Merging quantum dots, biomolecules, and polymers for record performance from solution-processed optoelectronics

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1. INTRODUCTION

We apply discoveries in nanoscience towards applications relevant to health, environment, security, and connectedness. A materials fundamental to our research is the quantum dot [1]. Each quantum dot is a particle of semiconductor only a few nanometers in diameter (Fig. 1).

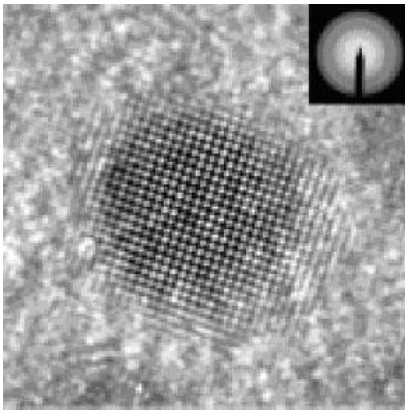

Fig. 1. A 4 nanometer PbS quantum dot.

These semiconductor nanoparticles confine electrons to within their characteristic wavelength. Thus, just as changing the length of a guitar string changes the frequency of sound produced, so too does changing the size of a quantum dot alter the frequency – hence energy – the electron can adopt. As a result, quantum dots are tunable matter (Fig. 2).

We work with colloidal quantum dots, nanoparticles produced in, and processed from, solution. They can be coated onto nearly anything – a semiconductor substrate, a window, a wall, fabric. Compared to epitaxially-grown semiconductors used to make optical detectors, lasers, and modulators, they are cheap, safe to work with, and easy to produce.

Much of our work with quantum dots involves infrared light – its measurement, production, modulation, and harnessing. While there exists an abundance of work in colloidal quantum dots active in the visible, there are fewer results in the infrared. The wavelengths between 1000 and 2000 nm are nonetheless of great practical importance:

- half of the sun's power reaching the earth lies in this wavelength range;
- 'biological windows' in which tissue is relatively transparent and does not emit background light (autofluorescence) exist in the infrared;
- fiber-optic networks operate at 1.3 and 1.5 um.

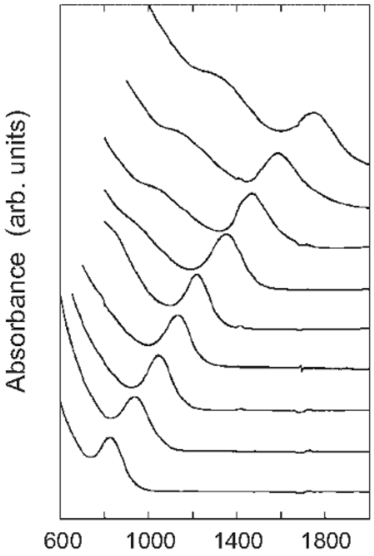

Fig. 2. The absorption spectra of PbS quantum dots ranging from 1 nm (bottom curve) to 8 nm (top curve). The horizontal axis is the wavelength of light in nanometers. The spectrum illustrates quantum size effect tuning.

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We are therefore pursuing the following goals:

1. Harvest light's power with high efficiency and at low cost
2. Sense life at the molecular level
3. Generate infrared light for high-speed networking

2. HARVESTING LIGHT'S POWER WITH HIGH EFFICIENCY AND AT LOW COST

Each day the sun bombards the earth with ten thousand times more energy than we consume. If we could cover 0.1% of the earth's surface with solar cells, and each solar cell was 10% energy efficient, we could satisfy our energy needs completely using this clean source of energy alone.

The world is not solar-powered today because solar panels cost more to build and install than we are willing to pay. We need to produce solar cells of very large area, but at the same time low cost, to capture a significant amount of power. Traditionally, rigid flat wafers of semiconductor have been used to make solar cells. We are instead working with physically flexible, solution-processed materials for harvesting light. Others have shown that photovoltaics made using such materials can be printed like newspapers, spinning seamlessly from roll to roll. The resulting solar cells are easy to transport and deploy. They could even be wearable.

Unfortunately, today's flexible, printable solar cells are not yet efficient enough for them to be of widespread use. One of the reasons is that they absorb only visible light. These devices "see" only about half of the sun's power reaching the earth. The other half lies in the infrared. In fact any warm object-even one not so hot as to glow visibly-emits energetic infrared rays in scaled-down mimicry of the sun's production of visible light. Photovoltaics are thus needed that can capture not only visible light, but infrared light as well.

In January 2005, we showed that we could turn infrared power into electricity in a solution-processed solar cell. Sensitizing conjugated polymers with infrared active nanocrystal quantum dots provided a spectrally tunable means of accessing the infrared while maintaining the advantageous properties of polymers. Earlier, we had reported a nanocomposite [2] in which quantum size effect-tuned PbS nanocrystals sensitized (MEH-PPV) into the infrared. This first report proved the principle but showed very low efficiency of 10^{-5} that necessitated the use of modulated illumination and a lock-in amplifier to observe the photocurrent. We more recently demonstrated [3], also using solution-processed materials, has been a three-order-of-magnitude improvement in infrared photoconductive internal quantum efficiency, allowing observation of the photocurrent under continuous-wave illumination without reliance on lock-in techniques; and also the first observation of an infrared photovoltaic effect in such materials. Under -5 V bias and illumination from a 975 nm laser, these detectors showed an internal quantum efficiency of 3%, a ratio of photocurrent to dark current of 630, and a maximum responsivity of 3.1×10^{-3} A/W. By varying the size of the nanocrystals during processing, photocurrent spectra were demonstrated with peaks tailored to 980 nm, 1.200 μm, and 1.355 μm.

