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## Photoluminescent core-shell particles of organic dye in silica

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#### Abstract

Using a single silica precursor, Rhodamine 6G organic dye molecules have been entrapped in silica particles resulting into core-shell particles of  $\sim$ 500 nm diameter. Energy dispersive X-ray analysis, X-ray photoelectron spectroscopy and transmission electron microscopy analysis reveals that dye molecules are trapped inside the silica particles. Photoluminescence investigations show that highly luminescent and photostable core-shell particles are formed. Such core-shell particles can be easily suspended in water and would be useful for a variety of applications. However, there is a blue shift in the photoluminescence wavelength in case of core-shell particles compared to bare dye powder sample.  $\bigcirc$  2004 Elsevier B.V. All rights reserved.

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#### 1. Introduction

There is a considerable interest in core-shell particles due to their applications in bar codes, drug delivery, DNA sequencing, proteomics, etc. Several types of core-shell particles are designed to suit different applications and some reviews have appeared recently [1–3]. Generally in core-shell particles, nanoparticles or some molecules are

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trapped as a core, which is coated by some polymer or inorganic protective material to form a shell. Even some liquid can be trapped as a core inside some solid shell. Protective shells avoid degradation of nanoparticles or trapped molecules. Surface-modified core-shell particles are quite useful as they can be targeted towards the complementary molecules and located using the luminescence technique [1]. Few nanometer [4] to hundreds nanometer thick [5] shells can be synthesized. Silica core-shell particles are often used in bio-analysis due to their possibility of suspending in water as well as their ability to adsorb variety of biomolecules on their surfaces

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[1,2]. In some cases, their large surface area can be used as a template to adsorb big molecules.

Organic dyes are often used in fluorescent biological labeling. However organic dyes are not photostable and bleach out very quickly. Besides, some of the organic dyes cannot be uniformly dispersed in water, as required in many biological applications. One alternative is to employ coreshell particles with semiconductor nanoparticles as the core and shell for protection. Hydrophilic shell enables to uniformly suspend the particles in water. Nanoparticles can be excited with the radiation for which shell is transparent. Although such methodology is quite successful, quantum efficiency of organic dyes for fluorescence is still unmatched. Therefore attempts are being made to make core-shell particles such that dye molecules are entrapped as core and organic or inorganic protective shell is built around them.

Rhodamine and other organic dyes have been incorporated in polymer shells such as polystyrene in the past [6]. Rhodamine dyes containing secondary amino groups belong to a class of xanthene derivatives. Among different dyes, they occupy an important position due to their useful photochemical and photophysical properties. Rhodamine dyes have high fluorescence quantum yield, which makes them useful in applications like lasers, fluorescence labeling, conversion and storage of solar energy etc. In the field of medicine, these dyes are used as antitumor agents by killing the photosensitized cells [7]. In all such applications photostability for repeated, successive applications is required. Limitations of photostability, water insolubility etc. of organic dyes can be overcome by entrapping dye molecules inside some robust, inorganic shells which can be easily suspended in water. Their incorporation in easily functionizable silica shell is however considered to be difficult. This is attributed to the hydrophobic nature of organic dye molecules. Trapping of organic dyes like napthazarin, quinizarin and Rhodamine 6G (RHO6G) in silica gels using sol-gel route at room temperature and pressure as high as  $\sim 4$  GPa is well documented [8]. Silica composites thus obtained were highly stable, transparent and resistant to a temperature of about 150 °C. However, in view of more applicability of silica particles due to their easy surface modification by thiol, amine or carboxylic groups Tapec et al. [6] recently developed a three-step process to synthesize silica core-shell particles in which two silica precursors viz. tetraethylorthosilicate (TEOS) and phenyltriethoxysiliane (PTES) were used. They showed that PTES was advantageous to incorporate organic dve molecules due to its better lyophilicity. In this communication we show that PTES can be eliminated and dye-silica core-shell particles can be synthesized using a single precursor viz. TEOS. We also find that these core-shell particles indeed are highly luminescent, can be easily suspended in water, photostable and RHO6G dye does not leach out from silica particles. Our analysis using a variety of techniques like transmission electron microscopy (TEM), energy dispersive analysis of X-rays (EDAX), photoluminescence (PL) and X-ray photoelectron spectroscopy (XPS) indeed proves that dye molecules are trapped inside the silica particles and are not present on silica surface.

#### 2. Experimental

In the present work, RHO6G dye was entrapped in silica particles. Core-shell particles so generated were investigated using PL, EDAX, XPS and TEM. Synthesis and analysis procedures are as follows.

### 2.1. Synthesis of dye core-silica shell particles

Silica particles were prepared following the standard Stöber method [9]. It involves the hydrolysis and polycondensation of tetraethy-lorthosilicate (TEOS) in water and ethanol solutions. The process was modified as shown in the flow chart of Fig. 1, so as to trap the dye inside silica shell. Briefly, RHO6G dye was dissolved in ethanol medium to which tetraethylorthosilicate (TEOS) was added. The solution was stirred for 10 min. Ammonium hydroxide (1 M, 0.78 ml) was added to this solution and further stirred till solution became completely homogeneous (solution A). Second solution (solution B) consisted of mixture of ethanol (30 ml) and TEOS (0.6 ml).

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