

Making waveguides containing nanocrystalline quantum dots

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ABSTRACT

A new material platform is described that enables inclusion of nanocrystalline quantum dots into a polymer. This technology is compatible with semiconductor processing and may enable integration of active materials into current waveguide technologies. We describe the steps performed to fabricate a waveguide chip that contains IR-emitting quantum dots. Optical tests demonstrate guiding and preservation of the quantum dots optical properties through the processing steps. Time resolved optical measurements indicate presence of gain in the InAs quantum dot impregnated polymer.

Keywords: Quantum Dots, Waveguides, Photonic Devices, Gain, nanocrystals, InAs, PbSe, PFCB, polymer waveguides

1. INTRODUCTION

As technology aims for higher functionality, precise control, and miniaturization of various devices, Nanocrystalline Quantum Dots (NQDs)^{†,1,2} appear very attractive to participate in this “nano revolution”. NQDs possess many desirable features including: (1) the ability to engineer their energy levels, or optical emission wavelength by controlling their size, (2) the ability to use a library of possible materials with various bandgaps, (3) the discrete energy level structure could enable room temperature, thermally insensitive, low threshold lasers and devices, (4) the nanometer size makes possible interesting nanophysics studies where small size is essential. It is due to these features that many possible applications³⁻⁶ spanning, lasers and switches for telecom, labeling in biology, and quantum cryptography and computation have been envisaged.

An interesting characteristic of the NQDs comes from the way they are synthesized; they are usually compatible with organic chemistry, a fact that delivers a lot of processing possibilities. Compared to their Molecular Beam Epitaxy (MBE) counterparts⁷ they can be fabricated to fill a much higher volume ratio in the material, which increases their potential effectiveness in devices. Also the equipment required to prepare NQDs is much simpler than an MBE machine.

While seeking to implement devices based on the NQD it is necessary to simply position the NQDs in the desired location. This is unfortunately not a trivial matter and there is not a fully developed technology to achieve it. The goal of our research is to develop a platform that makes design of optical devices where the NQDs can serve as an active medium. (It is also necessary to avoid environmental degradation, and quenching of NQD optical emission caused by the sensitivity of the QD to surface conditions of humidity and oxidation). We concentrated specifically on implementing a

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[†] often referred to as colloidal quantum dots, chemically synthesized quantum dots, or nanocrystals.

method that would work for NQDs emitting in the IR communication wavelength range (InAs with ZnSe shells and PbSe).

First it is necessary to find a host for the NQDs that will protect them from the environment and is optically transparent in the IR. As discussed below we have found a polymer that addresses these issues successfully. The initial simplest device we chose to implement was a waveguide impregnated with the NQDs. The processing steps included mixing the NQDs into the polymer and patterning a waveguide made with the mixture. Subsequently we verified that the emission properties are mostly unchanged. In addition we have found evidence for optical gain in InAs NQD/mixture for the first time. This will enable active devices such as lasers and amplifiers. The manuscript is organized as follows: in section 2 the preparation of the polymer NQDs mixture is described. Section 3 describes the preparation of the waveguide, Section 4 describes the optical characterization of the waveguide and the film for emission and gain, and section 5 is a summary where we speculate about possible future devices.

2. MIXTURE PREPARATION

NQDs usually consist of a crystalline semiconductor core, often no larger than just a few nanometers in diameter and a surrounding shell of a higher band gap semiconductor material. The shell provides the confining potential for the core electrons, and at the same time passivates the core, protecting it from the surroundings and reducing the effect of the surface. The shell is capped by organic ligands that give the NQDs their solubility and prevent aggregation.^{7,8}

While the NQDs easily mix in various solvents, in order to utilize their functionality in practical integrated photonic systems, they need to be distributed in a more robust but highly functional matrix. Once the NQDs are dispersed into the polymer, the liquid mixture can be treated in a way similar to the pure polymer and can be spin coated, cured, plasma-etched, or molded into desired shape onto various substrates. This matrix serves also for the most crucial role of isolating the NQDs from the immediate oxygen and humidity rich ambient that tends to degrade the NQDs with time.

