Synthesis of BAlq Embedded Silica Nanoparticles

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Introduction

Silica nanoparticles (NPs) are widely used in science for their well-known synthesis and easy functionalization. Silica nanoparticles doped with a fluorescent molecule have many biological and medical applications such as biological labeling, sensors, fluorescent markers in vitro and in vivo and as MRI contrast agents[1].

We have modified the recipe to synthesize silica nanoparticles by including different amounts of a fluorescent molecule, Bis(2-methyl-8-quinolinato)-4-phenylphenolate aluminum (BAlq) that can be seen in Figure 1. We will characterize the results in terms of the amount of molecule absorbed, the particle size and colloid's stability.

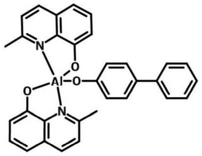

Figure 1. BAlq molecule structure. Spectrofluorometry was used to characterize the emission of this molecule. The emission band, with a peak at 480 nm, can be seen in Figure 5, in the Results section.

We aim to encapsulate the BAlq in silica nanoparticles as depicted in Figure 2.

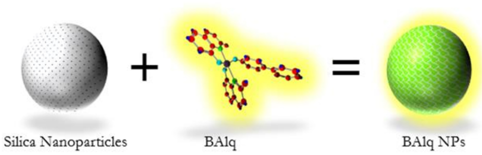

Figure 2. Encapsulation. Representation of the encapsulation process to obtain BAlq-Embedded nanoparticles.

Specifically, we present the results for silica particles loaded with the following amounts of the Balq fluorescent molecule: 10% (wt), 7.5% (wt), 5% (wt) and 2.5% (wt)

Objectives

- ✓ Learn silica nanoparticle synthesis and characterization techniques.
- ✓ Encapsulate the molecule BAlq in silica nanoparticles.
- ✓ Study the encapsulation in terms of the amount of molecule absorbed, and its influence in the particle size and colloids stability.

Acknowledgments

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References

- [1] **Well-Ordered Mesoporous Silica Nanoparticles as Cell Markers.** Yu-Shen Lin et al. Chemistry of Materials **2005** 17 (18), 4570-4573
- [2] **Phosphorescence emission from BAlq by forced intersystem crossing in a colloidal photonic crystal.** Luis González-Urbina, Javier Perez-Moreno, Koen Clays & Branko Kolaric**.** Molecular Physics. Volume 114, 2016 - Issue 15

Methods

Synthesis

- Stöber-Fink-Bohn method, the hydrolysis of Tetraethylorthosilicate in an alcoholic medium.

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH \quad \text{(Nucleation and growth)}$$
$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O \quad \text{(Termination)}$$

- Modified Stöber, replacing part of the alcohol with a BAlq solution in ethanol.

Purification

- Centrifuge: To induce solid to precipitate from the suspension and to remove the supernatant
- Ultrasound bath + vortex: For the resuspension of the nanoparticles in the dispersant medium.

Characterization

- Fluorescent emission: BAlq-NPs emission bands using Hitachi F-2500 spectrofluorometer.
- DLS: Dynamic Light Scattering is used to measure size and Z-potential (stability).
- SEM: For a precise measurement of the particles and their size dispersity.

Results

Silica nanoparticles were synthesized with different amounts of BAlq. All syntheses were done at 20°C.

Emission

Fig. 5 proves the encapsulation of BAlq in the NPs. BAlq-NPs were purified 3 times and no molecule emission was found in the supernatants. The emission band at 475 nm matches the typical emission from BAlq. The emission intensity and the content is quite consistent.

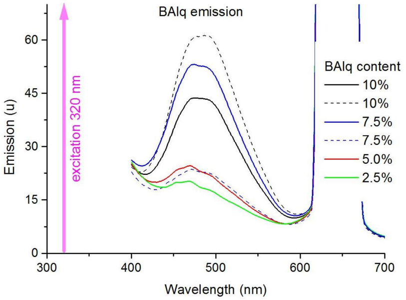

Figure 5. Emission spectra of nanoparticles with different BAlq content. Excitation wavelength at 320 nm. The large peak at 640 nm is the second order diffraction.

