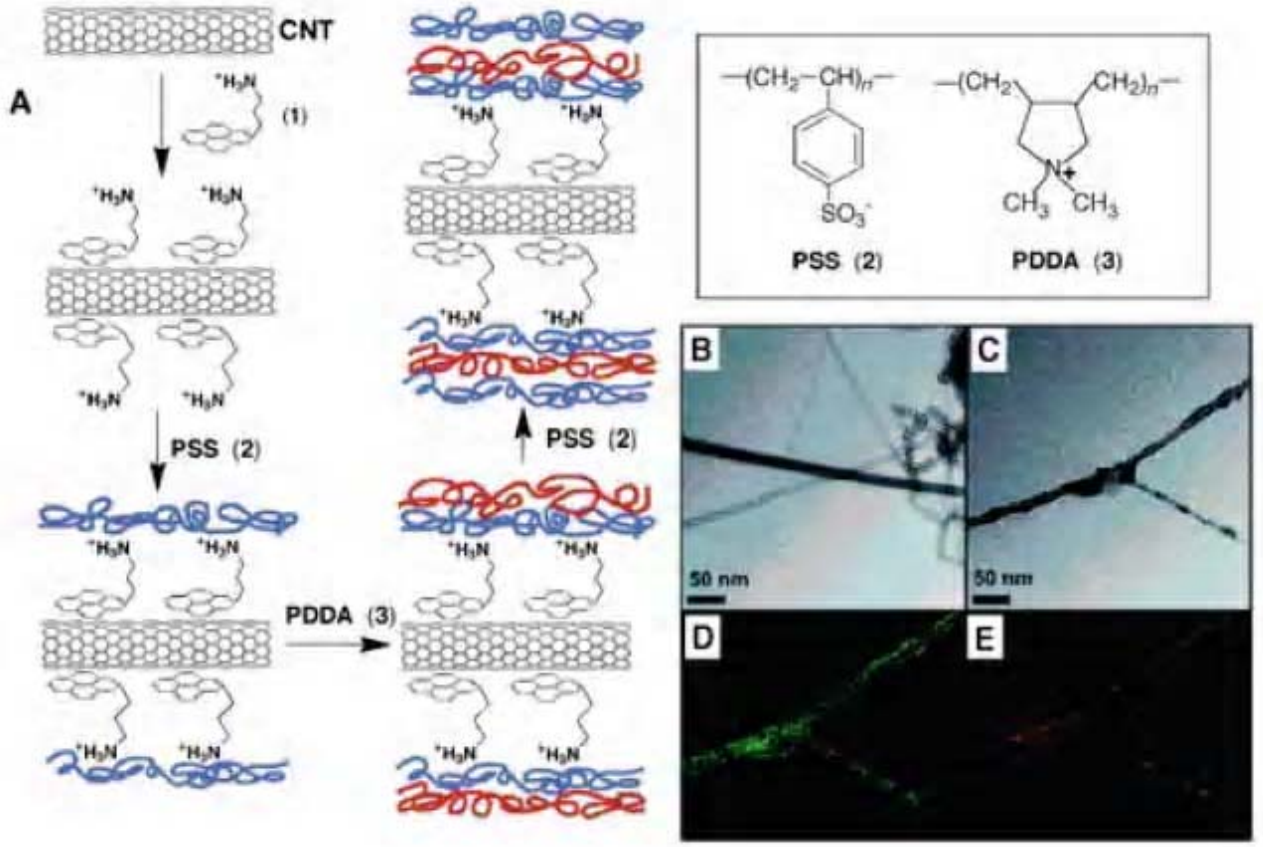


Figure 6. *A) CNT modification using layer-by-layer electrostatic self-assembly. TEM images of: B) The CNTs prior to the deposition of polymeric layers; C) The CNTs coated with four alternating PSS/PDDA polyelectrolyte layers; D) Sulfur and E) nitrogen element maps of the area shown in (C). (Adapted from ref. [77], Figures 2 and 3, with permission. Copyright American Chemical Society, 2004).*

