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Quantum dot dispersions in aerogels: a new material for true volumetric color displays

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ABSTRACT

The true volumetric displays project a 3D image within a cube viewable from most of its sides thus providing the ultimate physiological depth cues for countless applications. The ultra-light and highly transparent aerogels may provide the best optical medium for these displays as they can be easily fabricated in the form of a large-volume, low-scattering bulk material. On the other hand, the semiconductor nanocrystals (quantum dots, QDs) are a remarkable fluorescent material with optical properties superior to those of conventional materials. QDs dispersed in aerogels hold a promise to become the most efficient display material for volumetric 3D displays. The true volumetric displays described in the literature are built around the concept of two beams exciting the fluorescent material in their intersection. However, the optical properties of QDs are quite different from these of the fluorescent materials proposed for intersecting-beams displays and it may not be feasible to build such displays using QDs. Instead, we are proposing the use of a single focused infrared laser beam to excite a nanostructured material for volumetric color displays consisting of QDs dispersed in a transparent silica aerogel matrix. Presented are the theory and modeling results proving the feasibility of this approach.

Keywords: static volumetric displays, quantum dots, silica aerogels

1. INTRODUCTION

The world is three dimensional but the current display technology routinely visualizes it in two dimensions. The 3D visualization overcomes most of the problems related to this transformation providing many benefits, including the ability to convey additional information that is simply not possible with a 2D representation. Some of the 3D visualization technologies used today include holography, stereoscopic displays, and advanced 3D graphics engines that generally render three dimensional images on a two dimensional display by mapping the coordinates of the 3D images into a 2D perspective. The use of these "pseudo" 3D visualization technologies has a few drawbacks that result from the lack of true 3D rendering. To view a three-dimensional visualization on a two-dimensional display such as a monitor screen, some method of projection must be used to render the three-dimensional geometry. As a result, some amount of geometric information is lost through this projection, reducing user's perception and, eventually, distorting the very intention of the visualization[1]. Ultimately, these technologies lack the physiological depth cues needed for true 3D display imaging such as motion parallax, accommodation, convergence, and binocular disparity[2].

Another class of 3D displays includes the so-called *volumetric displays*. The difference between these displays and the 3D techniques mentioned above is that they form a visual representation of an object in three physical dimensions as opposed to the planar image of traditional screens. The comprehensive review on the various volumetric display designs is beyond the scope of this document; interested readers are referred to the relevant literature[3-5].

The ultimate evolution in the volumetric displays are the so-called "true" volumetric displays that project the image within a cube viewable from all or most of its sides, forming a visual representation of an object in three physical dimensions as opposed to the planar image of traditional screens, thus providing the ultimate physiological depth cues for countless applications in a number of areas. This is the most "direct" form of volumetric displays in which an addressable volume of space is created out of active elements that are transparent in the *off* state but are either opaque or luminous in the *on* state. When these elements or *voxels* are activated, they show a solid pattern within the space of the display[6]. These displays, in which there are no moving parts in the display volume, are sometimes called *static volumetric displays* to distinguish them from the *swept-volume volumetric displays* in which the three-dimensional image is formed by reflecting or transmitting light from a rotating or oscillating 2D surface within the 3D display volume[3].

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The current state in the true volumetric displays area presents a rather chaotic picture. A number of designs are described, mostly in the patent literature. Unfortunately, no static volumetric displays have left the labs to date and/or backed up by rigorous research and scientific evidence to prove the feasibility of their underlying principles. As a result, the suggested conceptual designs are intriguing but not practical and, in some cases, not even feasible. Most of these displays are built of solid glass and are heavy and expensive. Large-size displays are not feasible or practical. Displays based on dyes suffer from low quantum efficiency and weak fluorescence. Furthermore, dyes degrade fairly quickly[7].

