ELECTRO-OPTICAL PROPERTIES
of CdSe NANOWIRES

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Abstract

by

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This Thesis describes the results of electro-optical experiments performed on solution grown CdSe nanowires (NWs). TEM images reveal that such NWs have diameters between 6-40 nm, are highly crystalline and exhibit large aspect ratios (>1000, length/diameter). The morphologies of these NWs range from straight to hyper-branched.

Absorption cross-sections determine how efficiently a material absorbs light. In this Thesis we calculate single NW absorption cross-sections based on UV-VIS linear extinction, TEM, and inductively coupled plasma atomic emission spectroscopy experiments. Obtained numbers compare well with theoretical estimates, having order of magnitude values of $10^{-11}$ cm$^2$ per 1 μm length of a 10 nm diameter NW.

Synthesized CdSe NWs are emissive and are easily detectable at the single wire level. A surprising observation from these experiments is the modulation of the NW
emission intensity by applied electrical fields. Specifically, the part of the wire closest to
the positive electrode exhibits up to a 10x increase in intensity. Simultaneous quenching
of identical magnitude is detected on the other side of the wire. Our current working
hypothesis is that mobile electrons driven by the external electrical field passivate
emission quenching centers resulting in local emission enhancement. Similarly, the
smaller density of electrons on the other side of the wire yields emission quenching.

To confirm the existence of these mobile carriers we perform electrophoresis
measurements on NWs. Observed single wire translational and rotational dynamics can
be explained by mobile carriers residing on or within the NWs. A lower limit for the
carrier density of NWs in oleic acid is estimated to be \( \sim 1 \, \text{charge/\mu m} \).

Since light absorption results in both NW emission as well as the photogeneration
of carriers, photoconductivity measurements are also possible. While doing such
measurements, we unexpectedly discovered that randomly oriented NW networks could
exhibit a significant photocurrent polarization anisotropy with values of \( \rho=0.25 \) \( (\sigma=0.04) \)
under excitation with linearly polarized light. The remarkable conclusion from this result
is that polarization sensitive devices can be built from random NW networks without the
need to align component wires. To explain these results a simple geometric model has
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1.1 Project outline

Since the invention of the transistor in 1947 its size has shrunk ~ 100,000 times. Nowadays ~100 million transistors exist on ordinary Intel or AMD computer processors, occupying the same area as their grand-grand-grand-ancestor alone. By the same token, the invention of semiconductor hetero-structures at the end of 60’s resulted in a dramatic reduction in the size of lasers (from meters to millimeters). We have all benefited from these scientific and technological breakthroughs. For example, the miniaturization of optical and electronic components has led to new medical procedures, accessible global telecommunication, as well as live-time weather and disaster tracking. Furthermore, new educational technologies have quickly spread around the world making our lives full of new opportunities.

When progressing from micron to sub-micron length scales of electronic elements, the cost of traditional, Si-based, micro-fabrication fabs increases significantly. To illustrate, the current price for a turn-key 65 nm technology fab is $2-3 billion! Even if you have this money in your pocket and are ready to invest it in a new generation of nanoelectronic fabs, many scientific and technological challenges remain such as carrier scattering on single imperfections, heat dissipation issues, and the physical and chemical transformation of materials. All must be understood before any further steps are to be
made. Acknowledging the difficulties of “classical” Si technologies, researchers have started looking for alternative, easier, and less expensive ways to the nanoworld. One alternative way, which has gained recent popularity, considers the “bottom up” assembly of functional elements out of small nanostructures. It is here that chemistry plays a leading role since it is within the scope of chemistry to synthesize absolutely identical nanoparticles and to find ways for assembling them into more complex (functional) structures.

A number of reliable methods for synthesizing quantum dots (QDs), carbon nanotubes (CNT), nanorods (NRs), and nanowires (NW) have been developed within the last four decades. Since my Thesis is about the optical and electrical properties of nanowires, I will briefly describe their history. The story of NWs starts in the mid 60’s with Wagner and Ellis at Bell Labs. [1] They found that small molten Au particles formed out of a metal film heated to 950 °C can initiate the growth of Si “whiskers” in the presence of silane vapor. This new growth technique was named vapor-liquid-solid (VLS) growth because the chemical precursors involved successively undergo transformation from gas to liquid (within the molten metal catalyst) to solid in the form of a one-dimensional (1D) nanostructure. The interest in the properties of 1D structures grew quickly but then faded in the 80’s. The interest in VLS was renewed during mid 90’s when Lieber demonstrated that high quality crystalline nanowires with narrow diameters could be obtained via the laser ablation of a metal catalyst film. [2] Further developments in the method have resulted in heterostructured NWs [3, 4] as well as core/shell species. [5] A recent review on such heterostructures can be found in Ref. 6.
However, prior to the reincarnation of VLS, Buhro discovered an analogous process to VLS growth that could be conducted in solution. He called it solution-liquid-solid (SLS) growth. [7] As apparent from the name, it occurs in liquids where low-melting metal particles (In, Sn, Bi and Ga) are employed as growth catalysts. The decomposition of chemical precursors on molten metal particles causes subsequent saturation of the catalyst with metal ions, which ultimately precipitate leading to the one-dimensional growth of nanowires. [8] SLS has successfully been applied to the growth of Ge [9], InP, InAs, GaAs [10, 11], ZnTe, CdSe, CdTe [10, 12], PbSe [13], CdS [14], and PbS [15] wires.

Other methods for synthesizing nanowires include: a) template-based growth employing porous anodized aluminum oxide (AAO) followed by subsequent etching of the template [16]; b) oriented attachment of nanocrystals and the formation of chain-like structures due to dipole-dipole attractions [17]; and c) solvo/hydrothermal growth where the NWs are formed out of mixture of precursors by heating them in the presence of surfactants. [18] The bottom line is that many different chemical routes are available today for synthesizing high quality metal and semiconductor nanowires.

Many advantages of using NWs originate from their 1D nature. Namely, the two dimensional confinement of carriers in NWs leaves just one degree of freedom for carrier transport. This enables high carrier mobilities and a natural resistance to scattering from surface imperfections. [19] This discovery has stimulated intense research on carrier transport in single NWs. [20] On the optical side, quantization effects increase carrier binding energies [21] and may result in mobile one-dimensional (1D) excitons, emission and excitation polarization sensitivities as well as other interesting optical phenomena.
[22] Biological sensors [23], single electron diodes [24] and transistors [25], polarization sensitive detectors [26], lasing [27], and photovoltaic applications [28] are areas where nanowires will play a significant role in the nearest future. Relevant reviews regarding NW applications can be found in Ref. 29-31.

An intriguing system that combines numerous aspects of abovementioned 1D carrier physics is solution grown CdSe NWs. These wires potentially exhibit quantum confinement effects (diameter 7-10 nm, bulk exciton Bohr radius 5.6 nm) and possess alternating zincblende (ZB) and wurtzite (W) segments. From a structural perspective, this ZB/W phase admixture is responsible for the recent discovery of branching in CdSe NWs. [12a] From an electronic standpoint, however, such alternating ZB and W sections are theoretically responsible for the creation of a Type-II homomaterial heterostructure arising from staggered conduction and valence bands along the wire. [32] There exists numerous studies on the electrical properties of NWs but only a few focus on their optical characterization. In this Thesis I present results from optical and electrical measurements performed on highly crystalline, high aspect ratio (>1000:1 length-to-diameter), narrow diameter (10-20 nm) CdSe nanowires grown by SLS.

How effectively a particular substance absorbs electromagnetic radiation can be characterized by their absorption cross-section. Experimental estimates of these optical constants represent an area of key interest in nanoscience. Specifically, a direct measure of how well a nanostructure absorbs light holds wide use in fundamental studies as well as in applied interests, both involving low dimensional materials such as colloidal QDs and more recently, solution-based semiconductor NWs. For example, such values are useful in quantifying properties such as sample concentrations, fluorescence quantum
yields, QD/NW photodetector conversion efficiencies, external photovoltaic efficiencies, lasing thresholds and multi-carrier excitation regimes. Despite the recognized usefulness of these values, it has been a challenge to measure the absorption cross-sections of chemically synthesized NWs. Unlike molecules or other systems with well defined molecular weights, solution-based NWs do not possess such exact physical properties. This is despite recent successes in solution-based syntheses yielding narrow NW diameter distributions between 15-30%. [7, 8, 12, 13] However, no NW length control has been achieved in these reactions.

Further hindering the definitive structural characterization of chemically grown nanostructures, are organic surfactants used in abovementioned syntheses. These surfactants control the size, shape, growth kinetics, and even crystallographic phase of solution-based nanomaterials. [33] They also electronically passivate QD/NW surfaces, improve their fluorescence quantum yields, provide solubility in a variety of organic/aqueous solvents, and protect their surfaces from oxidation. However, as an unintended consequence, actual masses of solution-based nanostructures are greatly influenced by these surface bound species. Thus the weight of dried QD/NW powders is not necessarily representative of the actual number of nanostructures present in a sample.

In spite of these problems, absorption cross-sections and associated molar extinction coefficients have been evaluated on chemically grown nanostructures using thermal gravimetric analysis (TGA) [34], acid digestion followed by inductively coupled plasma mass spectroscopy [35] (alternatively, inductively coupled plasma atomic emission spectroscopy), atomic absorption spectroscopy [36-38], anodic stripping
voltammetry [39] or other approaches [40, 41], all in conjunction with absorption spectroscopy.

In this study, absorption cross-sections $\sigma_{abs}$ of solution-synthesized CdSe NWs are determined through concerted transmission electron microscopy (TEM), UV-VIS extinction spectroscopy and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Specifically, TEM characterization of high quality NW ensembles provides a measure of average nanowire diameters and corresponding diameter size distributions. ICP-AES measurements and subsequent comparisons to commercial Cd and Se atomic emission standards yield sample stoichiometries as well as overall NW concentrations. Accompanying solution linear absorption spectra of the same ensembles allow both NW absorption cross-sections and corresponding molar extinction coefficients to be determined.

Charges on metal, semiconductor, and dielectric particles can significantly alter their physical, chemical, and optical/electrical properties. This is especially true when the particle size falls below a micron given concurrent increases in the particle surface to volume ratio. Millikan was one of the first to observe such size-dependent properties having analyzed the trajectories of micron-sized oil droplets subjected to an external electric field. [42]

Charges on nanoparticles have since been utilized in countless studies and applications. For example, the simplest use of surface charges is the electrostatic stabilization of colloidal suspensions. [43] In this respect, Faraday’s colloidal gold sols can still be seen at the Royal Institution of Great Britain. [44] More recently the controlled electrophoretic deposition of smooth CdSe quantum dot films, as well as their
mixtures with other nanoparticles, has been reported. This opens up new ways for manufacturing nanostructured devices. [45] Furthermore, electrostatic forces between charged nanocrystals dictate their assembly into complex three-dimensional colloidal crystals, possessing potentially unique collective properties. [46, 47]

Charges and associated electric fields alter not only the self-assembly or electrophoretic motion of nanoparticles, but they also modify their optical [48-53] and electrical [54, 55] properties. In the case of colloidal QDs, both their fluorescence intensity and spectral position are influenced by the presence of mobile charges. Specifically, carriers migrating on a nanocrystal surface produce sufficiently strong electric fields to cause time-dependent spectral changes, as well as increases in linewidth. [49-51] These Stark-induced shifts are accompanied by abrupt jumps of the fluorescence intensity believed to be caused by sequential QD ionization and neutralization events. The phenomenon is often referred to as “blinking” and remains distinct from triplet-induced quantum jumps. [52, 53] Spectral shifts, line broadening, and fluorescence intermittency are also observed in semiconductor nanorods and arise for similar reasons. [56]

When nanostructures evolve from zero-dimensional (0D) QDs to one-dimensional (1D) NWs, the lowering of the overall structural symmetry further impacts the material’s optical and electrical properties. This leads to unique 1D phenomena. For example, the radial confinement of electrons and holes modifies the nanostructure’s joint density of states. Moreover, valence band mixing occurs, inducing variations in subband oscillator strength as well as introducing intrinsic polarization anisotropies. [57] Differences in
NW/local environment dielectric constants also significantly alter exciton binding energies, suggesting possible dielectric contrast “engineering” of 1D nanostructures. [58]

Corresponding differences in 1D optical and electrical properties of NRs and NWs are also expected when in the presence of mobile charges. Specifically, in the limiting case of NWs, we observe the appearance of unexpected optical effects such as field-induced fluorescence enhancement, [59] intrawire fluorescence intensity and spectral heterogeneity, as well as spatially correlated intensity fluctuations. [60] These effects likely stem from the presence of mobile surface charges. When studies of these properties are combined with the unique structural asymmetries of NWs, new insights into these ubiquitous, yet unexplained, optical phenomena are possible.

