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PHOTOELECTROCHEMISTRY OF SEMICONDUCTOR NANOWIRE ARRAYS

Final Report

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A. Period covered: September 1, 2005 – May 31, 2009

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B. Publications resulting from DOE grant DE-FG02-05ER15749:

1. Manuscripts published:

1. A. P. Goodey, S. M. Eichfeld, K.-K. Lew, J. M. Redwing, and T. E. Mallouk, "Silicon nanowire array photoelectrochemical cells," *J. Am. Chem. Soc.* 124, 12344-12345 (2007).
2. P. G. Hoertz, Y. I. Kim, W. J. Youngblood, and T. E. Mallouk, "Bidentate dicarboxylate capping groups and photosensitizers control the size of IrO₂ nanoparticle catalysts for water oxidation," *J. Phys. Chem. B.* 111, 6945-56 (2007).
3. S. M. Eichfeld, T. T. Ho, C. M. Eichfeld, A. Cranmer, S. E. Mohny, T. S. Mayer, and J. M. Redwing, "Resistivity measurements of intentionally and unintentionally doped template grown silicon nanowire arrays," *Nanotechnology* 18, 315201 (2007).
4. R. S. Woo, R. Xiao, Y. Kobayashi, L. Gao, N. Geol, M. Hudait, T. E. Mallouk, and R. F. Hicks, "Effect of Twinning on the Photoluminescence and Photoelectrochemical Properties of Indium Phosphide Nanowires Grown on Silicon (111)," *Nano Letters*, 8, 4664-4669 (2008).

2. Manuscripts in preparation, submitted, or in press:

1. S.M. Eichfeld, H.T. Shen, C.M. Eichfeld, E.C. Dickey and J.M. Redwing, "Thermodynamic limitations on the growth of epitaxial silicon nanowires by the vapor-liquid-solid technique using SiCl₄," manuscript in preparation.
2. C.E. Kendrick, S.M. Eichfeld, J.M. Redwing, Y. Yuwen, H. Yoon, T.S. Mayer, G. Barber and T.E. Mallouk, "Effects of surface preparation on the diode characteristics of radial p-n junction silicon wire arrays solar cells," manuscript in preparation.

C. Progress Summary

1. Project Objectives

The goal of our DOE-supported research has been to synthesize and study semiconductor nanowire arrays as photoelectrochemical and photovoltaic devices. Semiconducting nano- and microwire arrays represent a promising alternative to single-crystal and polycrystalline semiconductor solar cells for the photochemical production of hydrogen

from water. In addition to the possibility of attaining high energy conversion efficiency at low cost, these arrays enable novel designs for direct solar water splitting without wiring to an external electrochemical cell. The goals of this project were to demonstrate photoelectrochemical energy conversion in these arrays, first in simple liquid junction regenerative cells that make electricity, and then ultimately in multijunction electrolytic cells that can drive overall water splitting. The key tasks were to control the growth, doping, and interfacial chemistry of Si and compound semiconductor nanowires, to characterize the nanowires chemically and electronically, and to study photochemical charge separation and water splitting in different nanowire array architectures.

This project combined the expertise of the Redwing group in growing and electronically characterizing semiconductor nanowires with that of the Mallouk group in photoelectrochemical measurements, nanomaterials synthesis, and electrocatalysis. Previous work by Redwing showed that Si nanowires could be grown as arrays of high quality single crystals by chemical vapor deposition in the pores of anodic aluminum oxide (AAO) membranes. This method in principle offered a route to inexpensive, polycrystalline electrodes that will have solar conversion efficiencies similar to those of expensive single crystal devices. The major scientific questions that were addressed, beyond the question of whether the target structures could be produced, related to the roles of dimensionality, impurities, and interfaces in promoting light-induced charge separation and recombination. By fabricating simple electronic and electrochemical devices from high quality semiconductor nanowires, as shown schematically in Fig. 1, we have been able to develop an understanding of these fundamental properties at the same time as we developed and studied solid state and liquid junction photovoltaic cells.

a. Liquid junction solar cells based on semiconductor nanowires.

