

PMMA quantum dots composites fabricated via use of pre-polymerization

Lin Pang, Yaoming Shen, Kevin Tetz and Yeshaiahu Fainman

Department of Electrical and Computer Engineering, University of California,
San Diego, 9500 Gilman Drive, La Jolla, California 92093-0407
lpang@ece.ucsd.edu

Abstract: We present a novel method to produce a PMMA-quantum-dot (QD) composite fabricated by pre-polymerization of PMMA and dispersing commercially available colloidal semiconductor QDs. The QDs are stabilized in rapidly formed oligomer matrices, and the complete polymerization of the PMMA-QD composite is achieved by commonly used polymerization. The properties of the PMMA-QD composite are measured and compared with the QDs in colloidal solution. Patterning of the PMMA-QD composite by direct write electron beam shows its promising applications in optoelectronics.

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OCIS codes: (160.5470) Polymers; (230.4000) Microstructure fabrication; (160.6000) Semiconductors, including MQW

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1. Introduction

One of the most promising approaches to enhance and engineer linear and nonlinear properties of optical and optoelectronic materials is to utilize nanoscale quantum confinement of semiconductor materials in 1-D (quantum wells), 2-D (quantum wires), and 3-D (quantum dots) spaces. Semiconductor quantum dots (QDs) have attracted great interest in recent years due to their unique properties that carry a great promise for numerous optoelectronics and photonics applications including communications [1,2], display [3], and biology [4].

Since the first quantum dots made by use of the etched quantum well by Reed [5], various methods of fabricating semiconductor QDs have been investigated. Self-organized growth of QDs has been widely used to make electronic and optoelectronic devices [6] from the epitaxial structure to the random arrangement of islets by means of the Stranski-Krastanow transition [7]. These types of structures rely on complicated processing and high cost with metal-organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) facilities. Methods based on growing semiconductor microcrystals in glass dielectric matrices [8], and use of sol-gel films as hosts for QDs have also been considered as an alternatives [9,10]. Recently, semiconductor QDs fabricated in colloidal solution via synthetic routes have been shown to be promising alternative fabrication method of QDs [11-13]. In colloidal solutions, however, QDs are suspended in some solvent, making them less practical for fabrication and integration of photonic and optoelectronic devices. Thereby, the introduction of such QDs into a solid state matrix is of great interest for numerous applications. One of the

approaches uses incorporation of QDs into polymer thin films and has shown a great promise [3,14]. However, the incorporation of QDs into thick bulk polymer matrix has remained challenging. A large number of complicated synthesis techniques have been investigated to prevent aggregation of QDs during the polymerization process when QDs are dissolved in vinyl monomers and processed to radical polymerization. These methods include: Gao *et al.* [15] used Pb methacrylate to make PbS QDs, then polymerized the vinyl to form solid polymer composite. Frog *et al.* [16] incorporated QDs within a polymer containing phosphine donors attached to the polymer backbone to form polymerized QDs composite film. Lee *et al.* [17] used the same phosphine ligand covering QDs to prevent the QDs from phase separating during polymerization to form solid composite polymer. Zhang *et al.* [18] utilized the polymerizable surfactant to transfer QDs to styrene solution and polymerized to solid polymer composite.

In this paper, we describe a simple method of pre-polymerizing monomer QD solution to prevent the QDs from separating away from the polymer matrix. The pre-polymerized polymer could be cast into various molds to form solid-state polymer-QD composites via a complete polymerization step. This approach could be used for fabrication of various microstructures [19]. Moreover, its dilute solution can also be used to form films by spin coating, which can be further lithographically processed to construct nanostructures for realization of photonic devices [20].

2. Experiments

Our process is based on radical polymerization of methyl methacrylate (MMA). Under vigorous stirring, a quantity of nanoparticle colloidal solution of 620nm CdSe/ZnS core shell tri-n-octylphosphine oxide (TOPO) capped quantum dots in toluene (Evident Technologies) is slowly added into the distilled MMA with a concentration of radical initiator azobisisobutyronitrile (AIBN) of 0.1% in weight. The MMA QD solution was heated in a thermostatic water bath at about 90°C for 20 min. to get the suitable viscosity, or pre-polymerization, and then poured into molds, which were put into an oven at 60°C for post-polymerization. Generally, the whole process in the oven is conducted for more than 20 hours.