Obviously, a lot of resources have been and are being spent on the engineering task, i.e., on developing the hardware and software for the 3D displays. What is missing is a focused effort to systematically study and understand the fundamentals of these devices. There is a need, therefore, to start with the physical foundations on which, through engineering effort, to build practical and realistic designs for the future volumetric displays. In a previous publication[8], the authors investigated theoretically and experimentally the two-photon absorption (TPA) in the focal point of a pulsed infrared laser and the resulting upconvered photoluminescence in dispersions of semiconductor nanocrystals (quantum dots, QDs) as a means for generating voxels in a true volumetric display (a brief discussion of the results from this work is included below). The current paper extends this study to multicolor volumetric displays based on a unique nanostructured material consisting of QDs uniformly and randomly dispersed in a virtually transparent silica aerogel matrix, and excited with a focused infrared laser beam. The combination of aerogels and quantum dots can result in a very attractive novel material for true volumetric 3D displays. Aerogels are ultra-light and despite their high porosity, some aerogels are highly transparent in the visible spectral region[9]. Aerogels may provide the best optical medium for volumetric 3D displays as they can be relatively easily fabricated in the form of a large volume, low-scattering bulk material. Because of their high photo-stability, large TPA cross-section, and size dependence of the emission wavelength, QDs dispersed in a transparent host material hold a promise to become the preferred display material for practical volumetric displays. QDs are an excellent material for displays because their quantum efficiency is higher than that of the other fluorescent materials such as fluorescent gas, dye, or doped crystals[10].

2. DISPLAY MEDIUM

In our study, the voxels in the display space are generated through selective excitation of the QDs with a single focused infrared laser beam to produce visible light emission in the voxel volume via frequency upconversion by two-photon absorption. As discussed in Ref. 8, the upconversion luminescence due to two-photon absorption is the most efficient mechanism for generating voxels in QDs embedded in a transparent host medium and, ultimately, for building a static volumetric display.

2.1 Quantum Dots

The active optical material in our study, the quantum dots, are semiconductor nanocrystals of group II-VI or group III-V capable of emitting electromagnetic radiation upon excitation. The wavelength of the emitted light depends on the size of the nanocrystal and the material. QDs generally have a broad absorption band; the electromagnetic radiation absorption continuously increases from the onset, which occurs near to but at slightly higher energy than the emission band. In comparison with organic dyes and fluorescent proteins, QDs are about 20 times brighter, mainly due to their large absorption cross sections (the TPA cross section of quantum dots is several orders of magnitude greater than those of the organic fluorophores[11, 12]), 100–1000 times more stable against photobleaching[13], and show narrower and more symmetric emission bandwidth - from 20 nm to 40 nm - that scales with pump intensity.

The fundamental process in the proposed display material is the upconversion photoluminescence initiated in the QDs by a focused infrared laser beam. The upconverted or anti-Stokes photoluminescence (UCPL) is the emission of photons with energies higher than the excitation energy. The UCPL occurs when the QDs are excited with light sources operating at wavelengths much longer (i.e., lower energy photons) than the ones in the absorption spectrum that produces the normal photoluminescence (PL) band. Different UCPL mechanisms are suggested in the literature (more detailed discussion is available in Ref. 8). QDs with linear dependence of the UCPL can be used as fluorescence targets due to their efficient excitation, while QDs with quadratic dependence of the UCPL can be efficiently used for confocal imaging[14]. The focus in our study is on the latter material in which the UCPL is primarily due to TPA. As we have demonstrated, these materials can be successfully used for voxel generation in volumetric displays resulting from selective excitation near the focal point of the laser beam. A characteristic of the upconversion emission from these materials is the quadratic or near-quadratic laser power dependence, $I \sim P^K$, where I is the emission intensity, P is the instantaneous power of the excitation source, and K is an exponent with values between 2.0 and 1.7 that depends on the size (color) of the QDs[14]. We have derived theoretically a relationship for the dependence of the voxel luminance on the excitation intensity and voxel diameter using the physics of TPA and beam optics (see Eqn.1). The results indicate that the luminance of a voxel can be controlled by modulating the excitation laser power. This can be done with an ultrafast voltage-controlled variable polarization attenuator, such as a Pockels cell combined with polarizers. The Pockels cell modifies the polarization and a polarizer subsequently converts this to a change of transmitted laser power. The same device can be used as an optical switch to turn off the laser beam when it moves to the next voxel position.

2.2 Quantum Dot Dispersion in Silica Aerogel

Aerogels are transparent, highly porous, open cell, low density solid foams prepared by the sol-gel method followed by supercritical solvent extraction, which leaves the original gel structure virtually intact. Aerogels are materials with exceptional and even unique optical, thermal, acoustical, and electronic properties such as the lowest thermal conductivity, refractive index, sound velocity, and dielectric constant of any other material known[15]. The aerogels are the lightest solid known – their density could be close to this of the air, and if synthesized in helium, they may be lighter than air. Despite their high porosity, some aerogels, such as silica aerogels, are highly transparent in the visible spectral region[9]. At the UV region scattering increases, eventually cutting off transmission near 300 nm (Fig. 1). Aerogels may provide the best optical medium for volumetric displays as they can be relatively easily fabricated in the form of a large volume, low-scattering bulk material.