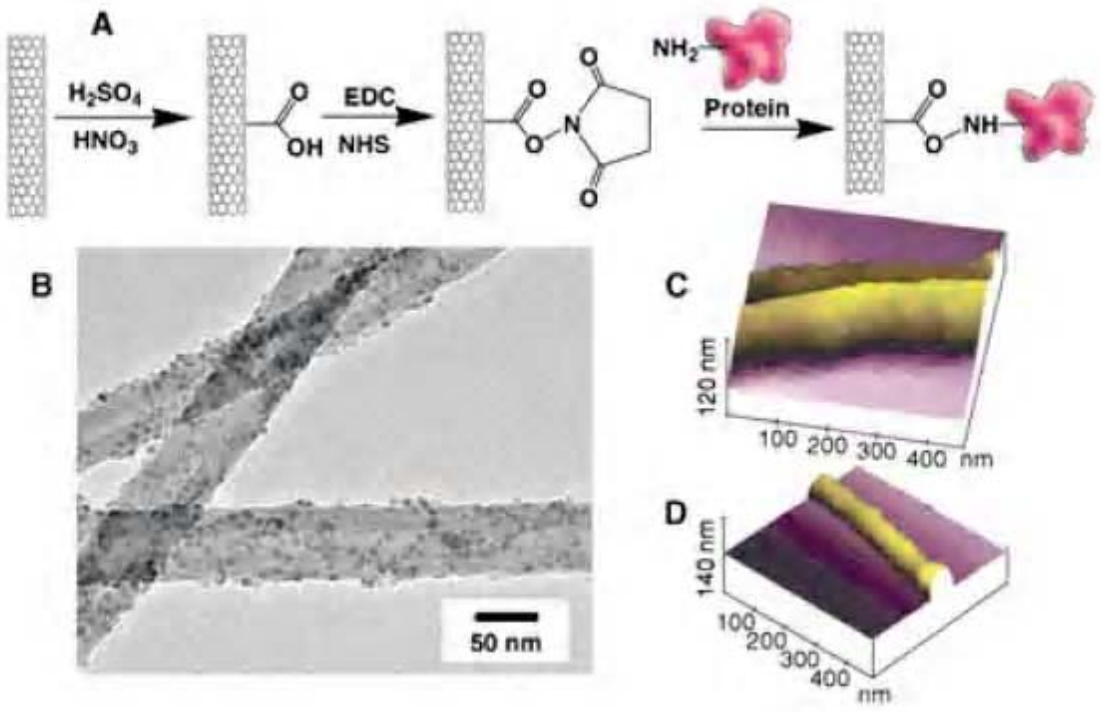


Figure 9. *A) Covalent binding of proteins to CNTs via a two-step process of diimide-actived amidation. B) TEM image of ferritin-functionalized MWCNTs. C,D) AFM images of BSA-functionalized MWCNTs. (Adapted from ref. [89], Figures 1, 2, and 3, with permission).*