It is commonly known that uniform dispersion of nanoparticles in the final solid phase polymer-QD composites is hampered by separation and cluster aggregation within the matrix. To minimize these effects, ligand and other surfactants were used to envelope the nanoparticles to prevent aggregation during the polymerization of the monomers [15-18]. In contrast, our method does not use such surfactants, indicating that the QDs are only suspended in the MMA monomers during polymerization step. The polymerization procedure of MMA to its polymer form, or poly methyl methacrylate (PMMA), could influence the QD distribution in the polymerized PMMA. We conducted a comparison experiment on complete polymerization into PMMA of the pre-polymerized and non-pre-polymerized MMA mixed with QDs. In this experiment we prepared 4 ml of 0.6 mg/ml QD-MMA solution of 0.1% AIBN which was split equally into two identical glass vials. One of the vials was placed into thermostatic water bath at 90°C for about 20 min. for pre-polymerization. Later it was transferred into oven at 60°C together with another vial containing non-pre-polymerized QD-MMA solution. The two samples were kept in the oven for 20 hours. The appearance of the two solidified composite polymers was completely different as shown in Fig. 1. For the pre-polymerization, the color is uniform, and there were no observable defects, as shown in Fig. 1 (a) (right). The directly polymerized counterpart, however, exhibits severe non-uniformity (see Fig. 1 (a) (left)). From the close-up in Fig. 1(a), large bunches of clusters can be observed, indicating the agglomeration of the QDs after direct polymerization. That is why attempts to obtain such composites from radical polymerization with the vinyl monomers showed limited success [17]. The sideview (see the left part of Fig. 1(b)) also shows non-uniformity of QDs distribution in the vertical direction. In fact, the QDs have clustered (i.e., split) into two parts with almost no QDs in the middle region of the sample.

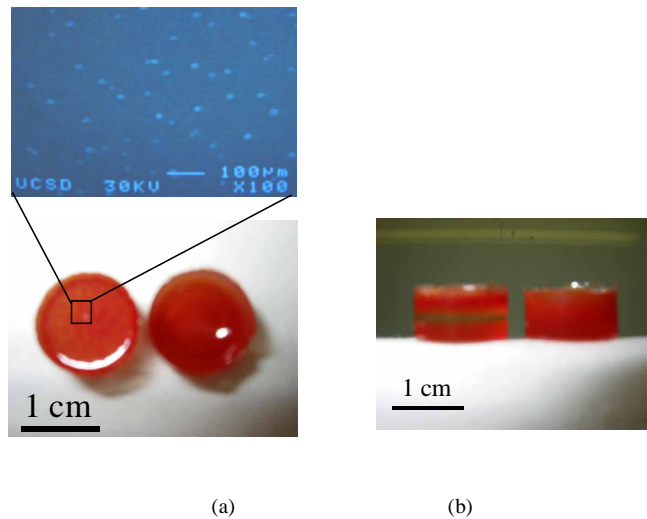


Fig. 1. Comparison of the pre-polymerization of MMA-QDs composite and the direct polymerization; (a) top view of the pre-polymerization (right) and direct polymerization (left); the close-up of the top surface of the direct polymerization was taken under a background; (b) sideviews of the pre-polymerization (right) and direct polymerization (left); the latter shows nonuniformity in the vertical direction.

The non-uniformity can be explained as follows: in general, the QDs dissolve in MMA easier than in polymerized PMMA due to the difference in the viscosity. Therefore, for direct polymerization process during 20 hours, when MMA is polymerized to PMMA, the large molecular mass PMMA with enveloped QDs sinks to the bottom of the container, whereas the non-polymerized MMA moves towards the top. Furthermore, due to the higher solubility of QDs in non-polymerized MMA, the non-wrapped QDs diffuse to the top MMA layer, leaving a gap in the middle region. After the polymerization process is complete, the composite has a non-uniform distribution of QDs in vertical direction as confirmed by our experiments. It is obvious that the aggregation of QDs need adequate control for most of the potential applications.

