

Heterojunctions of Gold Nanorods and Single-Wall Carbon Nanotubes

Aneta J. Mieszawska, Romaneh Jalilian, Gamini U. Sumanasekara, and Francis P. Zamborini*

Department of Chemistry, Department of Physics, University of Louisville, Louisville, KY 40292.

RECEIVED DATE (automatically inserted by publisher); f.zamborini@louisville.edu

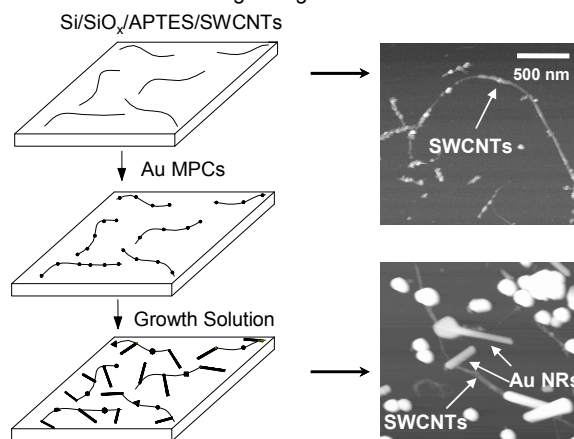
The synthesis of pure one-dimensional (1D) nanostructures is of tremendous importance, but for many electronic,¹ optoelectronic,² and sensing applications³ it is necessary to fabricate multicomponent structures with heterojunctions of different 1D nanomaterials. For example, carbon-semiconductor (SC),^{1a} SC-metal,^{1b,c} carbon-metal,^{1c,d} carbon-carbide,^{1e} and SC-SC² heterojunctions have been fabricated and shown to exhibit Schottky diode behavior,^{1a} ohmic contact,^{1d,e} thermoelectric properties,^{2a} photoluminescence,^{2c} and electroluminescence.^{2c} Striped nanorods comprised of different metal-metal junctions have served as biobarcode sensors.³ The methods used to prepare these heterojunctions have led mostly to end-to-end junctions by electrochemical deposition in porous templates,^{1b-d,3} solid-solid reaction,^{1e} or vapor phase growth onto catalysts.^{1a,2} In this report we describe a simple chemical reduction method for the synthesis of heterojunctions of metallic 1D gold nanorods (Au NRs) attached to the ends or sidewalls of single-wall carbon nanotubes (SWCNTs) assembled directly on surfaces.

Au NR/SWCNT heterojunctions were synthesized directly on Si/SiO_x substrates as shown in Scheme 1. First, an Si/SiO_x substrate was functionalized with aminopropyltriethoxysilane (APTES) by cleaning in 3:1 H₂SO₄:H₂O₂ (piranha) solution (**Caution: piranha reacts violently with organic compounds**), rinsing thoroughly with water and isopropanol (IPA), and then placing into a solution containing 100 μL APTES, 10 mL IPA, and 2-3 drops of water while heating just below boiling for 30 min. The substrate was removed, rinsed thoroughly with IPA, dried under N₂, and placed into a very dilute dimethylformamide (DMF) solution of SWCNTs for 25-30 min.⁴ The substrate was removed, rinsed with DMF and IPA, and dried under N₂. As shown in the top AFM image of Scheme 1, a low coverage of SWCNTs adsorb to the NH₂ groups on the Si/SiO_x/APTES substrate in the form of bundles containing ~7-10 nanotubes.

1.6 nm average diameter hexanethiolate Au monolayer-protected clusters (MPCs) were prepared by the Brust method⁵ and physisorbed onto the surface-attached SWCNTs, presumably through hydrophobic interactions, by simply immersing the Si/SiO_x/APTES/SWCNT substrate into a 9 mg/mL toluene solution of the MPCs for 10-15 min. The substrate was rinsed with toluene and IPA, dried under N₂, and placed into a “growth solution” containing 9 mL 0.1 M cetyltrimethylammonium bromide (CTAB), 450 μL 0.01 M HAuCl₄, and 50 μL 0.01 M ascorbic acid for 1 h. This leads to the seed-mediated growth of the SWCNT-bound Au MPCs into Au NRs and other shapes as described previously for Au NRs grown from citrate-stabilized Au nanoparticles in solution^{6a} or attached to surfaces.^{6b-d} The bottom AFM image in Scheme 1 shows the Au NR/SWCNTs junctions formed using this procedure.