We reported the first silicon nanowire solar cell in 2007,¹ and in the intervening two years, that paper has been cited 38 times and has stimulated research efforts in a number of other groups. We also reported the first nanowire solar cell made from indium phosphide, a compound semiconductor that is ideally matched to the solar spectrum.² Both studies revealed the critical role of defects and the nanowire surface in controlling the photovoltage of liquid junction solar cells. In subsequent work supported by DOE-EERE, we have built on these findings to design silicon microwire arrays that have greatly improved photovoltages in liquid junction cells, as well as radial p-n junction silicon microwire cells with solar conversion efficiencies of over 2%.³

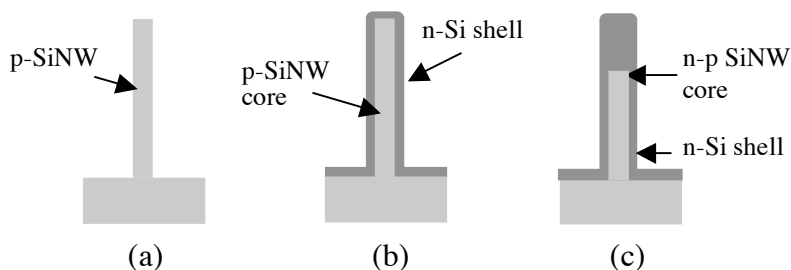


Fig. 1. Epitaxially grown Si nanowire structures:
 (a) p-type nanowires
 (b) core/shell p-n junction
 (c) axial/shell p-n junction

b. Multijunction nanowires for overall water splitting with visible light.

Nanowires offer some interesting new possibilities for device geometries that are not possible with single crystals. For example, doping of the nanowire array in “totem pole” fashion opens the intriguing possibility of making arrays of wires that can act individually as photocatalysts for overall water splitting. In this scenario, a series of p-n junctions (separated by thin tunnel junctions composed of p^+ and n^+ layers) would create an additive series photovoltage. In these devices each multi-junction Si wire is basically a