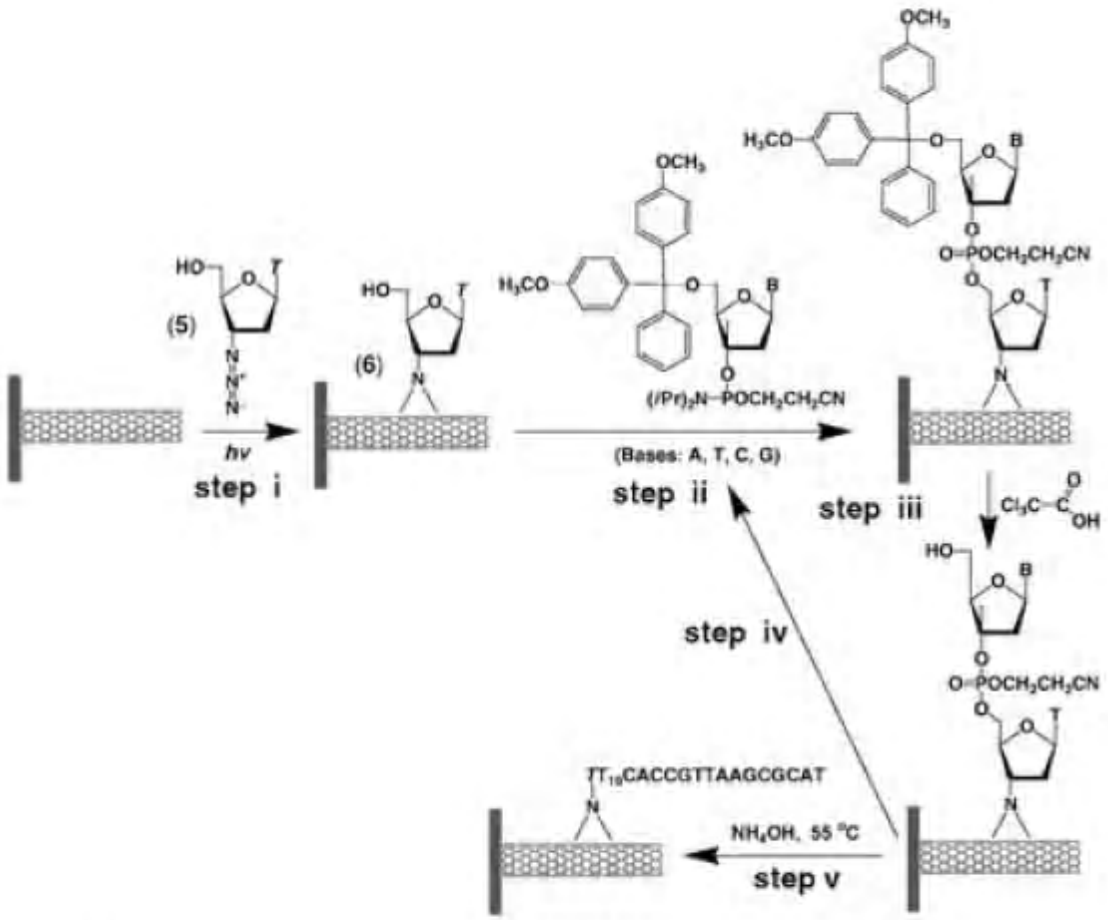


Figure 10. *In-situ DNA synthesis on sidewalls of CNTs photoetched with azidothymidine. (Adapted from ref. [90], Figure 1, with permission. Copyright American Chemical Society, 2004).*

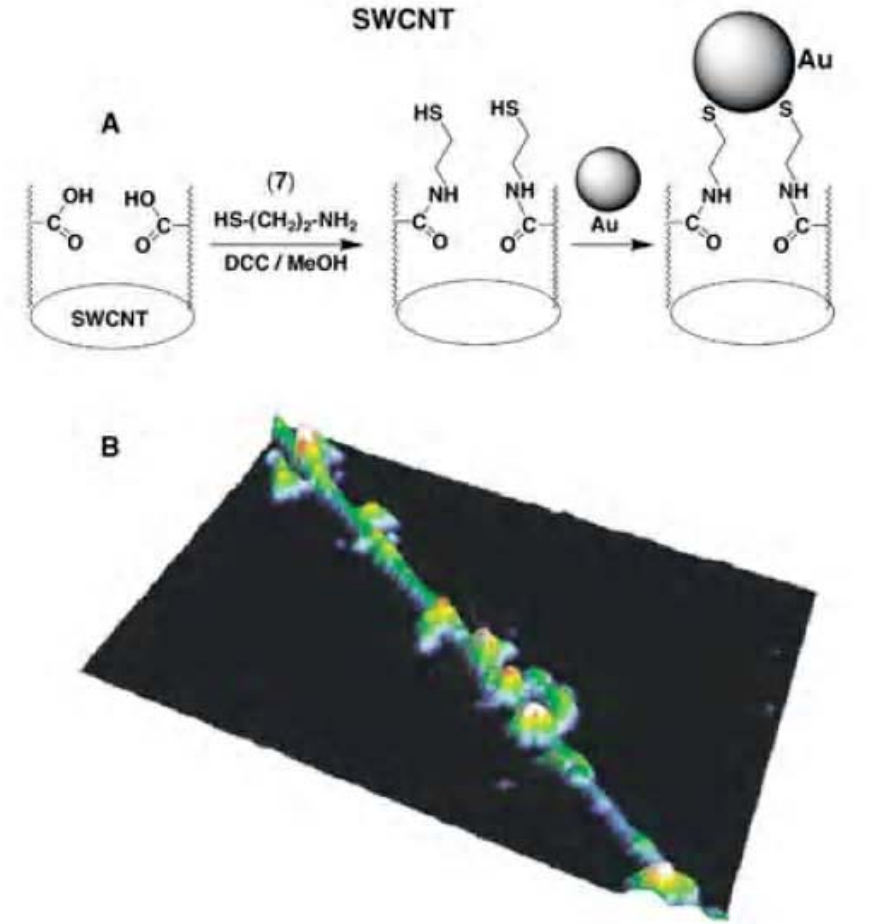


Figure 11. *A) Carbodiimide coupling reaction used to tether gold nanoparticles covalently to oxidized sites along SWCNTs. (DCC = dicyclohexylcarbodiimide). B) AFM three-dimensional topographic representation of a single SWCNT covalently decorated with gold nanoparticles 2–3 nm in diameter. The AFM image is approximately 50 × 150 nm² in size (z scale 0–3.5 nm). (Figure 11A was adapted from ref. [93a], Scheme 1; Figure 11B was adapted from ref. [93b], Figure 2; reproduced with permission of the Royal Society of Chemistry.)*