In this Thesis I describe the spatial and intensity modulation of single NW emission by external electric fields. In particular, we demonstrate that enhanced NW emission can be localized in the part of the wire closest to the positive electrode. A corresponding emission quenching of near identical magnitude occurs at the opposite end. When the polarity of the electric field is reversed, previously dark regions of the NW become bright. The NW emission can therefore be spatially “toggled”. In all cases, emission enhancements (quenchings) of 2-3 times are seen with occasional order of magnitude changes. Complementary AC electric field measurements show that the effect persists up to 500 kHz, limited by the bandwidth of the electronics.

Because the emission enhancement always occurs near the positive electrode, we suggest that mobile electrons inside the wire or on the NW surface are responsible for the phenomenon. Charged excitons are not considered due to their small room temperature binding energy. [61] To verify and to quantify the linear charge density of mobile
carriers, direct electrophoresis experiments of NWs dispersed in toluene, chloroform, immersion oil, and oleic acid were conducted. Analyses of NW rotational and translational dynamics show that mobile charges indeed exist on or within the wire with linear densities 1 charge per 1 μm of the wire. At least two contributions to these charges exist, stemming from both extrinsic and photogenerated sources.

Mobile carriers can be detected not only in dielectrophoresis experiments but also in photoconductivity measurements. In studying the photoconductivity of aligned NWs [62] we found, to our surprise, that photocurrent anisotropies ρ can be also obtained from a network of randomly oriented wires. The polarization anisotropy is defined by \( \rho = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp} \), where \( I_\parallel \) and \( I_\perp \) are photocurrents generated at two orthogonal polarizations of the excitation light. The 1D geometry of single NWs determines their polarization sensitivity since the light absorption strongly depends on the mutual orientation of the wire axis and the light polarization. Single NW experiments indeed demonstrate a \( \rho \sim 0.91 \) photocurrent anisotropy in agreement with theoretical predictions. [63] But the polarization sensitivity of a random NW network was unexpected.

A literature search revealed that a similar effect, namely a polarization “memory” existed in the emission of CdSe nanorods (NRs) dispersed in solution. The NRs emission was polarized collinear with linear polarization of the incident excitation. [64] The emission anisotropy was explained by the preferential excitation of rods whose growth axis coincided with the excitation polarization. Since the emission of individual rods is itself polarized along the growth axis, [65] this subset of preferentially excited rods polarizes the overall emission of the ensemble in solution. The net result is a suppression of randomness in this macroscopically isotropic system.
Following this line of thought, it was suggested that a similar effect could explain the photocurrent anisotropy of random NWs films. In such measurements, an external electric field imparts directionality to the NW network favoring higher dissociation rates for excitons and larger carrier mobilities in wires oriented primarily along the electric field lines. A simple geometrical model of the interaction between randomly oriented wires and linear polarized light has been developed and quantitatively explained the results. [26] The main conclusion of this research is that polarization sensitive elements can be constructed from random NW networks.

1.2 References


2.1 Nanowire chemistry

We utilize catalytic solution-liquid-solid synthesis for CdSe NWs growth. [1] Specifically, Au/Bi core/shell nanoparticles initiate NW growth due to the thermal decomposition of CdO and trioctylphosphine selenide (TOPSe) precursors on the nanoparticle surface. When the concentration of Cd and Se in a Bi shell reaches saturation, NW growth starts. Coordinating chemicals such as trioctylphosphine oxide (TOPO) are added to enable surface passivation of the wires. Depending upon the molar ratio between CdO and TOPSe, the morphology of the nanowires changes from straight to branched [7:1 (1:1) Cd:Se molar ratio for straight (branched) NWs].

2.2 Transmission electron microscopy

NW diameters and size distributions were evaluated by analyzing transmission electron microscope (TEM) images of NW ensembles. Survey TEMs were obtained during the synthesis with a JEOL 100SX TEM. All low and high resolution TEM micrographs were taken with a JEOL 2010 TEM operating at 200 kV. Images were subsequently scanned and analyzed using commercial software.
2.3 Atomic force microscopy

To evaluate the quality of NW coverages on substrates we scanned the samples using a Nanoscope IIIa or a Nanoscope IV atomic force microscope (AFM) from Digital Instruments. Intermittent-contact mode was utilized to image the samples over areas typically ranging from 100x100 $\mu$m$^2$ to 500x500 nm$^2$. To reveal the presence of organic surfactants on the sample surface, AFM scanning was performed under various pressures between the AFM tip and the sample.

To study the uniformity of local electrical fields in NW films, AFM surface potential measurements were carried out in photoconductivity experiments. One Au electrode of the sample (see 2.10 Photocurrent anisotropy section for details on the sample preparation) was grounded while ~10 V was applied to another. The AFM tip, operating in “interleave” mode, measured the potential profile of the field applied across the gap.

2.4 Linear absorption spectra

All UV/visible extinction spectra for CdSe and CdTe NWs were obtained at room temperature using a Cary 50-Bio UV-VIS spectrophotometer. A 1 cm pathlength suprasil cuvette was used in all experiments. Baseline corrections were conducted prior to each measurement.

2.5 Inductively coupled plasma-atomic emission spectroscopy

Concentrations of Cd and Se in NW samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Perkin Elmer Optima
3300XL instrument. Samples for ICP-AES were prepared by digesting NW samples (typically 300 μL) with concentrated nitric acid and diluting the resulting residue in 5% nitric acid (v/v, 10 mL). Specifically, adding concentrated nitric acid to NW solutions turns them orange. Subsequent heating at ~70-100 °C eventually renders the mixtures colorless. The remaining solvent is evaporated, leaving behind a residue which is redissolved in 5% nitric acid. Elemental concentrations were quantified by comparing NW ICP-AES data to results obtained from known elemental standards. Cd and Se calibration curves were prepared using solutions having trace concentrations ranging from 0.5 ppm to 25 ppm. All experimental calibration curves could be fit to straight lines with $R^2$ values greater than 0.999.

2.6 Optical instrumentation

The optical setup is constructed around a Nikon Eclipse 2000 inverted microscope (Figure 2.1) and the majority of the optical data acquired were recorded with a CCD camera (DVC-1412) attached either directly to the microscope or to an imaging spectrometer. The positioning of the sample with respect to the excitation is controlled by a three dimensional piezostage (Physik Instrumente). The excitation part of the optical setup includes a tunable broadband supercontinuum laser (Fianium, 470-1700 nm) as well as a Ar$^+$ ion laser (Melles Griot, 488 nm). In order to obtain narrow excitation lines out of the supercontinuum, we built a laser light dispersion/collimation system. The output of the Fianium laser is first dispersed into its component colors using a grating (600 grooves/mm, 500 nm blaze angle, Thorlabs, GR13-0605). This output is then collimated with a +150 mm achromatic lens. A ~0.5 mm wide slit, mounted on a
computer controlled motorized stage (LNR50K1/M, Thorlabs), selects the required wavelength for sample excitation by its lateral position across the dispersed supercontinuum. The resulting color is then focused onto a multimode fiber. At the other end of the fiber, the light is collimated with +50 mm lens and is then directed into the microscope. A retractable +400 mm lens widens the excitation spot from ~300 nm to 25 μm (from 5 μm to 30 μm) diameter for the Ar^+ (supercontinuum) laser. A retractable mirror switches between lasers (Fianium or Melles Griot). To smear out any speckle from the multimode fiber, we intentionally shake the fiber using a mechanical arm driven by a low speed AC motor. During a 1 s acquisition of the CCD camera, the optical field is averaged over many speckle configurations, providing a temporally stable and spatially smooth excitation profile.

Figure 2.1. Optical setup.
2.7 Sample preparation

Sample coverages are achieved by drop casting NWs in toluene onto flamed glass cover slips (Fisherbrand). To ensure that deposited NWs are clean and do not contain excessive organic ligands such as TOPO or TOP, we rinse post deposition substrates for ~3 min in toluene.

Figure 2.2 illustrates the effect of the post deposition toluene wash. AFM images of individual NWs reveal that the most of wires prior to the toluene wash bear excessive TOPO/TOP. Furthermore, the coverage is uneven (Figure 2.2 (a)). It was demonstrated that such patchy coverages can significantly alter the optical properties of NWs such as their excitation anisotropy. [2] Rinsing the sample for ~3 min with toluene removes this excessive organic layer (Figures 2.2 (b)-(d)) and results in a significantly improved reproducibility for the NW optical response.

For electric field measurements Au electrodes were patterned on glass cover slips with a narrow 20-100 μm gap. Interdigitated metal electrodes on the glass cover slips were fabricated using standard photolithography. This involves PMMA deposition, exposure through a mask, and etching with developer. A thin (~5 nm) Ti buffer layer is deposited on the substrate to act as a gold adhesion layer. Approximately 100 nm of Au is then added to create 20-100 μm gap electrodes. Subsequent liftoff is performed in acetone. In the majority of our optical experiments we select NWs with specific V-shapes or tripod morphologies since low and high resolution TEM photographs reveal that such shapes are characteristic of single NWs.
Figure 2.2 AFM images of NWs (a) prior to and (b)-(d) after a toluene wash.

2.8 Electric field induced emission enhancement/quenching

Samples are mounted on a closed loop piezo stage (Physik Instrumente). This enables accurate alignment of single NWs at the center of the excitation spot where the intensity profile is most uniform. A function generator (Tektronix) along with a 20x amplifier provides voltages to the interdigitated electrodes through a home-built probe station. Tapered tungsten wires are used as probes. Typical frequencies of the applied stepwise voltage vary from 0.01 Hz to 500 kHz with the high frequency limit determined by the amplifier bandwidth. The majority of our experiments are carried out on branched
wires with characteristic tripod, v-shape, y-shape and merge-y morphologies. Occasionally, straight wires with uniform emission intensities are used. The 20-100 μm gap between electrodes provides sufficient room to locate wires situated at least a few microns away from Au contacts. This prevents any charge transfer effects. Electric field measurements are carried out on NWs residing at the air/glass interface.

2.9 Micro-dielectrophoresis

The same optical instrument is used for micro-electrophoresis experiments. To conduct these studies, substrates consisting of glass cover slips with microcavities glued to their top were built (Figure 2.3). A deep, narrow slot is present between the electrodes to minimize any edge effects and to ensure subsequent field uniformity. Experiments were conducted with electric field amplitudes between 500 V/cm and 2 kV/cm and with NWs dispersed in either immersion oil or oleic acid.

Microcavities were constructed by cleaving 0.5–0.6 mm thick pieces of silicon and coating them with 50 nm of Au using a sputter coater (Emitech). Small 4x4 to 6x6 mm² sections were then glued to the cover slip using 5 minute epoxy. A small ~100 μm thick piece of paper is placed between the electrodes to define their spacing. This shim is subsequently removed once the glue has cured. Gold wires (~60 μm diameter) are then attached to the electrodes using conductive epoxy and are also connected to the above voltage source. To stabilize NW solutions inside the gap and to prevent any unwanted drift, the microcavity is surrounded by a small perfusion chamber.
2.10 Photocurrent anisotropy

Samples for photocurrent experiments were prepared by drop casting NW suspensions onto glass cover slips and by subsequent evaporation of Au electrodes over the film. The 40 nm thick Au electrodes were evaporated over the film using a shadow mask, consisting of a 30-110 μm diameter Au or Al wire. Subsequent removal of the wire resulted in a 30-110 mm gap filled with wires. SEM micrographs (Figure 2.4) exhibit the random distribution of NWs in the network. Estimated NW densities range from $10^9$ to $10^{10}$ NW/cm$^2$. It is also apparent that every wire is connected to many other randomly oriented wires.

For photoconductivity experiments, the sample was placed in the optical setup described previously in section 2.6, Optical instrumentation. For excitation, a 532 nm green laser diode and supercontinuum broadband emission laser were used. Corresponding excitation intensities varied from 3 to 5 kW/cm$^2$ while 16-20 μm diameter...
spot sizes were created with a +400 mm lens placed ~ 400 mm prior to the objective’s back aperture. A sheet polarizer with a 100:1 quality factor was mounted on computer controlled stepper motor prior to the lens enabling angular control of incident light polarization. Photocurrent and excitation power were measured at each position of polarizer to correct for power fluctuations; all analyses were conducted on photocurrents normalized to the excitation power. Photocurrent (excitation power) was measured using a Keithley picoammeter (Newport power meter). For spectral sensitivity characterization, the broadband emission of the supercontinuum laser was dispersed with a 600 groove/mm, 500 nm blaze angle grating and the appropriate excitation line between 480 and 670 nm was chosen by a motorized slit.

Figure 2.4 SEM image of ~30 μm gap formed between two gold electrodes.
To address anisotropy bandwidth measurements, the sheet polarizer/stepper motor was replaced with a ferroelectric liquid crystal polarization rotator (Displaytech). A stepwise +/- 5 V amplitude and 0.5-2 kHz signal from a function generator (Tektronix) rotated the polarization by 90° at the prescribed frequency. Photocurrent modulations were first converted into a voltage using a home built current-to-voltage preamplifier (10⁴-10⁷ gain) and was then fed into a lock-in amplifier (SRS). The lock-in amplifier measured (a) the amplitude of the signal modulation and (b) the phase delay with respect to the input signal. At frequencies lower than 0.5 Hz the current modulation was measured directly using a picoammeter.

