Oxide Nanowires for Sensing, Photonics and Photovoltaics

Matt Law
Department of Chemistry, University of California, Berkeley

One-dimensional inorganic nanostructures are a promising class of basic building blocks for future optoelectronic, mechanical and energy conversion devices. In this dissertation, single-crystalline SnO_2 and ZnO nanowires are used as model materials in proof-of-concept demonstrations of nanowire-based photodetection, chemical sensing, thermometry, photonics and photovoltaics. Each demonstration leverages specific attributes of the wire shape, such as its ability to confine and conduct electrons and photons, to produce miniature devices with novel functionality. To begin, single oxide nanowires made by vapor deposition are fabricated into ultraviolet photodetectors and fast, stable and responsive gas sensors. Next, a conceptually new synthesis of multi-component nanowires is presented in which nanowires with rectangular cross-sections act as templates for the deposition of a complementary material. The resulting bilayer structures act as nanoscale temperature sensors that bend when heated or cooled and offer an ideal geometry for studying the dynamics of interfaces by electron microscopy. In addition, SnO_2 nanowires thinner than the wavelength of visible light are shown to function as versatile waveguides that are suitable for signal routing, frequency filtering and spectroscopy in integrated nanoscale optical circuitry. The length, flexibility and strength of these nanowires enable the construction of nanowire emitter-waveguide-detector junctions and other prototype assemblies. The final topic of this thesis is the development of ordered solar cell architectures based on arrays of nanowires coated with a molecular dye or encased in a polymer. A facile and flexible aqueous synthesis of ZnO nanowire arrays is presented, and the performance of three different types of nanowire solar cells discussed.

Nanowire Photodetectors and Chemical Sensors

Semiconductor nanowires are attractive materials for photodetectors and chemical sensors because their electrical conductivity is highly sensitive to both illumination and the nature and number of chemical species adsorbed to their surface. The strong photoconductivity of ZnO nanowires synthesized by the vapor-liquid-solid process led to our invention of fast and reversible optical switches with switching ratios of 10^4 under low-intensity ultraviolet light (Figure 1).[1] The magnitude and time response of the photocurrent is a product of electron-hole pair formation and electron doping caused by the photoinduced desorption of oxidants (e.g., O_2) from the wire surface. This surface effect is particularly pronounced in nanowires because the subsurface space charge regions are comparable in thickness to the nanowire radius.

