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Synthesis and characterization of ZnS/SiO_2 photonic dots

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In this report, a facile, low-cost, and effective method has been employed to produce highly monodisperse colloids photonic materials ZnS QDs/SiO_2 were fabricated using chemical condensation reactions on poly-methyl methacrylate. The obtained results exhibit whispering gallery emission modes with 1.47nm spacing. In addition, the emission from ZnS QDs was modulated by a spherical microcavity. Furthermore, the spherical cavity dimension was calculated using the relation between modes spacing and cavity dimension and found to be 11.86 μm.

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1. Introduction

Bragg's reflections of colors depicted in nature had sympathized to animal communication or self-camouflage. Optical metasurfaces as reduced dimension photonics have noble optical properties and control light with surface confinement [2]. Periodic nanopatterns self-assembled dielectric materials had sowed controllable refractive index medium for a broad wavelength range, including the visible region [3]. Bloch's theory was said to be applicable for calculating photonic band structures in photonic crystal in analogy with electronic band structures calculations [4]. Due to the dielectric periodicity, photonic crystals acquire photon stop bands since the photon satisfies the dispersion relation. Photonic crystals, prepared by the colloidal chemical method, are limited due to the lower monodispersity and imperfect self-assembly. Silica sphere prepared chemically using condensation reaction method and self-assembled upon gravitation force acquires photon bandgap [5]. Highly monodisperse polystyrene latex self-assembled and forming hexagonal structure, the voids between PS spheres filled by TiO2 thermally annealed had exhibited photon band gap due to the air/TiO2 periodicity [6]. Topological photonic crystals made of highly ordered periodic structure dielectric and metallic materials had shown optical phenomena analogous to the quantum hall effect [7]. Three dimensions topological photonic crystal host Rhodamine 6G exhibits spontaneous emission in photon stopband and enhances the band edge emission from Rhodamine 6G [8]. Band edge emission from CdSe quantum dots embed in inverse opal photonic crystal enhances, and the intensity lifetime remains stable [9].

2. Materials and method

A high purity zinc acetate, sodium sulfide, and tetraethyl orzo silicate (TOES) are provided by Sigma Aldrich Company. In this experiment, 0.8 mM zinc acetate and sodium sulfide were added to a 40 ml TX-100 ethanol stabilizer solution, and TEOS was injected at room temperature to form SiO_2 colloids by Stöber method [10]. Afterward, the solution is stored in a

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dark environment to prevent QDs size growth and aggregation. ZnS/SiO2 photonic dots were imaged with an optical microscope, and the dimensions were determined as 11.851 μm.

3. Theoretical background

The dielectric optical cavity is defined as an optical device composed of a highly reflecting wall. It tends to trap electromagnetic fields and enlarged its intensity when bouncing between its walls. A trap of electromagnetic waves in the surface due to the total internal reflection gives rise to an optical mode known as whispering gallery mode (WGM), which is depicted in various cavities such as spherical, cylindrical, toroidal, etc. The formation of WGM indicates that the cavity has a high-quality factor, which is a good indication for high technological applications as photonic devices [11]. In this part, we will prove that the optical modes spacing is morphological dependent in nature. The refractive index of SiO_2 $n = 1.47$. Let us assume that our system composed of spherical mirrors with resonance conditions at positions ξ_1 and ξ_2, defining the optical beam waist, then the phase factor $\chi_{l,m}$, defined by the two modes resonance *l* and *m* and expressed as $\chi_{l.m}(\xi_2) - \chi_{l.m}(\xi_1) = q\pi$, where q is integer. The phase shift function is given by the relation; $\chi_{l.m}(\xi) = k\xi - (l+m+1)tan^{-1}\left(\frac{\xi}{\xi_0}\right)$, where $\xi_0 = \frac{\pi\omega_0^2 n}{\lambda}$. Resonance occurs only when the following relation satisfied;

$k_j r - (l+m+1)\left(tan^{-1}\frac{\xi_2}{\xi_0} - tan^{-1}\frac{\xi_1}{\xi_0}\right) = q\pi$, the resonator diameter seem to be; $r = \xi_2 - \xi_1$. As the beam mode bouncing between the mirrors along the optical axes without losing its transverse profile, then the radius of curvature R will be; $R_1 = \xi_1 + \frac{\xi_0^2}{\xi_1}$ and $R_2 = \xi_2 + \frac{\xi_0^2}{\xi_2}$. Using the optical resonator algebra construct the two quadratic algebraic equation and to compute their roots ξ_1 and ξ_2. $\xi_1^2 + \xi_0^2 - R_1\xi_1 = 0$ and $\xi_2^2 + \xi_0^2 - R_1 = 0$, then the roots will be;

$\xi_1 = \frac{R_1 \pm \sqrt{R_1^2 - 4\xi_0^2}}{2}$ and $\xi_2 = \frac{R_2 \pm \sqrt{R_2^2 - 4\xi_0^2}}{2}$. The difference between χ_1 and χ_2 is just integer multiple of π, hence $\chi_2 - \chi_1 = \pi$. In terms of wave number k and with reference to the resonance condition we have; $k_{j+1} - k_j = \frac{\pi}{r}$. Since $k = \frac{2\pi v n}{c}$. We can write $\Delta\nu = \nu_{j+1} - \nu_j = \frac{c}{2nr}$, also since $\Delta\nu = \Delta\left(\frac{c}{\lambda}\right)$, upon differentiation we get; $\frac{c}{\lambda^2}\Delta\lambda = \frac{c}{2nr}$ and finally the modes spacing as; $\Delta\lambda = \frac{\lambda^2}{2nr}$. Therefore, the modes spacing had found to be morphology dependent and the cavity dimension will be $r = \frac{\lambda^2}{2n\Delta\lambda}$ [12][13].