In addition to AFM surface potential measurements, the possibility of non-uniform local electrical fields was probed through another experiment. Rectangular slits with fixed height but with variable widths were inserted into the excitation beam prior to the + 400 mm lens to form a rectangular excitation spot on the sample. In this way, excitation spot sizes were adjusted from 0.75 μm x 20 μm to 12 μm x 20 μm (width x height). The resulting photocurrent was plotted vs. slit width. Without significant local charge accumulation we expect a linear photocurrent vs. width dependence, which was indeed observed in the experiment.

2.11 References


3.1 Crystallography of CdSe NWs

Low-resolution TEM micrographs confirm that straight and branched wires typically have large aspect ratios with lengths between 1-10 \( \mu m \) and with diameters between 5 and 20 nm. Because of the strong attractive interaction between wires, NWs have a tendency to bundle. The four panels in Figure 3.1 (a) are representative TEM images of straight CdSe NWs synthesized by SLS method. The excellent uniformity of the NWs, their flexibility, and bundle formation are obvious from images. In contrast, branched CdSe NWs preserve their individuality and NW bundling is greatly suppressed (the four panels of Figure 3.1 (b)).
High resolution TEM (HRTEM) images of straight (Figure 3.2 (a)) and branched (Figure 3.2 (b)) NWs reveal narrow diameter distributions (20-30%) in NW ensembles as well as small intrawire diameter variations (3-6%). Clearly visible crystal planes normal to the wire <0001> growth direction indicate high quality, defect free wires.

Figure 3.2 High-resolution TEM images of <110>-oriented (a) straight and (b) V-shaped CdSe NWs. Lines within ZB sections indicate twin planes.
HRTEM images also exhibit another interesting feature about SLS-grown CdSe nanowires. In particular, zinc blende/wurzite (ZB/W) phase mixtures are seen in all solution-grown CdSe NWs. This has been demonstrated through high resolution TEM micrographs of <110> oriented nanowires where twinning as well as ZB/W regions are identified through characteristic “zig-zag” fringes in lattice resolved images. [1] Notably, the branching point of tripods and V-shapes is always ZB. Measured ZB or W sections generally exceed 2-3 unit cell lengths, needed to establish nominal band structure. [2] Average ZB (W) sections are 3 (σ=1) nm [2 (σ=1) nm]. The origin of such admixtures/twinning is likely the low energy difference between the two lattice structures (2 meV/atom). [3] Moreover, the phenomenon is not uncommon having been observed in CdSe/CdTe tetrapods [4] as well as in bulk systems.

3.2 Optical properties

Single NW optical measurements show unexpectedly broad emission whose spectral position and width vary along the NW length. Figures 3.3 (a)-(c) form a representative set of spectra taken from different regions of tripod and v-shaped NWs. The numbered spectra in Figure 3.3 correspond to marked positions on the accompanying images (dashed circles). All data have been normalized to the same peak intensity and reveal noticeable shifts relative to the dashed line. Measurements on multiple (single) NWs yield an average peak shift of 62 (σ=27) meV. This spectral heterogeneity is not expected as previous single NW optical measurements show both uniform intrawire spectra and emission intensities. [5, 6] Adding to this heterogeneity, the average emission full width at half maximum (FWHM) is 103 (σ=22) meV [38 (σ=9) nm].
Figure 3.3 Intrawire spectral heterogeneity in (a) tripod and (b, c) V-shaped CdSe NWs. Corresponding emission spectra from numbered locations are provided and are offset for clarity. The dashed vertical line is a guide to the eye.
For NWs with diameters exceeding 10 nm, the peak is centered at ~712 nm which corresponds to bandgap emission (1.74 eV). In contrast, for thinner wires the emission peak is blue-shifted, which might indicate quantum confinement effects. For example, ~7 nm diameter NWs typically emit around 690 nm. This behavior is routinely observed for CdSe QDs when diameters become smaller than twice exciton Bohr radius (5.6 nm in bulk). We see the same effect, but with a weaker magnitude in CdSe NWs.

To investigate any emission spectral fluctuations, we acquired emission spectra from a single NW with a 3 minute integration time over the course of 20 minutes. One such example is shown in Figure 3.4. Although dynamics within the NW spectra are apparent, the origin of this behavior is not completely understood. However, the photoinduced Stark effect as well as a NW Type II heterostructure (due to the zinc blende/wurtzite phase admixture) likely contribute to these spectral fluctuations. [7]

In addition to temporal variations in the spectra seen in Figure 3.4, 20-200% temporal and spatial variations in emission intensity have been detected for many NWs. Under epi-excitation conditions “snap-shot” images of single NWs exhibit “zebra”-like structure with bright places having higher emission intensities alternating with nearby dark areas (Figure 3.5 (a), (c)). In most cases these bright/dark spots are relatively stable with time, and “waterfall” emission plots (Figure 3.5 (b) and (d)) show mostly straight vertical bright/dark lines. In rare cases, highlighted by arrows in Figure 3.5 (b), bright/dark spots appear to move along the NW.
It has been predicted that the attenuation of optical fields inside thin dielectric cylinders depends strongly on the light polarization. [9] Therefore NWs should exhibit strong polarization sensitivities. In agreement with the theory, CdSe NWs indeed reveal $\rho=0.72-0.91$ excitation and $\rho=0.4-0.6$ emission polarization anisotropies. [10, 11]

An example involving a single CdSe NW is provided in Figure 3.6 and illustrates the one-dimensional nature of the wires. Specifically, two polarization response curves are observed, originating from each arm of the v-shaped wire. Both responses are identical, with absorption maxima (minima) occurring when the incident
Figure 3.5 “Snap-shot” emission images of two V-shaped NWs in PMMA ((a) and (c)). Corresponding emission “waterfall” plots recorded for 2 minutes ((b) and (d)). On the panels the horizontal axis is the emission intensity measured along dashed lines of the accompanying right images; the vertical axis corresponds to time (2 min total) which increases toward the bottom. Arrows show time intervals where directional fluorescence migration is visible.
light polarization is aligned collinearly (perpendicularly) to each NW arm. Corresponding polarization anisotropies of the top and bottom arms are both \( \sim 0.80 \). The \( \sim 112^\circ \) phase shift between the two curves originates from the \( 109.5^\circ \) crystallographic angle separating both arms given their growth out of equivalent \{111\} faces of a common ZB core.

Figure 3.6 Absorption polarization anisotropy of a single V-shaped CdSe NW. Typical anisotropy values are on the order of \( \rho \sim 0.75 \). The red circles (blue triangles) are data from the NW arm marked with the corresponding symbol in the inset. Solid/dashed lines are \( \cos^2 \gamma \) fits to the data where \( \gamma \) is the angle between the NW axis and the incident light polarization.
3.3 References


CHAPTER 4:
ABSORPTION CROSS-SECTION OF CdSe NANOWIRES

4.1 Measuring the extinction cross section

There are two major obstacles which have to be addressed here. First, the NWs are not molecules or even quantum dots, where extinction and absorption cross sections can be calculated \textit{per particle}. In the case of NWs, each individual wire has a specific length. It therefore possesses a specific cross section. To overcome this problem, we calculate the absorption cross section \textit{per unit length} of the NW. Next, light scattering by NWs has to be considered for proper interpretation of any UV-VIS extinction spectra. Experimentally determined UV-VIS extinction data (extinction = absorption + scattering) are used to relate the total extinction of a NW ensemble to the total cross-section of a hypothetical single wire, responsible for all of the light extinction in solution. The length of this single NW is then calculated using ICP-AES determined sample concentrations of Cd and Se ions and TEM determined average diameters. Given the total length of the effective NW and its complementary extinction cross-section, an extinction “cross-sectional density” ($\chi_{\text{ext}}$) with units of $\text{cm}^2/\mu\text{m}$ can be determined.

As stressed above, complicating direct absorption measurements are contributions to the extinction from scattering. For nanoscale object such as nanoparticles with diameters between 5-10 nm (much smaller than the wavelength, $\lambda$, of light), scattering can generally be neglected. This is due to the faster decay of the nanocrystal scattering...
efficiency with size (~ r^6) relative to its absorption (~r^3) [1] and justifies direct use of UV-VIS extinction data for calculating QD absorption cross sections. [2, 3] However, when the nanostructure sizes exceed 20-100 nm, scattering begins to dominate the extinction. A NW is therefore an interesting object from a scattering perspective since one dimension (the diameter) is much smaller than the wavelength of light but the other (its length) is generally > 1 μm and hence exceeds λ by 1-2 orders of magnitude. Since the current study focuses on the NW absorption, measured UV-visible extinction data are corrected for scattering to properly determine the NW absorption cross-section. Towards this end, a model describing the interaction between a long, finite length, dielectric cylinder (standard model for wires) and a plane wave is used to calculate the scattering contribution to the measured UV-VIS extinction spectra. [4]

Obtained absorption cross sections compare well with previous theoretical estimates obtained by modeling the NW density of states as bulk-like far from the band edge.[5, 6] Practical (and immediate) implications of this study include a more quantitative measure of single NW fluorescence quantum yields (previously estimated to be ~0.1% [7]), better estimates of multicarrier excitation regimes in transient differential absorption experiments [8], and an estimate of external photoconversion efficiencies in recently developed NW photodetectors. [9]

In our approach, average NW diameters and corresponding size distributions are measured by analyzing TEM images of CdSe wires. For the evaluated CdSe ensembles, diameters range from 6 to 42 nm with associated diameter distributions between 20 and 40%. Resulting diameters and corresponding size distributions are summarized in Table 4.1 below.
For ICP-AES measurements a small fraction of the initial NW stock solution (typically ~300 μL) is digested with nitric acid. The resulting residue is diluted with 10 mL of 5% nitric acid whereupon ICP-AES measurements are conducted on the sample. The results are subsequently compared to those from calibration standards, yielding sample stoichiometries. Specifically, ICP-AES results show an approximate 1:1 Cd:Se ratio \([1:1.07 (\sigma = 0.15)]\) in CdSe NW ensembles. A table of NW stoichiometries is also provided in Table 4.1. Slight deviations from an exact 1:1 stoichiometry may arise from the abrupt termination of NWs at their surfaces.

**TABLE 4.1**

**NAME OF CdSe NW SAMPLES, AVERAGED NW DIAMETERS, CORRESPONDING STANDARD DEVIATIONS, TRANSIENT ABSORPTION (TA) BAND EDGE PEAK POSITIONS, AND ELEMENTAL STOICHIOMETRIES**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Diameter (nm)</th>
<th>Standard deviation (nm)</th>
<th>TA peak, band edge (nm)</th>
<th>Stoichiometry Cd/Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>jgnb2p37</td>
<td>6.4825</td>
<td>1.5699</td>
<td>698.0</td>
<td>1/1.11</td>
</tr>
<tr>
<td>mknb3p212</td>
<td>6.5836</td>
<td>1.1523</td>
<td>693.8</td>
<td>1/1.09</td>
</tr>
<tr>
<td>jagnb1p27</td>
<td>13.070</td>
<td>5.3393</td>
<td>707.1</td>
<td>1/1.21</td>
</tr>
<tr>
<td>jagnb1p39</td>
<td>15.227</td>
<td>3.5881</td>
<td>710.6</td>
<td>1/1.05</td>
</tr>
<tr>
<td>jagnb1p40</td>
<td>21.407</td>
<td>5.7967</td>
<td>709.2</td>
<td>1/1.02</td>
</tr>
<tr>
<td>jagnb1p45</td>
<td>22.370</td>
<td>12.541</td>
<td>714.7</td>
<td>1/0.77</td>
</tr>
<tr>
<td>db050906</td>
<td>42.408</td>
<td>14.416</td>
<td>714.7</td>
<td>1/1.24</td>
</tr>
</tbody>
</table>

Concentrations of Cd and Se in each sample (NW stock) are simultaneously obtained when the volume (dilution) of the ICP-AES solution is known. This allows one
to quantify the total moles of CdSe and CdTe in each ensemble, using formula weights for CdSe. The total length (in microns) of a single NW with a diameter matching the TEM-measured mean ensemble diameter is then calculated using

\[ L = \frac{4M_{nw}}{\rho \pi d^2} \times 10^4 \]  

(4.1)

where \( M_{nw} \) is the solution NW mass in 1 cm\(^3\), \( \rho \) is the density of CdSe (5.81 g/cm\(^3\)) and \( d \) is the average NW diameter (cm) determined from TEM measurements. Since experimental stoichiometric ratios typically differ slightly from 1:1, the smaller of the two elemental mole quantities is used for both elements in calculating \( M_{nw} \).