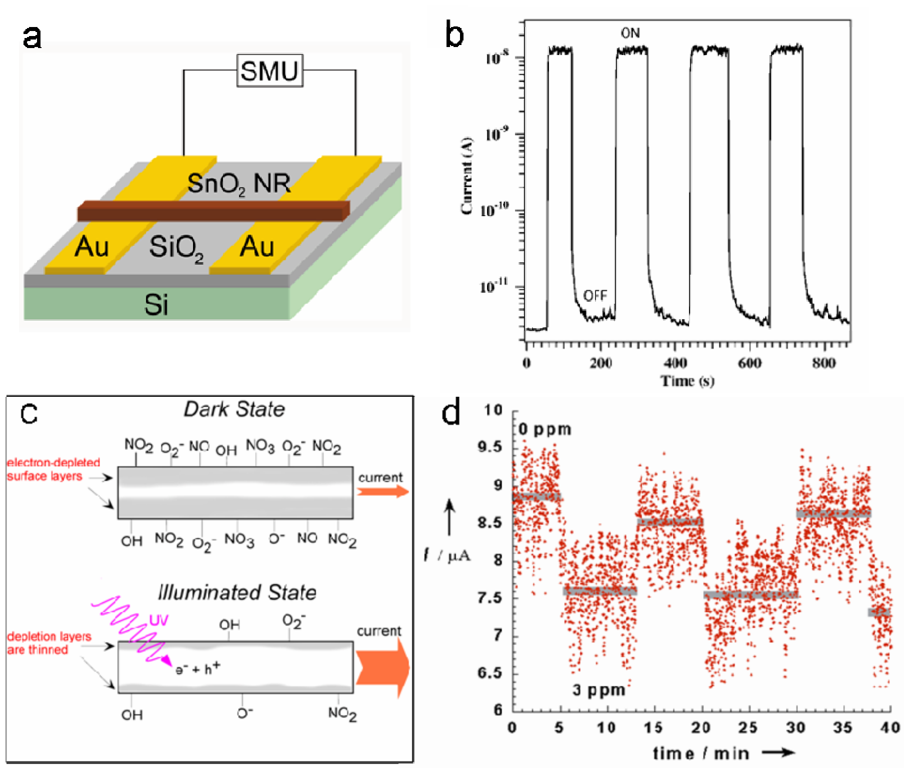

Figure 1. Nanowire light and chemical sensors. (a) Schematic of a single-nanowire device. (b) Photodetection with a ZnO wire. (c) The mechanism of sensing NO_2 with a SnO_2 nanoribbon. (d) Sensing NO_2 near the limit of detection.

Nanowire gas sensors can be more sensitive, stable and faster than traditional thin film sensors because they are ultrathin, single-crystalline channels with completely exposed surfaces. Nanoribbons[2] made of SnO_2 (a material common in commercial vapor detectors) have been investigated as sensors for NO_2, a smog-forming pollutant (Fig. 1c-d).[3] By using ultraviolet light instead of heat to activate NO_2 desorption, single-ribbon devices fabricated without lithography can operate at room temperature with ppm-level sensitivity and short response times. The specific mechanism of sensing was analyzed theoretically.[4] Nanowire sensors will remain interesting due to their potential for detecting very low concentrations of biomolecules[5] or pollutants with devices small enough to be integrated on a microchip or used in vivo.

Bilayer nanoribbons: interfacial dynamics and temperature sensors

Many potential applications require nanowires that possess built-in interfaces. For example, radial interfaces can function as *p*-*n* junctions, while longitudinal interfaces are useful as dielectric mirrors or for scattering phonons in thermoelectric nanowires. A new type of basic nanowire heterostructure is the bilayer nanowire, in which two nanowires are joined in a side-by-side configuration. A general synthesis of bilayer nanowires has been developed in which nanowires with rectangular cross-sections (nanoribbons) act as templates for the growth of a second material by pulsed laser or evaporative deposition.[6]

Bilayers are interesting because (*i*) they offer a route to making nanowires that are otherwise difficult to fabricate (e.g., doped semiconductors such as $Ti_{1-x}Co_xO_2$, perovskites and cuprate superconductors); (*ii*) they present heterojunctions in a geometry that is easily studied by TEM. For instance, epitaxial bilayers of copper and SnO_2 undergo a complex sequence of island formation, interdiffusion, chemical reactions and melting with increasing temperature[7] (Figure 2); (*iii*) they feature a radial asymmetry that can be used, for example, to produce bimetallic strips that bend when heated or cooled. The Cu-SnO_2 bilayers are ultrasmall and ultrasensitive heat detectors at low temperatures (Fig. 2). These bilayer nanowires are excellent platforms for investigating the mechanical properties of nanoscale composites.