In order to create the best material platform for the development of active devices it is most desirable to have as much of the active material in the matrix dispersed as evenly as possible (high loading). The challenge is that once the loading of the NQDs is too high agglomeration can occur where clumps and aggregates of dots form that can prevent good interaction between the dots and the light. Also when the aggregate sizes are comparable to the wavelength of the light, undesired scattering of light can occur. Below we discuss in some more details the preparation of the polymer, the NQDs, and their mixing procedure.

2.1. The polymer solution – PFCB

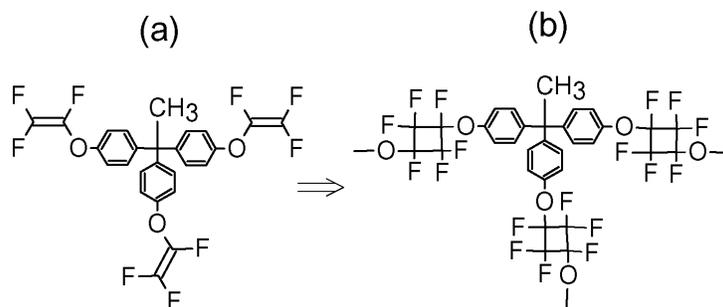


Figure 1. (a) the monomer: 1,1,1-tris (4-trifluorovinyl)oxy phenyl ethane. (b) the PFCB polymer structure after cyclopolymerization of the monomer.

A polymer from the perfluorocyclobutane (PFCB) family^{9,10} was chosen as the host matrix for the NQDs. PFCB is a semifluorinated polymer from the monomer 1,1,1-tris (4-trifluorovinyl)oxy phenyl ethane, as shown in Figure 1 (a), and when heated it undergoes a thermal cyclopolymerization (Fig 1b). The main motivation for choosing this polymer is its low optical loss over a very broad range of wavelengths ranging from the NIR (0.25dB/cm for 1.5 μ m) to visible

(0.1dB/cm for 700nm)^{11,12}. PFCB also has a low polymerization temperature, a low dielectric constant that is similar to that of glass, and is thermally stable.

2.2 Cap exchange

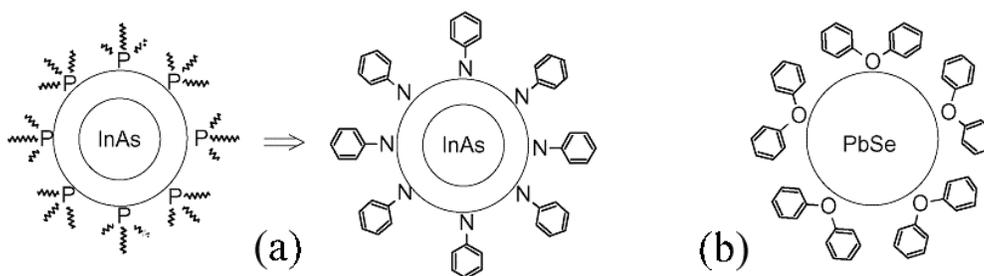


Figure 2. (a) Cap exchange: InAs/ZnSe NQDs with a TOP/TOPO cap that is exchanged with an aniline cap. (b) PbSe NQDs with diphenylether and oleic acid (not shown) caps.

The NQDs used were indium arsenide (InAs)⁷ and lead selenide (PbSe)⁸ prepared following the procedures described in Refs. 13 and 14 respectively. Both types of NQDs are 7-8 nm in diameter and are active in the infrared region of the spectrum with emission around 1.55 μm . The InAs NQDs have a zinc selenide (ZnSe) shell. A close-packed monolayer consisting mainly of ambiphilic trioctylphosphine/trioctylphosphine oxide (TOP/TOPO) molecules cap their outer surfaces, as shown in Figure 2 (a). The PbSe NQDs, however, do not have a shell and the caps, consisting of oleic acid and diphenylether, are directly bonded to the lead atoms in the core (Figure 2 (b)).

