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Efficient Entrapment of Dye in Hollow Silica Nanoparticles: Direct Evidence Using Fluorescence Spectroscopy

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Abstract Using hollow silica nanoparticles we demonstrate a simple and highly efficient way of removing hydrophilic dye (Rhodamine B) from water by encapsulation within these hollow spheres. The hollow silica spheres were obtained by using a surfactant templated procedure. Using fluorescence spectroscopy, we also show the evidence of the dye being absorbed within the hollow core of the silica shell (which is crucial for many applications) and differentiate from the adsorption of dye on the surface of the silica shell. It was found that that up to 94 % of the hydrophilic dye could be entrapped using these hollow shells within 72 h of exposure. Fluorescence spectroscopy shows a red shift in the dye encapsulated in the hollow silica which is due to aggregation of the dye and enables us to follow quantitatively the uptake of the dye molecules by the silica shells with time. The evidence for the encapsulation of the dye in these hollow spheres was reinforced by carrying out a comparative study, using solid silica particles.

Keywords Hollow silica · Rhodamine B · Entrapment · Fluorescence spectroscopy · Red shift · Encapsulation

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Introduction

With the rapid growth of industries, the problem of water pollution has been increasing at an alarming rate. The demand for water has been rising tremendously in the modern era as the industrial sector is alone consuming about 70 % of the available fresh water and thereby producing a huge amount of waste water [1]. Industrial waste water contains high percentage of toxic contaminants such as pesticides, dyes, surfactants and organic chemicals. These organic contaminants pose a threat to the aquatic life. Modern developments in nanoscale science and technology may provide solutions to some of the current problems related to the quality of water. These problems have been greatly minimized by using nano-absorbent, nanocatalysts, bioactive nanoparticles, nanostructured catalytic membranes, nanotubes and magnetic nanoparticles [2–4]. High surface area metal oxide nanoparticles and colloids have been successfully applied for the improvement of water quality in natural environment [5]. For the removal of dye molecules from water, materials like graphene-Fe_3O_4 nanocomposites [6], Fe_3O_4/C core–shell nanoparticles [7], jute processing waste [8] and also many other natural materials such as wood, peat, coal and lignite etc. [9] have been examined.

Although nanoparticles have found wide applications in the area of water purification as an efficient means for the detection and removal of toxic organic chemicals, plant nutrients and metal ions [10, 11], there is still a need to develop simple but efficient techniques to remove dissolved organic matter from water. Sand filtration, sedimentation, flocculation, coagulation, chlorination and adsorption on activated carbon are some of the conventional methods used for the removal of dissolved organic matter from water. However these methods are not highly efficient. Irradiation with UV light, ozonation and incineration are some of the alternative methods for the removal of the toxins present in

water though they are not economical for removal of trace pollutants [12].

Hollow silica spheres are capable of binding organic moieties. This property has been largely exploited in the field of bio-medical sciences for drug delivery [13–16]. They are also finding vast applications as nano-reactors, sensors and catalysts [17–20]. In literature, there are reports, on adsorption of dye molecules on the surface of nanoparticles. Hollow SnO_2 nanoparticles have been investigated for adsorption of basic dye [15], polyaniline hollow nanospheres for lead removal from water [21], hollow TiO_2 microspheres for adsorption of floating impurities in water [17] and hollow silica for the removal of methyl orange from water [22]. In literature, evidence for encapsulation of the dye has been provided using various analytical techniques like, Confocal laser scanning microscopy (CLSM) [23, 24], Transmission electron microscopy (TEM) [25], Scanning Electron Microscopy (SEM) [26] and Fourier transform infrared spectroscopy (FTIR) [27] etc. For establishing dye encapsulation inside vesicles, there is a report where fluorescence spectroscopy has been used, for self-quenching dye carboxyfluorescein [28]. However, to the best of our knowledge, a convincing proof of encapsulation of dye by hollow silica particles using fluorescence spectroscopy is not provided anywhere in the literature.

