ABSTRACT

We discuss our work on light emitters and photonic circuits realized using colloidal quantum dot composites. Specifically we will report our recent work on flexible microcavity laser, microdisk emitters and integrated active–passive waveguides. The entire microcavity laser structure was realized using spin coating and consisted of an all-polymer distributed Bragg reflector with a poly-vinyl carbazole cavity layer embedded with InGaP/ZnS colloidal quantum dots. These microcavities can be peeled off the substrate yielding a flexible structure that can conform to any shape and whose emission spectra can be mechanically tuned. The microdisk emitters and the integrated waveguide structures were realized using soft lithography and photo-lithography, respectively and were fabricated using a composite consisting of quantum dots embedded in SU8 matrix. Finally, we will discuss the effect of the host matrix on the optical properties of the quantum dots using results of steady-state and time-resolved luminescence measurements. In addition to their specific functionalities, these novel device demonstrations and their development present a low cost alternative to the traditional photonic device fabrication techniques.

Keywords: Quantum dot, nanocrystal, microcavity, photonic integrated circuits

1. INTRODUCTION

Colloidal quantum dots (QDs) have garnered much attention in the recent times due to their attractive spectral properties leading to wide range of potential applications in bio-imaging/sensing, display, telecommunication and quantum cryptography. The colloidal QDs allow spin-coating based processing, possibility of self-assembly, compatibility with silicon platform and tunability in absorption and emission spectra and have become one of the most attractive nanoscale fluorescent emitters. While colloidal QDs have become one of the most attractive nanoscale fluorescent emitters, they have still not found widespread application in practical photonic devices. This is in part due to the difficulty in incorporating these QDs into photonic structures. Practical ultrafast all-optical switches, modulators, flexible emitters, and room temperature single photon sources using these QDs can be realized if they can be patterned into waveguide or microcavity structures. Recently there have been several attempts to achieve this goal by embedding QDs in variety of photonic structures and hosts [1-15]. A significant challenge here is the incorporation of QDs into transparent host matrices without affecting their optical properties [16-18]. In addition, it is also desirable to achieve monodispersity, high fill factor and efficient charge injection.

Embedding photon emitters in microcavities alters their emission properties due to the ability of these structures to confine and enhance electromagnetic fields. Recently there have been several attempts to achieve this goal in QDs by embedding them in poly (methylmethacrylate) (PMMA) spheres, silica microspheres, one dimensional microcavities, two and three – dimensional photonic crystals and microdisk structures [1-15]. Most of the one-dimensional microcavity structures reported to date have used sputtered or thermally evaporated distributed Bragg reflecting (DBR) mirrors. While they do give good reflectivity, often they have undesirable effects on the optical properties of the QDs through surface defects. In addition, these techniques also require multiple deposition systems. Hence, it is highly attractive to develop a low-cost technique for the fabrication of the microcavities which is compatible with the solution processing of the colloidal QDs. Furthermore, solution processing allows the fabrication of the microcavity on wide variety of substrates including flexible ones.
In the present work, we report the realization of a one dimensional microcavity laser using colloidal InGaP quantum dots as the gain medium fabricated using spin coating and the development photonic integrated circuits using colloidal CdSe quantum dot composites fabricated through soft-lithography. We also discuss the effect of the host matrix on the luminescence properties of the QDs using steady state and time resolved luminescence measurements.

