devices, regardless of their channel lengths. These thin-film transistor (TFT) devices provided an average mobility of 0.09–0.15 cm²/V·s, together with a high current on/off ratio (∼10⁵) and low threshold voltage (∼6 V). All these results are in agreement with those observed for the devices using vacuum deposited gold electrodes. Gold electrodes printed from gold nanoparticles functionalized with longer homologues of alkanethiols such as octanethiol and dodecanethiol have also proven to be satisfactory, and yielded similarly excellent OTFT characteristics.

In conclusion, we have successfully demonstrated the simplicity in fabricating highly conductive electrode features for OTFTs from gold nanoparticles at sufficiently low temperatures to be compatible with most commercial plastic substrates. OTFTs with the printed gold source and drain electrodes of this nature have exhibited TFT properties that are similar to the devices using vacuum deposited gold electrodes. Other metal and metal alloy nanoparticles are being investigated as printable conductive materials.

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Figure 5. a) Plot of drain current I_D versus source–drain voltage V_D as a function of gate voltage V_G for an exemplary OTFT with printed source and drain electrodes having channel length of 240 μm and channel width of 2200 μm. b) Plot of I_D and (I_D)¹/² versus V_G at a constant V_G = –60 V (mobility and current on/off ratio extracted from this plot).
arrays, in which the electroactive components are positioned at the crossing junctions.[2-5] Uncoated and coated semiconductor nanowires[3] carbon nanotubes,[4] and functionalized metal nanowires[5-9] have been most extensively studied for this application. Reliable control can be had over the physical dimensions, surface chemistry, and transport properties of metal nanowires, and they can be easily prepared[5-9] and functionalized using low-temperature techniques.[5-9]

Our approach to electronically functionalizing metal nanowires combines templated electrochemical synthesis[6] with established wet-chemical methods for making thin-film devices.[11] Layer-by-layer assembly of electroactive shells around the wires can be achieved in two ways, namely, i) via growth of semiconductor or insulator tube-shells as thin films on the pore walls of an alumina (AAO) membrane, followed by electrodeposition of wires inside the tubes i.e., “in-membrane” assembly;[8,9] or ii) via growth of semiconductor or insulator shells on the walls of free-standing nanowires, or “on-wire” assembly.[7,8] Insulated metal interconnects and simple Schottky-barrier devices with rectifying properties have been made by these methods.[7-9]

Here we report the synthesis of nanowire diodes with highly structured tube-shells composed of electron- and hole-conducting multilayer segments. Semiconductor-particle/polymer interfaces have been routinely used to fabricate p-n heterojunctions in thin-film electroluminescent devices, photovoltaic cells, and diodes.[11a-3] A significant problem that limits the performance of thin-film polymer devices is their relatively low conductivity. Very recently, we showed that planar, multilayer films composed of subnanometer-thick polymer layers interlaced with monolayers of oxidized, single-walled carbon nanotubes (SWNT) exhibited conductivities several orders of magnitude higher than films of pure polymers.[12] In this work, we extend the layer-by-layer assembly of SWNT/polymer films to nanowire substrates. Three-layer polyaniline(PAN)/SWNT films were grown on the walls of gold nanowires coated with multilayers of n-type TiO$_2$ (anatase) nanoparticles and W$_{12}$O$_{41}$$^{10-}$ (paratungstate) ions (Au@TiO$_2$/W$_{12}$O$_{41}$)$_3$ to fabricate the “on-wire” p-n heterojunctions. To achieve this, we combined the “in-membrane” and “on-wire” assembly approaches. The “in-membrane” growth gave (TiO$_2$/W$_{12}$O$_{41}$)$_3$ tube-shells in which the roughness of the outer walls was determined by the smooth alumina pores. Electroplating metal inside these tubes resulted in intimate contact between the metal and the TiO$_2$ particles without having to add an organic priming layer to the metal surface.[13] However, growth in the AAO membranes required the tubes to be built from precursor molecules or particles that were much smaller than the pore diameters. To extend the synthesis to larger components, such as carbon nanotubes, one can deposit additional layers on the tube-shell after releasing the wires from the membrane. The material components used in this study had, by necessity, to meet the following set of requirements: i) an appropriate match had to exist between the electron affinity of the n-type semiconductor particles, the ionization potential of the p-type polymer, and the anode and cathode work functions; ii) it had to have been possible to regularly grow ultrathin, dense, and smooth multilayer shells; iii) the resistances of both the n- and p-type multilayers had to be relatively low; and iv) the materials had to be stable under the conditions of AAO membrane dissolution.

