Nanostructures Capable of Emission and Absorption in Near Infrared for Biochemical Applications

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1. Abstract.

1.1. Quantum Dots

Semiconductor quantum dots (QD) or nanocrystals (NC) are one of the most promising new tools in bio-medical research and its applications. They are already being used in such fields as in-situ imaging, as signal enhancers in surface enhanced Raman scattering (SERS)[1], for identification of bio-molecules, and in therapeutic applications (cancer / tumor treatments, for example).[2]

A quantum dot is a semiconductor crystal with a diameter of a few nanometers, also called a nanocrystal. Because of its small size it behaves like a potential well that confines electrons-hole pairs in three dimensions.[3] Fig. 1 shows a quantum dot and its band structure in which the hole is trapped by the potential of the dot, the electron is able to move around the dot, but is attracted to the hole by the Coulomb force.

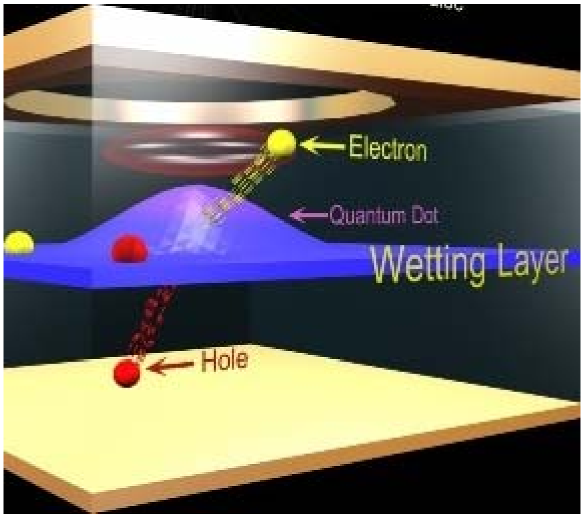

Figure 1 Process of Quantum Dots Formation

1.2. Nanoshells

Nanoshells are nano-sized semiconductor or dielectric balls, coated with thin layer of metal, usually gold or silver (Fig. 2). By manipulating the thickness of the metal layer one is able to make these nanoshells absorb light at specific wavelengths.

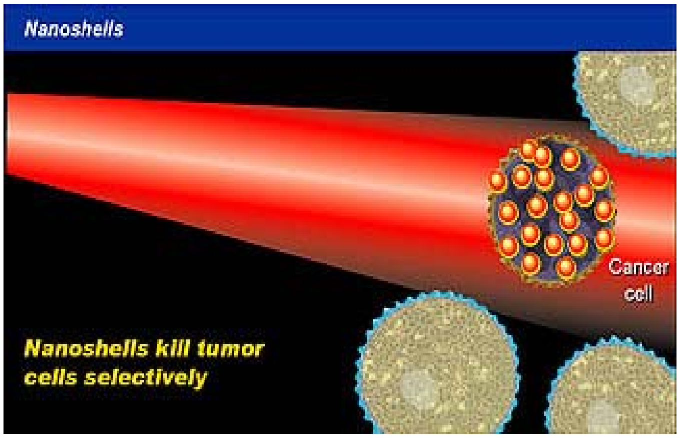

Figure 2 Nanoshells and Their Application to Tumor Treatments

Nanoshells that are capable of absorbing in near-infrared (NIR) spectral range (700nm – 1000nm) are most useful, since they can be heated up rapidly, and, as it is known, intense heat is lethal to the cells[4]; thus, one can, for example, use nanoshells to treat tumors.

1.3. Why NIR?

Most biological substances absorb and/or emit light with wavelengths between 190nm and 650nm. Therefore, quantum dots that are emitting and/or absorbing in the NIR (700nm – 1000nm) are the most useful, since NIR radiation penetrates relatively deeply into tissue with very low background auto-fluorescence and scattering[5]. Several nanosystems are being used for the NIR imaging and for therapeutic applications - e.g., CdSe/CdTe core-shell type II quantum dots[6] coated with polydentate phosphine are used for a major cancer surgery, sentinel lymph node mapping.

