Photoluminiscent nanocomposites PS/CdSe (quantum dots) via miniemulsion polymerization

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Abstract

In the present work miniemulsion polymerization was applied to encapsulate CdSe quantum dots in a polystyrene (PS) host matrix to produce photoluminiscent polymer nanocomposites. The latex was characterized by TEM and SEM. Nanocomposite film was characterized by absorption and emission UV spectrometry. Latex particles size ranged between 155 $\pm$ 30 nm. Fluorescence spectrums showed a 595 nm peak for an original solution of CdSe (QDs) and the resultant dried material PS/CdSe, suggesting that the polymerization method used preserves the optical properties of the quantum dots. The expectation for these materials is to create a new generation of hydrocarbon sensors.

Introduction

One of the most promising fields of application for nonostructured materials is that of semiconductors. In recent years, intense research has been developed about a kind of nanoparticles with very attractive electronic and optoelectronic properties, the *quantum dots (QDs).* These are semiconductor nanocrystals with typical size of 1 to 10 nm [1] and represent the ultimate limit of low dimensional structures. In quantum dots, free carriers are confined in all three directions [2]. They are often referred to as artificial atoms because their electronic properties resemble, for example, the ionization energy and discrete excitation spectrum of atoms [3].

When novel particular materials like quantum dots are envisaged to have strong potential according to their properties, is always interesting to think about their insertion in different matrices for the development of new and functional composites. In this direction, the incorporation of QDs in polymer hosts has been in recent years object of intense research, since it is considered ideal for certain applications [4]. Several strategies have been used to incorporate QDs into polymer matrices, i.e., the simple mixing of the QDs with the polymer, or the covalent or non-covalent bonding of QDs with the polymer. However, the simple mixing of the QDs with the polymer is not good enough due to phase segregation [5].

In the present study QDs of cadmium selenide (CdSe) of 2 to 3 nm were encapsulated into polystyrene particles of nanometric size. Through encapsulation it was expected to overcome some problems such as QDs phase segregation, chemical instability and compatibility. Miniemulsion polymerization was used as synthesis technique, since it is especially useful to incorporate hydrophobe compounds into polymer particles. The absence of micellar nucleation and the compartmentalization of the polymerization into the mini-emulsified droplets are some of the main characteristics that make this technique especially suitable for this task.

Experimental

Styrene monomer distilled under vacuum, 2,2-azobisisobutironitrile (AIBN) recrystallized from methanol, quantum dots of CdSe of 2 to 3 nm, cetyl trimethylammonium bromide (CTAB), hexadecane and hexadecylamine.
Miniemulsion polymerizations were performed at 70 ºC, 350 rpm and nitrogen atmosphere. Procedure: first, QDs (0.1 g) were dispersed in styrene monomer (20 mL); next, hexadecane, hexadecylamine and AIBN were also added to the monomer. Afterwards a surfactant solution, 0.2 g of CTAB in 80 mL of tridistilled water, was loaded to the reactor and kept in agitation for 15 min. Next, the monomer solution was poured to the reactor. The miniemulsion was formed by applying ultrasound for 45 min. Finally, temperature was raised to initiate polymerization.

Results

Fig. 1 an 2 shows SEM and TEM images, respectively, of PS particles from the latex of about 100 nm. In the photograph there is no evidence for another entity different from the polymer particles. According to that, it can be inferred that QDs are located inside the PS particles; other wise, intense agglomeration of quantum dots would be expected given that the surrounding of polymer particles is aqueous media, incompatible with the superficial covering of the QDs. Furthermore, the inclusion of CdSe quantum dots nanoparticles does not affect the size distribution of polymer particles, which is in agreement with some literature [6].