SEM

Scanning electron microscope (SEM) pictures of BAlq-NPs (Figure 6) show fluctuation in the shape and size of the nanoparticles. Some of the nanospheres are not completely spherical. Monodisperse spheres are necessary to ensure a good self-assembly in order to create well organized structures or crystals (Figure 7).

When the size of the NPs is in the order of the light wavelength (i.e. hundreds of nanometers) the crystals formed exhibit photonic properties and so they are called colloidal PhCs. The optical effect can be seen in Figure 9.

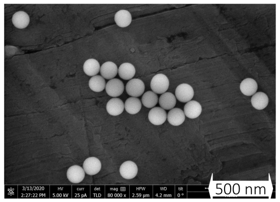

Figure 6. (Left). *SEM image of BAlq-doped silica nanoparticles.*

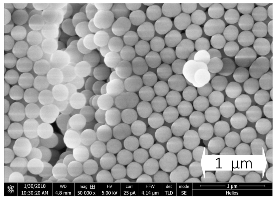

Figure 7. (Right) SEM image of a colloidal PhC.

Conclusions

- BAlq embedded nanoparticles were synthesized by modifying the Stöber method and obtaining a colloidal suspension of fluorescent silica nanoparticles.
- The emission intensity is consistent with the amount of fluorescent molecules in the synthesis, but the size of the particles changed dramatically and showed no clear trend.
- We have also noticed that the stability of the colloidal suspensions with the molecule was deteriorated.

Future Work

- We are currently working on improving the reproducibility of the synthesis and the size dispersity of the nanoparticles.
- We need to analyze the stability of the BAlq containing nanoparticles with Zeta-potential.
- We need to measure the emission from the dry photonic crystals with BAlq-NPs.
- We aim to optimize the size, shape, and stability of a colloidal silica nanoparticles with embedded BAlq by using core-shell encapsulation technique (see below).

Core-Shell encapsulation technique:

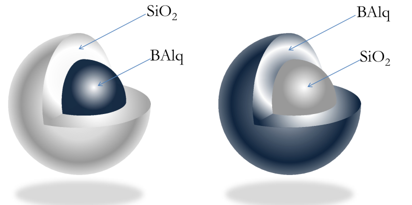

Figure 8. Core-Shell encapsulation technique. On the left, a BAlq containing NP is used as a seed to grow a pure silica shell. On the right, a pure silica NP is used to grow a shell with BAlq embedded.

In the core-shell technique, previously synthesized nanoparticles are used as seed. Two approaches are possible:

1. A suspension of pure silica nanoparticles is used as core and a layer of BAlq-doped silica is grown. The goal is to start with the best monodispersity and shape possible to minimize the standard deviation of the diameter and to achieve round nanoparticles.
2. A suspension of BAlq-doped nanoparticles is used as seeds and a shell of pure silica is grown. If the initial colloids are good in monodispersity this technique's goal is to increase the stability of the NPs in the colloidal solution.

In order to grow the shells, the addition of TEOS or a BAlq/TEOS solution to the suspension must be done at a slow, controlled rate.

Photonic Crystals

Photonic crystals (PhC) are periodical lattices capable of interacting with light due to their nanometer-size structure. Photonic crystals can be made using silica nanoparticles (NPs).

We aim to manipulate the emission of a molecule used in photovoltaic and LED devices, Bis(8-hydroxy-2-methylquinoline)-(4-phenylphenoxy) aluminum (BAlq). It has already been demonstrated[2] that photonic crystals can suppress the fluorescence emission from BAlq and obtain phosphorescence emission, which would in turn enhance the efficiency of such devices.

PhCs are formed by self-assembly vertical deposition – a collection of colloidal particles on a substrate driven by evaporation of the solvent at stable temperature (37 ºC). This process is done in a laboratory incubator and the resulting samples have iridescence colors like those in Figure 9.

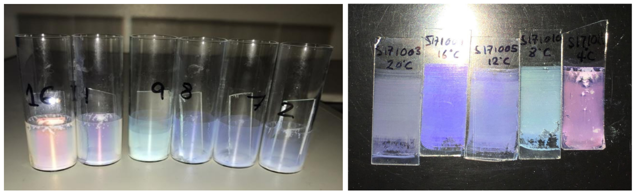

Fig. 9. (Left) Microscope glass slides in vials after deposition. (Right) Colloidal photonic crystals with different particle sizes. The different colors indicate different positions of the photonic band gaps.