Most currently employed nanostructures contain such toxic elements as Cadmium (Cd), Lead (Pb) or Mercury (Hg). These elements are dangerous by themselves, and, thus should not be used in medical applications. Therefore, it is important to look for new classes of materials that can be used to fabricate quantum dots and nanoshells, operating in NIR and that do not contain heavy metals.

Silver Sulfide (Ag_2S) does not contain toxic elements, and thus is a good candidate for application in the biomedical field.

1.4. Silver Sulfide Quantum Dots

Ag_2S is a direct band semiconductor with the bulk band gap energy of about 0.9eV (~1370nm)[8*]. The effective masses of electron and holes are $m_e^* = 0.286m_0$, $m_h^* = 1.096m_0$[9]. The Ag_2S dielectric constant, ε, is about 6. Assuming that confined excitons are responsible for optical transitions, one can estimate the size of spherical Quantum Dots that would emit or absorb electromagnetic radiation within 700nm-1000nm range via the following equation[10]:

$$E_{ex} = E_{bulk} + \frac{\pi^2\hbar^2}{2R^2\mu} - 1.8\frac{e^2}{\varepsilon_\infty R},$$

where E_{bulk} is the band gap of bulk Ag_2S, R is the radius of the nanoparticle, and μ $(\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*})$ is the effective reduced mass of the exciton. Thus, spherical Ag_2S Quantum Dots with diameters between 2nm and 4nm can be used for NIR applications.

2. Hypothesis

We proposed to develop quantum dots and nanoshells, for application in the bio-medical field, based on Ag_2S direct band gap semiconductor. We expect Ag_2S Quantum

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[*] To convert energy to wavelength, one can use the following equation: λ (nm) ≈ 1240/E(eV)

Dots to emit in the NIR, whereas both Quantum Dots and nanoshells absorb in the NIR. We also expect that due to chemical nature of this system one can fabricate Quantum Dots and nanoshells of comparable sizes. Therefore, such nanoparticle systems would have tremendous advantage over currently used materials as we expect them to emit as well as to absorb in NIR at the same time.

Indeed, use of quantum dots with nanoshells of comparable size would, for instance, enable one to image and treat cancerous cells simultaneously. This should drastically reduce time and number of invasive procedures, increasing the efficiency of the treatment, and, most important, the patient's quality of life.

In order to verify the hypothesis, we needed ≈3 nm Ag_2S particles. The task was to prepare these particles and to test their transmission and absorbance rates using CCD spectrometer, tungsten-halogen light source, and the software. Since such particles are difficult to make, we will start testing larger particles and then reduce the size to that required for the project.

3. Ag_2S Nanocrystal Synthesis.

The following chemicals were used to prepare silver sulfide nanocrystals.

1. Silver nitrate ($AgNO_3$)
2. Tetra-*n*-octylammonium ($(C_8H_{17})_4NBr$)
3. 1-Nonanethiol ($CH_3(CH_2)_8SH$)
4. Sodium Sulfide (Na_2S)

Method:

1. Thirty milliliters of an aqueous silver ion solution (0.03M $AgNO_3$) was mixed with 20mL of a chloroformic solution of phase transfer catalyst (0.20M $(C_8H_{17})_4NBr$) and stirred vigorously for 1 hour until all the silver salt was transferred into the organic layer.
2. The French gray organic phase was subsequently collected, and 150*u*L 1-nonanethiol was added. After the nonanethiol/Ag^+ solution were stirred for 15 min, 1.5mL of fresh aqueous sodium sulfide (0.43M Na_2S) solution was used.

$$2AgNO_3 + Na_2S \rightarrow Ag_2S + 2NaNO_3$$

3. After the Ag_2S solution was prepared, the centrifuge and 10nm filter were used for 30 min.

At the end of the procedure ≈50mL solution of 10nm Ag_2S particles was prepared. Because of the lack of equipment and the lack of time we were not be able to get 3nm particles.