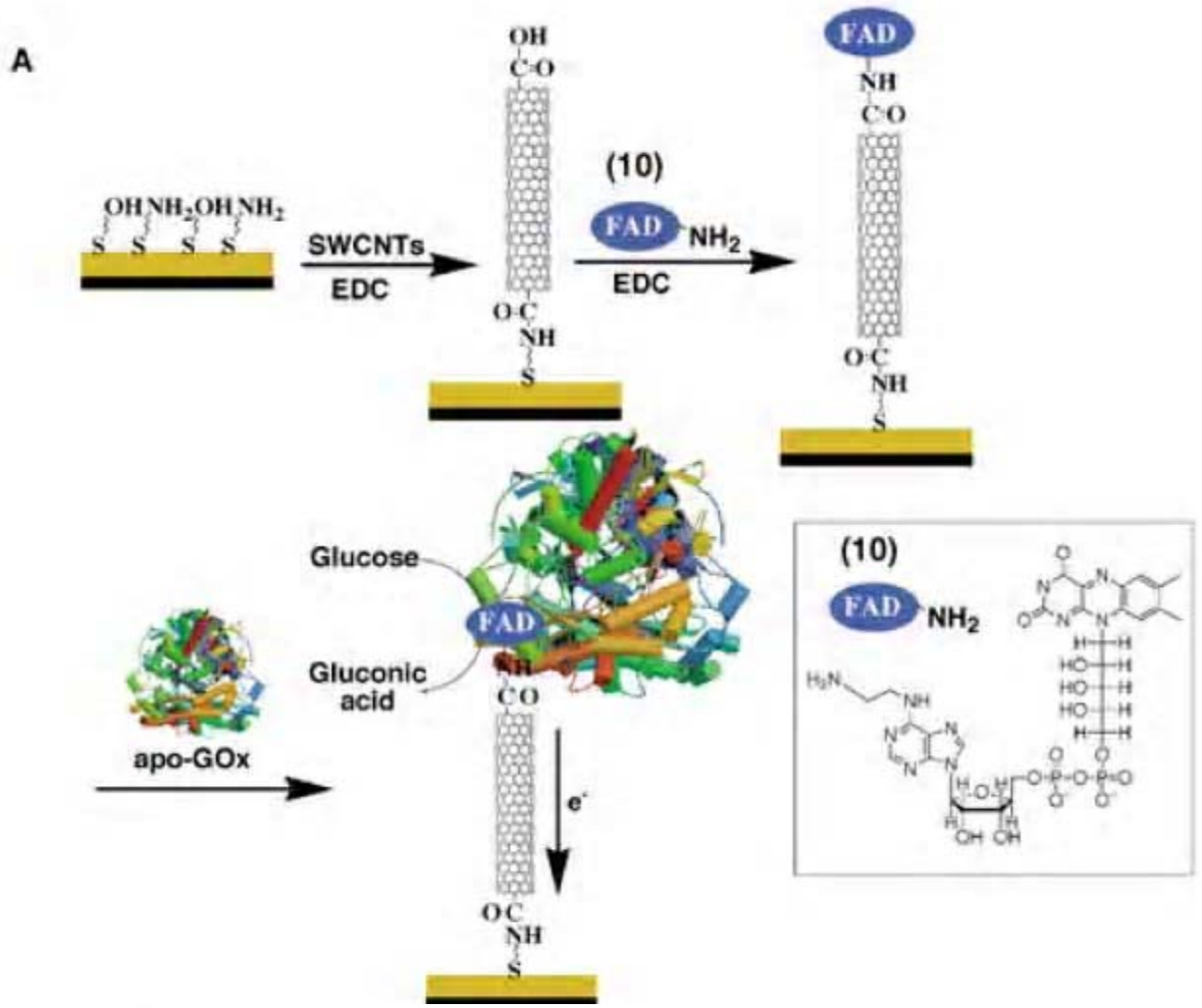


Figure 15. *A) Assembly of the SWCNT electrically-contacted glucose oxidase electrode. B) AFM image of the GOx reconstituted on the FAD-functionalized SWCNTs (about 50 nm) monolayer associated with the gold surface. C) Cyclic voltammograms corresponding to the electrocatalyzed oxidation of different concentrations of glucose by the GOx reconstituted on the 25 nm long FAD-functionalized SWCNTs assembly: a) 0 mM glucose; b) 20 mM glucose; c) 60 mM glu-*