The extinction \( (A_{ext}) \), which includes both absorption and scattering, from a given dilution of the original NW stock is then obtained using UV-VIS spectroscopy. This value is corrected for scattering contributions (described in more detail below) to yield \( A_{abs} \). With the solution concentration at hand, the angle- and crystallographic phase-averaged extinction cross-sections of all wires in solution are now established. This assumes negligible absorption contributions from NW ends and is reasonable given the typical \( \sim 1000:1 \) aspect ratios of the wires. Specifically, from \( A_{ext} = \sigma_{ext} n_{dens} l_{cuv} \log e \) and Equation 4.1 an absorption cross-section per unit length (or “cross-sectional density”), \( \chi_{ext} \), averaged over all angles and crystallographic phases is calculated using

\[ \chi_{ext} = \frac{A_{ext}}{n_{dens} \cdot l_{cuv} \cdot (\log e) \cdot L \cdot N} \]  

(4.2)

where \( N \) (a dilution factor) is the ratio of NW concentrations in the extinction and ICP-AES measurements \( ([NW]_{UV/Vis} / [NW]_{ICP-AES}) \), \( l_{cuv} = 1 \) cm and \( n_{dens} = 1/cm^3 \). It is apparent that for 1 \( \mu \)m long NWs values \( \sigma_{ext} \) and \( \chi_{ext} \) are equivalent by this definition.
4.2 Corrections for scattering

Complicating estimates of the absorption cross section are scattering contributions to the extinction ($A_{ext}$). Hence, to obtain $A_{abs}$ from measured $A_{ext}$ values, scattering contributions are accounted for theoretically using an expression that angle averages the NW scattering cross section, $\sigma_{scat}$, over all possible wire orientations relative to the incident (unpolarized) light. In the current study, angle averaged $\sigma_{scat}$ values from an ensemble of finite length cylinders, excited with depolarized light, is obtained using the results of References 4 and 10.

Specifically, in the limit of finite length cylinders with a diameter, $d$, less than the excitation wavelength $\lambda \left[ \frac{m'd}{\lambda} \ll 1 \right]$, where $n' = \text{Re} \frac{n_c}{n_i}$ is the real part of the ratio between the cylinder’s refractive index, $n_c$, and that of the surrounding medium, $n_i$, and

$$\left| \frac{n'}{n} \right| \ll 1 \quad (n' = \text{Im} \frac{n_c}{n_i})$$

as well as when the cylinder’s length, $l$, satisfies $l > \frac{\lambda}{2m_i}$, the scattering cross-section can be angle averaged for arbitrary orientations of the cylinder relative to the incoming light. An explicit mathematical expression for $\sigma_{scat}$ is obtained

$$\sigma_{scat} = \frac{\pi}{128} (\kappa d)^4 l^2 \left| \frac{n'^2 - 1}{n'^2 + 1} \right|^2 \int_0^\pi \left( \sum_{m=0}^3 \alpha_m(\theta) \cdot \text{Re} \left[ F_2 \left( 1,1;2,6-m;2i\kappa d\sin\frac{\theta}{2} \right) \right] \right) \sin\theta d\theta$$

(4.3)

where $\kappa = \frac{2\pi}{\lambda}$ is the wavevector of the incident light, $d$ ($l$) is the cylinder diameter (length), $n = \frac{n_c}{n_i}$ is again the ratio between the cylinder’s refractive index and that of the
surrounding medium, and \( \alpha_m(\theta) \) are coefficients defined in Reference 4.

\[
\text{Re}\left(\sum_{2} F_{2}\left(1,1;2,6-m;2i\kappa\sin\frac{\theta}{2}\right)\right)
\]

is the real part of the hypergeometric function, \( \sum_{2} F_{2}(a, b; c, d; z) \), having generic arguments \( a, b, c, d \) and \( z \) where \( z = 2i\kappa\sin\frac{\theta}{2} \), \([11]\), \( m \) is a summation index, and \( \theta \) (ranging from \( 0 \rightarrow \pi \)) is the angle between the incident light and the scattering direction.

Using Equation 4.3 we calculate \( \sigma_{\text{scat}} \) for CdSe NWs dispersed in toluene. Since the NW scattering efficiency depends on the excitation wavelength through \( n_c \) and because such numbers are not currently available for CdSe NWs, corresponding bulk values of the refractive index are used.\([12]\) The refractive index of toluene is 1.5.\([13]\)

Two interesting features of Equation 4.3 are noted. First, \( \sigma_{\text{scat}} \) appears to scale quadratically with \( l \). It therefore grows much faster than \( \sigma_{\text{abs}} \). In general, the absorption cross section is proportional to the NW volume and hence grows linearly with length. This would, in turn, suggest that an accurate accounting of NW ensemble length distributions is needed in order to properly calculate scattering contributions to the overall extinction. Fortunately, a detailed analysis reveals that the integral in Equation 4.3 is well approximated by \( \sim \frac{1}{l} \). This behavior is caused by an increasing localization of the hypergeometric function \( \text{Re}\left(\sum_{2} F_{2}\left(1,1;2,6-m;2i\kappa\sin\frac{\theta}{2}\right)\right) \) about values near \( \theta = 0 \) with increasing \( l \) and values of \( \sin \theta \rightarrow 0 \).\([4, 14]\)

Figure 4.1(a) illustrates the phenomenon by plotting the angular distribution of the normalized (relative to the \( \theta=0 \) value) scattering intensity for three different NW lengths...
and for arbitrary NW/light propagation direction orientations. From the graph it is apparent that in all three cases, light is preferentially forward scattered along the incident light propagation direction and is increasingly concentrated about $\theta = 0$ with growing NW length. As a consequence, $\sigma_{\text{scat}}$ from Equation 4.3 scales linearly with $l$. This is further illustrated in Figure 4.1(b) where Equation 4.3 is plotted at 555 nm for an arbitrary 14 nm diameter CdSe NW as a function of length. Similar results are obtained at all other sizes and wavelengths between 300-1200 nm. The final result is that the ratio between the NW absorption and scattering cross sections is independent of the length. Thus an accurate accounting of ensemble NW length distributions is not needed in subsequent evaluations of either $A_{\text{abs}}$ or $\sigma_{\text{abs}}$. Figure 4.2 illustrates the scattering contribution to the total extinction for a representative 12.8 nm diameter, 1 $\mu$m long CdSe NW. From the graph, it is apparent that scattering contributes only a small amount to the overall extinction. Absorption therefore dominates $A_{\text{ext}}$ in the spectral range of interest. However, scattering contributions steadily increase towards the blue. In this respect, Equation 4.3 shows that $\sigma_{\text{scat}}$ scales as $\frac{1}{\lambda^4}$. This is analogous to the behavior of small particles [1] and, as a consequence, NWs are predicted to scatter blue light efficiently. While not significant for thin wires and for red frequencies, the $\frac{1}{\lambda^4}$ scattering becomes important when dealing with large diameter (> 30 nm) NWs at near UV frequencies. The scattering contribution to the total extinction at 300 nm grows from 2.3% to 37% when $d$ increases from 6.4-22.0 nm.
Figure 4.1 (a) Polar plot of the scattered light intensity for different NW lengths. All intensities are normalized to the $\theta = 0$ value where $\theta$ is the angle between the scattered light and the incident light propagation direction. (b) Scattering cross-section of a 14 nm diameter CdSe NW excited at 555 nm, showing a linear dependence of $\sigma_{\text{scat}}$ with NW length.
Figure 4.2 Angle averaged extinction (solid line) and scattering (circles) cross-sections of 12.8 nm diameter 1 μm long CdSe NW. Inset: Resulting angle averaged absorption coefficients at various wavelengths.

Our subsequent evaluation of $\sigma_{abs}$ for all CdSe NW ensembles, which accounts for scattering contributions to the extinction, proceeds by subtracting $\chi_{scat}$ from $\chi_{ext}$ since

$$\chi_{ext} = \chi_{abs} + \chi_{scat}. \quad \text{(4.4)}$$

When $\chi_{abs}$ is multiplied by the average length of a NW in solution ($l$, in microns),

$$\sigma_{abs} = \chi_{abs} l. \quad \text{(4.5)}$$

angle averaged values of the NW absorption cross-section are obtained.

Measured $\chi_{abs}$ values for CdSe NWs with diameters between 6-42 nm range from $6.93 \times 10^{-13}$ to $3.91 \times 10^{-11}$ cm$^2$/μm at the band edge (1.73 to 1.79 eV). Further to the blue
at 488 nm, CdSe $\chi_{\text{abs}}$ increases to values between $3.38 \times 10^{-12}$ and $5.50 \times 10^{-12}$ cm$^2$/μm, depending on size.

Figure 4.3 compares model predictions (dashed lines) to experimental values (closed circles) by plotting $\chi_{\text{abs}}$ versus $d^2$. [7, 15] Solid lines are linear fits to the data, showing an apparent linear dependence between the two and a corresponding scaling of $\chi_{\text{abs}}$ with NW volume. In either case, however, good agreement is found between experiment and theory at 488 nm; predicted values are within a factor of 1.5. However, larger discrepancies are observed at the band edge (Figure 4.3 (a)) where approximately factor of three differences are seen. This may be due to the presence of subbands underlying the NW linear absorption spectra.

Proportionality constants between $\sigma_{\text{abs}}$ (cm$^2$) and $d^2$ (nm$^2$), extracted from above linear fits to the data in the region of interest are $2.33 \times 10^{-14}$ for CdSe at the band edge $[\sigma_{\text{abs,edge}} = 2.33 \times 10^{-14} d^2]$. Likewise, at 488 nm the proportionality constant is $1.06 \times 10^{-13}$ $[\sigma_{\text{abs,488nm}} = 1.06 \times 10^{-13} d^2]$.

Above cross sections include the effects of orientational averaging. However, to extract $\sigma_{\text{abs}}$ values free of this, we explicitly consider the $\cos^2 \gamma$ dependence of both $\chi_{\text{abs}}$ and $\sigma_{\text{abs}}$, where $\gamma$ is the angle between the incident light electric field and the NW growth axis.[16] Specifically, values of $\chi_\parallel$ (or $\chi_\perp$) can be extracted using above $\chi_{\text{abs}}$ estimates and the NW excitation polarization anisotropy $\rho = \frac{I_\parallel - I_\perp}{I_\parallel - I_\perp}$ where $I_\parallel$ and $I_\perp$ are the amount of absorbed light with polarization parallel and perpendicular to the NW axis.
Figure 4.3 Absorption cross-section (a) at the band edge and (b) at 488 nm (2.54 eV). Solid lines are linear fits to the data. Dashed lines are theoretical predictions, assuming a bulk-like density of states.

In deriving $\chi_{\parallel}$ or $\chi_{\perp}$, the NW growth axis is considered to be randomly oriented in space with angles, $\theta$, and $\phi_{NW}$ relative to the z and x axes of a Cartesian coordinate system respectively. (Figure 4.4) The direction of light propagation is along the z axis. As such, the accompanying electric field is within the XY plane. Its angle relative to the x axis is $\phi_E$. 
Figure 4.4 Cartesian coordinate system and angles involved in accounting for orientational averaging effects.

Previous single NW absorption/emission polarization anisotropy measurements have shown large anisotropies on the order of $\rho \sim 0.9$ with the data exhibiting a $\cos^2 \gamma$ dependence. [16] An expression for the absorption cross section can therefore be written as

$$\sigma_{abs} = \sigma_\perp + (\sigma_\parallel - \sigma_\perp) \cos^2 \gamma$$  \hspace{1cm} (4.6)
where $\sigma_\parallel$ and $\sigma_\perp$ are the parallel and perpendicular absorption cross sections of the NW. Alternatively, one may also write

$$\chi_{abs} = \chi_\perp + (\chi_\parallel - \chi_\perp)\cos^2 \gamma.$$  

(4.7)

In terms of $\theta$, $\phi_{NW}$, and $\phi_E$, $\cos \gamma$ can be written as

$$\cos \gamma = \sin \theta \cos(\phi_{nw} - \phi_E)$$  

(4.8)

enabling us to angle average Equations 4.6 and 4.7. One then obtains

$$\chi_{abs} = \frac{1}{2\pi} \int_0^{2\pi} d\phi_E \frac{1}{4\pi} \int_0^{2\pi} \left[ \chi_\perp + (\chi_\parallel - \chi_\perp)\sin^2 \theta \cos^2 (\phi_{nw} - \phi_E) \right] \sin \theta d\theta d\phi_{nw}$$  

(4.9)

where the limits of $\theta$ are 0 and $2\pi$. Similarly, the limits of $\phi_E$ ($\phi_{NW}$) are 0 and $2\pi$ (0 and $\pi$). After evaluating the above angle average, one obtains a relation between $\chi_{abs}$, $\chi_\parallel$, and $\chi_\perp$ as follows.

$$\chi_{abs} = \frac{\chi_\parallel + 2\chi_\perp}{3}$$  

(4.10)

Next the polarization anisotropy $\rho = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp}$ can be expressed in terms of $\chi_\parallel$ and $\chi_\perp$ through

$$\rho = \frac{\chi_\parallel - \chi_\perp}{\chi_\parallel + \chi_\perp}$$  

(4.11)

since $\chi$ and $I$ are directly proportional to one another. By combining Equations 4.10 and 4.11, one obtains the desired final expressions relating $\chi_\parallel$ and $\chi_\perp$ to $\chi_{abs}$. 