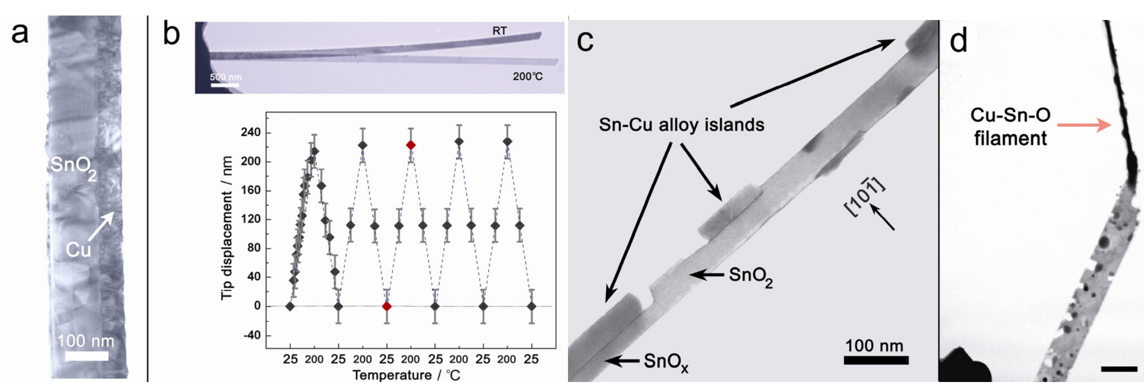

Figure 2. The thermomechanical behavior of Cu-SnO_2 bilayer nanoribbons: (a) An epitaxial bilayer (b) Reversible bending at temperatures <200ºC. (c,d) Island formation, etching and melting at higher temperatures.

Nanowire photonics: waveguides, multi-wire assemblies and spectroscopy

While the electrical integration of simple nanowire circuits has been achieved using lithography, optical integration, which promises more versatile, faster devices, is largely unexplored. Remarkably, the SnO_2 nanoribbons discussed in the previous sections are also excellent subwavelength optical waveguides that have been used to link nanowire light sources with detectors as a first step toward building photonic devices from nanowire circuitry.[8] The nanoribbon waveguides feature high aspect ratios (300-1500 μm × 100-300 nm), optical transparency, a large index of refraction, smooth surfaces, and sufficient flexibility and strength to be bent into complex shapes on silica surfaces with a sharp metal probe. These thin cavities preferentially confine blue light, making them natural short-pass filters. Prototype filter networks, directional couplers and optical grids based on multi-ribbon assemblies demonstrate that functional photonic elements can be built from nanowire units (Figure 3). Additionally, the injection of light pulses from multiple nanowire lasers into the same ribbon waveguide raises the exciting possibility of performing nanowire-based nonlinear wave mixing for spectroscopy-on-a-chip.

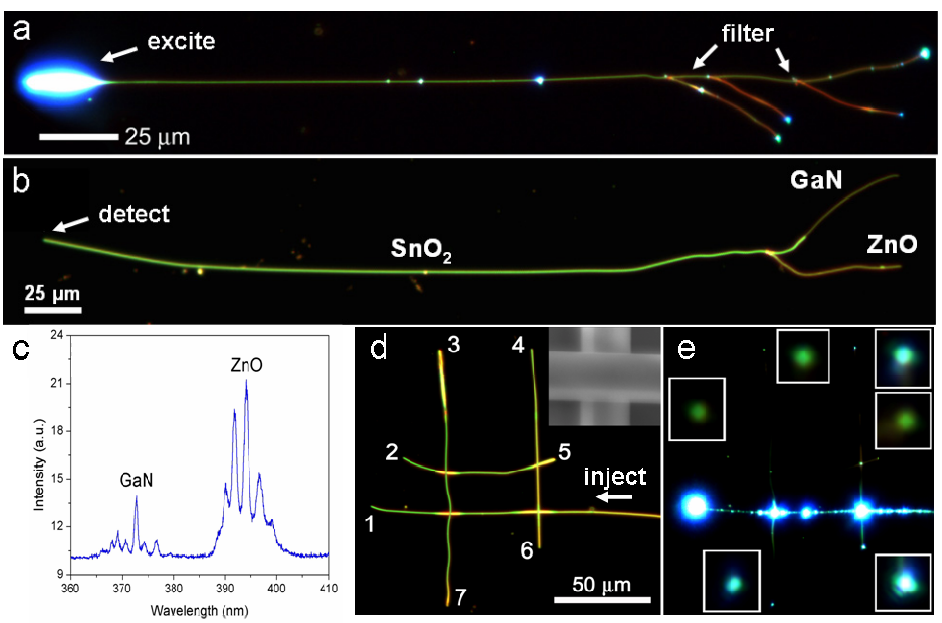

Figure 3. Multi-nanowire photonic elements: (a) A four-ribbon wavelength filter. (b,c) The optical coupling of multiple nanowire lasers to a single nanoribbon waveguide. (d,e) A nanoribbon optical grid, a prototype structure for nanowire-based optical relays and pixilated optical devices.