2. SPIN COATED FLEXIBLE MICROCAVITY LASER

Lasing has been observed from colloidal QDs by embedding them in a variety of microcavity structures such as microspheres, distributed feed back structures, cylindrical cavities, and microring structures [2-7]. The simplest class of such microcavities is the one dimensional microcavity consisting of a cavity layer sandwiched between two sets of Distributed Bragg Reflectors (DBRs) which comprise of alternating layers of materials with different refractive indices. Despite the simplicity of these structures, they have found wide range of applications in photonic devices such as vertical cavity surface emitting lasers (VCSELs), microcavity LEDs, detectors and filters. Most DBRs for VCSEL structures are fabricated using techniques such as MBE, MOCVD, plasma enhanced chemical vapor deposition, or sputtering. Recently, techniques such as self assembly of block copolymers, co-extrusion of two polymers and spin coating have been used to realize DBR and distributed feedback (DFB) lasers in organic medium [19-26]. Optically and electrically pumped surface emitting devices demonstrated to date in organic and inorganic material systems have used solid substrates with the exception of the recent demonstration of surface emitting lasers that utilized two dimensional photonic crystal based reflectors with a thick (~1 μm) organic dye based gain medium to realize a flexible laser structure [27 - 29]. In contrast, we present a one dimensional microcavity structure consisting of a half wavelength thick cavity sandwiched between two distributed Bragg reflectors to realize the laser structure.

Here we demonstrate the fabrication of a solution-processed mechanically-flexible optically pumped VCSEL emitting at 657 nm. The entire structure, including the DBR mirror, is fabricated via spin coating on a glass substrate. A schematic drawing of the one-dimensional microcavity is shown in Fig. 1(a). Alternating layers of polymers of two different refractive indices were stacked to form the DBR mirrors [24-26]. The high and low refractive index polymers chosen were poly-N(vinylcarbazole) (PVK), and cellulose acetate (CA), with refractive indices of 1.683 and 1.475 at 600 nm respectively. Solvents were chosen such that the solvent for one polymer does not dissolve the other. PVK is soluble in non-polar solvents such as chlorobenzene, whereas CA is soluble in polar solvents such as alcohol.

The microcavity structure was realized on a glass substrate. Alternating layers of poly-N(vinylcarbazole) (PVK), and cellulose acetate (CA) of quarter wavelength thickness were stacked to form the DBR mirrors. Here, PVK was dissolved in Chlorobenzene (28 mg/ml) and CA in diacetone alcohol (30 mg/ml). The PVK layer was spun at 3000 RPM for 40 seconds and then placed on a hotplate at 80°C for 15 minutes, resulting in thicknesses of ~ 90 nm. Following this the ~100 nm thick CA layer was spin coated at 4500 RPM for 40 seconds, and then placed on a hotplate at 80°C for 15 minutes to remove the solvent. This process is repeated to obtain the DBR stack mirror. Following the realization of the twenty period bottom DBR, a PVK cavity layer of $\lambda/2n_{PVK}$ thickness (~190 nm) embedded with InGaP/ZnS core/shell QDs is
spin coated at 2000 rpm. Here, $n_{\text{PVK}}$ is the refractive index of PVK. The InGaP/ZnS core/shell QDs dispersed in toluene (2.0 mg/ml) having peak emission wavelength of 650 nm and nanocrystal diameter of ~ 6 nm was obtained from Evident Technologies. The concentration of QDs in PVK was optimized to obtain the maximum emission intensity, which was found to be 30% v/v of colloidal QDs with respect to the PVK solution (39 mg/ml) by dispersing 0.3 ml of the QDs in 1 ml of PVK solution. This corresponds to a fill factor of approximately 2% of QDs in the cavity layer. Following this, ten and half period DBR consisting of alternating PVK/CA layers was realized on top of the cavity layer by spin coating. The thicknesses of the layers were controlled through spin speed and concentration of the polymer. The layer thicknesses were calibrated separately using reflectivity measurements prior the fabrication of the entire structure.

Following the fabrication of the microcavity structure, it was peeled off the glass substrate to form a free standing microcavity. Photographs of the free standing microcavity as well as on a cylindrical surface are shown in Fig. 1(b). These photographs clearly demonstrate the ability of these flexible microcavities to conform to any shape.

