Directed Linking of Carbon Nanotubes with Single CdSe Quantum Dots

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Abstract
Metallic single-walled carbon nanotubes (SWNTs or NTs) are the ideal nanometer-scale wire, as they can withstand current densities up to 2 to 3 orders of magnitude higher than copper currently used in electronic chips [1]. These conductive NTs can be utilized as nano-electrodes to electrically contact another nanoscale object, such as a single semiconductor quantum dot (QD) or metallic nanoparticle (NP). We have designed a strategy for directed assembly of fabricated QD–SWNT devices. NTs were grown across patterned catalyst islands on a silicon wafer followed by electrode placement. After cutting the NTs, the resulting carboxyl group moieties found at the cut NT edges were used to covalently attach amine-functionalized cadmium selenium (CdSe) QDs or gold (Au) NPs. Electrostatic force microscopy (EFM) was used to monitor NT conductivity before and after cutting, as well as after NP attachment.

Summary of Research
Combining the technique of NT chemical vapor deposition (CVD) synthesis with photolithography and metal deposition has resulted in the successful fabrication of a device with an active NT component, as shown in Figure 1a. Device validity is monitored by applying a voltage to the NT, followed by capturing an EFM charge image, as shown in Figure 1b. After NTs are grown on a substrate and device validity is assessed, the difficult process of NT cutting occurs. NTs have been cut successfully using two different methods: by applying a sequence of voltage pulses across a metal-coated atomic force microscopy (AFM) tip in close proximity to a grounded NT [2] and by using electron beam (e-beam) lithography in conjunction with an oxygen plasma to remove small sections of a NT (Figure 2) [3]. Whereas using an AFM tip yields gaps as small as 80 nm, the smaller (< 20 nm) gaps produced using e-beam lithography are necessary in order to successfully attach a single NP of less than 20 nm in diameter. EFM images captured before and after the cutting events clearly indicate the location of the cut.

When either cutting method is utilized, the exposed NT edges oxidize to form carboxyl groups that will be used to anchor a single NP. Previously, our group functionalized the ends of commercial NTs in solution with thionyl chloride and then covalently attached CdSe QDs coated with amine-terminated surface ligands [4]. In this project, similar chemistry has been used to attach single CdSe QDs to severed NTs on a silicon substrate (Figure 3). The hydrophobic surface ligands on CdSe QDs are exchanged with amine-terminated ligands, which can form amide bonds with carboxyl groups found on the cut SWNT edges to yield the consummate NP-NT circuit [5]. CdSe QDs have been attached along the NT sidewalls...
Materials

Successfully; however, due to the small size (~ 4 nm) of a single CdSe QD, conjugation across the larger NT is impossible.

Two possible solutions to the size mismatch problem are to create a smaller cut in the NT or to use larger NPs. Since e-beam lithography is currently the best method for patterning the smallest features and its resolution limit is < 20 nm, choosing larger particles to fit into the NT gap is the most plausible solution. CdSe nanorods (NRs) are a better candidate for filling the NT gap due to their elongation along the c-axis. These NRs can be coupled to NTs using the same procedure as for CdSe QDs (Figure 3). The difficult task of exchanging the hydrophobic surface ligands on NRs for hydrophilic ones is currently being investigated in our group. Another candidate for placement into the gap is an Au NP, which can be synthesized in sizes ranging from a few to hundreds of nanometers (Figure 4) [6, 7]. While it has been reported that dielectrophoresis can be used to move Au NPs between gold electrodes [8], placing an individual Au NP between NT nano-electrodes would be a major breakthrough.

After device optimization on silicon substrates is completed, fabrication of NP-SWNT structures on quartz substrates will allow for laser excitation and fluorescence measurements studies. The finished device will be used to study charge-transfer effects between the NPs and the NT, with possible applications in solar cell technology.

References


Figure 2: (a) AFM and (b) EFM images of a NT cut using e-beam lithography followed by oxygen plasma exposure. Scale bar = 500 nm.

Figure 3, left: Coupling of CdSe QD or QR with amine-terminated surface ligands using EDC (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride) bioconjugation reaction. After coupling, the QD is covalently held in place via amide bonds.

Figure 4, right: Coupling of Au NP (citrate-stabilized) to NTs. Ethylenediamine is attached to the carboxyl groups found at NT ends. Using dielectrophoresis, Au NPs are guided into the gap while amine groups hold the NP in place.