5. Experimental Setup

A charge-coupled device (**CCD**) is a sensor for recording images, consisting of an integrated circuit containing an array of linked or coupled, capacitors. Under the control of an external circuit, each capacitor can transfer its electric charge to one or other of its neighbors. CCDs are used in digital photography and astronomy (particularly in photometry, optical and UV spectroscopy and high speed techniques such as lucky imaging).[3]

A **LASER** (Light Amplification by Stimulated Emission of Radiation) is an optical device which uses a quantum mechanical effect called stimulated emission (discovered by Einstein while researching the photoelectric effect) in order to generate a beam of light from a lasing medium of controlled shape, purity, and size. One can make a laser beam to be a continuous, constant-amplitude (known as *CW* or continuous wave), or pulsed, by using the techniques of Q-switching, model-locking, or gain-switching. In pulsed operation, much higher peak powers can be achieved. A laser medium can also function as an optical amplifier when seeded with light from another source. Common light sources, such as the incandescent light bulb, emit photons in almost all directions, usually over a wide spectrum of wavelengths. Most light sources are also incoherent, which means that there are no fixed phase relationships between the photons emitted by the light source. By contrast, a laser generally emits photons in a narrow, well-defined, polarized, coherent beam of near-monochromatic light, consisting of a single wavelength or hue.[3]

A Fiber (see e.g. Fig. 3) is a very thin (1-1000 microns) silica strand, designed for light transmission. Fibers are able to "trap" the light beam using the principle that the light will fully reflect of a surface under a certain angle. When a beam of light gets into the fiber, it is being reflecting back and forth, and thus can travel through it without a significant loss. Because of light weight, amount and safety

Figure 3 Fibers

of transmitted information (up to 10Tb/sec), fibers are widely used in telecommunications, and in many other fields.[3]

4.1. Equipment used

Figure 4 HR 4000 Spectrometer From Ocean Optics, Inc.

a) An Ocean Optics, Inc. CDD based HR 4000 spectrometer (Fig. 4) operating in the spectral range between 250nm and 1100nm was employed for light detection. It functions as a conventional spectrometer, which brakes down the beam of light into a spectrum of wavelengths, and a detector using a CCD. It does not require external power source as it powered through USB connection to computer.

b) A Tungsten-Halogen Light Source LS-1-LL (Ocean Optics, Inc.) (Fig. 5) Tungsten-Halogen Light Source is a white-light source, optimized for the Visible-Near-

Figure 5 A LS-1 or a LS-1LL Tungsten-Halogen Light Source (Ocean Optics, Inc.)

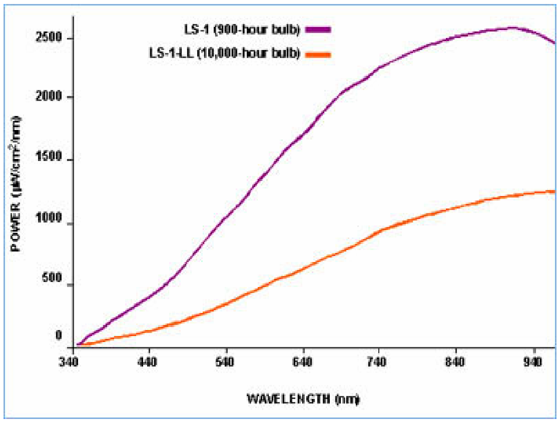

Figure 6 Emission Spectrum (lower curve) of a LS-1LL Tungsten-Halogen Light Source (Ocean Optics, Inc.)

Infrared spectral region from 350nm to 2000nm (Fig. 6).

c) Premium-grade Solarization-resistant Optical Fiber QP400-2-SR

Width: 400 µm; Transmission range: 200-1100 nm

d) OOI Base32 Spectrometer Operating Software

e) Lasers:

A solid state Frequency Doubled Nd:YAG laser (532nm)

A Gas He-Ne Laser (631nm)

f) Quartz SUPRASIL 1mm absorption cell

We used fused silica beakers to minimize the loss of light due to absorption. Also, exact control of the width at 1 mm makes calculations easier.