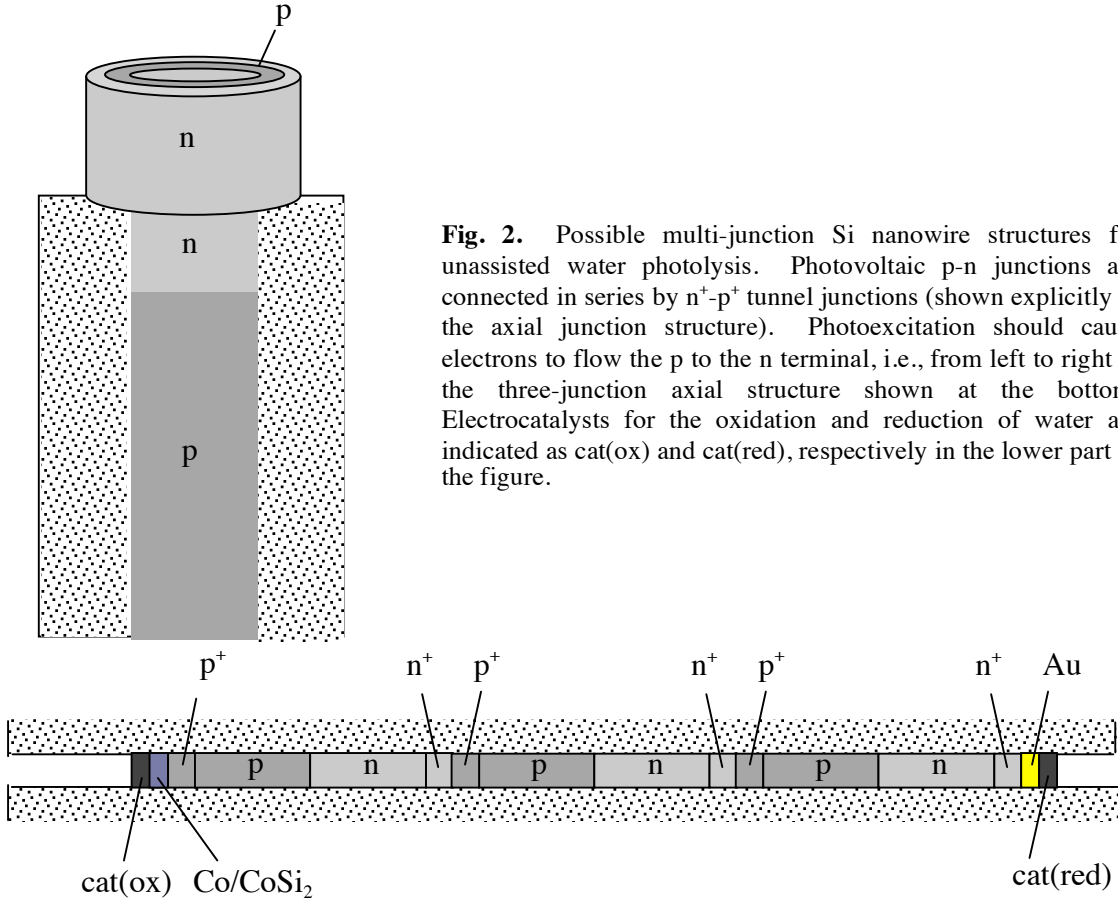


Fig. 2. Possible multi-junction Si nanowire structures for unassisted water photolysis. Photovoltaic p-n junctions are connected in series by n^+ - p^+ tunnel junctions (shown explicitly in the axial junction structure). Photoexcitation should cause electrons to flow the p to the n terminal, i.e., from left to right in the three-junction axial structure shown at the bottom. Electrochemical catalysts for the oxidation and reduction of water are indicated as cat(ox) and cat(red) , respectively in the lower part of the figure.

membrane bound, nanoscale version of the Texas Instruments Si p-n series photocell,^{4,5} or of the series photoelectrochemical cells developed by Smotkin, et al.^{6,7} The Texas Instruments system utilized two series p-n junctions for direct photolysis of HBr. With 3-4 series junctions and appropriate electrocatalyst particles grown at the ends of the wires, it should be possible to develop sufficient photovoltage to split water, generating hydrogen and oxygen on the n^+ and p^+ ends of the nanowires, respectively. Fig. 2 shows some possible architectures that combine involve axial and/or radial doping in order to achieve such as series arrangement of p-n junctions in individual nanowires. One of the major challenges in achieving this goal is to learn to control the doping profile of the nanowires along their length, and to understand the role of interfacial layers that control charge separation and recombination on the nanoscale. A second problem is to develop electrocatalysts for hydrogen and oxygen evolution from water, which can be grown at

the appropriate ends of the series of p-n junctions. Ideally, these catalysts should not absorb light too strongly and should perform the water oxidation and reduction reactions at low overpotential. Because the four-electron oxidation of water is the most kinetically demanding half-cell reaction, our efforts in this project have been concentrated on developing stable nanoscale iridium oxide catalysts that could be deliberately tethered to metal or semiconductor surfaces for electro-oxidation of water. In this project, we developed a robust chemistry for capping iridium oxide particles with bidentate ligands that prevent their aggregation and allow tethering to oxide surfaces.⁸ In subsequent DOE-BES supported research, we have demonstrated visible light water splitting in dye-sensitized solar cells containing these catalysts.⁹ We have also developed very active rhodium oxide cluster catalysts for the electrochemical reduction of water to hydrogen.^{10,11}

2. Growth of silicon nanowire arrays in anodic aluminum oxide membranes

We developed a process to grow single crystal Si nanowires within the pores of AAO, as shown schematically in Fig. 3. resulting in the directional growth of single crystal nanowires within the template. A thin layer of silver is initially evaporated on one side of the membrane to serve as a backside electrical contact. A segment of silver is then electrodeposited in the membrane, followed by a segment of a contact metal and finally a thin (<0.2 μm) segment of gold. The silver segment serves as a spacer to position the gold catalyst within the pore. The contact metal segment can be varied in order to optimize ohmic contact to the silicon nanowire. In our initial experiments, we used cobalt as a contact metal to p-type silicon nanowires where a cobalt silicide forms at the Co-Si nanowire interface. The thin gold segment serves as the catalyst for silicon nanowire