Layer-by-layer assembly of multilayer junctions on the side-walls of metal nanowires is a four-step procedure, which is shown schematically in Figure 1. In the first step, multilayer W$_{12}$O$_{41}$/TiO$_2$ nanotubes were grown as thin films on the AAO membrane pore walls as previously described.[8] In brief, an AAO membrane template with an evaporated Ag backing layer was alternately immersed in aqueous (NH$_4$)$_2$W$_{12}$O$_{41}$ (1.5 wt.-%) and TiO$_2$ (3.8 wt.-%, pH2); prepared according to a previously published method[8] solutions for 5-15 min. Each adsorption step was followed by several washings for 15 min in a beaker with H$_2$O (which allowed weakly bound particles to diffuse out of the pores) and by drying in an Ar stream. In the second step, the W$_{12}$O$_{41}$/TiO$_2$-filled membrane was used as the cathode in an electrochemical cell, and gold was electroplated inside the tubes.[8,10] The resulting Au wires coated with (TiO$_2$/W$_{12}$O$_{41}$)$_3$ nanotube shells were then released into a solution by successively dissolving the Ag backing layer and the AAO membrane in 50% HNO$_3$ and 0.5 M NaOH, respectively. Finally, the free-standing colloidal wires were used as substrates for layer-by-layer assembly of a (PAN/SWNT)$_2$-PAN shell on the W$_{12}$O$_{41}$-terminated surface of the wire sidewalls. To achieve this, the nanowire suspension was concentrated by centrifuging, then a PAN solution in dimethylformamide (DMF, 1.7 g L$^{-1}$) and an aqueous SWNT solution (PAN solution: emeraldine base, EB, synthesized according to a method given in the literature[13]), SWNT so-

![Figure 1. Layer-by-layer template synthesis of an on-wire p-n junction.](image-url)
olution: 0.4 g L\(^{-1}\), synthesized according to a method given in the literature\(^{[14]}\), were alternately added to the nanowires. After each 10 min adsorption cycle the reagent was removed by centrifuging and the nanowires were washed/centrifuged with three portions of appropriate solvent. The resulting heterojunction-coated wires were designated Au@(TiO\(_2\)/W\(_{12}O_{41}\))(PAN/SWNTox)\(_3\)PAN.

Transmission electron microscopy (TEM) images of free-standing (TiO\(_2\)/W\(_{12}O_{41}\)) nanotubes grown in an AAO membrane indicated that the tubes had outer diameters of 80±10 nm, which is equal to the diameter of the membrane pores (Fig. 2a). The thickness of the tube walls increased with the number of adsorption cycles and reached 9±1 nm for a three-layer TiO\(_2\)/W\(_{12}O_{41}\) tube. A typical TEM image of a Au@(TiO\(_2\)/W\(_{12}O_{41}\)) nanowire (Fig. 2b) showed a uniformly thick shell that was composed of densely packed particles around the wire. The tube walls were apparently defect-free and no metal penetration was observable. Both ends of the nanowires released from the membrane were open, because the tube shells broke within around 10 nm of the ends of the wires during the membrane dissolution process. This allowed one to make electrical contact easily (see below) by evaporating metal onto the wire ends. Layer-by-layer deposition of a (PAN/SWNTox)\(_3\)PAN film on the Au@(TiO\(_2\)/W\(_{12}O_{41}\)) wires added approximately 3 nm to the shell thickness (Fig. 2c). The shell surface remained smooth, indicating strong adsorption of the PAN chains and oxidized carbon nanotubes.