The optical microcavity was characterized using reflectivity and photoluminescence (PL) measurements. All optical measurements reported here were carried out at room temperature. Fig. 1(c) shows the experimental reflectivity of the microcavity structure at normal incidence. Reflectivity measurements were carried out using a fiber coupled Tungsten-Halogen lamp as the white light excitation source. Light from the excitation source was focused to spot size of approximately 0.5 mm in diameter and the reflected light was collected by a fiber coupled spectrometer. The spectral position of the cavity mode was designed to overlap with the emission maximum of the InGaP/ZnS core/shell QDs. The quality factor of the microcavity was found to be ~ 70. The inset of Fig. 1(c) shows the normalized reflectivity spectrum of a stand alone DBR consisting of 20 periods at normal incidence at five different locations. Greater than 95% reflectivity and a 100 nm stop-band was obtained using twenty periods of the structure. The reflectivity spectrum also showed excellent uniformity across the sample. The maximum reflectivity observed from the entire structure in the vicinity of the region where lasing was observed was 99%.

Steady state PL measurements were carried out using the 488 nm line of an Argon-Ion laser as the excitation source. The emission from the microcavity sample showed cavity linewidth limited narrower emission with the integrated spectral intensity being ~ 2 times that of QDs in free space (Fig. 2(a)). Results of angle resolved PL measurements are shown in Fig. 2(b). The emission spectrum follows the cavity mode till 40°. Beyond this point, the emission maximum of the QDs lies outside the stop band of the DBR and hence does not show any angle dependence. The above measurements were

![Fig. 2. (a) Steady state photoluminescence spectrum of the InGaP quantum dots in the microcavity (red). Luminescence maxima corresponding to the cavity mode and the band edge modes are indicated. The luminescence spectrum of the bare quantum dots in toluene is also shown for comparison (black). (b) Angle dependent photoluminescence spectrum of the microcavity device on a flat substrate. The emission spectrum follows the cavity mode till 40°. Beyond this point, the emission maximum of the quantum dots lie outside the stop band and hence does not show any angle dependence. (c) Photoluminescence observed at 20° collection angle from the microcavity wrapped around cylinders of different radii. The emission wavelength is found to blue shift and intensity of emission decreases upon bending the microcavity to smaller radii.](image-url)
carried out with the microcavity laid out on a flat substrate. Following this, the microcavity was wrapped around glass cylinders with different radii. The PL emission collected at 20° was compared for the three cases and is shown in Fig. 2(c). Clearly, the emission wavelength blue shifts and intensity of emission decreases upon bending the microcavity to smaller radii. As expected, this effect was observed only for non-normal collection angles since light being emitted normal originates from the cavity region that is not curved by the bending.

Time resolved PL measurements carried out on the InGaP QDs in toluene show bi-exponential decay with lifetimes of 16 ns and 85 ns. These lifetimes were found to decrease to 10.8 ns and 78 ns when the QDs were embedded in the PVK host. This is attributed to increased nonradiative processes that occur due to surface degradation when the QDs are dispersed in the PVK host. These lifetime measurements were carried out on spin coated samples with identical QD concentrations on glass substrate. More detailed study on the effect of the host matrix on luminescence properties of these QDs is currently underway.

To characterize the lasing properties of the flexible microcavity structure, the device was optically pumped using the second harmonic of an NdYAG laser (532 nm) with 5ns pulses operating at 10 Hz. The emission from the device was collected using a fiber coupled spectrometer. The input pump power was varied using a variable attenuator. Fig. 3 shows the average output power as a function of average pump power. As can be seen from Fig. 3, the lasing threshold is at 27 mW and the slope efficiency (top emission) is ~12%. At pump power greater than 50 mW, the laser output was found to saturate primarily due to heating effects. The variation of the full width at half maximum (FWHM) at the lasing wavelength as a function of pump power is also shown in the inset of Fig. 3. The FWHM shows a threshold behavior consistent with the light output versus input measurements. Also shown in the inset is the emission spectra obtained above the threshold. The observation of threshold in light output as well as significant linewidth narrowing above threshold provides clear evidence of lasing in the flexible microcavity discussed here.

