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High efficient fluorescent stable colloidal sealed dye-doped mesostructured silica nanoparticles

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ABSTRACT

The fluorescence properties of colloidal sealed Rhodamine 6G doped mesostructured silica nanoparticles prepared by a one-pot templated base-catalyzed sol–gel self-assembly method are reported. The hybrid organic–inorganic nanoparticles is tested against water and alcohols dye leaching showing larger resilience to leaching in water, high quantum yield despite the large dye concentration and huge relative brightness up to 1.5×10^5 emitting molecules per nanoparticle. This super fluorescence is 3 times larger of comparable systems and 100 times larger than the fluorescence of CdSe/ZnS quantum dots. The surfactant used for the formation of the mesostructure plays a key role both as dye splitting element and as sealing agent against leaching effect. The resilience to dye leaching in water is further justified by the formation of core–shell architectures made up of mesoporous core and homogeneous low-porous silica shell of 5–12 nm in thickness due to long aging condensation reaction of surface silanols in water. In addition, the comparison with a reference no-doped silica sample points out a possible alternative synthetic strategy to tune the structural, morphological and textural properties of silica-based nanosystems: properly engineering can exploit the effect of dye molecules addition on nanoparticles mean size, polydispersity and mean thickness of matrix silica walls.

1. Introduction

Fluorescent micro and nanoparticles (NPs) find applications in a wide range of fields, from biomedicine, as probes for tagging and labeling [1–5], in particular for super-resolution fluorescence microscopy [6], to photonics, as active medium for nanolasing [7–10]. Among the others, silica NPs are a suitable host for fluorescent elements because of its bio-compatibility and ease of functionalization [11,12]. For instance, hexagonal arrangement of one- or two-dimensional mesopores with diameters ranging from 2 to 10 nm (MCM-41 [13,14]) allows high surface area and good thermal stability, which make them an attractive molecular sieve for catalysis [15,16], sensor and sorbent applications [17], or quantum confinement of guest molecules [18,19]. In addition monodispersed silica NPs display very low cytotoxicity, being virtually nontoxic for diameters in the 100–350 nm range [20], and a silica shell of even few nm in a core–shell system can bestow nontoxic features to a potentially dangerous bare core nanosystem [21]. So far the brightest colloidal particles were synthesized with inorganic chromophores, like PbS and CdSe quantum dots, that, despite their high efficiency, have the main drawback of being largely toxic [22,23]. On the other hand, organic dyes offer a large variety, high quantum yield and relatively low toxicity, properties that, in conjunction with the ones of the silica host, make them very appealing for engineering fluorescent nanosystems [11,24]. Dye doped silica nanosized systems were largely studied in the past in the attempt to solve two main difficulties: the concentration

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phenomenon and the leaching effect [25–27]. In addition, the photoreactivity of the dye molecules largely decreases their potential applications [9,28]. Basically, there are two possible ways to incorporate organic molecules within inorganic host: physical encapsulation with electrostatic bonding between the dye and the surface host matrix (type I organic–inorganic hybrids), or chemical entrapment by means of covalent bonds [26,28]. The latter was shown to be the most promising in open pore systems, showing larger resilience to solvent rinsing and larger photostability. The host–guest interaction is also relevant to achieve a larger dye concentration before the formation of fluorescence quenching aggregates. Indeed, the presence of the host surface supplies an additional external potential that can drive the formation of different aggregation geometries depending on the polarity of the surface itself and the interaction with the guest molecules [29–39]. The aggregation geometry of dye molecules adsorbed at the host surface is a key parameter to define the fluorescent character of the synthesized systems and their efficiency in terms of quantum yield. Efficient J-dimers' fluorescence was reported in xanthene–silica hybrid systems for dye concentration up to 10^{-3} M (the concentration limit in water solution is 10^{-6} M because of the formation of non-fluorescent H-dimers' aggregates) [40–45]. Concerning nanoparticles, in the last years two different and somehow opposite approaches were proposed to solve both the leaching and concentration glitches, by means of chemical or physical entrapment. Chemical bonding of the dye molecules within the silica core was pursued in a nanoparticle core–shell closed structure [46–51]; whilst, in a sealing approach, the dye molecules are physically trapped within the silica pores whose open nanoarchitecture is sealed to water penetration with hydrophobic groups [24,25,52–57]. In the first case, highly fluorescent dye doped NPs were synthesized through a one-pot procedure exploiting Pluronic F127 micelles as a nanoreactor to produce, in water environment, water soluble monodispersed core–shell nanoparticles of about 30 nm in diameter. The brightness of these particles, that is the concentration of dye molecules per NP, was estimated of about tens, and multiple doping was achieved to efficiently tune the emission properties to the desired imaging target from the visible to the IR range [49]. In the sealed approach, ultrabright fluorescent mesoporous silica nanoparticles were synthesized in a templated base-catalyzed sol–gel method allowing achieving up to 670 Rhodamine 6G (Rh6G) molecules per NP (40 nm in diameter) without fluorescence quenching despite of the very large concentration of dye molecules within the nanostructure [57].