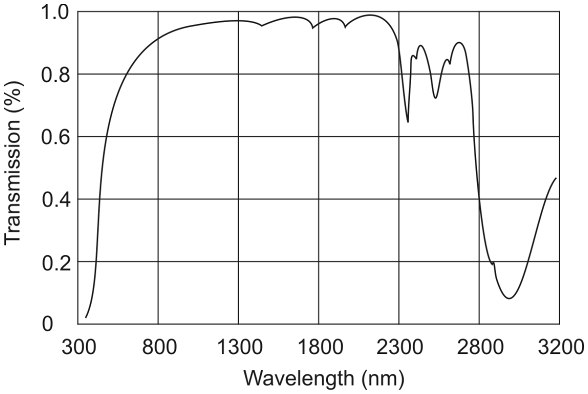

Figure 1. Transmission spectrum through silica aerogel[16].

QDs could be utilized as an aerogel display material in two different ways, (a) by synthesizing QD aerogels from sols of quantum dots, and (b) by embedding prefabricated QDs in the supporting aerogel matrix of another material.

In 1997, Gacoin and co-workers first reported the synthesis of transparent CdS gels from concentrated sols of CdS nanocrystals[17, 18]. S. L. Brock and co-workers[19-22] have expanded this work to fabricate unsupported CdS aerogels in which CdS is three-dimensionally linked together into a solid architecture. However, these materials do not appear to be highly transparent to be useful as a volumetric display medium.

Studies outlining the successful dispersion of QDs in a monolithic silica sol–gel material have recently appeared[23, 24]. One particular problem with these materials is their emission stability over an extended period of time. It was reported that the fluorescence of the QDs in the monolithic silica glasses could be preserved through for several months, but, ultimately, emissive intensity was lost. In 2006, Sorensen and co-workers reported the first successful fabrication of stable low-density silica aerogels with covalently integrated CdSe–ZnS core/shell QDs that maintain their optical properties for months[25]. Aerogels were formed from the supercritical CO_2 extraction of an alcogel containing quantum dots surface passivated with 3-aminopropyltriethoxysilane. The resulting aerogels are low scattering and display intense with a stable luminescence. Based on these early results, the use of silica aerogel-embedded ZnS capped CdSe QDs appears ideal for 3-D display applications. Recently, quantum dots of CdS have been incorporated into silica aerogels through a novel laser-writing technique[26]. However, the method developed by Sorensen and co-workers appear to be more suitable for the intended application as it can be utilized to fabricate monolithic bulk aerogels (laser writing has been demonstrated to only 4 mm depth) and uses the more stable and readily available ZnS capped CdSe QDs.

3. VOXEL GENERATION IN QD DISPERSIONS

3.1 Theoretical Background

In the previous study[8], we reported an expression for the luminance of voxels excited in a dispersion of QDs by a focused infrared laser beam (Eqn. 1). The luminance, B, of the light emitted by a voxel as a function of the peak intensity of the excitation source, I_p, and the QD concentration, C, is given by

$$B = \kappa \sigma_{2p} \Phi C I_p^2 W_{vx} \Delta t f_{rep} \frac{\lambda_{exc}}{\lambda_{emi}} \exp\left(-\sigma_{a,emi} C L_{view}\right). \tag{1}$$

where λ_{emi} is the peak emission wavelength, λ_{exc} is the wavelength of the excitation source, $\sigma_{a,emi} = 0.23\sigma_a$ is the effective absorption coefficient at the emission spectrum of the QDs (approximately 23% of the absorption coefficient at the 1st exciton peak), L_{view} is the optical path between the voxel and the observer inside the QD dispersion, and P_p and Δt are the laser peak power and the pulse width, respectively. The constant κ is required to express the luminance in nits.