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\[ \chi_\parallel = \frac{3(1 + \rho)}{3 - \rho} \chi_{abs} \]  

(4.12)

\[ \chi_\perp = \frac{3(1 - \rho)}{3 - \rho} \chi_{abs} \]  

(4.13)

Thus, when the NWs are aligned collinearly with the polarization of the incident light, all \( \chi \) values increase by a factor of \( \sim 2.7 \), given previously measured \( \rho \) values of \( \sim 0.9 \). [16] Relevant limits of the prefactor are 3 and 1 when \( \rho = 1 \) and \( \rho = 0 \) respectively. Given \( \chi_\parallel \) and \( \chi_\perp \) values, the absorption cross section, free of angle averaging, can then be determined using Equation 4.5. These results help quantify observations of strong NW excitation/emission polarization anisotropies due to dielectric contrast effects [17] as well as confinement-induced optical selection rules.[18] They also show that the wires absorb most effectively when the incident light polarization is aligned along the NW growth axis.

4.3 Nanowires vs quantum dots

With values of \( \sigma_{abs} \) for CdSe NWs in hand, absorption cross-sections can be scaled to account for volume differences between nanowires and corresponding colloidal quantum dots. Comparison of these values may then highlight fundamental differences between the two, stemming from their intrinsic 0D or 1D nature. To illustrate, absorption cross-sections of CdSe NWs with diameters between 5-12 nm were compared to those of their QD counterparts, having the same diameters. The previously discovered linear relationship between CdSe NW cross-sections and \( d^2 \) \( [\sigma_{abs,edge} (CdSe) = 2.33 \times 10^{-14} d^2] \) was used to calculate model \( \sigma_{abs} \) values. Corresponding CdSe QD cross-sections were
estimated using experimentally determined $\varepsilon$(M$^{-1}$cm$^{-1}$) versus $d$ relationships found by Peng and coworkers [$\varepsilon_{\text{CdSe}}=21145d^{2.0226}$]. [19] Resulting $\varepsilon$ values were subsequently converted to absorption cross-sections using

$$\sigma_{\text{abs}} = \frac{2.303(1000)\varepsilon}{N_A}. \quad (4.14)$$

Obtained NW $\sigma_{\text{abs}}$ values were scaled to account for volume differences between nanowires and QDs. Resulting volume normalized NW cross-sections are then plotted in Figure 4.5 along with corresponding QD cross-sections.

Figure 4.5 Scaled cross-sections of CdSe NWs compared to those of corresponding QDs. (b), (d) NW to QD cross-section ratios estimated for (a) band edge and (c) 350 nm absorption.
Figure 4.5 shows that, even after accounting for volume disparities, scaled CdSe NW cross-sections are larger than those of complementary colloidal QDs. Within the diameter range of interest, factor of ~1-2 differences are readily apparent (Figures 4.5 (b) and (d)). The larger scaled NW cross-sections may originate from differences in the joint density of states between NWs and QDs. In the former, 1D subbands underlie the linear absorption when confinement effects are present. In the latter, discrete atomic-like transitions are responsible for the absorption. This motivates the comparison in Figure 4.5.

Despite apparent differences, NW/QD cross-section comparisons are actually more complicated since $\sigma_{abs}$ is, in fact, related to the product of the oscillator strength ($f_{osc}$) and the underlying 0D or 1D joint density of states. Since QD oscillator strengths likely experience significant size-dependent changes, large variations of the QD cross-section at the band edge could compensate for the smaller volume and reduced density of states relative to NWs. A more detailed and in depth cross-section comparison therefore awaits better knowledge of relevant QD and NW $f_{osc}$ values.

4.4 References


[11] A. Erdelyi, *Higher Transcendental Functions*, McGraw-Hill, New York, **1953**, vol. 2. In MatLab the hypergeometric function \( \, _2F_2(a, b; c, d; z) \) is called “hypergeom([a b],[c d],z)” In Mathematica the same function has the name “HypergeometricPFQ([a,b],[c,d],z)”.


CHAPTER 5:

NW EMISSION COUPLED TO AN EXTERNAL ELECTRIC FIELD

5.1 NW emission intensity response to an electric field

Optical experiments conducted on individual (electrically isolated) NWs in the presence of external electric fields show unexpected behavior. Namely, the emission from each NW localizes in regions of the wire closest to the positive electrode. This is accompanied by a noticeable (2-3 fold) enhancement of the emission intensity, as defined by the ratio of emission intensities with the electric field on versus off. In certain cases, near order of magnitude increases are seen. At the same time, emission quenching occurs in opposite regions of the wire where the quenching factor is defined as a ratio of the NW emission with the field off versus on. Both effects are described below in more details.

When the field polarity is reversed, the emission enhancement/localization “moves” to the opposite end of the wire closest to the (new) positive electrode. Figures 5.1 (a)-(c) illustrate this effect for a tripod-shaped NW. In particular, between images (b) and (c) the field points in opposite directions. However, clear differences in the spatial position of the emission and its intensity relative to the zero-field case (Figure 5.1 (a)) are apparent. In Figure 5.1 (b), the emission is localized/enhanced on the right side of the wire whereas, by contrast, in Figure 5.1 (c) the enhancement/localization occurs on the left side of the wire. Another example for a v-shaped NW is shown in Figures 5.1 (d)-(f).
Figure 5.1 Effects of an external electric field on the emission from an isolated (a)-(c) tripod and (d)-(f) V-shaped NW under the following conditions: (a) and (d) no external field, (b) and (e) a negative, and (c) and (f) a positive potential applied to the left electrode. Emission enhancement (quenching) is observed in the NW region closest (furthest) from the positive electrode.

Repeated switching of the external electric field orientation causes cycling of the emission enhancement and quenching. This is illustrated in Figure 5.2 where the emission intensity from specific regions of the wire is plotted as a function of time. In the particular case considered, points 1 and 2 show a ~1.5 fold fluorescence enhancement/quenching during each half cycle of the modulated field. No electric field was applied during first 20 seconds of the trajectory to obtain a baseline reference level. In Figure 5.2, the electric field points from left-to-right or right-to-left. Similar enhancement/quenching trajectories are seen in other wires within the same image.
Figure 5.2 (a) Emission images of two v-shapes and a straight wire. (b) Plot of the intensity in locations 1 and 2 while an oscillating step-wise electric field (28 kV/cm amplitude) is applied from left to right and vice versa. No field was applied during the first 20 seconds of the trajectory to obtain a baseline reference level.

When the external field is turned off, the NW emission redistributes itself over the entire wire. Both the enhanced emission intensity and quenching behave non-linearly with field strength. In the analysis, only components of the electric field parallel to NW axis are considered for wires not perfectly aligned with the field. Results of the measurement for twelve single wires at the air/glass substrate interface are shown in Figures 5.3 (a) (enhancement) and 5.3 (b) (quenching).

From both figures, the enhancement and quenching show similar field dependencies below ~20 kV/cm. Quenching slightly dominates enhancement above 20kV/cm where the enhancement appears to saturate at factor of 2.5 in contrast to the quenching which continues to increase. Higher field experiments are limited by the output of the high voltage amplifier. In Reference 1 we previously estimated the emission
quantum yield (QY) of CdSe NWs to be approximately 0.1%. Since the current study uses analogous CdSe NWs we assume similar QYs here. A 2-3 fold fluorescence enhancement/quenching induced by external electric fields thus implies NW QYs of 0.2-0.3% (0.03-0.05%) when enhanced (quenched).

Figure 5.3 Field induced (a) enhancement and (b) quenching factors averaged over 12 single NWs. Error bars represent one standard deviation. Experiments were conducted by slowly modulating the field between 0.01 and 0.5 Hz and comparing the maximum (or minimum) emission intensity to the zero field value. These ratios then provide “pure” enhancement and quenching factors. A third order polynomial fit is provided as a guide to the eye.

Interestingly, the field-induced emission enhancement/localization for NWs at the air/glass interface is metastable. Specifically, under a constant electric field, the enhanced NW emission eventually re-distributes itself over the entire wire during the course of several seconds. This can be seen in Figure 5.4 where images of a straight NW under zero field conditions (Figure 5.4 (a)) as well as under a constant electric field at two different times are shown (Figures 5.4 (b) and 5.4 (c)). From Figure 5.4 (c) it is apparent that over the course of several seconds, the emission redistributes itself over the entire length of the wire despite the constant electric field. The emission intensity also becomes comparable
to that of the zero field case. This can also be seen in Figure 5.2 (b) where, on applying an electric field, the emission intensity changes sharply and within a few seconds relaxes to near zero-field intensities. The intensity heterogeneity and intermittency reported previously for NWs under zero-field conditions [1] are still present here under moderate strength fields. This can be seen through the non-uniform emission intensities along the NW length in Figures 5.4 (a)-(c).

Figure 5.4 A CdSe NW at the air/glass interface under (a) zero field (b) field on, no delay and (c) field on, 3 second delay conditions. Electric field: 14 kV/cm, 0.1 Hz. Graph (d) is the frequency response of the emission enhancement. Blue diamonds were calculated without taking into account relaxation of the enhancement as discussed in the text.
5.2 Frequency-dependent response

At low frequencies the metastable NW emission includes a fast intensity response to reversals of the electric field direction. This is followed by eventual relaxation to the zero-field level over the course of several seconds. The varied behavior thus suggests phenomena governed by different physical processes. Measurements of the NW emission intensity modulated by AC electric fields were therefore conducted. We found that the enhancement/quenching effect at a given field strength persists up to 500 kHz. This is illustrated in Figure 5.4 (d) for experiments carried out with $E=22.0 \ (\sigma=7.9) \ \text{kV/cm}$. Since the data were recorded with a CCD using typical integration times of 0.1-10 seconds (in general) many switching events occur during a given frame. As a consequence, the effective enhancement is analyzed differently from the previous section.

At low frequencies (0.01 to 0.5 Hz; typical acquisition time per frame: 0.1 to 0.5 second) movies are analyzed by evaluating the average emission intensity ($I_{mean}$) from a given point of the wire over all frames. This value contains contributions from periods where the NW emission is enhanced and periods where it is quenched. To determine the net effect of the field, $I_{mean}$ is compared to the intensity at the same location under zero field conditions, $I_o$ (separate movie). The ratio $I_{mean}/I_o$ then indicates a net enhancement of the NW emission when in the presence of an external electric field.

Because of relaxation, emission trajectories acquired during low frequency (<1 Hz) modulation experiments show clear decays during a given half cycle (Figure 5.2 (b)). This relaxation phenomenon therefore lowers estimated emission enhancement factors. If analyses of the emission enhancement are conducted using peak (not average) emission intensities, slightly higher enhancement factors are obtained (blue diamonds, Figure 5.4)
(d)). These numbers more closely approximate the pure enhancement values in Figure 5.3 (a).

At high frequencies (1 Hz-500 kHz) the electric field switches on and off many times during a given frame (typical acquisition time: 10 s/frame, field switching synchronized to the frame integration time). We therefore alternate sequences when the AC field is on and when it is off. Off periods enable one to estimate $I_0$. Similarly, on periods provide $I_{\text{mean}}$. The ratio $I_{\text{mean}}/I_0$ (obtained from the same movie) then reveals the overall effect of the external field, which is again a net enhancement of the NW emission.

Although Figures 5.3 (a) and 5.3 (b) show that quenching slightly dominates enhancement, an overall emission enhancement is seen at all frequencies at the employed field strength [$E=22.0 \ (\sigma=7.9) \ kV/cm$]. This is because even when the polarity is reversed, the NW emission is never completely quenched (i.e. never goes to background levels, See Figure 5.2 (b) for example) and the pure enhancement is approximately 2 at the considered field. As a consequence, the net emission intensity in frames where multiple on/off cycles are averaged is enhanced. Corresponding enhancement factors between 1.3 to 1.6 are seen, which differ from the values of 2-3 in Figure 5.3 (a) (identical field strengths) because the latter values consider the enhancement or quenching independently. Notably, the enhancement in Figure 5.4 (d) does not change significantly over the range of frequencies investigated. This leads us to conclude that the field-induced enhancement/quenching persists up to 500 kHz or even higher since this is the cut-off frequency of our high-voltage amplifier.
5.3 Suggested mechanism for the electric field/NW emission coupling

We have shown that the spatial position of the NW emission as well as its intensity can be modulated using external electric fields. It appears that the strong correlation between an external electric field and the emission of nanostructures is a ubiquitous phenomenon. [2-4] For example, spectral diffusion in single colloidal QDs has been attributed to the random migration of surface charges causing time-dependent Stark shifts. [5] Furthermore, spectral diffusion and QD fluorescence intermittency (also called “blinking”) appear to be connected. [6] The latter phenomenon is thought to be related to the sequential charging and discharging of individual QDs. [7, 8] In either case, charges, possibly surface localized, play a role in the phenomenon.