4. Result and discussion

The image of SiO_2 photonic dots has obtained by a sensitive digital camera attached to an optical microscope, as shown in figure (1). The diameter of the ZnS/SiO_2 photonic dots determined from the micrograph was found to be 13.987 mm. The emission of ZnS/SiO_2 spheres upon illumination had shown total internal reflection, which might indicate whispering gallery modes (WGM) generated due to the propagation of the surface of the light incident with an angle greater than p/2.

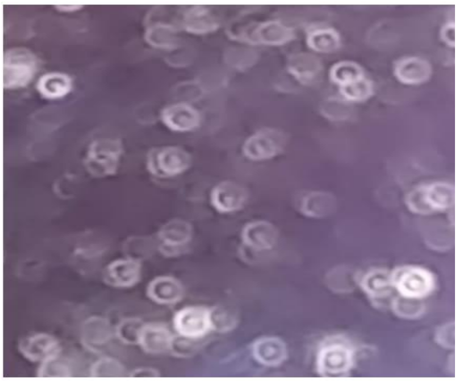

Fig. 1. Shows the photonic dots illuminations.

Photoluminescence of ZnS QDs stabilized by TX-100 had exhibited a single narrow peak centered at 366.5 nm, as shown in figure (1). The emission peak had found to be blue-shifted for that of bulk structures ZnS. Such a peak might be due to the band edge emission of ZnS QDs [14]. The full width at half maxima (FWHM) of the emission band had said to be 24.5 nm, which implies the formation of highly monodispersed ZnS QDs [15]. From the feature of the spectra, the absence of any red-shifted emission band. Such feature might mean complete surface passivation and removal of dangled bonds; occur due to the stoichiometry from the surface of ZnS QDs capped by TX-100 [16].

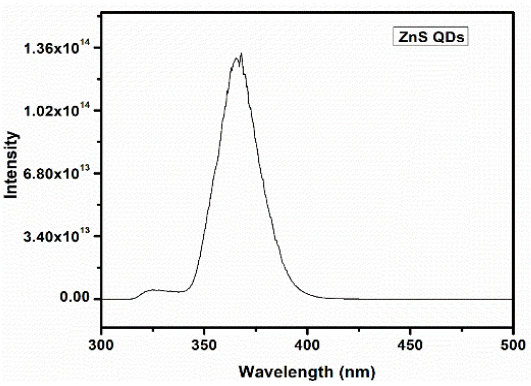

Fig. 2. Shows the photoluminescence of ZnS/SiO_2 QDs.

Emission spectra of SiO_2 optical cavity embedded by ZnS QDs shown in figure (2). The spectra obtained had shown a wider emission band associated with emission modes, which indicate coupling between the emission of ZnS QDs and SiO_2 optical cavity. The photoluminescence referred to as the composite system of ZnS QDs has shown modified emission. Such emission modification might be referred to as the coupling between the QDs emitter and ZnS/SiO_2 cavity. The successive emission peaks obtained in figure (3) might correspond to the WGM [17]. The previous results show that the WGM modes generated due to total internal reflection leading to surface trap light propagation [12]. Theoretical and experimental studies on optical emission from photonic dots had shown that the modes' degeneracy is proportional to the photon density inside the optical cavity. To realize the three-dimension confinement of radiation in the ZnS/SiO_2 dielectric cavity, it is essential to model the cavity as a mirror with spherical curvature of high reflectivity [18]. The formulations based on geometrical optics algebra of the spherical symmetry had led to a dispersion relation, which implies that the spacing between emission modes is morphology dependent [17]. The emission obtained by the photonics dots might be due to the electron-hole recombination process in ZnS QDs that arises near the band edge [19].

The cavity dimension calculated from optical emission data based on the mode spacing formula $r = \frac{\lambda^2}{2n\Delta\lambda}$, has found to be 13.982 μm, which agree with that obtained by microscopic method.

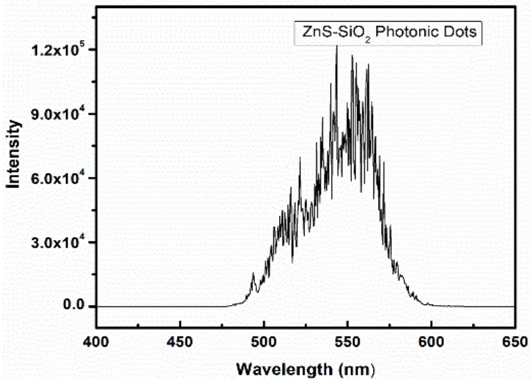

Fig. 3. Shows the photoluminescence emission of photonic dots.

5. Conclusion

ZnS QDs embedded in ZnS/SiO_2 spherical cavity exhibit modified emission. WGM observed is due to the total internal reflection leading to the surface propagation of tap photon. The cavity dimension calculated from the emission mode spacing has found to be around 13 μm, which agree with dimension determined from the cavity micrograph.

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