The minimum concentration of QDs for a Q-switched Nd:YAG excitation laser that satisfies the minimum luminance for normal display operation, $B \geq 100$ nit with $L_{\text{view}} = 17.5$ cm, was calculated from (1) at $C_{\text{min}} = 2.36\times10^{14}$ cm^{-3}. This value was confirmed experimentally for an equivalent experimental setup. For a Ti:Sapphire laser operating at $\lambda_{exc} = 977$ nm, the minimum concentration that satisfies the required minimum luminance was calculated at $C_{\text{min}} = 1.037\times10^{12}$ cm^{-3}. Because of the higher peak power produced by the Ti:Sapphire femtosecond laser, this value is two orders of magnitude lower than the minimum concentration required if a Q-switched Nd:YAG laser was used.

3.2 Prove of Concept Experiments

A series of two-photon absorption (TPA) experiments were carried out using a *Teem Photonics* passively Q-switched 1064 nm Nd:YAG microchip laser to prove the technical feasibility of the proposed approach. The display medium was a dispersion of 10mg 550nm Core-Shell CdSe/ ZnS QD in toluene, procured from *Ocean Nanotech*. The experimental dispersions were placed in a 10 mm GL14-C quartz cuvette from *Starna Cell* with 10 mm pathlength size and two polished parallel optical windows. The beam of the 1064 nm Q-switched laser was focused in the middle of the dispersion. To avoid the use of a beam expander, we used a lens with the focal length equal to 25 mm located at the beam waist of the laser, whose beam waist radius was equal to 250 µm. The first voxel was clearly visible with a naked eye at a concentration of 5.83×10^{14} cm^{-3}, an experimental value fairly close to the theoretical value of 3.88×10^{14} cm^{-3} predicted by (1) with $L_{\text{view}} = 0.5$ cm for a voxel with luminance $B = 100$ nit. The difference between experiment and theory can be attributed to the imperfect optics that leads to a non-Gaussian profile of the beam at the voxel, and to the loss of light due to the reflection at the toluene-quartz interface and at the quartz-air interface.

Figure 2. Single green voxel generated by TPA in a 5.0×10^{14} cm^{-3} concentration of 550nm Core-Shell CdSe/ZnS QDs in toluene. Photograph taken with a 950-1070 OD7+ filter.

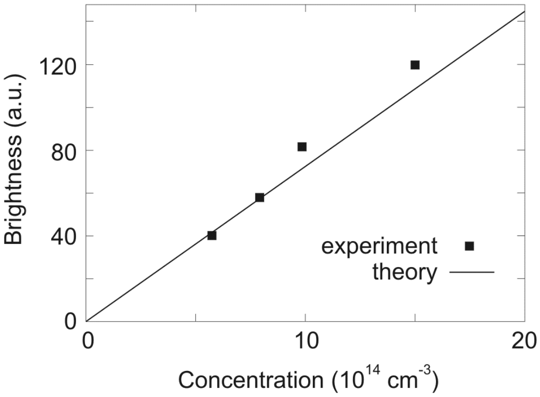

Figure 3. Relative luminance of voxel as a function of the QD concentration in the dispersion. The dots are the experimental results. The solid line represents Eqn. 1 with the vertical axis rescaled by a factor of 0.4.

Fig. 2 shows a typical result from the TPA experiments in which a well-defined voxel was successfully generated in the dispersion. The voxel luminance was measured from the histogram in the green channel of the image. The luminance values represent the median of the histogram on a scale of 0 (dark) to 255 (light). These values are also plotted as a function of the QD concentrations in Fig. 3 showing the good agreement between the experimental and theoretical results.