Interestingly, the same behavior has been observed in individual solution grown NWs. Specifically, solution-based CdSe NWs exhibit large intrawire spectral heterogeneities with average shifts of 62 (σ=27) meV. Accompanying linewidths of 103 (σ=22) meV are also seen, inconsistent with lifetime-limited values. Intrawire intensity fluctuations akin to fluorescence intermittency are likewise observed and exhibit near identical power law on/off kinetics. [1] This similarity to QD behavior, despite dissimilar electronic structures, suggests surface localized charges as a point of commonality.

We therefore hypothesize the following (see also Figure 5.5). Mobile carriers exist on NW surfaces. They originate either through, as of yet unidentified, charge transfer events or are photogenerated. The presence of such charges effectively passivates NW surface defect states and in turn changes the exciton non-radiative recombination rate. As a consequence, photogenerated excitons in the vicinity of the localized carrier recombine radiatively. Passivated non-radiative decay channels likely quenching centers
relate to surface defects as supported by the low overall ensemble emission quantum yield (QY) of CdSe and CdTe NWs. [1, 9]

In general, the effective passivation is local to the immediate vicinity of surface bound carriers. However, applying an external electric field causes charges to migrate to opposite ends of the wire. The subsequent passivation of multiple electron acceptor states near the positive electrode causes the wire to become significantly brighter due to postulated changes in exciton non-radiative relaxation rates. The frequency response of the average enhancement (Figure 5.4 (d)) suggests carrier mobilities on the order of 0.04 cm²/Vs. These values are not consistent with the band transport of carriers in NWs (100-1000 cm²/Vs). Furthermore, in principle, were carriers to be inside the NW Auger-mediated relaxation would likely increase, not decrease, the non-radiative exciton decay
rate. [10] Both provide the reasons for suggesting surface localized carriers as responsible for the NW emission enhancement/localization.

We further speculate that a few mobile electrons can effectively passivate regions of the NW surface through the Coulomb repulsion of like charges. When coupled to their mobility, significant sections of the NW surface can therefore be passivated using only a few carriers. This picture is therefore, in many ways, an “electrostatic blockade” model for preventing carriers inside the NW from accessing non-radiative decay channels related to surface defects. Precedence for the hypothesis exists. Namely, the proposed scenario is virtually identical to a model developed by Maenosono to explain the fluorescence brightening of close packed CdSe QD films. [11] In either the current study or Maenosono’s earlier work, a more quantitative model for the Coulomb passivation is needed. Furthermore, it is clear that more detailed studies identifying the origin, energy as well as lifetime of long-lived surface (charge) trap states are needed. However, the postulated mechanism would seem to be the simplest model for self consistently explaining all of the presented data. It involves mobile charges. It further invokes surface carriers, avoids competing Auger effects, and ties into previous observations of intrawire NW spectral heterogeneity and intensity fluctuations. More importantly, the model requires few, not many charges to explain the effective passivation of the NW surface. The existence of low number of mobile electrons is confirmed in NW electrophoresis experiments described in the next Chapter.
5.4 References


CHAPTER 6:
DIELECTROPHORESIS OF CdSe NANOWIRES.

6.1 Dielectrophoresis of NWs

The presence of mobile charges can be directly tested through NW electrophoresis experiments. [1, 2] This is perhaps the simplest study that provides quantitative information about the magnitude and possible origin of stray charges. Experiments were conducted on NWs in toluene, chloroform, hexane, oleic acid and immersion oil. Early studies involved NW ensembles although it was ultimately concluded that such experiments provided only the sign and number of net excess charges on the NW. No information about the absolute number of mobile carriers present could be extracted, given the possibility of charge compensation by mobile species of the opposite sign. The experiment did, however, suggest the origin of these unbound charges as will be described shortly.

To circumvent these limitations, microelectrophoresis experiments were conducted on small NW bundles in immersion oil or oleic acid. These experiments involved the use of an inverted microscope with a microcavity built atop a cover slip. Wires were observed either under epi-illumination (i.e. through their emission) or under brightfield conditions. In epi-illumination mode, typical laser excitation intensities were 100-200 W/cm² with constant DC fields between 500 V/cm and 2 kV/cm. In all cases, single wire/bundle experiments showed that in either solvent, the wires behaved as
though positively charged. Moreover, the high viscosity of the solvent enabled an accurate recording of their dynamics. Nominal mobilities of $4 \times 10^{-4} - 10^{-3} \, \mu\text{m/s/V/cm}$ ($10^{-3} - 10^{-2} \, \mu\text{m/s/V/cm}$) were seen for wires in immersion oil (oleic acid).

At the outset of these experiments, many wires do not happen to be oriented along the (eventual) direction of the applied electric field. Thus, when a potential is applied, the wires first rotate to align themselves with the field. Figures 6.1 (a)-(r) show a series of frames illustrating NW rotational and translational motions in oleic acid. While this behavior can potentially be explained by the presence of internal dipoles due to the spontaneous polarization of wurtzite NW sections [3-5] the wires eventually move towards the negative electrode, indicating an excess of positive charges.

These experiments also suggest that permanent dipoles are not responsible for the NW torque and subsequent field alignment. In this respect, NWs always align themselves by *minimizing* their angle with the electric field. By contrast, were a permanent dipole or a static distribution of positive and negative charges to be present, observed rotation angles should exceed $90^\circ$ half of the time. This is because of the random orientation of wires in the channel prior to turning on the electric field. Furthermore, when the polarity of the field is suddenly reversed during an experiment, wires still rotate in the same direction. These results therefore rule out static dipoles and charges as the source of NW rotation and translation. The role of induced dipoles is also excluded since no NW translational motion should be observed in a uniform electric field. Instead, an accumulation of mobile charges at either NW end is suggested as the cause of the phenomenon.
Figure 6.1 A montage of images (a-r) illustrating NW bundle rotational and translational dynamics in oleic acid after a 500 V/cm DC electric field has been applied between the third and fourth frames. Image size: 100 x 100 μm². Image acquisition time: 0.2 seconds. Time interval between images: 0.4 seconds. Temporal variation of the NW bundle (s) angle $\alpha$ and (t) position from the images. Solid lines are a fit to the data using the model described in the text.

Furthermore, since NWs in oleic acid are positively charged and mobile electrons are thought to be responsible for the emission enhancement, an anti-correlation between the direction of NW electrophoretic motion and the spatial localization of its emission is expected. Figure 6.2 provides an example of NW translation in immersion oil with a
slowly modulated AC electric field. Asterisks in the images show the position of the emission localization and enhancement. In the case where the field polarity is reversed (Figures 6.2 (e), (f), (q)) a second asterisk appears indicating the new NW region experiencing emission enhancement. In all cases, the effect occurs at the NW end opposite to the direction of its translation. Such observations suggest that even though both negative and positive charges exist on the NW surface, electrons are responsible for the emission enhancement/spatial modulation. These experiments also show that NW mobile carriers are responsible for the effect since no substrate is involved in the measurement.

6.2 Hydrodynamic model for NW dynamics

To quantify the number of free carriers present, we introduce a simple model for the NW rotational and translational dynamics. In our approximation, forces acting on the wire include electrostatic forces between unbound NW charges and externally applied electric fields as well as viscous forces from the fluid. For simplicity, no intrawire Coulomb attraction between carriers of opposite sign is considered. On applying an
For viscous fluids with a small Reynolds number (Re) one has Re = \( \frac{\rho UL}{\mu} \). In the expression, \( U \) and \( L \) are the NW translational speed and length while \( \rho \) and \( \mu \) are the surrounding fluid’s density and viscosity. In the case of small Re, laminar flow exists and the force acting on a long slender cylinder with \( L/d \gg 1 \) (\( d \) is the NW diameter) is given by the following equation [6]

\[
d\vec{F} = -ds \frac{2\pi \mu}{\ln(L/d)} \left( 2\tilde{I} - \frac{d\tilde{R}}{ds} \cdot \frac{d\tilde{R}}{ds} \right) \tilde{U} + O \left( \frac{1}{\ln(L/d)^2} \right),
\]

where \( \tilde{R}(s) \) is the body centerline location, and \( s (0 \leq s \leq L) \) is a distance along the body centerline itself (NW growth axis).

In the general case of a wire moving within the \( xy \) plane and with an electric field pointed along its \( x \)-axis, \( \frac{d\tilde{R}}{ds} = [\cos(\alpha), \sin(\alpha)] \) is a unit vector tangent to the wire centerline, \( \alpha \) is an angle between the NW growth axis and the field, and \( \tilde{I} \) is the identity matrix. The wire translates with a velocity vector \( \vec{U} = (U, V) \) (\( U \) component along the \( x \) direction and \( V \) component along the \( y \) direction), rotating with an angular velocity \( \omega = \frac{d\alpha}{dt} \). The resulting forces \( \vec{F} = (F_x, F_y) \) acting on the wire are then

\[
F_x = -\frac{2\pi \mu L}{\ln(L/d)} \left( (2 - \cos^2(\alpha))U + \cos(\alpha)\sin(\alpha)V \right) + O \left( \frac{1}{\ln(L/d)^2} \right)
\]
\[ F_y = -\frac{2\pi \mu L}{\ln(L/d)}(\sin(\alpha)\cos(\alpha)U + (2 - \sin^2(\alpha))V) + O\left(\frac{1}{\ln(L/d)^2}\right) \quad (6.3) \]

An expression for the viscous torque, \( G \), on the wire can similarly be obtained from Reference 6

\[ G = -\frac{\pi \mu L^3}{3\ln(L/d)} + O\left(\frac{1}{\ln(L/d)^2}\right) \quad (6.4) \]

Higher order terms in Equations 6.1-6.4, of order \( O\left(\frac{1}{\ln(L/d)^2}\right) \), are excluded in subsequent calculations since, in long wires with large aspect ratios \((L/d \sim 1000)\), these extra terms contribute less than 10% (estimates are provided below) to the final result while making all calculations complex. The rigid NW is then driven by the constant force exerted by the electric field and its effective torque, \( T \). In general, \( T \) is a function of \( E, \alpha \) and time \( t \). As viscous forces act to counteract motion due to the electric field, a set of equations governing NW motion can therefore be written as

\[ \frac{dx}{dt} \frac{2\pi \mu L}{\ln(L/d)} \left[ 2 - \cos^2(\alpha) - \frac{\cos^2(\alpha)\sin^2(\alpha)}{2 - \sin^2(\alpha)} \right] = EQ \quad (6.5) \]

\[ \frac{d\alpha}{dt} \frac{\pi \mu L^3}{3\ln(L/d)} = -T \quad . \quad (6.6) \]

If a NW is placed in an electric field at an angle \( \alpha \) between its growth axis and the field lines, it will eventually develop an effective stationary charge \( Q_+ \) at the NW end closer to negative electrode and \( Q_- \) at the other end. The total nanowire charge becomes \( Q = Q_+ + Q_- \) and the resulting torque is \( T = \frac{L}{2} E(Q_+ - Q_-)\sin(\alpha) \). The torque originates
from mobile charges separated by the electric field and we model its orientation dependence through $T\cos(\alpha)$. After rearranging Equations 6.5 and 6.6 and defining new parameters $B(\alpha)$ and $\tau_\omega$

$$B(\alpha) = \frac{\ln(L/d)}{2\pi \mu L} \left( 2 - \cos^2(\alpha) - \frac{\cos^2(\alpha) \sin^2(\alpha)}{2 - \sin^2(\alpha)} \right)^{-1}$$  \hspace{1cm} (6.7)$$

$$\tau_\omega = \frac{2\pi}{3} \frac{\mu L^2}{\ln(L/d)(Q_+ - Q_-)E}$$  \hspace{1cm} (6.8)$$

we obtain the final Equations

$$\frac{dx}{dt} = B(\alpha, L, d, \mu)|E|(Q_+ + Q_-)$$  \hspace{1cm} (6.9)$$

and

$$\tau_\omega(Q_-, Q_+, L, d, \mu, E) \frac{d\alpha}{dt} = -\cos(\alpha) \sin(\alpha)$$  \hspace{1cm} (6.10)$$

where Equation 6.9 describes NW translation and Equation 6.10 models their rotation.