W\(_{12}O_{41}\)/TiO\(_2\) multilayer growth inside the AAO membrane, which was monitored by mass-uptake measurements, was line-

![Figure 2](image_url)

**Figure 2.** TEM images of a) a free-standing (W\(_{12}O_{41}/\)TiO\(_2\)) nanotube; b) a (W\(_{12}O_{41}/\)TiO\(_2\)) nanotube electrochemically filled with an Au wire; and c) a Au@(TiO\(_2\)/W\(_{12}O_{41}\))(PAN/SWNTox)\(_3\)PAN nanowire prepared in the pores of AAO membranes as shown in Figure 1. Pore diameters are a) 80±10 nm; b) c) 280±20 nm. d) AFM image (450 nm × 250 nm) of a (W\(_{12}O_{41}/\)TiO\(_2\))W\(_{12}O_{41}\)(PAN/SWNTox)\(_3\)PAN film grown layer-by-layer on a planar Au substrate.

300 nm and the pore density as 10\(^8\) cm\(^{-2}\), one can estimate the total surface area of the alumina membrane (diameter: 2 cm; thickness: 56 μm) to be 1800 cm\(^2\). An ideally packed monolayer of spherical anatase particles (diameter: 5 nm) adsorbed on this area should have a mass of 2.2 mg, which is consistent (given the approximate nature of the calculation) with the mass uptake per cycle observed experimentally. Increasing the TiO\(_2\) concentration in the stock solution from 3.8 wt-% to 20 wt-% did not result in higher mass-uptake values, indicating that the adsorption was limited to one monolayer of particles.

The layer-by-layer deposition of the same multilayer film on a planar Au substrate also showed regular growth of both the W\(_{12}O_{41}/\)TiO\(_2\) and PAN/SWNTox bilayer components of the film (Fig. 3, Trace 1). The ellipsometric thickness of the three-bilayer segments was estimated to be 8.6 nm for (W\(_{12}O_{41}/\)TiO\(_2\)),W\(_{12}O_{41}\) and 3.6 nm for (PAN/SWNTox)\(_3\)PAN. This is in good agreement with the thicknesses of the (TiO\(_2\)/W\(_{12}O_{41}\))\(_3\) (9±1 nm) and (TiO\(_2\)/W\(_{12}O_{41}\))(PAN/SWNTox)\(_3\)PAN (12±1 nm) shells grown around the Au nanowire (Figs. 2b,c) estimated from TEM. A tapping-mode atomic force microscopy (AFM) image of the planar Au(W\(_{12}O_{41}/\)TiO\(_2\))W\(_{12}O_{41}\)(PAN/SWNTox)\(_3\)PAN film (Fig. 2d) revealed complete coverage of the substrate by the densely packed film, which is consistent with the dense packing of the tube-shells.

The mass of an individual, spherical, anatase particle (average diameter: 5 nm) can be approximated to be 2.5 × 10\(^{-19}\) g, and that of a W\(_{12}O_{41}\)\(^{10-}\) polyanion, 4.8 × 10\(^{-21}\) g. From the mass-uptake data, an average of 17 paratungstate polyanions

![Figure 3](image_url)