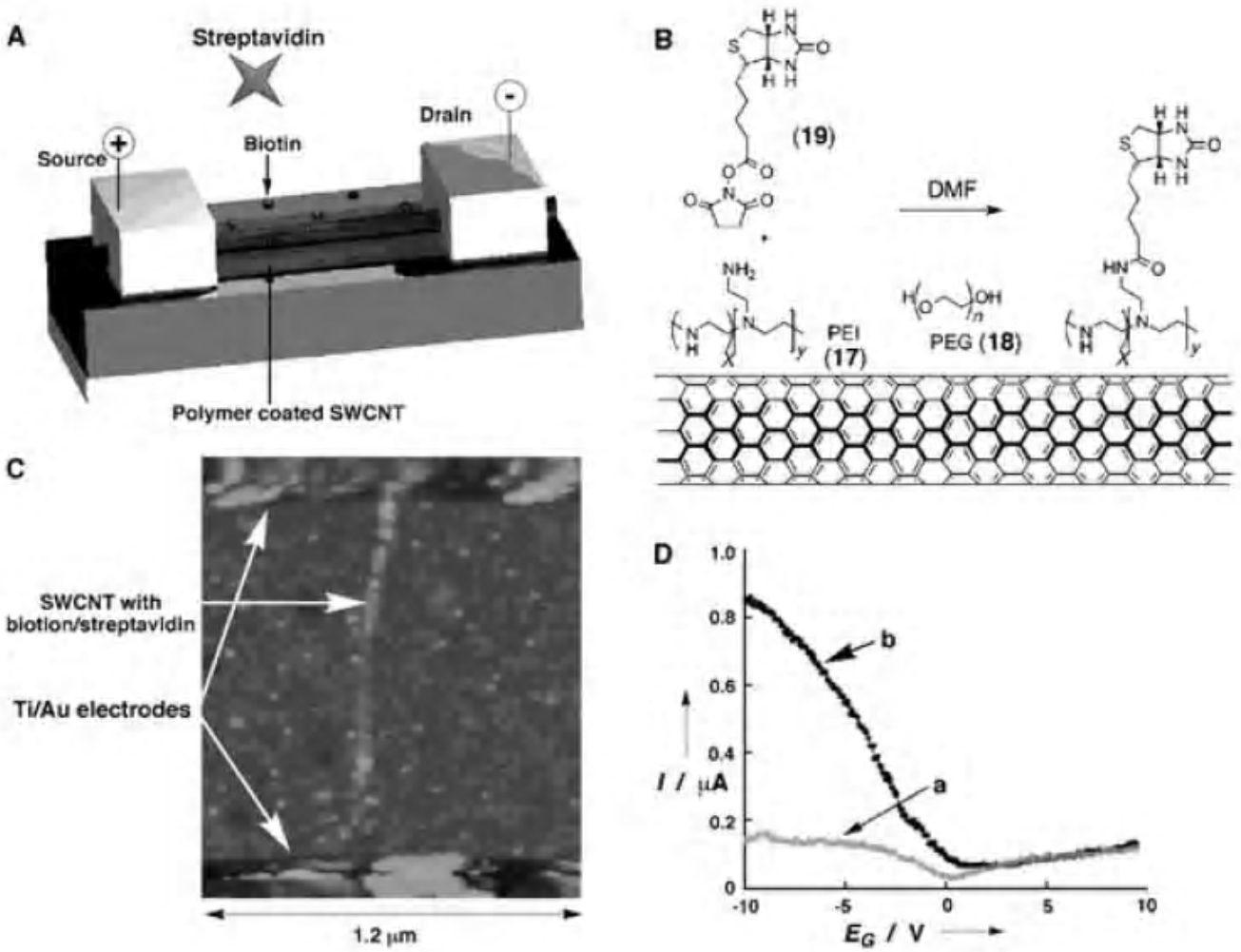
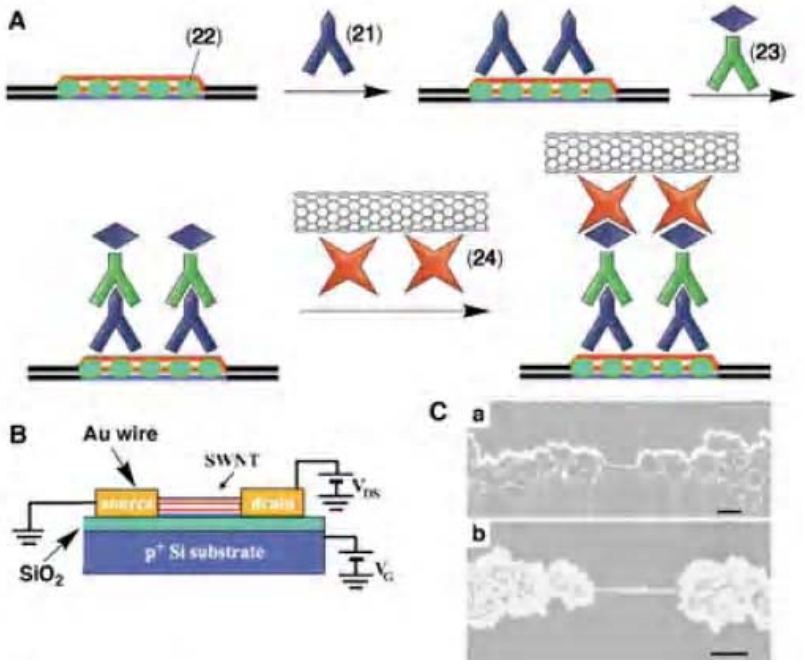