Fig. 3. Output power of the flexible microcavity surface emitting laser as a function of input optical pump power. A clear threshold for lasing can be observed at 27 mW at wavelength of 657 nm. The insets show the emission spectra above threshold and the full width at half maximum of the lasing spectra as a function of pump power clearly indicating a threshold behavior

### 3. PHOTONIC INTEGRATED CIRCUITS USING QUANTUM DOT COMPOSITES

Next generation smart sensors and adaptive sensors would require the development of high performance optical signal processors and data routing technologies that will facilitate efficient and fast transfer of information, on-demand connection and ultrafast data processing. Chip-scale multifunctional photonic integrated circuits (PICs) are essential for reducing cost, and for realizing high component performance required in modern optical data transmission and telecommunication systems. A major impediment to the rapid development of integrated photonic systems has been the difficulty of integrating multiple, high performance photonic functions on a chip at low cost. While a wide array of fabrication processes and photonic functions have been demonstrated based on Indium Phosphide material for integration
of active and passive photonic components - such as re-growth, selective area growth, quantum well intermixing, and asymmetric twin waveguides, etc. - most of these techniques are very material specific and require expensive fabrication tools in addition to being incompatible with silicon.

Here we are developing three dimensional photonic circuits using a bottom-up approach. This differs considerably from the more traditional top-down approach that is widely used in traditional semiconductor based PICs. The vertical integration scheme allows realizing PICs with smaller footprint with multiple functionalities. Furthermore, the use of colloidal quantum dots as the active medium allows us to realize PICs on silicon platform and cover wide spectral range. All the circuits currently being pursued are being fabricated on silicon on insulator (SOI) substrate. The passive structures such as waveguides, resonators and couplers are fabricated in silicon and thus permit smaller footprint devices. The active medium for emission, amplification and detection is colloidal QD composite consisting of QDs in a polymer host matrix [16-18]. Currently we are working on efficient passive to active couplers.

In a different version of the vertically integrated devices, the passive structures are made using polymer – SU8, a negative photoresist. The motivation here is to build active microring and microdisk resonators integrated with passive bus waveguides similar to the one shown schematically in Fig. 4(a). Here, the coupling between the passive waveguides and the resonators happen vertically and is controlled through the intermediate layer between them. Result of beam-propagation simulation showing excellent coupling efficiency between such stacked waveguides is shown in Fig. 4(b).

Stacked waveguides using polymers with one of them being active has been realized by us. In these structures the passive waveguides are fabricated using SU8 (Microchem Corp.) and the active waveguides are fabricated using QDs in SU8 or in a UV curable resin (Evident Technologies). SU8 has been used in the past to realize microelectromechanical systems, holographic lithography, microfluidic chips, waveguides and ring resonators. Using SU8, it is possible to realize single mode waveguides with low surface roughness and reasonable cross sectional area. Furthermore, SU8 also allows the use of both electron beam lithography and standard photo lithography to pattern structures. With QDs embedded in SU8, it is possible to realize active waveguides and resonators.

In the present work, CdSe/ZnS core/shell colloidal QDs in hexane (Evident Technologies) was dispersed in SU8. The QDs have to be dispersed slowly to avoid clustering. Due to the lower dispersability of QDs in SU8, one cannot achieve high concentrations of QDs in the composite system. The stacked structures were fabricated using photo lithography. SU8 and the Su8 QD composite were applied on the substrate by spin coating followed by soft baking at 90°C for 2 minutes. Following this, the sample was exposed to UV light and then post exposure baked for 2 minutes at 95°C. Finally, the sample was developed in propylene glycol methyl ether acetate. The passive waveguide was first patterned using pure SU8 and this was followed by the active waveguide patterning. The waveguides were aligned using carefully placed alignment marks on the photomask. Figure 5(a) and (b) shows scanning electron microscope (SEM) images of a vertically coupled waveguide system and a vertically coupled ring resonator system, respectively.
An alternate technique being pursued for patterning the QD composite system is soft-lithography. Here we use a master pattern realized on silicon and polydimethyl siloxane (PDMS) stamp to transfer the pattern SU8 is drop coated on to the substrate and the PDMS stamp is pressed on this. With the PDMS stamp in place, the sample is exposed to UV light and then post exposure baked for 3 minutes at 95°C. Finally, the PDMS stamp is peeled off. Figure 5(c) and 5(d) show patterning achieved on a QD composite using soft-lithography. The inset of Fig. 5(c) shows emission from the QD embedded microdisk samples. The out coupling from the microdisks was not efficient due to the rough edges as seen in Fig. 5(d).