Stabilization of the NQDs within the PFCB requires the cap on the NQDs to resemble the chemical structure of the PFCB. Since PFCB is aromatic, the InAs NQDs with the native TOP/TOPO caps aggregate and are not miscible with the PFCB matrix. Therefore, the TOP/TOPO caps were partially substituted with an aromatic aniline capping ligand, which assisted in the miscibility of the NQDs. The existing TOP/TOPO aliphatic ligands are removed using an alcohol with a suitable polarity. The new aromatic caps are incorporated onto the NQDs surfaces by adding the aniline while slowly heating the NQDs to 70°C and then keeping the mixture stirring at that temperature for four hours. The NQDs are then rinsed once more in the alcohol and centrifuged to remove any unattached capping material. The PbSe NQDs have no protective shells. Therefore, their optical properties are very sensitive to the core/cap interfaces and luminescence can be easily quenched due to the changes on the NQDs core surfaces during a cap exchange process. To avoid any such optical quenching the capping material originally deposited in the NQDs synthesis was chosen to be compatible with the polymer matrix. This cap consists of a mixture of oleic acid and diphenylether. The miscibility of PbSe NQDs in PFCB was therefore achieved without cap exchange.

2.3. The mixture

As mentioned earlier, achieving maximum loading of dots in to the polymer matrix is crucial for a potent technology. There are many parameters that can influence the resultant loading. Above we described the cap exchange that is performed in order to make the dots and the polymer more compatible. We found that the polymer conversion and the polymer weight fraction affect the maximum loading possible. These probably have both a microscopic effect on the miscibility and a direct effect on the visco-elastic mixing properties. We have used annealing to increase conversion and NMR to measure the conversion of the polymer.¹⁰ As of now the best results of loading were achieved for about 50 % conversion and 60 % weight content of the polymer solution.

The mixing of the NQD and the polymer was achieved using a magnetic stirring bar. We found it crucial to use ultrasound to further improve the mixing of NQD-PFCB solution. The solution was then filtered through a 0.25 μm PTFE filter to make sure that any aggregates that may have formed will not be present in the final step of device fabrication. The filtered NQD-PFCB mixture remains relatively stable over an extended period of time (months). The resulting mass fraction of dots in the filtered polymer solution is measured to be about 2 %. The measurements are based

on a comparison of the absorption coefficients (of a HeNe laser beam at 632.8nm which PFCB is transparent to) between the filtered NQD-PFCB solution and a reference NQD-solvent solution with known dot concentration.

Figure 3 shows TEM micrographs of thinned PFCB-NQD films. The images demonstrate how the ultrasound assisted mixing and the filtering eliminate the presence of aggregates in the solution. The polymer solution was diluted with the polymer solvent, mesitylene, in order to achieve a thin film that could be imaged in the TEM.