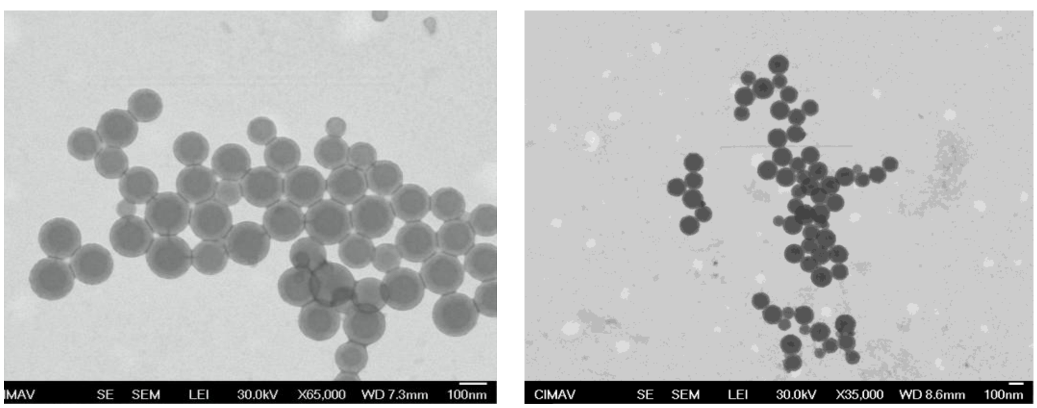

Fig. 1. SEM images of PS/QDs latex

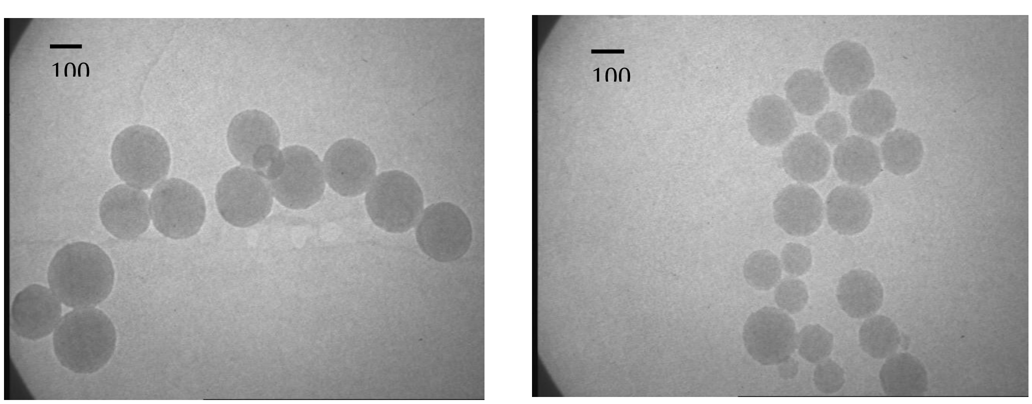

Fig. 2. TEM images of PS/QDs latex

In Fig. 3 it is observed a distinctive peak in the UV spectrum at 575 nm only for the CdSe QDs after the synthesis.

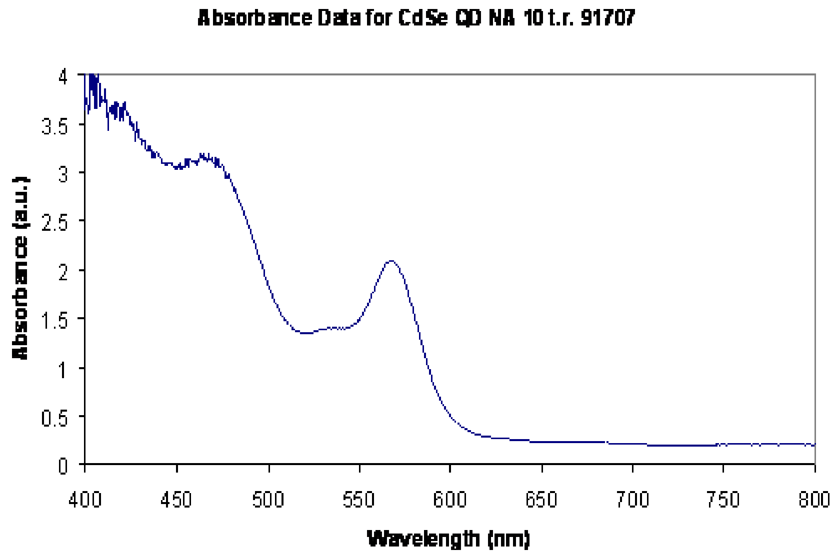

Fig 3. UV spectrum for the CdSe quantum dots in a chloroform dissolution.