Close inspection by AFM or scanning electron microscopy (SEM) shows that >90% of the Au nanostructures emanate

Scheme 1. Method for growing AuNRs on SWCNTs.



directly from SWCNTs, consistent with physisorption of Au MPCs onto the SWCNTs and seed-mediated growth into NRs and other shapes. As further confirmation, Figure 1 shows the visible spectra of glass/APTES/SWCNT samples that were placed in Au MPCs for 15 min or 10 min and then growth solution for 1 h to form Au NR/SWCNT heterojunctions (spectrum 1 and 2, respectively). The spectra exhibit a large absorbance in the visible region with a surface plasmon (SP) band at 527 nm, consistent with the formation of Au nanostructures on the surface. As expected, the substrate soaked in Au MPCs for 15 min has a slightly higher absorbance compared to that for 10 min due to the larger coverage of Au MPCs with longer time. The bottom two spectra are glass/APTES/SWCNTs (no Au MPCs) placed in growth solution (spectrum 3) and glass/APTES placed in Au MPCs for 15 min and growth solution (spectrum 4). Neither of

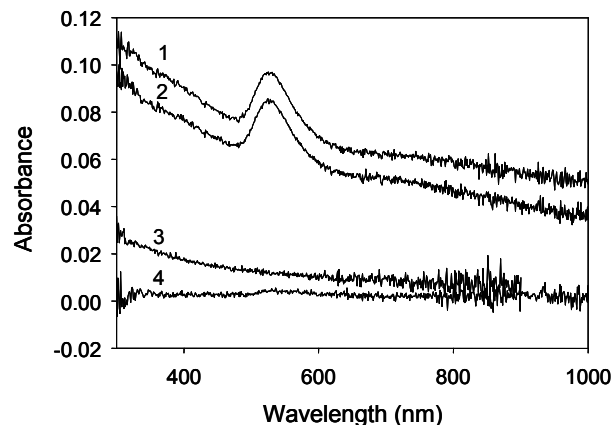


Figure 1. Visible spectra of 1) glass/APTES/SWCNT/Au MPCs (15 min), 2) glass/APTES/SWCNT/Au MPCs (10 min), 3) glass/APTES/SWCNTs (2 days), and 4) glass/APTES/Au MPCs (15 min) placed in growth solution for 1 h.

these samples exhibit significant absorbance or evidence of a SP band for Au, indicating that the Au MPCs do not adsorb appreciably to the glass/APTES surface and that neither glass/APTES nor SWCNTs alone (without MPCs) catalyze the growth of Au nanostructures. It has been previously shown that SWCNTs can nucleate the deposition of Au from HAuCl₄ solutions,⁷ but this is prevented in our case by the excess CTAB.

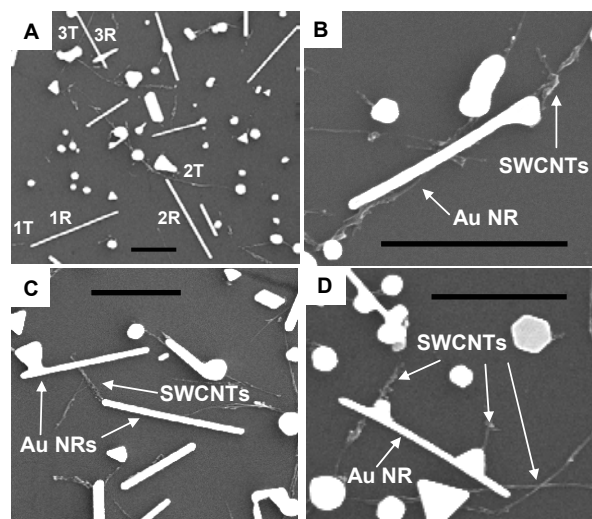


Figure 2. SEM images of Au NR-SWCNT heterojunctions grown directly on Si/SiO_x/APTES substrates. (A) typical image of Au NRs grown directly on SWCNTs, (B) Au NR grown parallel to a SWCNT bundle, (C) Au NR-SWCNT-Au NR junction, and (D) Au NR connecting three different SWCNT bundles. Scale bars are 500 nm in all images. SWCNTs were soaked in Au MPCs for 10 min in Frames A and B and 15 min in Frames C and D.

Figure 2 shows scanning electron microscopy (SEM) images of different regions of a surface containing Au NR/SWCNT heterojunctions. The bright regions represent Au NRs and nanoparticles, the dark regions represent the underlying Si, and the intermediate shade represents SWCNTs. Frame A is a typical image, showing that NRs, particles, triangles, and other shapes grow from the SWCNTs. The yield of Au NRs is ~19%, which is slightly higher than previous reports of high aspect ratio Au NRs grown in solution^{6a} and on surfaces.^{6b-d} The diameter of the NRs is fairly uniform (25-30 nm) and the average length is 572 ± 203 nm (AR ~20). Consistent with the spectroscopy, the images reveal that Au nanostructures exist where SWCNTs exist. Frame A shows that junctions may form at different places on the SWCNTs. For example, Au NR 1R attached to the end of nanotube 1T, NR 2R attached to the sidewall of nanotube 2T, and NR 3R formed a cross-junction with nanotube 3T. Junctions may form by direct growth of NRs from SWCNTs or by NRs growing into a SWCNT. Frame B shows an example of an Au NR growing parallel along the sidewall of the SWCNTs.