In the present paper we followed the indications of the second approach, by preparing Rh6G doped silica NPs by means of a one-pot templated base-catalyzed sol–gel self-assembly method with tetraethyl orthosilicate as the main silica precursor, cetyltrimethylammonium bromide surfactant as the structure-directing agent, Rh6G aqueous solution and water as solvent. Usually, the preparation of ordered hexagonal or cubic mesoporous silica materials [13,58] consists in the formation of micelles of the chosen templating surfactant in aqueous solution, the polymerization of the inorganic source and the final removal of surfactants from the pores of the material [14]. In the present case, the dye molecules are physically trapped within the silica matrix and the samples were not subjected to calcination, since the surfactant is also exploited as a splitting element between Rh6G molecules in order to allow large doping concentration and to achieve large brightness with reduced aggregation. Starting from a quite high dye concentration (of about 10% in weight), the samples were subjected to different washing procedures in water and ethanol to verify the resilience to the leaching phenomenon as a function of the applied solvent, showing very good sealing properties against water. Both the nanodimensions of the pores and the presence of the surfactant allowed achieving an outstanding relative brightness of doped nanoparticles with low fluorescence quenching despite the large dye concentration tested. When scaled to comparable dimensions, the synthesized nanoparticles (164 nm in diameter) are more than 3 times brighter than previously prepared similar nanostructures [57] and up to almost 100 times brighter than CdSe/ZnS quantum dots (a single ZnS-capped CdSe QD is about 20 times brighter than a single Rh6G molecule) [59,60].

2. Experimental

2.1. Synthesis

Chemicals: tetraethyl orthosilicate (TEOS, 98% Aldrich), cetyltrimethylammonium bromide (CTAB, 96% Aldrich), ethylacetate (EtOAc, 99% Aldrich), liquor ammonia (38 wt.%, Aldrich), and Rhodamine 6G (Rh6G, 99% Exciton) were used in this study. All the chemicals were used without further purification.

2.2. Preparation

A relative molar ratio composition of 1CTAB:2.03-H_2O:0.1Rh6G:0.82TEOS:8.3NH_3:1.87EtOAc was applied. In a typical synthesis, CTAB (0.1 g) is first solubilized in distilled water (100 mL) and kept at room temperature in constant stirring for 1 h (300 rmp), then Rhodamine aqueous solution is added (0.026 g Rh6G in 5 mL of water) and left for another 25 min under mild stirring (300 rpm). Under vigorous stirring (1000 rpm), ammonia (3 mL), TEOS (0.5 mL) and ethylacetate (0.5 mL) are added one after the other to the orange solution and left for 3 h in constant stirring (300 rmp). Silica NPs are recovered by centrifugation at 4500 rpm and then washed several times with water, ethanol or mixture water:ethanol (1:1 molar volume ratio) solutions. Reference samples made up of silica NPs prepared in the same conditions but in the absence of Rh6G were synthetized. Table 1 reports the list of the samples and the different rinsing procedure they were subjected to different solvents and/or number of successive treatments.

2.3. Structural analysis

Structural characteristics of the samples were investigated by low-angle and wide-angle X-ray diffraction patterns recorded on a Seifert 3000 diffractometer with 2θ Bragg Brentano geometry with Cu Kα wavelength. Low-angle diffraction patterns were recorded using a zero-background silicon sample holder. Transmission electron microscopy (TEM) investigation was carried out using a JEOL 200CX microscope operating at an accelerating voltage of 200 kV and a high resolution TEM (HRTEM) JEOL 2010 UHR equipped with a Gatan imaging filter (GIF) with a 15 eV window and a 794 slow scan CCD camera. The water suspensions were directly dropped on carbon-coated copper grids for the TEM and HRTEM observations. Textural analysis was carried out on a Sorptomatic 1990 system (Fisons Instruments) by determining the nitrogen adsorption–desorption isotherms at 77 K. Prior to analysis, the samples were heated (heating rate 1 °C $\min^{-1}$) overnight under vacuum to 80 °C (samples no thermally treated) or to 250 °C (samples thermally treated at 600 °C). The Brunauer–Emmett–-Teller (BET) specific surface area and pore volume were assessed from the adsorption data. The mean pore diameter was determined by applying the Barrett–Joyner–Halenda (BJH) model to the isotherm desorption branch. Thermogravimetric analysis (TGA) and simultaneous differential thermal analysis (SDTA) were performed on a Mettler Toledo TGA/SDTA 851 thermobalance, under the