Nanowire waveguides also represent a new type of evanescent wave sensor, in which the evanescent electromagnetic field that extends outside of a wire cavity is used to detect nearby molecules in solution by absorption, fluorescence or inelastic scattering[9] (Figure 4). This is the first example of performing spectroscopy with nanowires, and highlights their potential for highly sensitive and specific sensing of biomolecules in microfluidic assays and in living tissue.

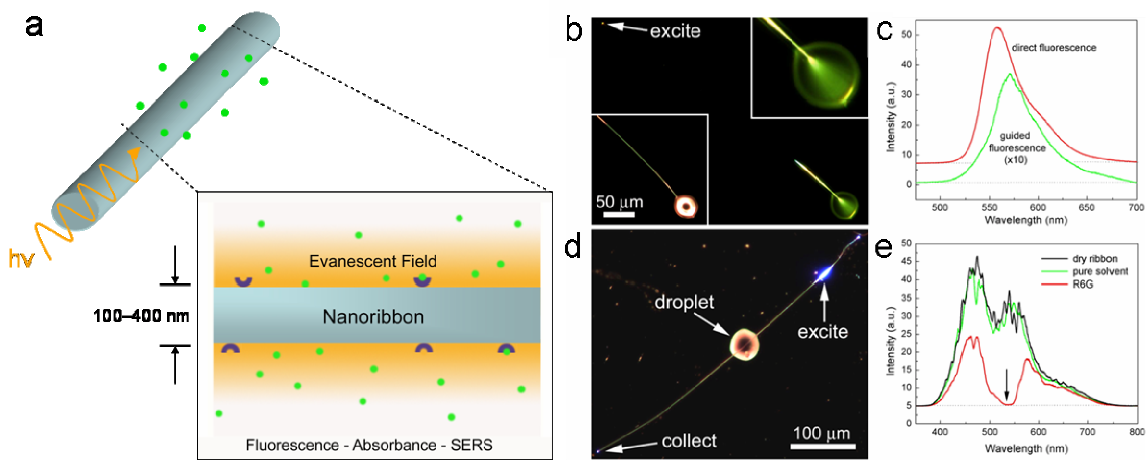

Figure 4. Optical spectroscopy with nanowire evanescent wave sensors: (a) General schematic of the process. (b,c) Fluorescence sensing of a droplet of Rhodamine 6G in 1,4-pentanediol at the tip of a nanoribbon. (d,e) Absorbance sensing of R6G. White light is created with the waveguide by photoluminescence of SnO_2.

Nanowire Solar Cells

Over the past decade, innovative photovoltaic architectures based on thick films of dye-sensitized oxide nanoparticles or blends of organic and inorganic materials have been introduced, with overall efficiencies reaching 11% and 5%, respectively.[10,11] Common to these nanostructured devices is a convoluted internal interface and a high degree of structural disorder, which results in slow charge transport that often limits the carrier collection yield and device efficiency. Replacing these disordered architectures with ordered nanowire arrays of optimal dimensions is a promising approach to boosting the carrier collection yield and power conversion efficiency of nanostructured solar cells.