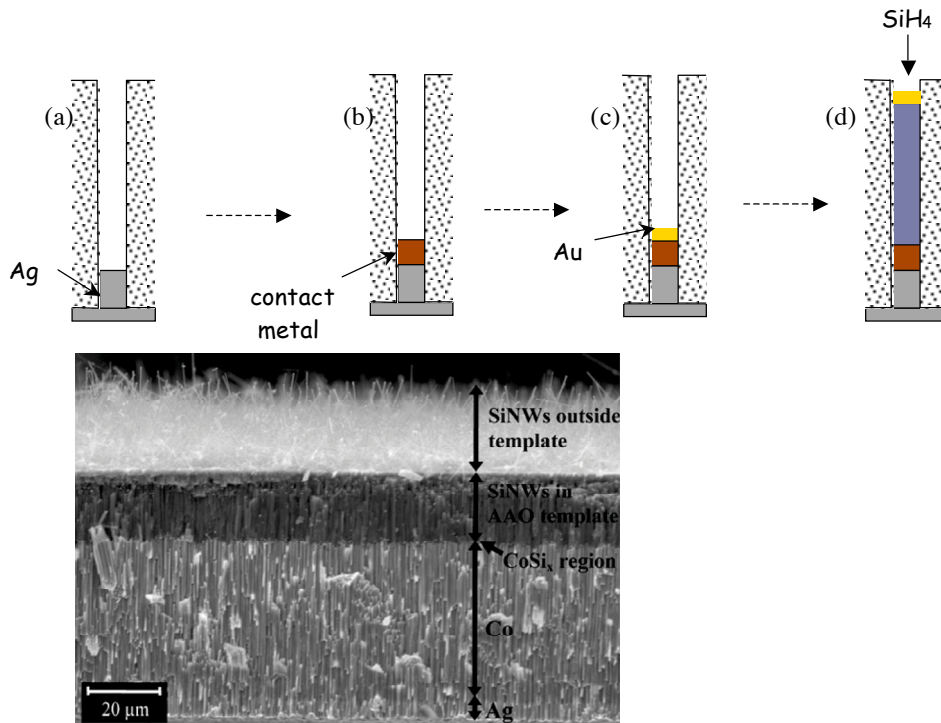


Fig. 3. Nanowire array fabrication process. (a) thermal evaporation of Ag backside contact layer and Ag electrodeposition, (b) electrodeposition of contact metal and (c) Au catalyst and (d) VLS growth of Si nanowire. SEM image at the lower left is a cross-sectional view of an AAO membrane in which Si nanowires have been grown on ~50 micron long Co contacts. Hemispherical Au catalyst particles can be seen at the tips of the nanowires.

growth. VLS growth was then carried out by heating the metal-impregnated membrane

in an ambient containing silane gas (SiH_4). In the VLS process,¹² gold catalyzes the decomposition of SiH_4 resulting in the formation of a liquid Au-Si alloy droplet at temperatures greater than $\sim 360^\circ\text{C}$ (the Au-Si eutectic temperature). Upon supersaturation, silicon is precipitated from the melt in the form of a nanowire, which grows in length along the axial direction. At reduced temperature ($< 500^\circ\text{C}$) and pressure (< 10 Torr), the silicon thin film deposition rate from SiH_4 is low, consequently, the SiH_4 diffuses into the pores and selectively decomposes on the gold catalyst surface.¹³ The liquid alloy catalyst is then pushed upward in the pore as the silicon nanowire grows in length, and the nanowire eventually emerges from the top surface of the membrane.

The resistivity and carrier type of individual silicon nanowires, released from the membrane, were measured using a back-gated four-point electrical test structure (Fig. 4). Field-assisted assembly^{14,15} was used to align the nanowires from solution onto pre-patterned contact pads on the test structure. In general, the nanowire resistivity decreased as increasing amounts of both p-type and n-type dopant are added during growth. The silicon nanowires grown without the addition of a dopant source (undoped) were determined to be p-type and the unintentional acceptors fully compensated donors at low n-type doping levels ($\text{PH}_3/\text{SiH}_4 = 2 \times 10^{-5}$). We measured substantially higher resistivities ($\sim 10^3 \Omega\text{-cm}$) on undoped silicon nanowires grown on oxide-coated silicon substrates under similar conditions in our reactor, which suggests that the alumina membrane was the source of background p-type doping in the wires.¹⁶