**Figure 3.** Plots of 1) ellipsometric thickness of a multilayer (W\(_{12}O_{41}/\)TiO\(_2\))W\(_{12}O_{41}\)(PAN/SWNTox)\(_3\)PAN film grown on a planar Au-substrate and 2) mass of TiO\(_2\)/W\(_{12}O_{41}\) deposited in an AAO membrane versus the number of adsorption cycles. Solid squares (■) and diamonds (♦) correspond to TiO\(_2\) and solid triangles (▲) to SWNTox-terminated surfaces. Film refractive indices were taken as 2.0 for TiO\(_2\)/W\(_{12}O_{41}\) and 1.54 for PAN/SWNTox segments, and the planar Au substrate was used without priming. The AAO pore diameter was 280±20 nm.
were adsorbed for each TiO₂ particle in a bilayer cycle. This number is about half that needed to completely cover the exposed surface (top hemisphere) of the TiO₂ particles. It is likely that the highly charged W₁₂O₄₁⁻ ions avoided each other and were thus relatively evenly distributed over the surface of each TiO₂ layer. This picture is consistent with the average thickness of the planar W₁₂O₄₁⁻ monolayer (0.5 nm) obtained from ellipsometric measurements, versus the value of 0.9–1 nm expected from the van der Waals dimensions of the anion (Fig. 3, Trace 1).

UV–vis spectra of TiO₂/W₁₂O₄₁ films grown on a quartz substrate (not shown) showed a regular increase in absorbance with the number of deposition cycles, which is again consistent with regular, layer-by-layer growth. The spectrum of the (W₁₂O₄₁/TiO₂)₃ film was identical to that of a TiO₂ film drop-cast from a dilute TiO₂ solution. The same was true if we compared the UV–vis spectrum of a mixture of TiO₂ and W₁₂O₄₁ solutions, at a particle/anion ratio of 1:150, to the spectrum of a pure TiO₂ solution. The absorption-edge energies of TiO₂ and W₁₂O₄₁ appeared at 3.21 eV and 3.54 eV, respectively, in individual spectra, but the contribution of W₁₂O₄₁ in the mixture was quite weak. In contrast, the UV–vis spectrum of a PAN solution changed upon addition of SWNTox. The absorption center at 596 nm gradually shifted to shorter wavelengths with increasing SWNTox concentration, and finally merged into the wide π-plasmon absorption band of the nanotubes[15] (Fig. 4). At high SWNTox concentrations, the absorption band at 650 nm (~1.9 eV), characteristic of metallic SWNTs, became pronounced (Fig. 4, Traces 6,7). The band at 596 nm (2.08 eV), which is characteristic of the PAN EB state, was assigned to electronic transitions from the highest occupied energy level centered on the benzenoid rings to the lowest unoccupied level centered on the quinoid rings.[16] As we have suggested previously, changes in this band may have been caused by partial filling of the “quinoid” band due to charge transfer from the π-system of the nanotube walls.[15] Although the interaction with SWNTox lead to the protonation of the EB imine moieties,[12] no evidence of electronic reorganization, leading to the formation of bipolaron or polaron bands, appeared in the UV–vis–NIR spectra of the PAN–SWNTox blends.[17] It seems, therefore, unlikely that the previously observed[12] dramatic increase in the conductivity of PAN (EB) after its assembly into a multilayer film with SWNTox is caused by the formation of a more conductive redox form of this polymer. This confirms our previous suggestion that the enhancing effect of SWNTox on the conductivity of ultrathin PAN (EB) layers is mainly due to improved electrical contact between relatively short polymer chains.[12] The extrinsic π–π* bandgap of PAN (EB) is estimated to be 3.92 eV, and the absorption edge energy is about 3.24 eV. An energy-level diagram of all the components is presented schematically in Figure 5 (top, left). Conduction band energies were approximated using literature data.[17,18]

For electrical measurements, the coated metal nanowires were electrofluidically aligned[19] on a lithographically patterned Si/SiO₂ substrate so that one wire bridged a gap between two gold pads on which the wire ends rested, while the middle of the wire rested on top of a gold line deposited in the middle of the gap. This line provided an electrical contact to the coating on the wire walls. Au pads, 200 nm thick, were then evaporated on top of the wire ends to ensure good electrical contacts. Figure 5 (top, right) shows an optical micrograph of this test structure and an Au@TiO₂/W₁₂O₄₁/PAN/SWNTox/PAN nanowire aligned for electrical measurement. The structure of the multicomponent shell and the electrode positioning relative to the component layers is shown schematically in Figure 5 (top, middle).