Thus, we have focused our study mainly on the encapsulation of dye in hollow silica spheres and their practical application in removal of toxic organic contaminants from aqueous environment. Hydrophilic toxins from water can be entrapped very efficiently by just dispersing these hollow silica shells over the polluted water and then these toxin-encapsulated particles can be removed by ultra-filtration technique.

We have used surfactant templating method [29] for the synthesis of hollow silica shells which have been used to study the dye encapsulation in the hollow particles. Rhodamine B, which is the commercial name for [9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride has been used in this work. It is a highly water soluble dye and it can be easily monitored spectrofluorometrically. Here we show that fluorescence spectroscopy can be used effectively to establish the encapsulation of the dye within the hollow silica shells.

Experimental Section

Chemicals Oleic acid (OA) from Fisher Scientific, tetraethyl orthosilicate (TEOS) and (3-aminopropyl)triethoxysilane (APES) from Sigma Aldrich, were purchased and used without further purification.

Synthesis of Hollow Silica Nanoparticles

The anionic surfactant templating method used for the synthesis of hollow silica nanoparticles has been reported elsewhere [29].

In brief, 1 mmol of OA was dispersed in a solution of deionized water (28.8 mL) and ethanol (2.3 mL) at room temperature under vigorous stirring. A mixture of 6.7 mmol of TEOS and 1 mmol of APES was added to the solution with stirring. After 10 min, the stirring was stopped, and the reaction mixture was kept at room temperature for 2 h and then aged at 80 °C for 1 day. The precipitate was filtered, dried at 80 °C and calcined at 550 °C for 6 h. For the preparation of solid silica particles, the procedure discussed above was followed without the addition of OA.

Encapsulation of Rhodamine B

15 mg of silica particles were dispersed in 20 mL of deionized water by ultrasonication. 17.64 mL of this was added to 360 μL of 0.01 mM Rhodamine B solution in a glass vial and stirred for 30 min and after which, 3 mL of this mixture was taken out and centrifuged. The supernatant and the residue were kept separately. At time intervals of 1 h, 6 h, 24 h, 48 h and 72 h, 3 mL of solution (continuously stirred) was taken out and the above procedure was followed. Later, each residue (obtained after different time intervals), was dispersed in 3 mL of deionized water. Each supernatant solution and also the dispersed residue was analyzed by fluorescence spectroscopy.

Characterization

Synthesized silica particles were characterized by Powder X-ray Diffraction (PXRD) technique, Infrared (IR) spectroscopy and Transmission electron microscopy (TEM). PXRD studies were carried out on a Bruker D8 Advance diffractometer with Ni-filtered Cu-Kα radiation with a scan speed of 0.5 s and scan step of 0.02°. FT-IR studies were carried out on a Nicolet Protégé 460 Fourier transform infrared (FTIR) spectrometer. The data were recorded with a KBr disk in the range of 400–4,000 cm^{-1}. Fluorescence measurements were carried out in Horiba Fluoromax-4 spectrofluorometer. The fluorescence spectra of the pure dye solution were also recorded. TEM was carried out on a FEI Technai G^2 20 electron microscope operated at 200 kV. The nitrogen adsorption/desorption isotherms were measured at 77 K with a Quantachrome Nova 2000E surface area and pore size analyzer. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method and the pore size was obtained from the pore size distribution curve calculated by the Barrett-Joyner-Halenda (BJH) method. The pore volumes were estimated from the amount adsorbed at a relative pressure of ~ 0.99.