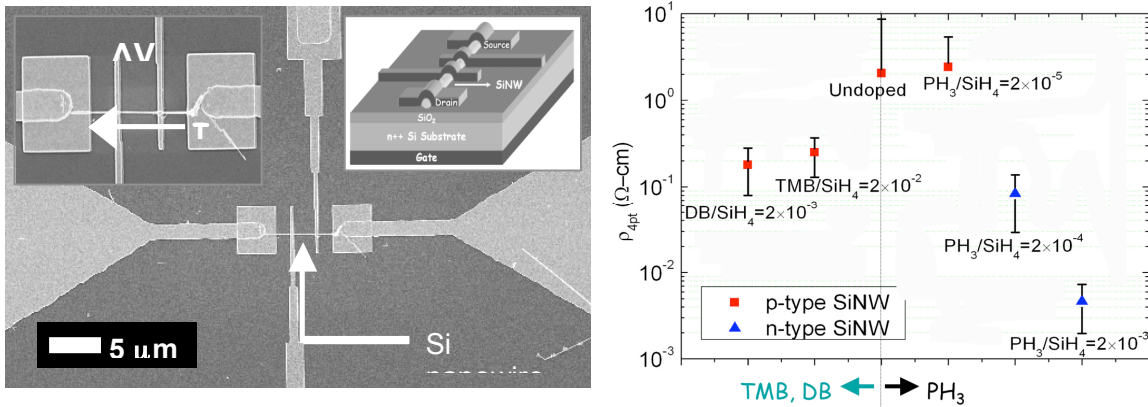


Fig. 4. Left: FESEM image of the back-gated test structure used for four-point resistance and gate-dependent conductance measurements. A high magnification image of the SiNW is shown as an inset along with a 3D schematic of the cross-section of the test bed structure. Right: Resistivity of undoped and intentionally doped silicon nanowires as a function of dopant/Si gas ratio. Carrier type (p versus n) was determined from gate-dependent current-voltage measurements.

In order to circumvent the p-type impurity problem encountered with the AAO templates, the VLS growth of SiNW arrays on gold-coated (111) Si substrates was investigated using SiCl_4 as the silicon source. Wire orientation was found to be strongly dependent on the growth temperature with $\sim 80\%$ of the SiNWs being $\langle 111 \rangle$ oriented perpendicular to the substrate at 900°C but dropping to $\sim 18\%$ at 800°C . At low SiCl_4 partial pressures (P_{SiCl_4}), the growth rate of the wires increases linearly with increasing P_{SiCl_4} reaching a maximum of $\sim 3 \mu\text{m}/\text{min}$ at P_{SiCl_4} of 3.7 Torr. Beyond this point, the growth rate begins to decrease with increasing P_{SiCl_4} due to a shift in gas phase equilibrium which promotes the reverse HCl etching reaction. The resistivity of nominally undoped SiNWs grown

under these conditions was studied using four-point measurements carried out on individual SiNWs released from the substrate by ultrasonic agitation and assembled onto pre-patterned back-gated test structures using field-assisted assembly. Nominally undoped SiNWs grown on p-type (111)Si substrates ($r=1-15$ W-cm) were determined to be p-type with a room-temperature resistivity on the order of 800 W-cm, which was two orders of magnitude higher than that of SiNWs grown in the AAO templates indicating a reduction in unintentional impurity incorporation. SiNW samples grown under these conditions were used in subsequent photoelectrochemistry studies.

3. Photoelectrochemistry of silicon nanowire arrays

Our initial photoelectrochemical experiments with p-type SiNW electrodes grown in AAO were quite disappointing in that no photoeffects were observed. These experiments employed a non-aqueous electrolyte (acetonitrile) and a redox mediator ($[\text{Ru}(\text{bpy})_3]^{2+}$) with a sufficiently negative formal potential that one obtains an open circuit photovoltage of 450-500 mV with single crystal p-Si illuminated with white light. In light of the data shown in Fig. 4, we reasoned that adventitious p-type doping from Al^{3+} ions in AAO resulted in a very thin space-charge layer, and therefore large dark currents. In order to

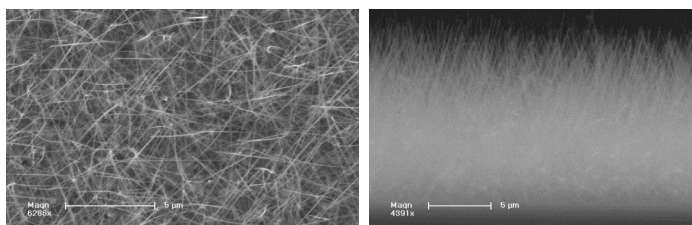
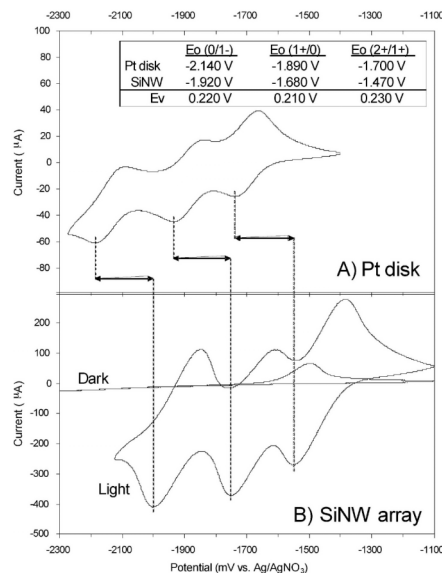