Different types of heterojunctions are formed on the surface that will be interesting to study electronically. Frame C shows an example of two Au NRs attached to different regions of the same SWCNT and Frame D shows three different SWCNT bundles connected by one Au NR. Au NRs could serve as nanoscale contacts, which could lead to integrated devices and greater reproducibility in the electrical measurements of SWCNTs.

Raman spectroscopy is commonly used to characterize SWCNTs^{8a,b} and Au NRs are known to enhance Raman scattering signals.^{8c} Figure 3A and 3B shows the high frequency regime (containing G and D bands) and low frequency regime (containing radial breathing modes), respectively, of the spectrum of SWCNTs before (bottom spectrum) and after growth of Au

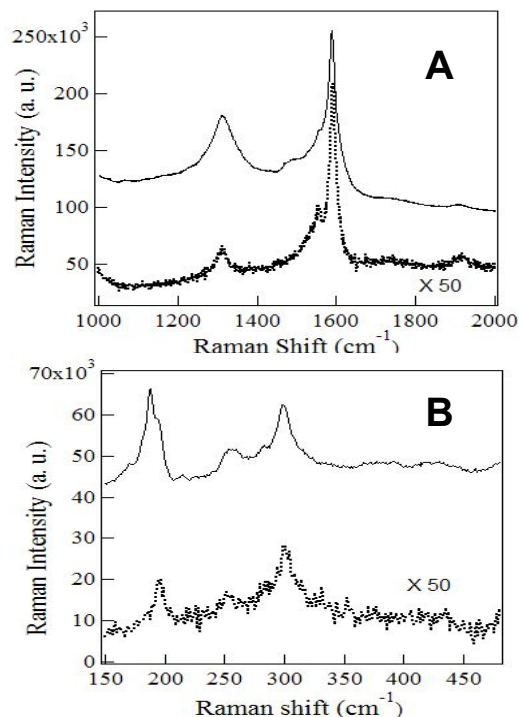


Figure 3. Raman spectra depicting (A) G and D bands in the high frequency regime and (B) radial breathing mode in the low frequency regime of SWCNTs for pristine (bottom spectra) and Au NR-SWCNT heterojunctions (top spectra). The spectra were collected at 632.8 nm excitation using a Renishaw micro Raman system.

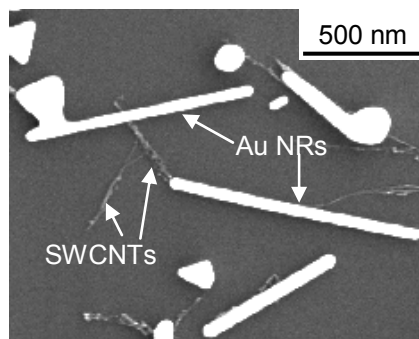
NRs and other nanostructures (top spectrum).^{8a,b} The close proximity of Au to the SWCNTs resulted in an approximately 50-fold enhancement of the SERS signal.

In summary, we have described a simple chemical method for synthesizing surface-attached heterojunctions of 1D Au NRs and SWCNTs. These structures may be promising for nanoelectronic and sensing applications as well as for studying the structure and functionality of SWCNTs by SERS. Experiments aimed at characterizing the junctions electronically and understanding the affect of Au nanostructure size, shape, and proximity to the SWCNTs on the SERS enhancement are currently underway.

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This paper describes the synthesis of gold nanorod (Au NR)/single-wall carbon nanotube (SWCNT) heterojunctions assembled directly on Si/SiO_x substrates. SWCNTs are attached to amine-functionalized Si/SiO_x substrates and Au monolayer-protected clusters (MPCs) are adsorbed to the surface of SWCNTs through hydrophobic interactions. Seed-mediated reduction of HAuCl₄ with ascorbic acid in the presence of cetyltrimethylammonium bromide (CTAB) onto the Au MPCs leads to the growth of larger Au nanostructures directly on the SWCNTs. Au NRs account for 19% of the nanostructures, some of which are attached directly to the sidewall and some at the ends of the SWCNTs. Raman spectroscopic measurements of SWCNTs before and after growth of the Au nanostructures reveal that the presence of Au leads to an approximately 50-fold enhancement of the Raman scattering signal. Combining 1D nanostructures of different materials (Au and carbon in this example) is of fundamental interest and may find use in nanoelectronics, chemical sensing, and spectroscopy applications.