For comparison, planar, thin-film devices with the same layer sequences were prepared and characterized. Multilayer (TiO₂/W₁₂O₄₁)₃(PAN/SWNTox)₉(PAN and (TiO₂/W₁₂O₄₁)₃TiO₂ films were grown layer-by-layer on Au pads that were lithographically patterned on Si/SiO₂ wafers, and 200 nm thick Au pads were evaporated on top of the films. A striking qualitative similarity was found in the I–V characteristics of the “on-wire” and planar devices (Figs. 5a, b), which implies that the I–V characteristics are mainly determined by the multilayer device structure.

The I–V curve of a typical “on-wire” Au@TiO₂/W₁₂O₄₁/PAN/SWNTox/PAN device is asymmetric with turn-on potentials of 1.1 V and ~2 V for forward (negative voltage on the TiO₂/W₁₂O₄₁ region) and reverse bias, respectively (Fig. 5a, Traces 1, 1+). A typical ratio of reverse starting resistance (R₉) to forward starting resistance (R₉) was R₉/R₉ ~ 14, and it rapidly increased with voltage above the forward turn-

![Figure 4](image-url)
Figure 5. Top: Energy level diagram of materials used in the assembly of the p–n junction (v.b.: valence band, c.b.: conduction band) (left). Schematic diagram of the (TiO$_2$/W$_{12}$O$_{41}$)$_2$/(PAN/SWNTox), PAN multilayer film structure and electrode positioning for electrical measurements (middle). An optical micrograph of the test structure and Au@[TiO$_2$/W$_{12}$O$_{41}$]$_2$(PAN/SWNTox) nanowire aligned for electrical measurements (right). Top: I–V characteristics of a) Au@[TiO$_2$/W$_{12}$O$_{41}$]$_2$(PAN/SWNTox)Au (Traces 1, 11) and Au@[TiO$_2$/W$_{12}$O$_{41}$]$_2$/Au (Traces 2, inset top) nanowire devices. Trace 1* shows details of the low-current region of Trace 1. The bottom inset shows I–V characteristics of Traces 1, 2 plotted in semi-logarithmic coordinates. The characteristics 1 and 2 are typical for groups of 12 and 10 devices, respectively. The variation in the current values was ± 11%. End-to-end measured I–V characteristics of the Au wire cores with evaporated Au-electrodes were linear with total resistance (nanowire plus two contacts) of ∼20 Ω. b) Au@[TiO$_2$/W$_{12}$O$_{41}$]$_2$(PAN/SWNTox)Au (Au) (Au@[TiO$_2$/W$_{12}$O$_{41}$]$_2$/Au (Au (2), and Au@[TiO$_2$/W$_{12}$O$_{41}$]$_2$/Au (3, inset) thin-film devices. The measurements were performed at ambient temperature with an HP 4156B Precision Semiconductor Parameter Analyzer. For both types of Au@[TiO$_2$/W$_{12}$O$_{41}$]$_2$(PAN/SWNTox)Au devices, the variable electrode was in contact with the PAN/SWNTox (i.e., outer) part of the film.

on potential. This device had a current-rectification ratio >120 at 3 V and above.