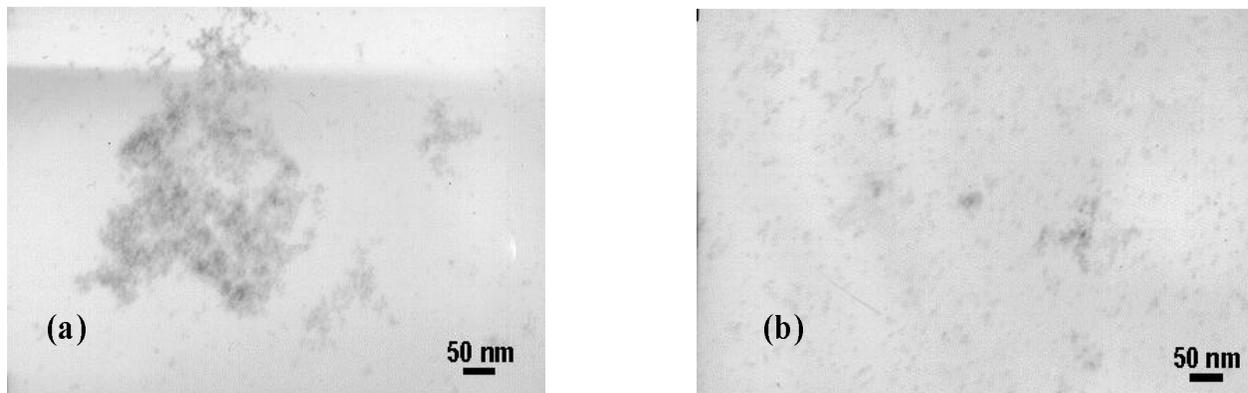


Figure 3. TEM micrographs of InAs-PFCB solution. (a) shows typical aggregate size in a PFCB-NQD mixture that was not filtered or mixed with the aid of ultrasound. (b) a PFCB-NQD mixture prepared with ultrasound enhanced mixing after being filtered through a 250 nm filter. This shows the effectiveness of the mixing and filtering

3. WAVEGUIDE PREPERATION

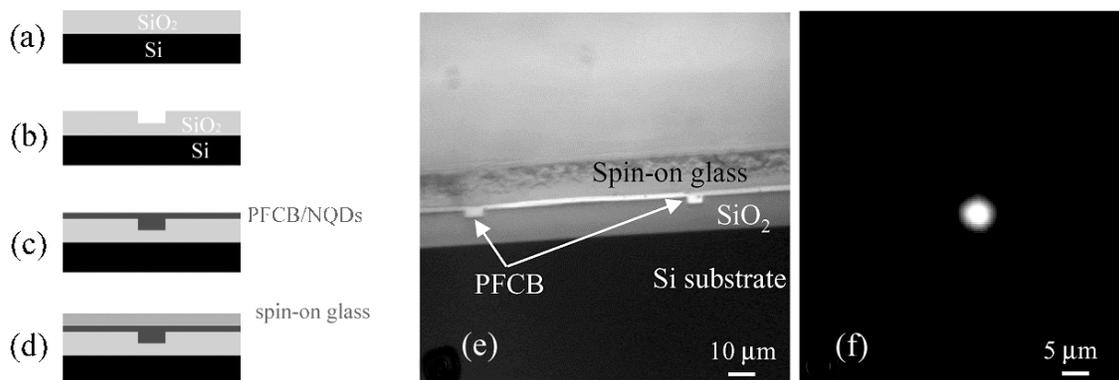


Figure 4. The process flow, and the waveguide: (a) start with a Si substrate with a thick oxide; (b) etch 3 μm trenches in the glass to form waveguides; (c) spin the NQD-PFCB solution and anneal in nitrogen; (d) lastly spin on-on glass is applied for the upper cladding and annealed. (e) Optical image of a polished facet of a PFCB polymer ridge waveguide structure. The fuzzy layer above the spin-on glass is a glue layer used to attach a cover glass on top of the waveguide for polishing purposes; (f) Far field image of the optical mode at 1.55 μm transmitted through a PFCB ridge waveguides containing InAs NQD, similar to the one shown in (e).

Fig 4. shows the procedure for the fabrication of NQD/polymer waveguide devices. A thick 15 μm layer of silica glass (with a refractive index of 1.445) was thermally grown on top of a silicon wafer and was used as the lower cladding for the waveguides, (Fig 4 (a)). Trenches were then etched into that glass cladding using reactive ion etching, (Fig 4. (b)). The trenches are 3 μm deep and of various widths between 2 to 9 μm . The NQD-polymer resin was then spun on the wafer, filling up the trenches and forming a thin wetting layer with thickness depending on the spinning speed, ranging from 0.5 to 1.5 μm . The films were then slowly cured at $T=120^\circ\text{C}$ in a nitrogen atmosphere over night, (Fig 4 (c)). The refractive index of the cured PFCB layer is around 1.52 and becomes slightly higher with the NQD incorporated. An

upper cladding layer consisting of a spin-on glass[†] with a refractive index of 1.49 was spun to finalize the ridge waveguide structure, (Fig 4 (d)). The end facets of the waveguides were then fine polished to minimize optical coupling losses. Figure 4 (e) presents a polished facet of one of the fabricated devices. The layer structure and the ridge waveguides can be clearly seen.