An aqueous solution process has been developed to grow high-density arrays of single-crystalline ZnO nanowires with tunable aspect ratios and controllable orientations on virtually any substrate.[12] In this process, ZnO quantum dots deposited onto a surface by dip-coating serve as seed crystals for the subsequent growth of nanowires from solutions of zinc nitrate and amines.[13] The addition of polyamines that hinder the radial growth of the nanowires leads to an order-of-magnitude increase in the wire aspect ratio and surface area. Completely vertical wire arrays have been grown from crystallographically aligned ZnO islands made via a novel seeding approach based on the decomposition of zinc acetate (Figure 5).[14]

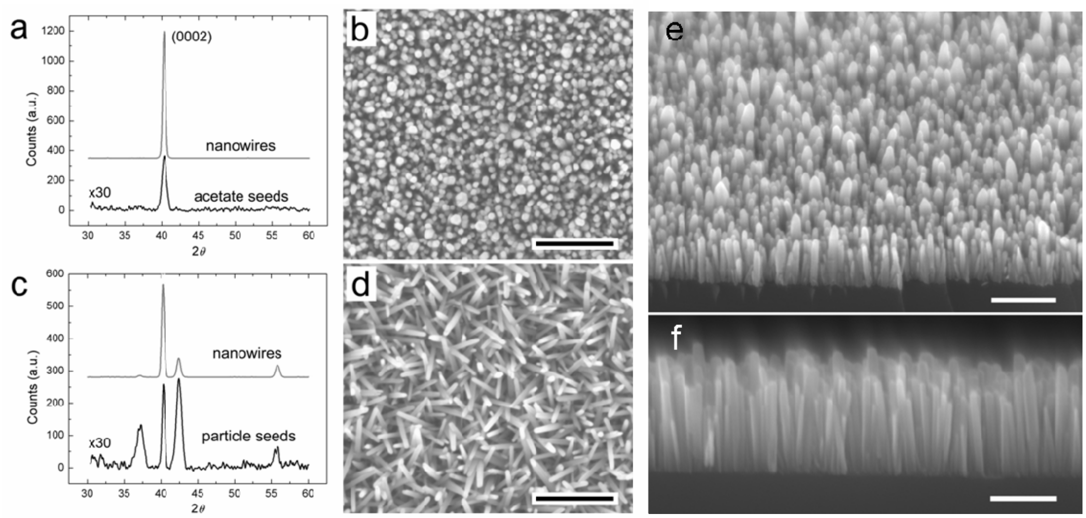

Figure 5. Growth of vertical ZnO nanowire arrays: (a,b) Aligned acetate-derived seeds result in vertical wires, while (c,d) preformed particle seeds grow into wires with a variety of orientations. Scale bars = 500 nm. (e,f) Tilted and cross-sectional images of the vertical arrays. Scale bars are 500 nm and 200 nm, respectively.

Dye-sensitized solar cells built from these ZnO wire arrays are highly efficient carrier collectors, showing 50-75% higher short-circuit currents than ZnO nanoparticle films and achieving conversion efficiencies of up to 1.5%, limited mostly by the inadequate surface area of our nanowire films[15] (Figure 5). Coating the nanowire electrode with a thin TiO_2 shell by atomic layer deposition causes a doubling of the cell efficiency as a consequence of a higher voltage and fill factor (Figure 6). Our best ZnO-TiO_2 core-shell nanowire dye-sensitized cells have efficiencies of 2.5%. Additionally, ZnO nanorod arrays have been encapsulated in spin-cast films of the hole-conducting polymer poly(3-hexylthiophene) to create vertical nanorod-polymer solar cells. Nanowire-based photovoltaic architectures represent an important advance in the fabrication of high-efficiency, inexpensive solar cells from nanoscale materials.