Most recently [4], we have reported a processible infrared photovoltaic device active beyond 1 um that exhibits an external quantum efficiency exceeding 1% and an estimated monochromatic internal quantum efficiency greater than 10%. This represents an improvement by more than 1000 compared to the best previously reported processible greater-than-1-um infrared photovoltaics. We employed a device architecture in which the infrared-absorbing active layer is based purely on semiconductor nanoparticles with no semiconducting polymer matrix. The replacement of a polymer-quantum dot composite with a pure nanoparticle layer, combined with improvements in control of organic ligands passivating nanoparticle surfaces, facilitates improved electronic transport, enhancing carrier extraction prior to recombination.

3. SENSING LIFE AT THE MOLECULAR LEVEL

Nucleic acids such as DNA code life. Semiconductors process, store, and convey information. We are uniting nucleic acids with semiconductors to create materials to help advance the early detection of disease.

We recently reported the successful growth of infrared-emitting quantum dots with the aid not of monomeric ligands such as TOP/TOPO or oleic acid, but instead based on the biopolymer DNA [5]. The resultant nanoparticles were soluble in water, a crucial requirement for biological applications. The synthetic procedure resulted in PbS nanoparticles with exceptional stability and photoluminescence quantum efficiency. Energy-filtered transmission electron microscopy revealed cubic-latticed PbS quantum dots 4 nm in diameter on a network of DNA. We obtained photoluminescence quantum efficiencies greater than 10%. Aged in standard plasma at 37°C, the DNA-grown PbS nanocrystals exhibited a quantum efficiency half-life of one week.

We are now working to create smaller, more biocompatible quantum dots that also emit at the wavelengths at which live tissue is maximally transparent and minimally autofluorescent.

4. GENERATING INFRARED LIGHT FOR HIGH-SPEED NETWORKING

Using quantum dots to produce, detect, and act on light offers advantages relative to classically-sized (bulk) materials. Tunability based on the quantum size effect allows a single material to address a vast set of wavelengths. It is attractive to be able to use a single family of processes designed around a single class of materials to build devices spanning such a broad spectral range. The approach contrasts with the need in single-crystal epitaxy to develop material- and substrate-specific processes for each spectral range of interest.

Since size determines the set of optical transitions, even slightly polydisperse ensembles of quantum dots exhibit inhomogeneous broadening. While in some applications this is a problem, in others, controllable broadening is useful. A new standard in fibre-optics, coarse wavelength-division multiplexing, mandates use of the emerging low-optical-loss fibre spectrum 1270 - 1610 nm with 20 nm spacings between channels. Since homogeneous line widths are at room temperature in the few meV, corresponding at these wavelengths to ~ 10 nm, a single designably-homogeneously-broadened quantum-dot-based material could independently address all CWDM channels. If crosstalk among these dots could be avoided, signal processing could be done in parallel on these eighteen channels within a single medium with the need for demultiplexing, separate processing, and remultiplexing.

Electroluminescent sources in the infrared thus link electronics-based communications and signal-processing systems with the carrier used in optical communications. Measures of practical interest include external quantum efficiency – the ratio of photons extracted to electrons injected – and brightness. One inferred quantity often estimated and reported is the internal quantum efficiency – the number of photons generated within the per injected electron. Size-tunable infrared electroluminescence in the telecom wavelengths, resulting in devices with internal efficiency 1.2%, was recently reported based on PbS colloidal quantum dots [6]. Photoluminescence excitation spectra were subsequently used to study the influence of ligand chemistry and ligand length on energy transfer from a polymer matrix to nanocrystals [7]. PbS nanocrystals capped a variety of organic ligands were combined with the host matrix MEH-PPV and formed into films. Composites based on as-synthesized PbS nanocrystals capped by oleate ligands provided transfer efficiencies – excitons transferred to the nanocrystals divided by total excitons generated in the polymer – of 20%. Replacing oleate with the shortest ligand gave a threefold improvement in excitation transfer efficiency. Photoluminescence quantum efficiency optimization has also been reported through combined ligand and polymer matrix engineering [8]. By uniting advances in photoluminescence quantum yield and energy transfer, electroluminescence efficiency has recently been further improved [9].

Room-temperature amplified spontaneous emission and spectral narrowing at infrared wavelengths have been reported in solution-processed films made up of PbS [10] quantum dot nanocrystals. The results are relevant to optical amplification and, ultimately, the possibility of realizing lasers integrated on a variety of substrates. In the case of PbS, the active optical medium provided amplified spontaneous emission at 1300 nm and operated at room temperature without any additional matrix material, providing an optical gain of 260 cm^{-1} and a pump threshold of 1 mJ/cm^{-2}. Nanocrystals synthesized in aqueous solution and stabilized using short ligands resulted in a high quantum dot volume fraction in solid films and a three-dimensional superlattice effect which red-shifts emission relative to absorption.

CONCLUSIONS

The field of infrared solution-processed quantum dots may hold great promise, but this promise remains to be materialized until stringent performance requirements are fulfilled. We are working towards demonstrating:

- infrared photodetectors with D* (normalized detectivity, a.k.a. specific detectivity, the measure of detector sensitivity) exceeding $1\text{x}10^{12}$ Jones at room temperature;
- infrared photovoltaics with monochromatic power conversion efficiency exceeding 10%;
- a solution-processed infrared laser; and
- efficient (> 10% quantum yield), biocompatible, rapid-clearance (< 4 nm hydrodynamic radius), aqueous-soluble, long-lived quantum dots excited in, and emitting in, the infrared biological windows.

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