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Enhanced luminescence stability of quantum dot-based inorganic nanocomposite particles for white-light-emitting diodes

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ABSTRACT

We have synthesized quantum dot (QD)-embedded inorganic nanocomposites by effective combination of spray pyrolysis and subsequent sol–gel processing. The rapid depression of emission intensity of QDs just after addition of ammonia for sol–gel processing was effectively retarded by intermediate addition of boron alkoxide to the self-assembled QD ensembles. White-light-emitting diodes with low color correlated temperature were fabricated by combining QD-inorganic nanocomposite particles and conventional oxide. In contrast to previous reports describing fabrication of wLED by simple blending of bare quantum dots with silicone encapsulants, QD-embedded in B_2O_3–SiO_2-based nanocomposite particles provide much enhanced stability of light emission during the prolonged operation.

1. Introduction

White-light-emitting diodes (wLEDs) with high luminous efficacy, high color rendering index (CRI) and low correlated color temperature (CCT) were quested as alternatives to commonly used incandescent bulb with low efficiency and mercury-containing fluorescent lamps [1]. The demand of new lighting source with low CCT and high CRI to replace incandescent lamps emitting "warm" white color have driven phosphors beyond conventional Ce-doped yttrium aluminum garnet (YAG:Ce). Conventional red light emitting phosphors can be applied to compensate red-deficient emission spectra of the yellow phosphors and they emit visible light as well as infrared light which is invisible to human eyes due to the broad emission spectra of red phosphors. Then, there should be tradeoff between color quality and power efficiency of white LED [2].

Recently, quantum dots (QDs) with capability of down converting blue light to green or red light were introduced as possible candidates for light emitters to correct emission spectrum of wLEDs without significant loss of power efficiency [3]. QDs are efficient emitters of visible light with high quantum yield and provide very narrow emission spectra with finely tunable emission wavelengths [2]. Hence, highly efficient wLEDs are expected to be realized with QDs [3]. Sometimes, surface ligands on QDs can disturb polymerization or reduce mechanical stability of silicone polymer, one of the most popular packaging materials for LEDs. Then, full utilization of the optical properties of QDs requires uniform mixing with silicone polymer to stabilize in packaging process of wLEDs, and the long chain surface ligands with hydrophobicity reduce their compatibility with polar silicone polymers which is preferred in the LED fabrication. Since QDs are a set of nanocrystals of chalcogenide semiconductors, they easily react with oxygen and form oxide on the surface which can be promoted by excitation from blue light of LED chips. It needs an efficient surface passivation route to circumvent oxidation of QD surface and to maintain the excellent light emitting capability of QDs. One possible solution to this requirement is encapsulation of QDs with hydrophilic inorganic matrix [4]. Various methods have been applied to synthesize oxide-encapsulated QDs [4–8]. However, discussion about light emission stability of QD-oxide nanocomposite particles is quite rare. Recently, one of the authors have synthesized SiO_2-based nanocomposites containing CdSe/ZnS quantum dots at high concentration by spray dispersion of QDs and further encapsulation through hydrolysis and condensation of TEOS [8]. The wLEDs with QD–SiO_2 nanocomposites showed good luminous efficacy comparable to the YAG:Ce-loaded blue LED and displayed high CRI. However, prolonged irradiation of blue light to QDs in white-emitting LEDs usually resulted in decrease in emission intensity and blueshift in emission wavelength of QDs due to reduction in size by corrosion. Although silica is one of the ideal matrices for QDs because of its good optical and mechanical properties, further modification of QD-based inorganic nanocomposite particles will be required to ensure stability of photoluminescence (PL) even after prolonged irradiation with blue light from

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LEDs. In this study, we have synthesized inorganic matrix for nanocomposites to passivate surface of quantum dots from oxidation and corrosion assisted by intermediate addition of boron alkoxide during sol–gel process for matrix formation. We report highly enhanced stability of QD-based white LEDs with low CCT.

2. Materials and methods

The toluene solution of CdSe/ZnS QDs was sprayed ultrasonically at 250 °C to evaporate solvent and assembled hydrophobic QDs were finally dispersed into hydrophilic ethanol. The sprayed QDs formed highly porous aggregates with complex shapes. Although QDs were experienced heating at 250 °C for a few seconds, they conserved hydrophobic nature of surface and could be uniformly dispersed in toluene. As a second step, inorganic matrix was formed around spray-dispersed QD aggregates by sequential addition of triisopropyl borate (TIB) and tetraethylorthosilicate (TEOS) followed by addition of aqueous ammonia solution after time interval of 10 min. In this stage of processing, we added 1 ml of TIB to 500 ml ethanol solution of QD aggregates and reacted for 5 min. under stirring. Subsequently, we added 5 ml of TEOS to the same solution followed by addition of 1 ml of aqueous ammonia solution. After hydrolytic reaction of TIB/TEOS and ammonia during vigorous stirring for 1 h, the solution became turbid and QD-based inorganic nanocomposite powders were centrifuged. The recovered powders were dried under vacuum at room temperature for characterization and further packaging.