Two remarks about the hydrodynamic motion of NWs in an AC field and the accuracy of the model should be mentioned. When NWs are placed in an AC electric field with a frequency $f$, unsteady hydrodynamic effects come into play when $fU$ (the fluid inertia) has the same order of magnitude as the viscous term, $\mu U/(\rho L^2)$, in the Navier-Stokes equations. This means that such effects will be important only at frequencies where $f \sim \mu/(\rho L^2)$. Thus for a typical wire with $L \sim 10 \mu m$ in oleic acid ($\mu = 0.028 \frac{kg}{m \cdot s}$, $\rho = 863 \frac{kg}{m^3}$), the cutoff frequency is $\mu/(\rho L^2) \approx 320 \text{ kHz} \sim 3.2 \text{ MHz}$.
for immersion oil). Below this, Equations 6.9 and 6.10 should be valid. Another limitation exists. Namely, the model only provides an estimate for the total number of mobile carriers present. It does not account, for example, for intrawire Coulomb interactions between charges which result in a spatial delocalization of carriers. [7]

Several relevant parameters in Equations 6.9 and 6.10 can be estimated beforehand. Specifically, oleic acid has a dynamic viscosity of $\mu = 27.64 \times 10^{-3} \text{ kg m}^{-1}\text{s}^{-1}$. Likewise, the electric field magnitude is typically $|E| = 500 \text{ V/cm}$. The NW length ($L$) and diameter ($d$) can also be determined from optical and TEM experiments. In general, straight NWs used in these experiments form small bundles, consisting of approximately 3-8 wires. We therefore model such bundles by cylinders having the same total volume as all component wires put together. The equivalent diameter is $d = d_{\text{single}} \sqrt{n_{\text{NW}}}$ where $d_{\text{single}}$ (~10 nm) is the diameter of a single NW and $n_{\text{NW}}$ is the number of wires per bundle. In practice, this latter value is estimated from an analysis of the bundle’s overall emission brightness as compared to the known emission intensity from single wires.

$B$ and $\tau_0$ in the model depend weakly on $d$ and scale as $1/\ln(L/d)$. Variations in these parameter yield only small changes in predicted translational (Equation 6.9) and rotational (Equation 6.10) speeds. To illustrate, for a typical wire with $L$~10 μm and $d$~20-30 nm, $\ln(L/d) \sim 5.8$-6.2. Thus factor of two variations in diameter yield only discrepancies on the order of 10%. Similar behavior is seen with $L$. Its uncertainty arises from the ~300 nm diffraction-limited optical resolution of the microscope. This translates into ~3-6% variations of $L$ (5-10 μm long NWs) and corresponding ~4-8% variations in $B$ and $\tau_0$. 

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With these estimates in hand, Equations 6.9 and 6.10 can be fit to experimental data in order to extract values of $Q_+$ and $Q_-$. These are essentially the net magnitudes of positive and negative charges localized on the NW ends. Experimental values were obtained by analyzing movies such as the one in Figure 6.1. Experimental data (open circles) and accompanying fits (solid line) for the translational and rotational NW motion are shown in Figures 6.1 (s) and 6.1 (t). Best fit parameters are provided in Table 6.1. Extracted values of $Q_-$ vary from -33.5 to 9.2\( q\) ($q=1.602\times10^{-19}$ C). In the most optimal case, corresponding single wire charge densities, $Q_-(L\times n_{NW})$, range from 0.45 to 1.2 electrons per micron. In agreement with experimental observations, not only do mobile positive and negative carriers exist on or within the wire, but an excess of positive charges allows for the observed electrophoretic motion towards the negative electrode in oleic acid.

Calculated values of the linear charge density are actually lower limits. This is because the underlying model excludes attractive intrawire Coulomb interactions and implicitly assumes that all mobile carriers accumulate indefinitely at opposite ends of the NW. Clearly this is not physical due to the eventual Coulomb repulsion of like charges and in the opposite extreme, partial compensation by oppositely signed species. Instead, what likely happens is that charges accumulate at NW ends distributed in such a way as to reduce their overall interaction potential energy. As a consequence, more charges are actually needed to produce the same torque, $T = \frac{L}{2} E(Q_+ - Q_-)$, experienced by NWs during rotational alignment. Supporting this are images such as those in Figures 5.2 (a) and 5.4 (b) which clearly show, through the emission, that the field enhancement extends across a significant length of the NW. More detailed accountings of the actual NW
charge distributions and attractive Coulomb interactions are therefore required if more precise \( Q^+ \) and \( Q^- \) values are to be obtained.

### TABLE 6.1

**PARAMETERS IN THE MODEL**

<table>
<thead>
<tr>
<th>( L, \mu m )</th>
<th>3.5</th>
<th>7.4</th>
<th>9.1</th>
<th>9.6</th>
<th>12.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q, e )</td>
<td>38.4</td>
<td>30.0</td>
<td>41.1</td>
<td>68.1</td>
<td>78.9</td>
</tr>
<tr>
<td>( Q^+, e )</td>
<td>51.2</td>
<td>28.6</td>
<td>31.9</td>
<td>101.6</td>
<td>72.4</td>
</tr>
<tr>
<td>( Q^-, e )</td>
<td>-12.8</td>
<td>1.4</td>
<td>9.2</td>
<td>-33.5</td>
<td>6.5</td>
</tr>
<tr>
<td>( Q/L ) (bundle density), e/( \mu m )</td>
<td>-3.6</td>
<td>0.2</td>
<td>1</td>
<td>-3.5</td>
<td>0.5</td>
</tr>
<tr>
<td>( Q/(L \times n_{NW}) ) (single NW density), e/( \mu m )</td>
<td>-1.2 to -.45</td>
<td>0.03 to .07</td>
<td>0.13 to .33</td>
<td>-1.2 to -.44</td>
<td>0.06 to .17</td>
</tr>
</tbody>
</table>

6.3 Two sources of mobile carriers

Where do these mobile charges come from? Two experiments provide clues for answering this question. Electrophoresis experiments, conducted in a variety of solvents, show that the sign and magnitude of the net *excess* NW charge is solvent dependent. Wires in toluene behave as though negatively charged. Figure 6.3 (a) is a color photograph of a NW ensemble in toluene prior to turning on a DC field. The wires are placed in a cuvette between two optically transparent indium-tin-oxide electrodes. Upon applying a DC field (~300 V/cm), NWs migrate to the positive electrode. After a few minutes, a uniform NW coverage is obtained on the positive electrode. Figure 6.3 (b) is a
color photograph of the resulting sample. Wires in oleic acid and immersion oil, by contrast, behave as though positively charged (Figure 6.3 (d)). This varied behavior suggests that some fraction of mobile charges originate from sources extrinsic to the wires, possibly due to (as of yet unidentified) charge transfer events with impurities in solution.

Figure 6.3 Photographs showing an ensemble of CdSe NWs dispersed in toluene (a) before (b) after applying a -100V DC potential between two optically transparent indium-tin-oxide electrodes. The right electrode is grounded and is at a higher potential relative to the left electrode. Similar experiments conducted in oleic acid (Figures (c) and (d)) exhibit positive charging of NWs.

Figure 6.3 Photographs showing an ensemble of CdSe NWs dispersed in toluene (a) before (b) after applying a -100V DC potential between two optically transparent indium-tin-oxide electrodes. The right electrode is grounded and is at a higher potential relative to the left electrode. Similar experiments conducted in oleic acid (Figures (c) and (d)) exhibit positive charging of NWs.
Other sources of mobile carriers exist. In this respect, we have observed that the AC dielectrophoretic (DEP) alignment of CdSe and CdTe NWs contains contributions from photogenerated carriers. [1] Images of aligned NWs are shown in Figure 6.4. By comparing the DEP alignment efficiency in the presence of 488 nm (2.54 eV, 100-200 W/cm$^2$) light versus under “dark” (i.e. ambient light) conditions we see that deliberately excited NWs move more quickly to the electrodes. Conversely, wires exposed only to ambient light show much slower, less efficient, DEP alignment. Because the operating principle of DEP involves the interaction of field- and light-induced dipoles with electric field gradients, [1] these results suggest contributions to the overall NW mobility from photogenerated carriers.

Figure 6.4 DEP alignment of CdSe NWs (a) in the presence of 488 nm light (~100 W/cm$^2$, centered about the dashed circle) and (b) under ambient light conditions for the same exposure time. Gap: 50 μm in both cases.
Apart from estimates of the total number of mobile carriers present ($Q_+$ or $Q_-$), it is difficult to definitively determine the fraction of charges that are solvent related versus those that are photogenerated. This is, in some part, due to limitations of above electrophoresis experiments. More involved studies are thus required and likely involve trying to deliberately add charges to the NW surface through chemical means or by conducting NW electrophoresis experiments under different excitation intensities.

6.4 References


[7] Note that $Q_+$ and $Q_-$ do not necessarily mean the absolute number of positive and negative charges present. While the subscripts indicate the net charge accumulated on the wire closest to the positive ($Q_-$) and negative ($Q_+$) electrode, in fact, attractive Coulomb interactions between more tightly bound electrons and holes potentially cause $Q_{+,+}$ to reflect net charges accumulated at NW ends.
7.1 Experimental data

When we first observed photocurrent anisotropies from a film of randomly oriented CdSe NWs, we thought that this effect was due to imperfections in the optical system. Reflection from dielectric coated mirrors, dichroic beam splitters, and the polarization ellipticity of the laser beam could all potentially yield a measurable photocurrent anisotropy. Replacing dielectric mirrors for Al coated ones and correcting the excitation polarization quality by inserting a $\lambda/4$ waveplate resulted in a great improvement of circularity of the incident laser excitation. However, the photocurrent anisotropy of random CdSe NW films was still present. We then started to monitor the magnitude of the photocurrent normalized to the excitation power. It significantly improved the appearance of the data on corresponding plots (Figure 7.1 (a) and (b)) while better highlighting the residual anisotropy. A subsequent measurement using a commercial polarization insensitive Si photodetector revealed significant reduction of the anisotropy caused by imperfections in the laser excitation polarization. It also indicated that we were observing an actual physical phenomenon since imperfections in the optics only account for ~15% of the NW film signal.
Figure 7.1(a) Photocurrent anisotropy of a random CdSe NW network and a photodiode: $\rho = 0.28$ and 0.03 respectively. (b) Corresponding polar plot. (c) UV-VIS absorption and photocurrent action spectrum of a CdSe random NW network.
As a final experimental check, photocurrent action spectra of CdSe NW films were measured. Resulting spectra were then compared to their complimentary UV-VIS extinction spectra (Figure 7.1 (c)). The good agreement between the two verified that the photocurrent indeed originated from CdSe NWs.

What remained unclear was the source of the photocurrent anisotropy. A literature search revealed that a similar effect, a polarization “memory”, was observed in the emission from a solution of CdSe nanorods (NRs) with the emission preferentially polarized along the polarization direction of the excitation. [1] Rigorous modeling [2] explained the phenomenon by the dielectric constant mismatch between CdSe nanorods and the surrounding solution. Basically speaking, the subset of rods oriented collinear with excitation polarization absorbed the most of light. As a result, these rods emitted the most. This constitutes the source of emission anisotropy in the system.

Figure 7.1 (a) provides a hint for the origin of the photocurrent anisotropy in random CdSe NW solids. Namely, the DC electric field applied between two Au electrodes imparts a directionality to the NW network such that every time the excitation polarization $\vec{E}_0$ coincides with the applied electric field $\vec{E}_{DC}$, the highest level of normalized current is detected. Conversely, when $\vec{E}_0 \perp \vec{E}_{DC}$, a minimum occurs. This strongly suggests that the photocurrent anisotropy is greatly influenced by the directionality of externally applied DC field.

Prior to moving forward and trying to model the phenomenon, two important issues must be considered. First, on what length scale can the NW film be considered as being uniform? Second, when we can neglect the nonuniformity of the local electric field? It is apparent from Figure 2.4 that the NW film appears uniform on a macroscopic
scale, but appears greatly inhomogeneous on length scales below 1 μm. Therefore, on a micron scale we might expect clusters of wires to exhibit local directionality. These locally aligned NWs might then interfere with the directionality imparted by the external electric field. To rule out this possibility, the diameter of excitation spot was varied using an iris between 10 and 40 μm. Corresponding anisotropies were calculated as a function of excitation diameter (Figure 7.2). Less than 10% variations in calculated anisotropies were observed. This suggests the uniformity of CdSe films on length scales greater than 10 μm. In accordance with prior control experiments, anisotropy values did not change significantly when the excitation spot was moved across the gap.

![Figure 7.2 Excitation spot size dependence of the photocurrent anisotropy at a given point within the gap. Dashed lines are \( \cos^2 \theta \) fits to the data. Diameters employed are (a) 10 μm, (b) 15 μm, (c) 20 μm and (d) 40 μm.](image)
The net electric field at any given point of the NW network is the geometric sum of the external field and that produced by trapped carriers. Considering the high resistivity of such CdSe films (typical currents fall in the range of 100 pA – 10 nA) the existence of localized carriers is quite possible. This would then alter the magnitude of global $\rho$-values because of the compromised directionality of local electrical fields. We carried out two measurements to address this concern.

Measuring surface potentials with sub-μm spatial resolution using an AFM is common in semiconductor film experiments. During this procedure, the AFM probe first maps the surface topography. On a subsequent pass it measures the local electrostatic potential. We employed this technique for measuring the profile of a potential drop across the gap when ~10 V was applied to one of the electrodes (the second electrode was grounded). Figure 7.3 combines the AFM topographic image of the NW film with the surface potential cross section. In spite of the small “bumpiness” of the potential profile the overall data exhibits a linear drop between the electrodes. One drawback of these measurements is the difficulty in bringing in a laser beam to illuminate the sample area. As a consequence, AFM potential measurements were carried out without illumination.

