Amplified spontaneous emission in polymer films doped with CdSe/CdS/ZnS colloidal quantum dots

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Abstract. Cd- and Pb-based colloidal quantum dots (QDs) and nanoplatelets are perspective materials for fabrication of active layers in photonic and plasmonic devices due to high values of optical gain (hundreds to 1200 cm⁻¹) under sufficient pump conditions [1, 2]. To obtain an optical gain, these nanocrystals are usually deposited densely and close-packed. Several drawbacks like scattering and difficulties associated with fabrication of such layers limit their use. We report successful aggregate free doping of polymer layers with homogeneously dispersed CdSe/CdS/ZnS QDs and provide description of two compositions that can accommodate up to 30-50 mass. % of QDs. The compositions can be polymerized with usual acrylate photoinitiation process or via thiol-ene polymerization process. QDs are well dispersed before and after heat- and photopolymerization, form no aggregates and, thus, the formed layers are almost free from scattering losses. Amplified spontaneous emission (ASE) in QD doped polymers was observed with 532 nm wavelength laser excitation in the variable stripe length (VSL) configuration.

1. Introduction
Plasmonic nanostructures can be used to localize electromagnetic radiation and to govern plasmon-polariton wave propagation [3]. Active plasmonics concept uses active medium with sufficient gain characteristic to mitigate intrinsic losses of metals (a usual plasmonic material) and improve characteristics of devices like waveguides [4] and spasers [5,6,7]. Quantum dots are especially good for such active media because of having large transition dipole moment; optical gain is proportional to its square and is only linearly proportional to volume concentration of excited quantum emitters [8]. Films of specially designed colloidal quantum dots (QDs) and other semiconducting nanocrystals (like colloidal quantum wells, nanorods etc) demonstrate optical gain coefficients over 1000 cm⁻¹ and are successfully used to obtain spaser devices [7]. Compared to dyes with limited gains below 100 cm⁻¹ [9] they also show improved photostability.

The most used are cadmium chalchogenide colloidal quantum dots, emitting in the visible. Since the first works on QDs lasing [10] synthetic chemistry have been improved; Cd-based core-shell QDs with CdSe cores demonstrate near unity single exciton quantum yields and improved biexciton and multiexciton quantum yields with non-radiative Auger recombination largely suppressed [11, 12]. The latter was the main factor limiting QDs lasing to femto- and picosecond pump regime. Most recent works demonstrate CW lasing and electrical pumping of Cd-based QDs layers [13].

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QDs thin layers are usually made by spin-coating, dip coating or any other suitable method that can provide densely packed nanocrystals film. Some usual complications are: heat management, fluorescence quenching due to Förster resonant energy transfer and unacceptable optical and mechanical properties of such films. One can also mention large losses of QD material during deposition.

Another rarely used approach is to disperse quantum dots in polymer matrix, which leads to lower optical gain, but improves all abovementioned issues if done properly. Since Cd-based QDs are not easily dispersed in common polymers like PMMA [14], we developed several liquid compositions where QDs were first dispersed evenly and randomly, and then these were used to obtain nano- to micrometer thick films via photopolymerization or heat-induced polymerization. Absence of significant aggregation lowers optical scattering and associated losses. Since these compositions are applied in a liquid form and have no solvent evaporation step (100% material conversion), the method can be scaled up to more environmental friendly and ecological production.

2. Materials and methods

2.1. Materials and chemical processes description

Mercaptopropyltrimethoxysilane (MPTMS), Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), 2-ethylhexyl acrylate (EHA), 1,6-hexanediol diacrylate (HDDA), oleylamine (OLA) are from Sigma-Aldrich. Deionized water, toluene, methanol, butanol, isopropanol (IPA), tetrahydrofuran (THF), hexane and other solvents (Sigma-Aldrich) were used as received.

CdSe/CdS/ZnS (QD630) quantum dots in toluene are synthesized according to [11] in NIIPA, Dubna, Russia. Their photoluminescence (PL) maximum is 630 nm and quantum yield is about 60%. QDot 655® CdSe/CdS/ZnS quantum dots (Invitrogen) 4-6 mg are supplied in 4 ml decane. All of the QDs were first precipitated from solvent with 1:3 IPA:methanol solvent mix, centrifuged and redispersed in hexane for subsequent processing. All quantity of QDot655 was heated with 100 uL OLA under nitrogen flow and then reprecipitated two times with IPA:methanol and methanol and redispersed in hexane.