In the forward-bias mode, the shape of the I–V curve was quite similar to that of the “on-wire” Au@[TiO$_2$/W$_{12}$O$_{41}$]$_2$/Au device (Fig. 5a, inset, top). This similarity was especially apparent for the corresponding planar devices shown in Figure 5b, Traces 1, 2. The turn-on voltages (1.1 V) were in good agreement with the difference between the Au work function (∼5.2 eV) and the electron affinity of TiO$_2$ (∼4.1 eV). Both I–V characteristics can be linearized in (ln(I), V) coordinates, giving relatively parallel plots (Fig. 5a, inset, bottom). These observations suggest that current transport is determined by charge injection at the Au/TiO$_2$ interface in the forward-bias mode. No barrier was apparent at the Au/PAN(SWNTox) interface, because the I–V characteristic of the planar Au(PAN/SWNTox)$_{10}$/PAN/Au device was almost linear in the low-current region$^{[12]}$ (Fig. 5b, inset). It should be noted that, compared to TiO$_2$ thin-film and multilayer TiO$_2$/polymer film devices$^{[8]}$ the presence of anionic W$_{12}$O$_{41}$$^{10-}$ spacers considerably improved the stability of the device characteristics and almost completely eliminated hysteresis in the I–V curves.

In reverse bias, the turn-on potential was slightly lower than the difference between the electron affinity of TiO$_2$, 4.1 eV, and the valence band energy of PAN (EB), 6.4 eV (Fig. 5, top left). The latter has been estimated by taking the optical π−π* bandgap as 3.92 eV, the position of the absorption band maximum (Fig. 4, Trace 1). However, this broad absorption band with an absorption-edge energy of 3.24 eV indicates the presence of occupied electronic states with energies down to 5.7 eV (dotted line in Fig. 5, top left). The EB conduction band is very flat with a width <0.05 eV and might not contrib-
ute to the electronic transitions lower in energy.\cite{17} This brings the expected reverse-bias turn-on potential into the range of 2.3–1.6 V, which is in reasonable agreement with the experimentally observed potential of 2.0 V. Hence, in reverse bias no current was observed until the bias overcame a potential approximately equal to the difference between the electron affinity of TiO$_2$ and the ionization potential of PAN, which suggests that a p–n junction was formed at the PAN/TiO$_2$ interface.

The possibility of barrier formation at the W$_2$O$_4$TiO$_2$/TiO$_2$ and W$_2$O$_4$TiO$_2$/PAN interfaces is not considered because of the small size (<1 nm) of the W$_2$O$_4$TiO$_2$ anions and the absence of continuous paratungstate layers in the multilayer films. In any case, the electron affinity of W$_2$O$_4$TiO$_2$ is relatively close to that of TiO$_2$ and would not significantly change the whole picture.

In summary, metal nanowires coated with 12 nm thick multilayer TiO$_2$/W$_2$O$_4$/PAN/SWNTox tube-shells have been shown to exhibit the characteristics of a built-in p–n junction at the TiO$_2$/PAN interface. These concentric shell structures were grown on metal nanowires by a simple, low-temperature, adsorption method using a combination of “in-membrane” and “on-core” layer-by-layer assembly. A rectification ratio >120 has been observed at 3 V, which represents a significant improvement over simpler, “on-core”, semiconductor-particle diodes.\cite{8} The characteristics we observe are close to those found in p–n junctions formed by crossing p- and n-type single-crystal Si nanowires\cite{38} and InP nanowires,\cite{39} although the rectification ratio is still inferior to that of single-crystal p-Si/n-GaN nanowire cross-point diodes.\cite{39} A strong similarity in the thickness, morphology, and electrical properties of films grown on metal nanowires and on planar substrates was found. This emphasizes the versatility of the wet, layer-by-layer, adsorption method. In particular, the availability of rectifying tube-shells on metal nanowires, which can be assembled into various kinds of cross-point structures, opens up the possibility of constructing logic gates and more complex circuits by means of electrofluidic, microfluidic, or chemically driven nanowire assembly.

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**One Volt Organic Transistor**

By Leszek Artur Majewski, Raoul Schroeder, and Martin Grell*

Organic field-effect transistors (OFETs) promise cheap, flexible, and disposable “plastic” electronics. Performance of organic electronics will be limited by the lower carrier mobility compared to inorganic semiconductors; however, there are a large number of potential OFET applications that require only moderate computing power, but demand low price.

A major problem that hinders the development of practical OFET devices is that current devices require rather high voltages to operate, while in a typical low-end application, the

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