In contrast, pre-polymerization of MMA-QD solution, processed for a short time at a higher temperature, assures the rapid polymerization of couples of MMA monomers to form oligomers, which envelope the QDs and prevent them from aggregation. Moreover, the great compatibility of the oligomer in both MMA and polymerized PMMA assures that the capped QDs will disperse uniformly during the post polymerization process. This also explains the formation of the bottom section of the PMMA-QD composite in the direct polymerization (Fig. 1(b) (left)), in which the partially formed oligomers capping the QDs polymerize to PMMA-QD composite, coalesce and descend. It should be mentioned that the capping ligand on the QDs, TOPO, plays an important role in solubilizing the QDs in the MMA. Clear PMMA-QD composites have also been produced with different sizes of CdSe/ZnS and PbSe colloidal QDs using above procedure.

For characterization of QD properties in the PMMA-QD composites fabricated using the pre-polymerization approach, we conducted experiments on absorption and photoluminescence (PL). An argon laser with wavelength of 488nm was used to pump for PL measurements, whereas LS-1 broadband (Ocean Optics) halogen lamp was used to measure the absorption spectrum. We used CVI DK480 monochromator and Hamamatsu H7421-50 (GaAs) photcounter to measure the absorption as well as PL from the samples. First, for comparison purposes, the spectra of QDs in toluene solution of concentration 2.5 mg/ml were

measured as shown in the Fig. 2(a). The first absorption peak of the CdSe/ZnS QDs is 612 nm, and its PL peak is at 625 nm with full width half maximum (FWHM) of about 16 nm. Fig. 2(b) shows the absorption and PL spectra of PMMA-QD composite in a slide-like shape with thickness of 1mm produced by casting the pre-polymerized MMA polymer (0.6 mg/ml) into a flat chamber made from glass slides. Absorption spectrum of a 1 mm thick pure PMMA slide is also shown for comparison, demonstrating that pure PMMA material absorbs little light at visible and near infrared regions.

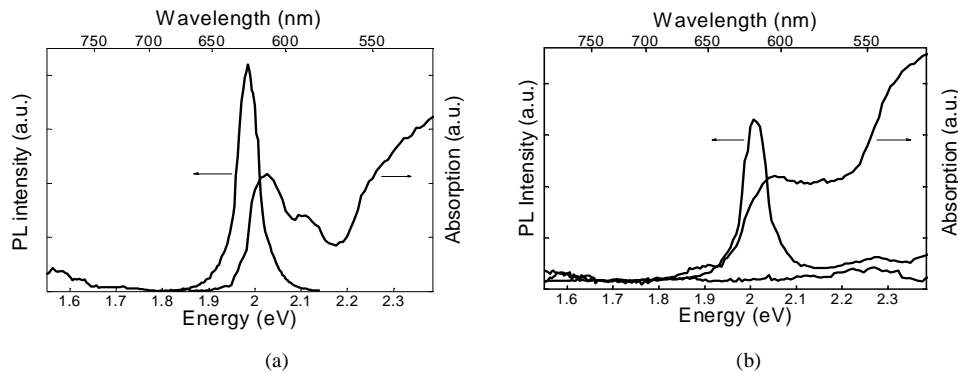


Fig. 2. Absorption and PL spectra of QDs in (a) toluene solution and (b) PMMA-QD composite, where the dash line shows the absorption spectrum of a 1 mm thick pure PMMA slide.

The PL peak of the solid PMMA-QD composite matrix occurs at about 617 nm with FWHM of about 19nm. The blue shift of the PL peak seems to be in contradiction with Ref 17, where a PL peak of 625 nm in toluene shifted approximately 17 nm to longer wavelength when incorporated into the composite matrix. The red shift of Ref. [17] was interpreted as due to light reabsorption by the larger QDs in the distribution as the emitted light from the smaller QDs travels along the composite rod. Because of different synthesis of colloidal QDs, a direct comparison between these two procedures cannot be conducted.