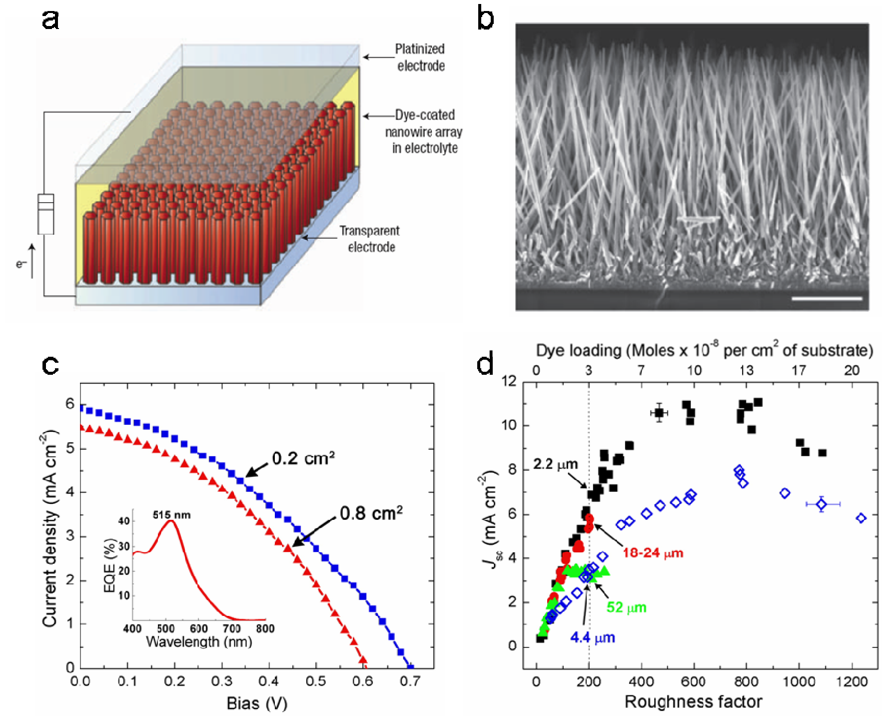

Figure 6. The nanowire dye-sensitized solar cell: (a) Device schematic (b) Cross-sectional image of the nanowire film (scale bar = 5 μm) (c) Performance of our best cells (d) Comparative short-circuit currents of nanowire and nanoparticle cells for different dye loadings. Circles = nanowires; squares = TiO_2 nanoparticles; diamonds = small ZnO nanoparticles; triangles = large ZnO nanoparticles.

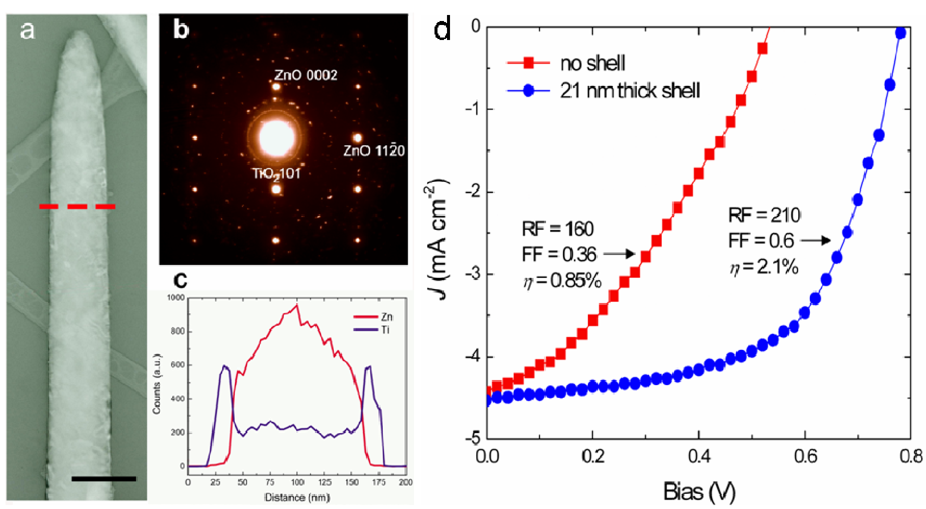

Figure 7. ZnO-TiO_2 core-shell nanowires and solar cells: (a-c) TEM characterization of a single core-shell wire with a 13.5 nm thick shell. The elemental line scan in (c) is taken across the dotted red line in (a). (d) Effect of a TiO_2 shell on device performance. RF = surface area, FF = fill factor and η = efficiency.

Conclusion

This dissertation pioneers the use of chemically-synthesized nanowires in photodetection, gas sensing, nanomechanics, photonics and solar cells. In doing so, it highlights a few of the many exciting possibilities for oxides in fundamental and applied nanoscience.

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