Fig. 4 presents the UV spectrum for a composite powder of PS/QDs obtained from drying of its correspondent latex. The maximum in the signal appears at 585 nm, approximately, a little shift to higher wavelengths respect to the CdSe QDs. This difference could be attributed to a different level of dispersion between systems. It was expected that in the dried powder, conditions for some agglomeration were given. However, it could be confirmed trough this test that polymerization process of miniemulsion was carried out in such a way that photostability of quantum dots was not affected.

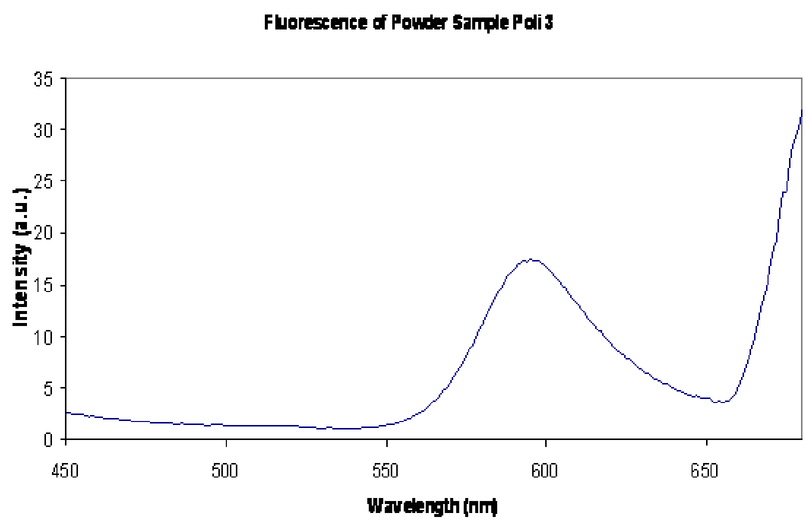

Fig. 4. UV spectrum for dried powder composite PS/QDs.

Fig. 5 shows the characteristic peaks of luminescence in composites film of different concentration, obtained from dilutions of an original concentration. It is clearly observed that peak intensity lowers substantially as amount of photoluminescence entities is reduced. There is no shift along the wavelength axis, inferring that dispersion and distribution of quantum dots are rather homogeneous in all cases.

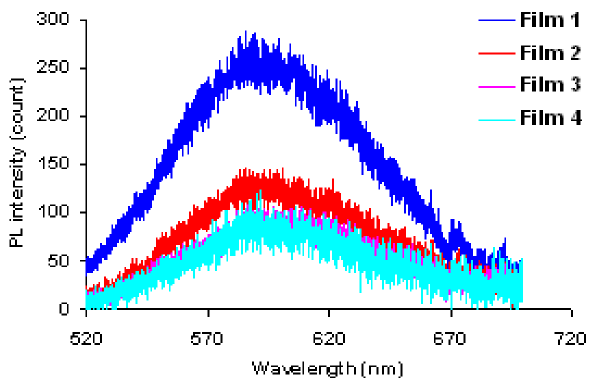

Fig. 5. Photolumimiscent spectra of PS/QDs films at different concentrations

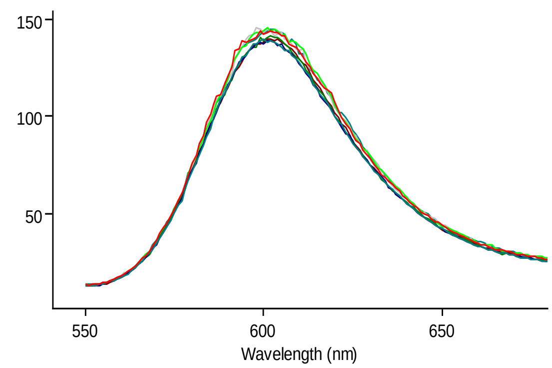

Fig. 6. Photoluminiscent spectrum of a PS/QDs film at different times periods of measurement.

In Fig. 6 a nanocomposite film was characterized at different time intervals in order to asses the photoluminescence stability. Each color represent a 30 minutes period between intensity measurements. Overlapped spectra accounts for the permanence of the luminescence effect.

Conclusions

Miniemulsion polymerization showed to be an appropriate method to produce CdSe/PS films composites without QDs quenching. Also, it is possible to obtain composites with high stability about their photoluminescence properties with time.

References

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