The trench filling or molding method¹⁵ for defining the waveguides and other possible devices has a few advantages over conventional photo-lithographical method of directly etching of polymer films. First, since the trenches are pre-etched on the substrate, the NQD filled polymer experiences fewer processing steps. The optical properties of the NQD are consequently less likely to be affected. In addition, etching glass is a mature and repeatable process, whereas a high quality PFCB/NQD mixture etching needs to be developed. In our trials, the glass etching approach yielded smoother waveguide sidewalls leading to reduced scattering in the waveguide.

4. CHARACTERIZATION

4.1. Waveguide

Figure 4 (f) shows the far field image of light (1.55 μm) transmission through the waveguide structure shown in Figure 4 (e), displaying a well defined circular mode, similar to that calculated based on the structure dimension and refractive index profile discussed above. In order to quantify their optical quality, loss measurements were performed on a set of PFCB based waveguides without NQDs. The measurements were done using a single mode fiber for both input and output coupling. An upper limit of 1dB/cm was extracted (e.g. a loss of 5dB/cm was measured on a 5 cm waveguide including the coupling losses to the fibers). Measurements with waveguides of different length indicate that coupling losses dominate over propagation losses.

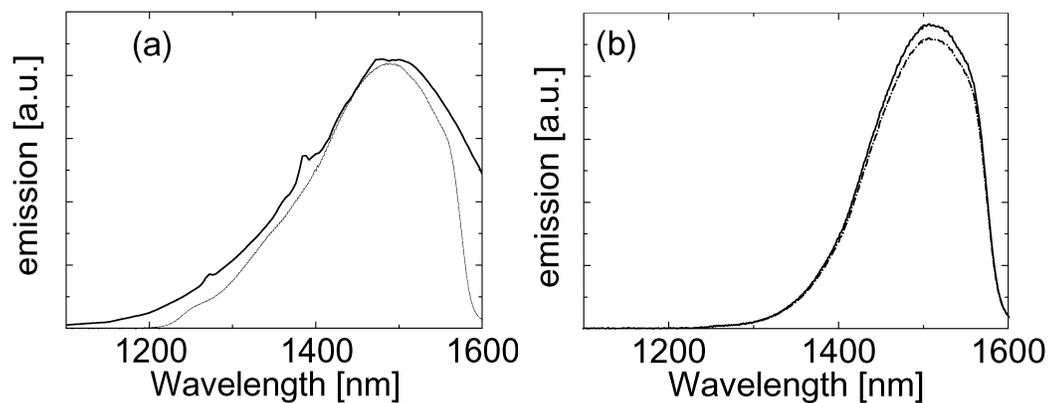


Figure 5. Emission spectra taken for InAs NQD (a) and PbSe NQD (b) before (solid lines) and after (dash-dotted lines) the waveguide fabrication processes. The "before" spectra were taken immediately following the growth of the NQD. The "after" spectra were taken from the cured NQD-PFCB films.

The most crucial test for the effectiveness of the whole process is the preservation of the optical properties of the NQDs. This is not *a priori* trivial because of the sensitivity of the NQDs optical properties, and especially their emission, to surface passivation. Any change in the surface chemistry (such as oxidation) may affect the surface passivation and create excess surface states that will serve as non-radiative traps for the carriers, thus quenching the NQD luminescence. To test the effect of our process (particular the cap exchange and the curing of the NQD-PFCB mixture) on the NQDs optical properties, emission spectra were collected after every step, and we have obtained identical emission profiles and intensities. A comparison between emission spectra of the as-grown NQDs and the cured NQD-PFCB thin film is presented for the InAs NQDs in Figure 5 (a) and for the PbSe NQDs in Figure 5 (b). The solid line shows the corresponding original NQDs emission profile in solution, while the dash-dot line shows the emission from the finished film. A very similar emission is observed for both types of NQDs before and after the process. This demonstrates that the

[†] The spin-on glass consists of 60% of methylsilsequioxane, dimethylsilsequioxane and phenyl silsequioxane blend (1:1:1), 37% of BuOH, and 3% of phenylphosphonic acid.