Fig. 5. Left: Top and side view scanning electron micrographs of a free-standing p-Si nanowire array grown on Si. Right: Cyclic voltammograms (200 mV/s) of (A) a Pt disk electrode and (B) a silicon nanowire array photocathode, both light and dark, as indicated. The inset table shows the midpoint potentials (E_0) of the $\text{Ru}(\text{bpy})_3$ anodic and cathodic peaks at the metallic and semiconductor electrodes, and the calculated photovoltages (E_v).



grow SiNW arrays with lower doping density, a p-type (111) Si wafer with a 1 nm Au film was used as the substrate. Doping was controlled by simultaneous introduction of trimethylboron (TMB). The nanowires were approximately 14 μm long, with an average diameter of 57 ± 12 nm. Fig. 5 shows that these nanowires gave greatly reduced dark currents and photovoltages in the range of 230 mV under white light illumination in $[\text{Ru}(\text{bpy})_3]^{2+}/\text{acetonitrile}$ solutions.¹ Importantly, the scan rate dependence of the peak current demonstrated unequivocally that the photocurrent came from the nanowire array rather than from the p-Si substrate. This experiment established at the proof-of-concept level that one could make a liquid junction solar cell from SiNW arrays grown by the VLS method. The relatively low photovoltage obtained, relative to single crystal p-Si (500-550 mV) suggests that bulk or surface carrier recombination is significantly faster with the high surface area nanowire array than it is at a planar single crystal

photoelectrode. These effects could arise from Au impurities, from crystal defects within the nanowires, or from dangling bond states at the Si surface.

Based on these findings, we investigated the dependence of the open circuit photovoltage of liquid junction Si wire arrays on the wire diameter. Nominally undoped Si wire arrays were grown by the VLS method from SiCl_4/H_2 mixtures using lithographically patterned Au catalyst islands. Following a procedure developed by Atwater and coworkers,¹⁷ silicon oxide “corrals” were fabricated lithographically in order to prevent the coalescence of the gold catalyst islands and to define their diameters. Fig. 6 illustrates results obtained by this technique. The photoelectrochemical open circuit voltage in this case was typically 300-400 mV, comparable to values obtained by the Atwater/Lewis group for n-Si microwire arrays.¹⁸ We have recently measured substantially higher

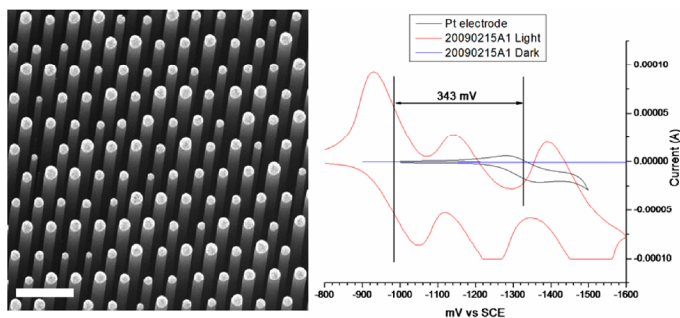


Fig. 6. Top view SEM image of an array of p-Si microwires grown by VLS from SiCl_4/H_2 on a patterned Si substrate, and cyclic voltammetry in 2 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ acetonitrile solution showing ~ 340 mV open circuit photovoltage in a liquid junction cell.

photovoltages (550 mV) with similar columnar structures made by reactive ion etching of p-Si wafers, suggesting that Si wires grown by the VLS method from Au, despite their single crystalline texture, have bulk or surface defects that compromise the photovoltage. We are currently investigating annealing and surface chemical treatments, as well as alternative catalyst metals, that may allow us to overcome this problem.

4. Photoelectrochemistry of indium phosphide nanowire arrays

Indium phosphide is an interesting photoelectrode material because of the high reported photovoltage of liquid junction cells fabricated with p-type InP, as well as reports of efficient hydrogen evolution from liquid junction p-InP solar cells. [12,13] It is also a prototypical material for studies of nanowire arrays of III-V direct gap semiconductors. One expects different issues in this case than with p-Si wire arrays, which as an indirect gap material has a much longer absorption length.

Most indium phosphide nanowires are prepared by the classical VLS method,¹⁹ using gold catalysts. The possibility of gold contamination is problematic since, as noted above, Au introduces deep-level impurity states that adversely affect solar cell performance.²⁰ Self-catalyzed growth using liquid indium droplets was therefore investigated to overcome this problem. In addition, InP nanowires are known to possess twinning defects due to the low stacking fault energy of the semiconductor crystal.^{21,22} We also investigated the effects of these defects, as well as the effect of nanowire diameter, on the photoelectrochemical properties of p-InP nanowire arrays.

