PHOTOLUMINESCENT DI-UREASIL HYBRIDS CONTAINING CdSe/ZnS QUANTUM DOTS

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Introduction

In recent years, there has been a growing interest in the synthesis of inorganic-organic functional materials exhibiting novel optical properties. A common procedure involves the association of already made inorganic nanostructures with an organic matrix, which is usually a polymer and that can be generated *in situ* by chemical means but maintaining the chemical integrity of the other component. The main advantage in using *in situ* methods is the often improved microstructure homogeneity of the materials, with important consequences in terms of their performance for example in optical devices and sensors. Using this strategy, a number of polymer nanocomposites have been reported in the literature [2].

Ureasilicate derivatives, often referred as di-ureasils, form a class of hybrid materials whose properties in terms of homogeneity are relevant for their optical performance, for example as a transparent host material in luminescent displays and integrated optical devices. The synthesis and optical properties of QDs, in particular for II/VI semiconductors, have been fully documented during the last decades and several reviews on the subject can be found in the literature [3]. An effective way to achieve highly photoluminescent CdSe QDs has been the passivation of surface defects either using organic capping agents or, more efficiently, to fabricate core/shell nanostructures in which the shell is made of a wide band-gap semiconductor [4]. As a result, radiative decay through emission of photons is a likely event in surface modified CdSe QDs, at room temperature, comparatively to bulk CdSe.

Chemical synthesis of d-U(600)CdSe and d-U(600)(CdSe/ZnS) hybrid materials

Several nanocomposites consisting on di-ureasil matrices doped with organically capped CdSe QDs have been prepared in this work. Despite the optical homogeneity of the CdSe/di-ureasil nanocomposites obtained, preliminary experiments performed on these nanocomposites also showed a low PL emission at room temperature. In principle, this reflects the properties of the individual QDs, since previous reports have shown that highly photoluminescent CdSe QDs need surface passivation with a wide band gap semiconductor (e.g. ZnS). We anticipate that this type of coating might have also a protective role in relation to detrimental effects on the CdSe QDs surfaces during the synthesis of the di-ureasil nanocomposites. In order to coat the CdSe QDs (prepared by Peng *et al* method [5]) with a ZnS phase we have developed in our laboratory a new strategy that is now described here. This involves in a first step the reaction of $Zn(S_2CNEt_2)2$ and thylenediamine (en), and then the thermolysis of the resulting complex $[Zn(en)_3(S_2CNEt_2)_2]$ in OL in the presence of CdSe QDs.

Photoluminescence of the as prepared hybrid materials

In preparing the di-ureasil nanocomposites, the primary effect of using coated CdSe QDs with ZnS was the bright luminescence observed in final transparent materials (figure 1), at least

when compared to their analogues using non-capped CdSe QDs. The lack of understanding on surface phenomena underlying the interaction between the di-ureasil matrices and the CdSe QDs led us to carry out a comparative study on the PL behaviour of the di-ureasil hybrids containing the as prepared CdSe QDs and those containing CdSe QDs which have been previously coated with ZnS.

Conclusions

The chemical synthesis of transparent, flexible and photoluminescent di-ureasil based nanocomposites was achieved by a sol-gel method, in the presence of CdSe and ZnS coated CdSe QDs (Fig. 1) [6]. For the latter a new and alternative process has been investigated, which involves the coating of previously prepared CdSe QDs with ZnS shells derived from an ligand mixed amine-alkyldithiocarbamate Zn(II) complex. The incorporation of such CdSe/ZnS QDs into the d-U(600) di-ureasil hybrid host result in final nanocomposites with emission quantum yields up to 0.11, displaying a huge increase (between 3 and 6 orders of magnitude) in the lifetime of the QDs, relatively to the isolated QDs, induced by d-U(600)-to-CdSe/ZnS QDs energy transfer active channels. Further work is at the moment in progress in our laboratory, including the development of nanocomposites whose photoluminescence can be tuned using distinct particle size distributions. This may be expressed in the future development of new functional nanomaterials which can be processed using already established sol-gel methodologies.

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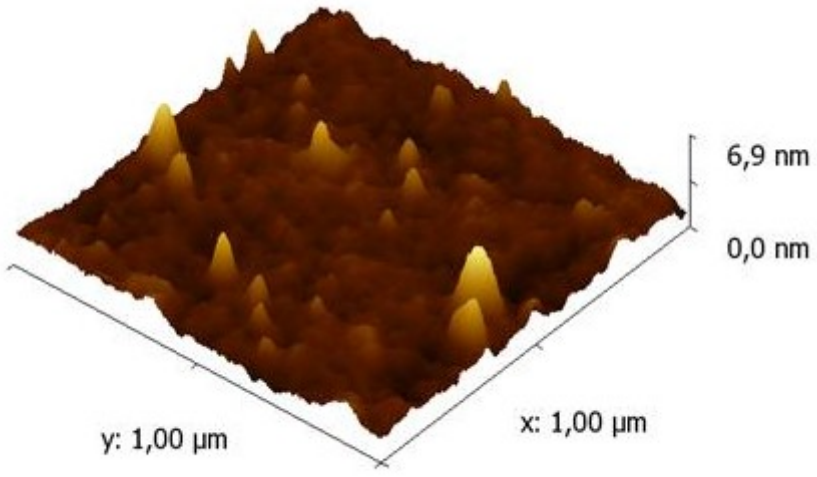

Figure 1: AFM image of a dU(600) di-ureasil hybrid containing CdSe/ZnS QDs