To more thoroughly investigate possible charge accumulation within the CdSe NW network under more realistic illumination conditions, we performed the measurements with a variable size excitation spot. In contrast to the previously utilized circular excitation area, the excitation profile in these experiments was shaped into a rectangular form with the longer side (20 μm) parallel to the Au electrodes (insert of Figure 7.3 (c)). This configuration ensures that the external electric field strength is the
Figure 7.3 (a) AFM topography of NWs in the gap. (b) Corresponding surface potential measured across the same gap (9.5V, $E \approx 1.1 \times 10^7$ V/cm). (c) Changes in the photocurrent with excitation slit width (constant height of 20 μm).
same in the excitation area and that changes in local fields are solely due to the presence of trapped charges. The slit width was varied between 0.75-12 μm and measured photocurrents were plotted vs. spot width. If charge accumulation exists, inhomogeneities in the local field strength and direction should occur within the excitation area. By increasing the slit width, a larger number of traps can be sampled. We therefore expect an averaging effect as well as a linear proportionality between the photocurrent and the excitation slit width. Indeed, the experiment exhibited such a linear dependence between the photocurrent and the slit width (Figure 7.3 (c)). This confirms that the net electric field on length scales > 1 μm is produced by the externally applied bias.

Both the frequency and the spectral bandwidth of random NW films were measured. To measure the frequency response, a ferroelectric polarization rotator was inserted into the excitation optical path. Applying +/- 5 V stepwise voltage from a function generator rotates the excitation polarization by 90° at a prescribed frequency (0.5 Hz to 2 kHz). As apparent from Figure 7.4(a), at modulation frequencies >100 Hz the film weakly responded to such polarization flips. This probably reflects the high resistivity of the NW networks. Indeed, based on a ~100 Hz bandwidth, approximately 10 ms was required for carriers to travel ~ 10 μm under the influence of a ~1 kV/cm electric field. Estimated carrier mobilities in films are ~10^-4 cm^2/Vs and are 6-7 orders less than that detected for single NWs. This small value may then be explained by hopping transport within the film. In spectral response measurements (Figure 7.4 (b)) approximately the same anisotropy values were found between 480 to 670 nm. This behavior is consistent with predictions of the model presented in the next section.
7.2 Rudimentary model for the photocurrent anisotropy

In the model we consider two origins for the photocurrent anisotropy: the polarization sensitive absorption of light by single NWs and charge separation facilitated by an externally applied electrical field. For thin wires with free carriers experiencing radial confinement (NW diameters below twice their corresponding bulk exciton Bohr
radius) selection rules for optical transitions likely exhibit confinement-induced modifications resulting in absorption polarization anisotropies.[3] Furthermore, for wires embedded in a medium with a dielectric constant $\varepsilon_m$ different from that of NWs, $\varepsilon$, the dielectric mismatch also contributes to the absorption polarization anisotropy. In this regard, for wires with diameters larger than twice the Bohr radius, dielectric contrast becomes the dominating source of the polarization anisotropy. [4-6] Since NW diameters employed in the current study exceed twice the bulk exciton Bohr radius of either CdSe ($a_B=5.6$ nm) or CdTe ($a_B=7.5$ nm), observed polarization anisotropies are thought to originate primarily from this latter phenomenon. [4]

Due to the mismatch in dielectric constants, the attenuation of the optical field inside the wire is determined by the mutual orientation of the wire axis and the incident field polarization. [7] For the optical field inside the wire, solutions yield a field, $E_\parallel$, identical to the external field, $E_0\parallel$. However, the perpendicular component $E_\perp$ is largely attenuated ($E_\perp = \frac{2\varepsilon_m}{\varepsilon + \varepsilon_m} E_0\perp$). In the following calculations, we use the dielectric constant of bulk CdSe $\varepsilon_{\text{CdSe}}=7.21+2.61i$ measured at 532 nm.[8] Since the NWs are deposited at the air/glass interface of a glass microscope cover slip, both the dielectric constants of glass $\varepsilon_{\text{glass}}=2.3$ and air $\varepsilon_{\text{air}}=1.0$ were averaged to give $\varepsilon_m=1.65$.

The amount of light absorbed by the wire, $P$, is proportional to the square of the internal electric field ($P \propto E_\parallel^2 = E_0^2 + E_\perp^2$).

$$P \propto E_0^2 \left| \frac{2\varepsilon_m}{\varepsilon + \varepsilon_m} \right|^2 \sin^2(\beta - \alpha) + E_0^2 \cos^2(\beta - \alpha)$$  \hspace{1cm} (7.1)
where $\alpha (\beta)$ denotes the angle between the external DC field and the NW growth axis (the incident light polarization vector) (Figure 7.5 (a)). The difference between these angles yields the angle $\theta$ between the NW growth axis and the excitation polarization. Each photon absorption event immediately results in the generation of one electron and one hole which might radiatively (or nonradiatively) recombine (both undesirable processes) or escape this fate by being separated by the applied DC electric field (a desired process for current generation). In this case, the strength of the external electric field determines the number of free carriers contributing to the observed photocurrent.

Similar to the optical field, an external DC electric field experiences the attenuation of parallel ($E_{DC} |\cos \alpha|$) and normal ($\left| \frac{2\varepsilon_m}{\varepsilon + \varepsilon_m} E_{DC} \sin \alpha \right|$) components inside the wire. Although the exact mechanism for the electric field assisted dissociation of electron-hole pairs inside the NWs has not been determined, we assume that the number of electrons and holes, $n_{e(h)}$, contributing to the current is proportional to the external DC electric field strength through

$$n_{e(h)} \propto E_{DC} \left( |\cos \alpha| + \frac{2\varepsilon_m}{\varepsilon + \varepsilon_m} \sin \alpha \right). \quad (7.2)$$

This linear proportionality is hypothesized to originate from significant 1D exciton binding energies predicted to occur within NWs. [9]

Once separated, mobile electrons/holes travel through the NW network towards their respective electrodes. Since estimated NW densities ($10^9$ to $10^{10}$ NWs/cm$^2$) are well above the percolation threshold [10] (1/$<L>^2$ - $4 \times 10^6$ NWs/cm$^2$, where $<L>$=5 $\mu$m is the average length of a single NW), each NW connects to many other wires having different
Figure 7.5 (a) Cartoon schematic of a model utilized in photocurrent anisotropy calculations. In the diagram, $\alpha (\beta)$ represents the NW (incident polarization) orientation relative to the external field and $\theta$ is the angle between the light’s polarization and the NW growth axis. $E_0$ is the magnitude of the optical electric field. Likewise, $E_{DC}$ is the magnitude of the applied DC electric field. (b) Effect of applied bias on the photocurrent.
orientations (Figure 2.4). Furthermore, given an electrode gap larger than $<L>$, carriers likely undergo hopping transport to the electrodes. The measured mobility of carriers in the NW network $\sim 10^{-4}$ cm$^2$/Vs is easily 4-6 orders of magnitude smaller than intrawire carrier mobilities 150-650 cm$^2$/Vs measured for single NWs. [11] A model of carrier transport then accounts for this through a corresponding reduction of the carrier velocity in the film

$$V_{e(h)} \propto \mu_{e(h)}^\text{film} E_{DC} \quad \text{(7.3)}$$

where $\mu_{e(h)}^\text{film}$ is the effective electron and hole mobility. Since the current density, $j$, is proportional to the product of $n_{e(h)}$ and $v_{e(h)}$, Equations 7.2 and 7.3 yield

$$j \propto E_{DC}^2 \mu_{e(h)}^\text{film} \left( |\cos \alpha| + \frac{2 \epsilon_m}{\epsilon + \epsilon_m} \sin \alpha \right) \quad \text{(7.4)}$$

The overall current, $I$, is then the product of 3 terms, the number of photogenerated carriers (proportional to the amount light absorbed, Equation 7.1), the probability for electrons and holes being separated (Equation 7.2), and the mobility of carriers in the film (Equation 7.3)

$$I \propto E_0^2 E_{DC}^2 \mu_{e(h)}^\text{film} \left( \frac{2 \epsilon_0}{\epsilon + \epsilon_0} \right)^2 \sin^2 (\beta - \alpha) + \cos^2 (\beta - \alpha) \left\{ \cos \alpha + \frac{2 \epsilon_m}{\epsilon + \epsilon_m} \sin \alpha \right\} \quad \text{(7.5)}$$

When Equation 7.5 is averaged for the random orientation of nanowires ($0 \leq \alpha \leq \pi$), expressions for the entire nanowire network maximum and minimum photocurrent values are obtained

$$I_{\text{max}} (\beta = 0^\circ) \propto E_0^2 E_{DC}^2 \mu_{e(h)}^\text{film} \left( \frac{4}{3} \frac{2 \epsilon_m}{\epsilon + \epsilon_m} \right)^3 + \frac{2}{3} \frac{2 \epsilon_m}{\epsilon + \epsilon_m} \right]^2 + \frac{2}{3} \frac{2 \epsilon_m}{\epsilon + \epsilon_m} + \frac{4}{3} \quad \text{(7.6)}$$
The resulting polarization anisotropy for a random NW network is then

$$I_{\text{min}}(\beta = 90^\circ) \propto E_0^2 E_{DC}^2 \mu_{\text{film}}^{\text{film}} \left( \frac{2}{3} \frac{2m}{\varepsilon + m} + \frac{4}{3} \frac{2m}{\varepsilon + m} + \frac{2}{3} \right). \quad (7.7)$$

The dielectric mismatch between $\varepsilon$ and $m$ yields $\rho_{\text{CdSe}}=0.122$ for CdSe NWs.

If we assume that the separation of carriers inside the NW is determined solely by the electric field parallel to the NW axis, the $\sin \alpha$ term in Equation (7.5) can be neglected. We obtain the following expressions for the maximum and minimum values of the photocurrent

$$I_{\text{max}}(\beta = 0^\circ) \propto E_0^2 E_{DC}^2 \mu_{\text{film}}^{\text{film}} \left( \frac{2}{3} \frac{2m}{\varepsilon + m} + \frac{4}{3} \right) \quad (7.6)$$

$$I_{\text{min}}(\beta = 90^\circ) \propto E_0^2 E_{DC}^2 \mu_{\text{film}}^{\text{film}} \left( \frac{4}{3} \frac{2m}{\varepsilon + m} + \frac{2}{3} \right). \quad (7.7)$$

The resulting polarization anisotropy in the absence of the $\sin \alpha$ term is then

$$\rho = \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}} = \frac{1}{3} \left( 1 - \left( \frac{2m}{\varepsilon + m} \right)^2 \right) \left( 1 + \frac{2m}{\varepsilon + m} \right), \quad (7.8)$$

which yields $\rho_{\text{CdSe}} \approx 0.26$. The close agreement to our experimental numbers probably indicates that the normal component of DC electric field does not contribute much to carrier separation.

Additional corroborating evidence for the model include experiments aimed at examining the magnitude of the observed photocurrent as a function of applied bias.
Specifically, Equation 7.5 implies that the photocurrent scales as $E_{DC}^2$ (or as $V^2$). Results from these experiments are shown in Figure 7.5 (b) and indicate that measured photocurrents change linearly with $V^2$. This is either a signature that our model adequately explains the phenomenon or tells us that a space-charge limited current exists in the nanowire network. [12]

This study has demonstrated the existence of current polarization anisotropies in random NW networks. The underlying principle for the existence of such anisotropies is that external DC electric fields impart directionality into the random NW film. As a consequence, a strong underlying asymmetry exists in the device even though the NW network as a whole exhibits no preferred orientation. All, in turn, suggest the feasibility of constructing polarization sensitive NW devices without the need to align component NWs.

7.3 References


CHAPTER 8:
CONCLUSIONS

My hope is that this Thesis covers and explains some basic observations of CdSe NWs interacting with optical and electrical fields. Indeed, absorption cross-sections are important parameters whose values are often required in many optical experiments. We provided a routine to quantify this parameter and to determine limits stemming from the 1D nature of the wires. High NW aspect ratios enable an easy detection of emission enhancement/quenching triggered by external electrical fields. We have explained this by the passivation of emission quenching centers by mobile electrons present on NWs. The presence of mobile electrons has subsequently been confirmed in dielectrophoresis experiments. Furthermore, analysis of rotational and translational dynamics of NWs dispersed in liquids undoubtedly argues in favor of such mobile carriers. Finally, the photocurrent anisotropy of random NW networks has been explained by the 1D dimensionality of the wires. Again, the 1D geometry of the NWs and the presence of mobile carriers were naturally combined in a simple model to qualitatively and quantitatively characterize the phenomenon. All optical experiments described in the Thesis involve two significant NW properties: a) SLS synthesized CdSe NWs possessing high aspect ratios (>1000, length/diameter ratio) and b) mobile carriers present on or inside of NWs. The recognition of these facts might lead to a deeper understanding about other unusual phenomena, such as NW emission intermittency.
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