2.1.1. First polymer composition. Hexane dispersions were transferred to glass microvials and evaporated, then 5% TPO (photoinitiator) solutions in EHA were added and heated to 90 °C to obtain QDs dispersions with 1-20 mass. % concentrations of QDs. Obtained acrylate dispersions were deposited on clean quartz substrates via spin-coating and photopolymerized under UV LED 380 nm under nitrogen to obtain 100-200 nm thin films. Alternatively 10 uL of dispersions were dropped on quartz substrates, covered by hydrophobized glass, cured under UV LED light; glass cover was easily removed afterwards and from 3- to 30-μm-thick films were obtained; thickness was regulated via amount of liquid dispersion and applied pressure.

2.1.2. Second polymer composition. QD630 100 mg was redispersed in 15 ml toluene and reacted with 30 uL MPTMS in 5 ml toluene for 3 hours under inert atmosphere. Then 900 uL of 1% water in THF was added and left stirring for 3 days. The resulting QDs with modified surface (thiol groups through intermediate SiO₂ layer) were cleaned through evaporation of excess solvent and precipitation/redispersion with hexane and IPA. TPO 5% in HDDA were added to obtain 10-30% dispersions; 50% dispersion was obtained via careful evaporation of intermediate solvent. These dispersions can be polymerized by heating to 120 °C in inert atmosphere or by UV cure analogous to described above; acrylate and thiol-acrylate radical polymerization reactions are involved.

2.2. Characterization

The thickness of all obtained samples was measured via white light profilometry and AFM where necessary. Aggregation of QDs was analyzed from photoluminescence maps obtained by NTegra microscope (excitation with 532 nm wavelength laser). The most informative were measuring of
photoluminescence and observation of ASE by utilizing the VSL method. In these experiments, a Nd:YAG laser second harmonic (532 nm, 13 ns, 10 Hz) was focused into a narrow line 200 μm x 10 mm, 800 kW/cm². Emission was collected via a 20x objective and fed into a monochromator via fiber waveguide. The collected light was analyzed by scanning in the 590-700 nm range with a 0.3 nm resolution and was measured at the exit slit of the monochromator via a Si detector.

3. Results and discussion

Visual examination and optical microscopy of all obtained samples shows high degree of their homogeneity. PL maps show absence of aggregates with sizes above 0.5 μm and low variation of PL intensity (<20%) over areas as large as 20 μm x 20 μm. For the first composition, some aggregation becomes prominent at 20 mass % concentration of both quantum dot types. The second composition yields better results even at 30 mass % for both QDs types and some visible aggregation at around 50 mass % for modified QDot655.

When the samples were exposed to laser radiation, emission collected from the end of the pump stripe showed characteristic signs of ASE – narrowing of photoluminescence spectra. The pronounced narrowing up to 4 nm is achieved for different types of samples when the stripe length exceeds 2 mm. For example, 8 μm thick sample containing 10% QDot655 under pump has a spectra shown on Figure 1. The onset of ASE could be attributed by the narrowing of the FWHM of the spectrum to 7 nm (line 3) at a stripe length L of 8 mm, contrary to the wide spectra achieved when the stripe length is less than 2 mm (lines 1 and 2). At the same time, samples with detected aggregation demonstrate typical QDot655 PL spectra with FWHM of 25-28 nm.

![Figure 1. Dependence of QDs PL spectra on stripe length (VSL method).](image)

4. Conclusions

The fabricated compositions employed in this work allowed us to obtain layers with homogeneously dispersed quantum dots in concentration range 1-50%. Methods that are reported here can be utilized
if one is limited in amount of quantum dots for experiments or if 100% material conversion is desired during making of active layer. Absence of aggregation leads to low scattering losses, which allowed us to observe large magnitudes of optical amplification of spontaneous emission. Optical peculiarities and magnitudes of the modal and material optical gain values for different samples are to be reported.

5. Acknowledgments
This study was carried out with support from Russian Foundation for Advanced Research Projects (contract № 7/004/2013-2018 dated 23.12.2013).

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