Results and Discussion

PXRD study shows amorphous nature of the synthesized silica nanoparticles (Figure S1). TEM images of the hollow

Table 1 Details of the absorption bands in the IR region

Bands	Hollow shell cm^{-1}	Solid silica cm^{-1}
$\nu_{Si-O-Si}$ Stretching	1107 and 1071	1110 and 1080
ν_{O-Si-O} Bending	459	463
ν_{O-H} Stretching	3425	3420
ν_{O-H} Bending	1631	1630

silica and solid silica are shown in Fig. 1(a) and (b) respectively. The hollow silica spheres of diameter 50–70 nm were obtained with uniform shell thickness of 8–10 nm. The solid silica particles of spherical morphology were obtained in absence of OA with an average diameter of 120 nm. The particle size is bigger than that of hollow silica as no surfactant was used during the synthesis of solid silica particles. IR studies of both, solid and hollow silica particles show bands

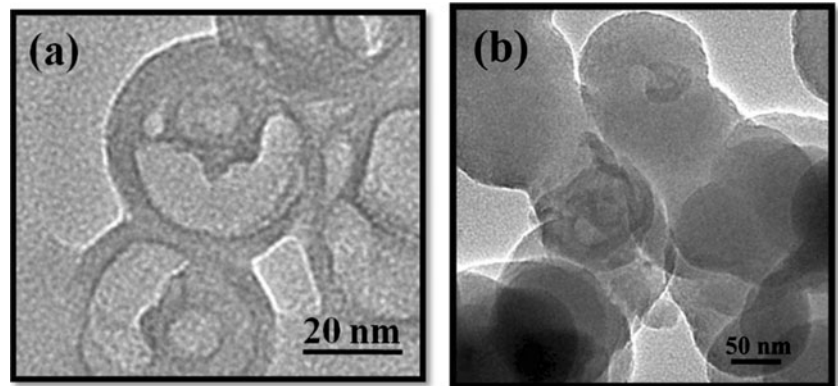**Fig. 1** TEM image of **a** hollow SiO$_2$ particles and **b** solid SiO$_2$ particles

Fig. 2 Nitrogen adsorption desorption isotherm of particles for surface area measurements on **a** hollow silica and **b** solid silica
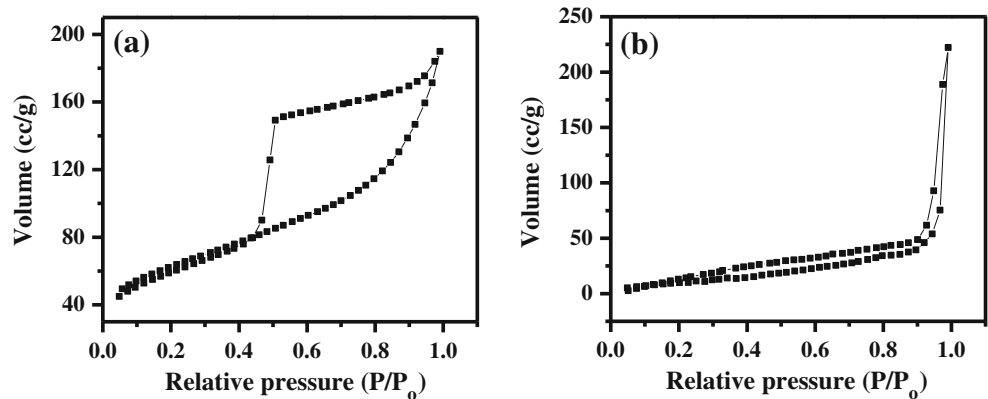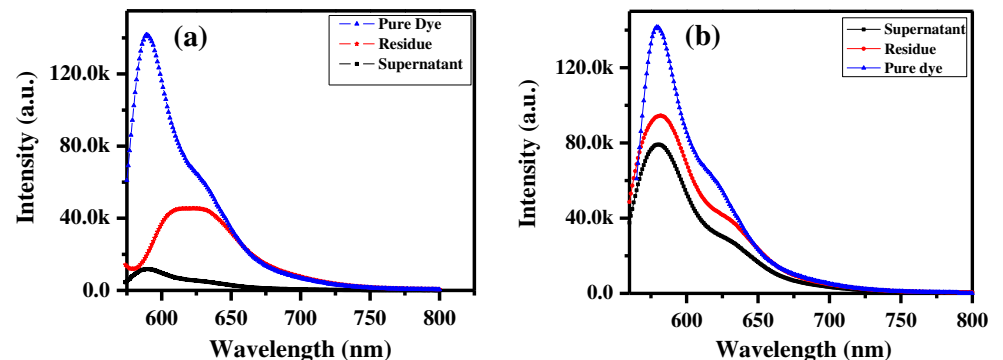