optical properties of the NQD were minimally affected by the various stages of the process. In comparison, the emission spectrum of PbSe NQD in PFCB polymer after polymerization in ambient atmosphere instead of in nitrogen is clearly found to be blue shifted, indicating a change in the NQD optical properties, probably due to core surface oxidation of the shell-less PbSe NQD. To quantify the cap exchange process efficiency further, we measured the integrated emission intensity before and after cap exchange. The integrated emission intensity and the emission profile were first measured for the NQD in Toluene inside a transparent cuvette, before cap exchange. Then cap exchange was performed as described above on the originally measured NQD. After the cap exchange process, the NQD with the new caps were mixed with the PFCB resin with the same volume as that of the original solution. This results in a NQD-PFCB mixture with the same volume and same NQD concentration as in the original Toluene solution. Next, the emission profile was measured under exactly the same experimental conditions as in the first set of measurements. Both the emission lineshape and the integrated intensity were found to be identical. This indicates that the NQD emission quantum yield remains unaffected by the cap exchange and in the polymer chemical environment.

4.2. Optical gain in the annealed InAs-PFCB film

One of the ultimate goals of a NQD application would be the fabrication of active devices such as lasers and amplifiers based on optical gain of NQDs. Although very challenging, gain and Amplified Spontaneous Emission (ASE) in NQD have been repeatedly observed in the visible regime,¹⁶⁻¹⁸ and have also been reported in the IR using PbSe NQDs.¹⁹ In order to measure gain it is favorable to increase the density of active material (or loading) in the host, an effort made as described above. In our measurements gain is induced using high intensity pulsed laser beams emanating from two optical parametric amplifiers, which are pumped by a common regenerative amplifier. In the case that the intrinsic gain is small, the loss overwhelms the measurement and it is hard to demonstrate gain (one has trouble differentiating between true gain and increased bleaching). In order to alleviate this limitation we used a 3-pulse technique similar to the one in reference²⁰. This method investigates the change in transmission of a probe pulse due to an extra resonant pulse inserted after the high-energy gain pulse, and before the low power probe pulse. The high intensity gain pulse is at a wavelength of ~1250 nm and has power of about a μJ per pulse. The strong resonant pulse and the weak probe pulse are both at ~1550nm. The laser repetition rate is 1Khz and pulse widths are about 100fs. In the case that gain is present the extra resonant pulse would act to decrease the population inversion by transferring electrons from the high to the low level and would decrease transmission, whereas in the case of bleaching the resonant pulse would promote electrons to the high level increasing transmission. We have observed intrinsic gain of 4cm^{-1} at a NQD density of $8 \times 10^{16}/\text{cm}^3$. The gain peaks as expected around the 1550nm wavelength.

5. CONCLUSION

In conclusion we have described the development of the NQD-PFCB system for optical devices. In this process the NQDs' surfaces are conditioned by a cap exchange to make them resemble the monomer and blend in more easily into the solution. The PFCB polymer solution is prepared in the right conversion and mixed together with the NQD. Finally a waveguide device was fabricated. The waveguide tests indicated guiding and preservation of the optical properties of the NQD. A 3-beam probing technique shows an indication of gain in the NQD-PFCB system.

The ability to incorporate NQDs into an optically transparent polymer host and enable fabrication of hybrid planar photonic devices in various useful platforms such as glass or silicon. This opens up opportunities for harnessing various NQD optical properties in a realistic photonic integrated system. Future efforts should concentrate on increasing the volume fraction of NQD in the polymer and building different functional structures such as optical resonators. Seeking to observe amplified spontaneous emission in the waveguide is an obvious goal as well.

The possibilities that a technology like this opens up are exciting. Integrated nonlinear optical switches, amplifiers, and lasers for optical communication may be on the horizon. As better control and smaller feature definition becomes available, other application where a small amount of active material is integrated into an optical device are plausible. This approach should be easily integrable into planar lightguide circuits (PLC) platforms realized in silicon on insulator (SOI), silica or other semiconductors, perhaps combining light sources detectors and waveguides on one platform. Single NQD devices, and experiments, with application in quantum computation and cryptography may be plausible.

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