The combination of blue LEDs, yellow emitting YAG:Ce phosphors and red emitting QD-based inorganic nanocomposite powders were prepared by following conventional LED packaging routes. QD-based inorganic nanocomposite powders and YAG:Ce yellow phosphors (Nanophosphor Technology Inc.) were mixed with OE6636 resin (silicone-based optical encapsulation material for LED, Dow corning) for LED packaging. After removal of pores and solvent in vacuum for 1 h, the mixture was dropped on unpackaged blue LEDs (B2410A, kindly donated by Iljin Materials Inc.) and cured for 1hour at 150 °C in oven. The prepared white LEDs were operated at ambient conditions with operating voltage of 3.3 V with power flux of 30 mW. The performance of LEDs were characterized with BTS256-LED (Gigahertz-Optik, GmbH).

3. Results and discussion

The toluene solution of QDs was sprayed ultrasonically at 250 °C to ethanol. The QD solution was scattered to be micron-sized droplets just after spraying and QDs were assembled to form highly porous aggregates with complex shape after evaporation of solvent. The spray drying method was often applied to evaporation assisted self-assembly of colloidal nanoparticles [9]. Evaporation of solvent during the spray-drying process induces the shrinkage of droplets containing nanoparticles and the nanoparticles inside droplets are assembled due to capillary forces. The aerosol spray technique maximizes evaporation of solvent and restricts self-assembly of nanoparticles within the droplet. In fact, various nanoparticles were self-assembled to be mesospheres using the aerosol-based spray process [10]. Ethanol, a poor solvent to hydrophobic QDs was used as a dispersing media to conserve the structure of assembled QDs. Since hydrophobic solvent can destroy the assembly of QDs and subsequent addition of aqueous ammonia can give rise to severe phase separation which may result in inhomogeneous oxide layer formation.

Fig. 1 shows evolution of photoluminescence (PL) spectra for QD-based inorganic composite particles during the oxide growth step. The PL spectra were shifted after oxide encapsulation on QDs.

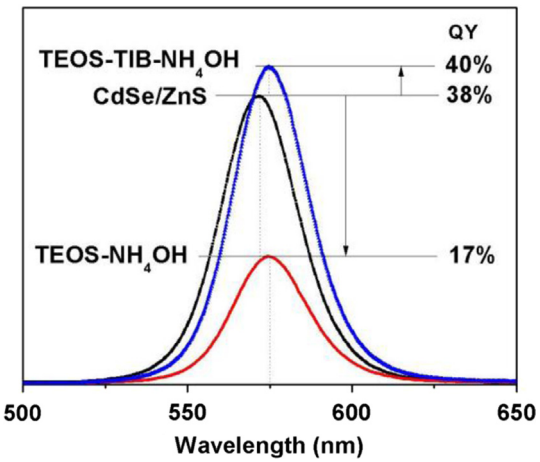

Fig. 1. Variation of emission intensity during each processing steps for inorganic nanocomposite particles incorporated with CdSe/ZnS nanocrystals. The quantum yield (QY) of each samples was also presented.

One possible explanation of redshift after surface modification with oxide matrix is the pressure effect. Since the pressure dependence of band gap for CdSe is negative (-4×10^{-3} eV/GPa [11]), pressure formed by oxide matrix can decrease band gap and the resultant redshift of PL spectrum. In particular, redistribution of surface electronic density after ligand exchange can result in redshift of the PL spectrum of CdSe QDs [12]. The emission intensity of the QD-silica nanocomposite was highly minimized just after addition of TEOS/NH_4OH for the silica matrix formation as reported in the previous paper [8]. The surface ligand of as-prepared QDs was oleic acid and trioctylphosphine. After surface modification with sol–gel processing, it is believed that the surface ligands are replaced by alkoxide [13]. The degradation of PL intensity after silica encapsulation was usually interpreted as formation of non-radiative recombination channels such as surface defects by the adsorption of ammonia [14,15]. The possible origin of these non-radiative recombination channels were attributed to increase in energy transfer from QDs to adsorbed ammonia [14].

In order to minimize deterioration in PL intensity of QDs during the silica matrix formation, several routes such as initial silanization [16], formation of multiple shells on QDs [17] have been suggested. In particular, the initial silanization approach was proven to be effective for conservation of quantum yield of initial quantum dots after silicza encapsulation. Although hydrolysis of TEOS in anhydrous organic solvent is quite slow (more than 20 h; [16]), initial silanization of QDs can form thin and uniform barrier layers preventing adsorption of fluorescence quenchers such as ammonia molecules. In this study, we used TIB for the initial thin barrier formation on QDs to prevent adsorption of ammonia on QDs and retain initial luminescence efficiency. Addition of B_2O_3 to silicate or titanate was popularly attempted to reduce the melting temperature and to obtain dense microstructure [18–20]. Since hydrolysis of TIB is much faster than TEOS due to highly electrophilic nature of trigonal boron compared to silicon [21,22], the surface of QDs were conjectured to be passivated with thin layers of B_2O_3 or $B(OH)_3$. As shown in Fig. 1, the drastic reduction in PL intensity of QD aggregates was successfully hindered by addition of TIB; that is, the initial PL intensity of QD aggregates was maintained without significant depression even after TEOS/NH_4OH addition.

Fig. 2 showed transmission electron microscopic (TEM) images of QD-inorganic nanocomposite particles synthesized from initial passivation of QDs with TIB and subsequent silica layer formation with the addition of TEOS and ammonia. The composite particles are irregularly shaped and less than 200 nm in thickness. Small particles are embedded in transparent matrix as shown in the