Fig. 3 **a** The fluorescence spectra of the pure dye, dye encapsulated in hollow silica particles (*after 72 h*) and supernatant solution of dye obtained after centrifugation. **b** The fluorescence spectra of the pure dye, dye bound solid silica particles and supernatant solution of dye obtained after centrifugation (*after 72 h*)

corresponding to Si-O-Si, Si-O-H and O-Si-O stretching. The results of the IR studies have been summarized in Table 1. The surface area of the hollow silica particles was found to be 217 m^2/g by BET nitrogen gas adsorption–desorption method [Fig. 2(a)]. The shape of the isotherm suggests that the material is macro-porous (pore size >50 nm) with ink bottle shaped pores [30]. This implies that the surface of the hollow spheres has small openings through which dye molecules can easily percolate through the silica shells into the hollow core. The surface area of the solid silica particles was found to be 41 m^2/g (1/5 th of the surface area of the hollow spheres) and the shape of the isotherm [Fig. 2(b)] indicates the presence of cylindrical pores with diameter smaller than 50 nm.

In literature, there are many reports on use of hollow structures for encapsulation of organic molecules [31–33] for various applications like drug delivery, catalysis etc. However, a systematic study wherein it is proved that organic molecules are encapsulated within the hollow interior of the nanostructures and not adsorbed over the surface is missing. In this study we have used fluorescence spectroscopy effectively to differentiate encapsulation of organic dye molecules within the hollow silica spheres and possible adsorption of the dye on the surface of the particles by investigating the solid silica particles under identical conditions.

Figure 3(a) shows the fluorescence spectra of the pure dye, dye encapsulated hollow silica particles and supernatant solution of dye obtained after centrifugation. It was observed that the fluorescence intensity of the supernatant dye solution decreased with time compared to the pure dye solution. This indicates that the concentration of the free dye molecules in water decreased upon interaction with the hollow silica particles. Figure 4 shows the change in the fluorescence intensity of the dye solution with time, upon exposure to solid silica and hollow silica particles. The reduction in the intensity of the fluorescence spectra was greater in case of hollow silica than in solid silica.
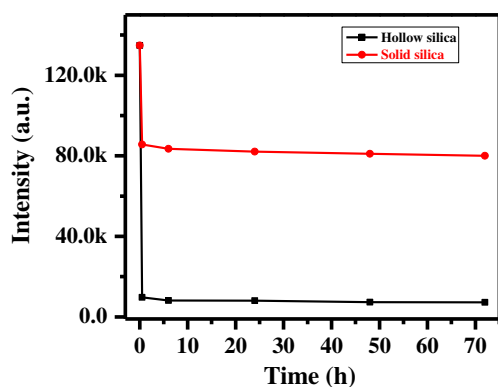
With time, the amount of encapsulated dye increases which is evident from both the decrease in the intensity of the supernatant solution and increase in the intensity of the dispersion containing dye encapsulated hollow silica (Fig. 5). It appears that the maximum amount of encapsulation is achieved in 72 h. Results of our studies show that upto 94 % of Rhodamine B was removed from the solution. We have carried out another experiment with the same protocol where we have used solid silica particles instead of hollow silica to differentiate the encapsulation and adsorption behavior of the dye. Figure 3(b) shows the fluorescence spectra of the pure dye along with the spectra of the solution containing dye adsorbed solid silica particles (redispersed after 72 h) and supernatant solution of dye obtained after centrifugation.