The growth experiments were carried out by Prof. Robert Hicks and coworkers at UCLA, by vapor-phase epitaxy (MOVPE), using trimethylindium and tertiarybutylphosphine. Two different types of substrates, Si (111) with 0° and 4° miscut angles, were used in order to modulate the density of twinning defects in the nanowire arrays. Although the growth process was far from optimized, we obtained encouraging results in the sense that the nanowire arrays showed both photoluminescence and open circuit photovoltages in liquid junction cells that were dependent on the defect density and the diameter of the nanowires.² These results are summarized in Fig. 7.

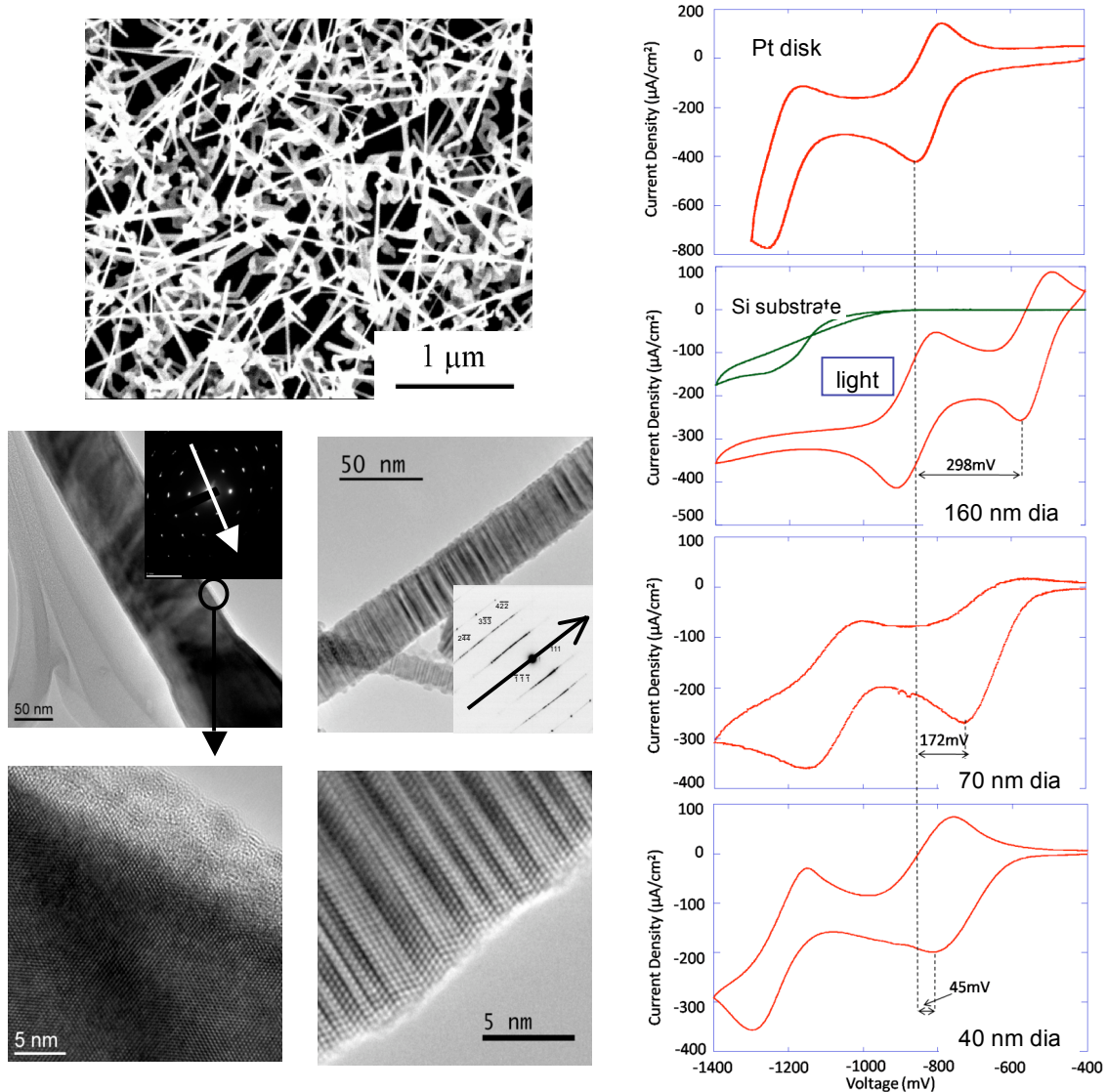


Fig. 7. Top view SEM image of an array of p-InP nanowires grown by MOVPE on Si (111) substrates. The wire defect density (lower left TEM images) was controlled by using miscut substrates and by annealing in the presence of the phosphorus source prior to In deposition. Cycling voltammetry showed, for wire arrays without twin defects, an increasing photovoltage with increasing wire diameter, consistent with the results obtained for VLS-grown arrays of Si nano- and microwires.

5. Catalysis of the water oxidation reaction

An important issue to address for the ultimate goal of photochemical water splitting using semiconductor nanowire arrays is the catalysis of the water oxidation and reduction reactions. The oxidation of water is arguably the most difficult problem. Because it is a four-electron process, water oxidation at moderate overpotential (100-300 mV) is slow even with the best catalysts. For photoelectrodes operating under one sun illumination, catalyst site turnover rates in the range of several hundred per second are needed. Despite much recent progress in the design of molecular water oxidation catalysts,²³⁻²⁹ such fast site turnover rates have not been achieved at low overpotential.