From Fig. 2(b), we observe that the first absorption peak of PMMA-QD composite sample occurs at about 602 nm, showing a shift to shorter wavelength (blue shift) by about 10 nm as compared to the absorption maximum of 612 nm measured for QDs in toluene. Blue shift in the PL and absorption spectra had been reported for different kinds of quantum dots when exposed in air (oxygen) [21-23], even was utilized for patterning [24]. For our case, the blue shift could also be attributed to the oxidation of the QDs surface. The in-depth investigations are being carried on, and will be addressed in the future work.

Our method of preparing PMMA-QD composites could be used not only to achieve QD-polymer displays [3] and precisely duplicated microstructures [19], but also used for direct write electron beam lithography to make nanostructures and other nanoscale patterned polymer-QD structures by exploiting the nature of sensitivity of PMMA to an electron beam. This fabrication approach may be very attractive for numerous applications of QDs composites for photonics and optoelectronics. For the proof-of-concept experiment the pre-polymerized PMMA-QD composite was dissolved in MMA and then spin coated on a SiO₂ substrate. After the soft baking step, the PMMA-QD layer was patterned by E-beam lithography in a modified SEM (JEOL JSM-6400), followed by development in solution of methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA) of MIBK:IPA=1:2. Figure 3 shows an SEM photograph of a structure with 1.5 μm period and feature sizes of 200 and 300nm.

Different from the photoactivation of QDs for large structure patterning [24], and self-assembly for small structure [25], the grating structure shown in Fig. 3 demonstrates that our PMMA-QD composite is a good E-beam sensitive material for patterning nanostructures. Although its organic matrix is not as environmentally stable as semiconductor QDs structure fabricated via MBE and MOCVD techniques, its flexibility and compatibility with organic optoelectronics make it a very attractive candidate for many applications. Use of PMMA-QD composite as a new electron beam writing material is being further investigated as a new e-beam resist as well as a new patterned optoelectronic material.

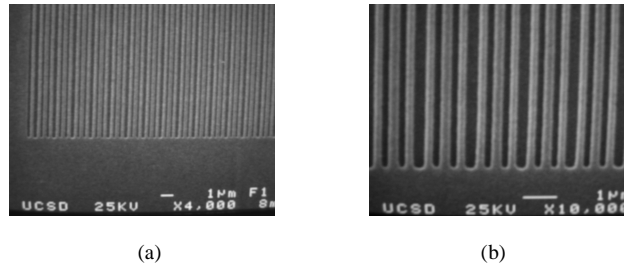


Fig. 3. Scanning electron microscopy image of PMMA-QD composite structure by directly patterning the composite with electron beam; (a) a composite grating with 1.5 μm period and features of 200 and 300nm, (b) magnified view of (a).

3. Discussions and conclusions

Generally, QD polymer film could be obtained by incorporating QDs into solvent and polymer [26], however, non-uniform dispersion and the insolubility of QDs in large mass molecule polymer would seriously affect its quality and limit its use for application. Due to the compatibility of the MMA and the solvent of the QDs, i.e., toluene, there is no limit to raise the concentration of our PMMA-QD composite. The limit comes from the availability of the QDs concentration in toluene. Devices made of QD composite, such as waveguides, can be fabricated by use of optical lithography, followed by etching process [26]. However, directly patterning the PMMA-QD composite with electron beam lithography allows for precise control of the position of the QDs, and the shape of the QD nanostructure in device fabrication such as photonic crystals, ring resonators, and other waveguide devices [20,27,28].

In conclusion, we have presented a novel approach to fabricate PMMA-QD composite using pre-polymerization of MMA and commercially available colloidal semiconductor QDs. The QDs were stabilized in the rapidly formed oligomer matrices, and the complete polymerization of PMMA-QD composite was performed by common post-processing. The absorption and the PL properties of the PMMA-QD composite were measured and compared with the QDs in solution. The blue shift of the emission peak in PMMA-QD composite as well as the blue shift of the first absorption compared to that of QDs in solution is attributed to the QD environment changes. Investigation of patterning PMMA-QD composite in the electron beam lithography demonstrates promising application of our PMMA-QD composite for patterning optoelectronic devices.

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