Figure 5 Quartz SUPRASIL Fused Silica 1mm Cell

8. Experimental Results

Passing the light through Silver Sulfide particles dispersed in the Chloroform and

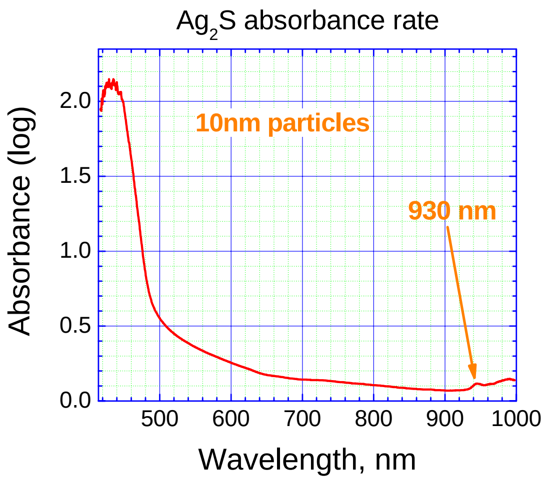

Figure 8 Absorbance of 10nm Ag_2S nano-particles

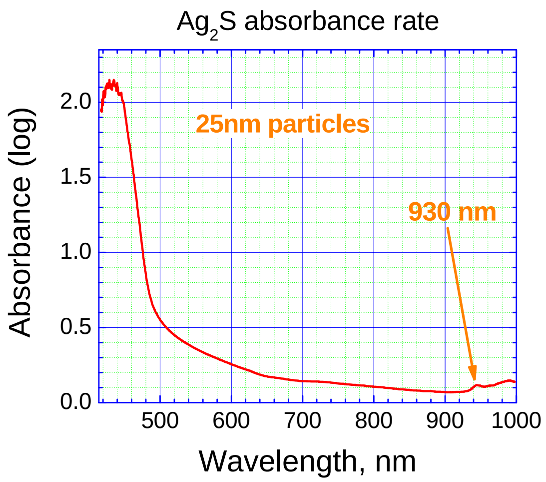

Figure 9 Absorbance of 25nm Ag_2S nano-particles

stored in the fused silica cell, we obtained the results shown in Figs. 8 - 10 for the particle with diameters of 10nm, 25nm, and 200nm, respectively.

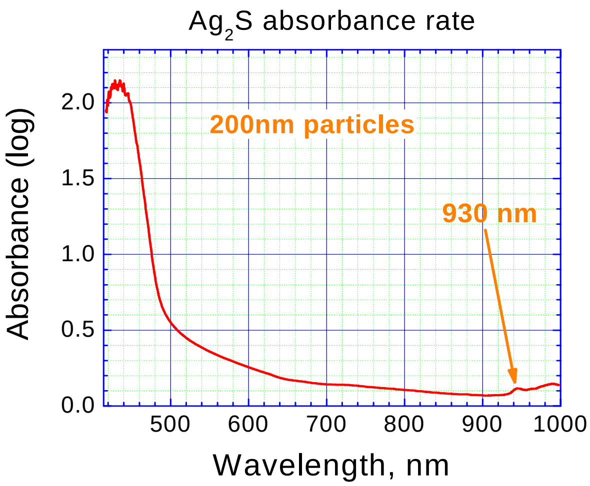

Figure 6 Absorbance of 200nm Ag_2S nano-particles

There is a peak in NIR at about 930 nm; however, it is a very weak and we are not sure if it is a real peak or just a noise. The peak at ~ 460nm is not well understood too, and future studies are required.

9. Conclusion

The results illustrate (compare Figs. 8 – 10) that there are no significant differences between the particles sizes that we tested. For our project we should have seen a stronger absorption peak in the NIR. We thus conclude that the particles we tested are too large. This is not surprising since we earlier predicted that 3 nm particles would be required for successful applications in biomedical field.

10. Future Work

Since we have shown that particle sizes 10 nm or above are not useful, we will continue to make and test increasingly smaller particles until we achieve the results we require.

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