4. MULTI-COLOR EMISSION

We propose to generate multicolor emission in the display material by randomly dispersing in an aerogel matrix a mixture of QDs with emission peak in the red, green and blue visible wavelength ranges with different concentrations and excited by lasers with different wavelengths and intensities. To produce RGB pixels, the display needs to turn on voxels with up to 100 cd/m^2 of luminance for each of the three basic colors: red, green and blue. Since it is not possible to selectively excite QDs with each of these emission wavelengths because of the broad absorption band of QDs, the laser exciting the blue QDs (Ti:Sapphire femtosecond laser tuned at 940nm) will also excite the QDs with peak emission in the red and in the green. The laser exciting the green QDs (Ti:Sapphire, tuned at 1030nm) will also excite the red QDs. Because the red QDs can be excited by all three sources, they must have the lowest concentration and the blue QDs must have the highest concentration. As a consequence, the laser beam used to excite the red QDs (same, tuned at 1300nm) must be the most intense of all three to achieve the same luminance in each of the three basic colors. The green QDs should have a concentration at least two orders of magnitude above the red QD concentration. This will ensure that the luminance of red photons emitted by the voxel will be 20 dB lower than the luminance of the emission of green photons when the 1030 nm laser beam is the only laser beam in operation. However, the intensity of the laser emission at 1030 nm should be substantially smaller than that of the 1300 nm laser to ensure that the green voxels will produce a maximum luminance consistent with that of red voxels (mixture excited by the 1300 nm laser). Likewise, the blue QDs should have a concentration below the maximum acceptable concentration and at least two orders of magnitude above the green QD concentration. This procedure will ensure that the green background emission will be below 20 dB when compared with the blue emission when only the 940 nm laser is on. The maximum concentration is achieved when over 5% of the visible photons emitted by the voxels are absorbed by the QD mixture inside the display, which produces an undesirable distributed background emission in the display. Again, to ensure that the maximum luminance of green voxels is consistent with that of green and red voxels, when excited by their respective excitation lasers, the blue laser should have the lowest intensity of the three excitation lasers. The colors from the RGB palette can be then created by controlling the intensity of excitation lasers using the theoretical model (Eqn. 1), which allows one to calculate the luminance of the light emitted by a voxel excited in a dispersion of QDs by a focused infrared laser beam as a function of the peak intensity of the excitation source and the QD concentration.

Calculations were performed to determine the optimum configuration of RGB QD concentrations and their corresponding excitation source characteristics for a volumetric display. These calculations assumed that the display volume is a cube with each dimension measuring 35 cm and that each voxel 'turned-on' is at the center of the cube, which results into an optical path length inside the display volume of 17.5 cm. Moreover, the wavelength of the excitation sources were selected for the simulation to be directly at the twice the wavelength of the peak excitons of the QDs and match those of COTS systems. The three QDs identified for the display have specifications listed by the manufacturer[27].

The relations identified in our simulation between RGB QD concentrations and their respective excitation source characteristics, known as the *display configuration* and the achieved resolution are consistent with those discussed in the previous section. Using Eqn.1 and the QD absorption curves[27], one can determine that limiting factors in the performance of the system are the peak power levels and the pulse repetition rate of the IR excitation sources. As mentioned earlier, for an optimum display medium configuration the laser source that 'turns-on' the red QDs must have the largest combination of high peak power and pulse repetition rate. A COTS OPA system is available which according to published specifications will provide peak powers of ~800kW at a pulse repetition rate of 250 kHz[28]. A peak power of 700kW was used for the red QD excitation source in the calculations.

In addition to providing the desired luminance, the identified configuration should also provide the optimum extinction ratios of the amount of green and red luminance emitted by a blue voxel and the amount of red luminance emitted by a green voxel. These calculations were carried out assuming the TPA cross section curves follow the same relation as the single photon absorption curves presented in Ref. 27. The relative extinction ratios for the type of display described above were calculated and are listed in Table 1.

Table 1. Calculated amount of unintended excitation.

	Green	**Red**
Blue source	-14 dB	-25 dB
Green source	-	-14 dB

Table 1 presents the calculated amounts of unintended excitation, which occurs as a result of the absorption curve overlap as seen in Ref. 27. These values assume a 35cm cube and a voxel luminance of 100 cd/m^2 for RGB QDs 'turned-on' at the center of the display volume and viewed along the cube's principle axis. A larger negative dB value is desirable because it indicates the color cross talk is minimized. The values presented in Table 1 should be well within acceptable range for a functioning multicolor display.

5. CONCLUSION

Proposed is a novel material for multicolor volumetric displays consisting of quantum dots for red, green, and blue emissions randomly dispersed in a highly transparent and ultra-light silica aerogel at carefully calculated concentrations. The multicolor emission can be achieved by a selective excitation of the quantum dots with a single focused beam from infrared lasers with different wavelengths and intensities. The fundamental process for generating voxels in the described material is the upconversion photoluminescence in the quantum dots by two-photon absorption. Through experiments and by using previously reported theoretical constructions in conjunction with the material specifications supplied by the manufacturer, we have demonstrated that the construction of the proposed displays is feasible. Such displays would have numerous military and civilian applications.

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