Fig. 5. Scanning electron microscope images of a) vertically integrated waveguides and b) vertically coupled ring resonator fabricated using photolithography, (c) Microdisk composed of CdSe quantum dots in SU8 which is fabricated using soft lithography. The inset of Fig (c) shows emission of QD in microdisk. Figure (d) shows the rough edges of the microdisk which affects the coupling of light into and out of the disks.

In addition to patterning the QDs using SU8 host matrix, we also explored the effect of different host matrices on the luminescence properties of the CdSe QDs. Results of steady state and time resolved luminescence measurements are shown in Fig. 6. The room temperature steady state photoluminescence measurements were carried out using a spectrofluorometer with Xenon lamp as the excitation source. Time resolved luminescence measurements were carried out using a time correlated single photon counting set up (Horiba Jobin Yvon). Measurements were carried out with CdSe QDs in toluene, PMMA, SU8, and a UV curable resin obtained from Evident Technologies.

![Fig. 6](image)

Fig. 6.(a) Steady state photoluminescence (PL) spectrum of QDs in various hosts is shown. It is observed that the PL line width and emission maxima for the quantum dots is not affected significantly in all four hosts, SU8, PMMA, UV resin and Toluene. (b) Time resolved photoluminescence spectra of QDs embedded in various hosts with Toluene as the control sample. The decay rate of the QDs in SU8 is much faster than the other hosts. This indicates the presence of an undesirable non-radiative decay channel. PMMA does not have a detrimental effect. The UV curable resin has the least effect on the lifetime.

Results of steady state and time resolved luminescence measurements indicate that the luminescence efficiency is not affected substantially by the various hosts. The UV curable resin from Evident Technologies is the best host matrix in terms of its effect on the luminescence properties of the QDs. Despite the faster decay rate and lower luminescence
efficiency of QDs in SU8, it is an attractive host matrix due to its higher refractive index when compared to the other hosts. Further work needs to be done in this context to identify a suitable host with high refractive index while having very small effect on the luminescence properties.

4. SUMMARY AND FUTURE WORK

We have demonstrated the fabrication of flexible microcavity laser using colloidal QDs as the gain medium. This demonstration of a new class of hybrid optically pumped surface emitting laser realized through a simple spin coating technique that combines the advantages of organic and inorganic systems represents a significant step towards low-cost, mechanically flexible lasers that have efficient luminescence properties, can cover a wide spectral range, and can conform to any shape. In addition to lasing, we have also demonstrated the possibility of tuning the emission wavelength of the flexible microcavity through mechanical bending. Such flexible microcavities are expected to play a key role in reconfigurable photonic switches and conformal optical apertures.

We have also successfully incorporated CdSe QDs into photosensitive polymer host, SU8 and patterned waveguides and microresonators using this composite. Vertically coupled waveguides and microring structures were realized using photolithography. Microdisk resonators with CdSe QDs embedded was also realized using soft-lithography. Results of steady state and time resolved luminescence measurements carried out on the CdSe QDs in various host matrix indicated that the polymer hosts did not have significant effect on the luminescence properties of the QDs while they maintained their photosensitivity.

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