It may also be noted that the fluorescence band of hollow silica bound Rhodamine B shows a red shift with time, which was found to be absent in case of solid silica bound dye solution. It is earlier reported that aggregation of the dye molecules leads to a red shift in the fluorescence spectra [34]. We can rationalize our fluorescence data for the hollow silica shells with dye showing a red shift due to significant aggregation caused by entrapment of the dye molecules within the hollow spheres. This also can explain the decrease in fluorescence intensity since free dye is not present in the solution. In case of solid silica, few dye molecules get adsorbed onto the surface of the particles, and the shape of the fluorescence spectra for silica bound dye molecules is similar to the spectra of dye adsorbed on solid substrates reported in the literature [35]. Since fluorescence is an environment dependent property, the peak positions do not change if the dye molecules remain in the same chemical environment. The kind of similarity of the fluorescence spectra obtained in case of free dye and the dye bound on solid silica surface, except for the slight decrease in the
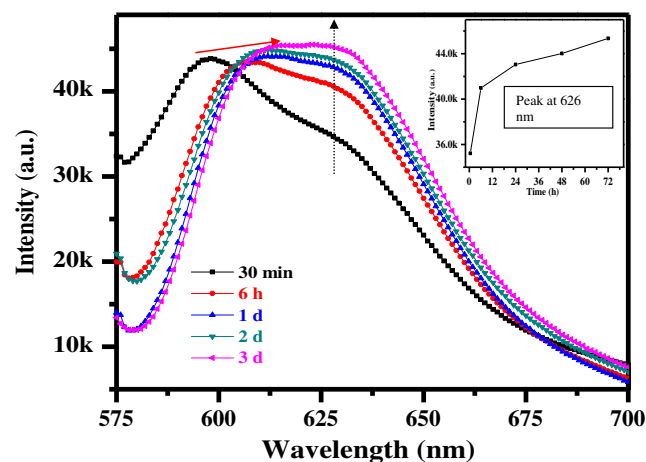

Fig. 4 Variation in the fluorescence intensity of the band at 595 nm of the supernatant dye solutions with time, upon interaction with the hollow silica particles and solid silica particles

Fig. 5 Fluorescence spectra of dye encapsulated in hollow silica particles, at different time intervals (inset: variation with time in the intensity of the band at 626 nm in the fluorescence spectra of dye encapsulated in hollow silica particles)

intensity due to adsorption, clearly indicates that free dye molecules and adsorbed dye molecules are in a nearly identical environment. It was observed that in the fluorescence spectra of the dye encapsulated in hollow silica spheres, the peak at 595 nm shifted gradually towards longer wavelength with time and the intensity of the band at 626 nm got enhanced (Fig. 5) with prolonged exposure of the dye solution to hollow silica shells (shown in the inset of Fig. 5). This observation can be attributed to the dimer formation by the dye molecules [36] due to their considerable aggregation caused by encapsulation inside the hollow core of the silica shells. In case of dye bound solid silica, we don't see such a dependence of the fluorescence intensity with time.

The release study was done by dispersing the dye bound hollow silica particles in water and ethanol. It was observed that only a small fraction of the bound dye molecules came out into the dispersing medium (which was being monitored by fluorescence spectroscopy) when sonicated for 15 min. Therefore, these hollow silica spheres can be successfully applied for the purpose of dye encapsulation from water and hence for water purification.

Conclusions

Hollow silica nanoparticles synthesized by anionic surfactant templating route were found to be highly effective in entrapping hydrophilic dye present in water in trace amounts. More than 90 % of the hydrophilic dye was entrapped in about 72 h. Fluorescence spectroscopy was shown to be an effective tool to follow the entrapment of the dye. Use of hollow silica for dye encapsulation suggests their possible use for water purification.

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