Figure 18. *A) A carbon nanotube field-effect transistor with a biotin-functionalized SWCNT operating as a gate sensitive to streptavidin. B) Biotinylation reaction of the polymer layer (PEI and PEG) on a sidewall of the SWCNT. C) AFM image of the polymer-coated and biotinylated CNTFET after exposure to streptavidin labeled with gold nanoparticles (10 nm diameter). D) The source–drain current I_{sd} dependence on the gate voltage of the CNTFET device based on carbon nanotube functionalized with biotin in the absence (a) and presence (b) of streptavidin . (Adapted from ref. [150], Figures 1, 2, 3, and 5 a, with permission. Copyright American Chemical Society, 2003).*



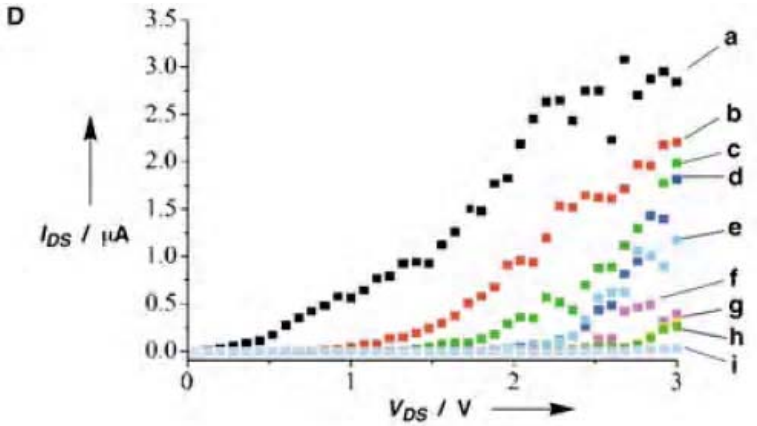


Figure 21. *A) Assembly of a SWCNT-based nanosized field-effect transistor using a patterned DNA template. B) Electrical wiring of the nanosized FET. C) SEM images of: a) An individual SWCNT contacted by two DNA-templated gold wires; b) A rope of SWCNTs bridging the gold wires; Bars, 100 nm. The scaffold DNA molecule and the RecA were not resolved by the SEM. D) Electrical characteristics of the DNA-templated carbon nanotube FET: drain–source current versus drain–source bias for different values of gate bias: a) −20 V; b) −15 V; c) −10 V; d) −5 V; e) 0 V; f) 5 V; g) 10 V; h) 15 V; i) 20 V. (Adapted from ref. [156], Figures 4 A and B), with permission.)*