Transition metal oxides have been known for many years to be good catalysts for water oxidation.^{30,31} Several groups have now studied water oxidation by $\text{IrO}_2 \cdot n\text{H}_2\text{O}$ nanoparticles in both electrochemical and photochemical systems.³²⁻³⁵ With these amorphous, hydrated nanoparticles, O_2 turnover rates of $\sim 40 \text{ s}^{-1}$ per surface Ir atom were measured under photochemical conditions at pH 5.7, where the overpotential for water oxidation by $[\text{Ru}(\text{bpy})_3]^{3+}$ is 370 mV.³⁴ Murray and coworkers found electrochemical turnover rates of $5\text{-}6 \text{ s}^{-1}$ per Ir atom (of which about 50% are on the surface) at 250 mV overpotential with mesoporous films of 2 nm $\text{IrO}_2 \cdot n\text{H}_2\text{O}$ particles.³⁵

In order to “package” active $\text{IrO}_2 \cdot n\text{H}_2\text{O}$ nanoparticles for attachment to semiconductor surfaces, we investigated a variety of oxophilic capping ligands. We found that the alkaline hydrolysis of IrCl_6^{2-} in the presence of dicarboxylic acids, especially succinate and malonate derivatives, gave stable 1-2 nm diameter capped particles. Fig. 8 compares the aggregated “raspberry” morphology of iridium oxide particles prepared with citrate capping ligands to the stable 1-2 nm diameter colloids made with butylmalonate ligands.

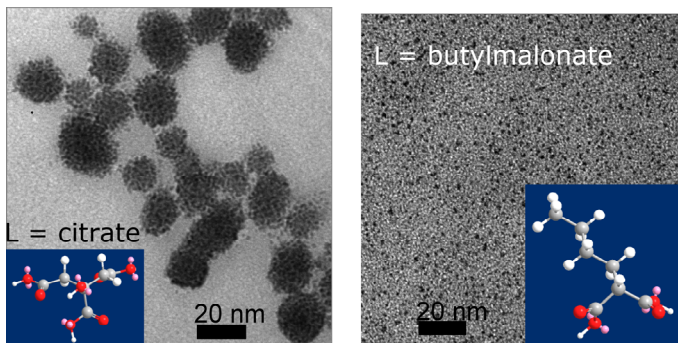


Fig. 8. $\text{IrO}_2 \cdot n\text{H}_2\text{O}$ colloids prepared by alkaline hydrolysis of IrCl_6^{2-} in the presence of citrate (left) and butylmalonate (right) capping ligands.

These stabilized catalyst particles could be linked to $[\text{Ru}(\text{bpy})_3]^{2+}$ derivatives through the capping ligands.⁸ In these covalently linked sensitizer- $\text{IrO}_2 \cdot n\text{H}_2\text{O}$ diads, the first-order electron transfer rate from Ir(IV) to Ru(III) was $8 \times 10^2 \text{ s}^{-1}$, corresponding to electron transfer on the millisecond timescale. These results suggest that it should be possible to pattern semiconductor wire surfaces with silane molecules that terminate in dicarboxylate ligands, to grow stabilized iridium oxide catalyst clusters where they are needed for overall water splitting systems.

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