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Porous microcapsules comprised inter-locked nano-particles by evaporation-induced assembly: Evaluation of dye sorption

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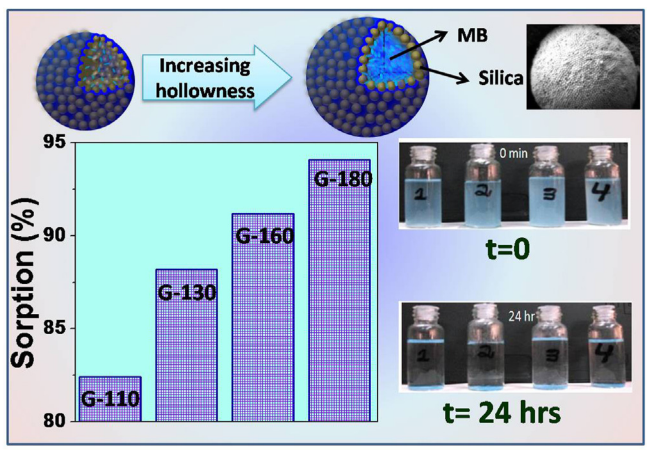
HIGHLIGHTS

- Nano-structured silica micro-capsules by EISA.
- Efficient sorption of cationic dye from aqueous solution and quick settling.
- In-situ monitoring of sorption using UV–vis spectroscopy.
- Preferential sorption depending on granular interstitial pore size and dye molecular structure.

GRAPHICAL ABSTRACT



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ABSTRACT

Evaporation induced assembly of colloidal particles in an aerosol droplet has been utilized to synthesize nano-structured porous silica microcapsules comprising of interlocked correlated nano-particles. Morphology of the microcapsules was tuned by controlling the rate of evaporation. In the present work, we demonstrate that such porous capsules can efficiently take up cationic dye from aqueous solution. In-situ UV–vis spectroscopy has been utilized to monitor the time dependence of sorption by these capsules. Small-angle X-ray scattering and scanning electron microscopy have been used to probe the multi-level structure of the powder granules. Thermal analysis was performed on the dye-sorbed granules to investigate the effect of confinement on the thermal degradation behaviour of the dye molecules within the granules.

1. Introduction

Evaporation induced self assembly (EISA) of colloidal particles [1] has become a well-established method in nanotechnology due

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to its ability to synthesize various nano-composites, colloidal crystals, porous material [2], etc. [3]. Spray drying [4–6], a well known technique in pharmaceutical and food industries, has been found effective in realizing such assembly [6] through evaporative drying of tiny droplets in a contact-free environment [7–9]. It is essentially a one-step process in which atomized micro-metric colloidal droplets are dried in a fairly rapid manner. The emergence of attractive capillary forces [10,11] in course of drying [12] drives the assembly and the constituent nano-structures get interlocked [13,14] by overcoming the repulsive forces. This results in the formation of 3-dimension micro-capsules with internal correlated nano-structures. Various physico-chemical parameters [15–17] during the drying process govern the resultant morphology of the capsules as well as the internal correlation of the constituent nano-structures. The interlocked nano-particles in a granule enclose interstitial empty spaces or pores. It is well known that a system of close-packed uniformly sized spherical particles, the packing is 74% [18] while that for random jamming of nano-particles, the packing is nearly 64% [19]. In a closely packed structure, containing N spherical particles, there are 8N trigonal voids, 2N tetrahedral voids and N octahedral voids. Further, the ratio of radius of void to that of a particle is 0.155, 0.225 and 0.414 for trigonal, tetragonal and octahedral voids, respectively [20]. Thus, the size of the voids/pores is typically of the order of the size of the nano-particles. It is needless to mention that such porous granules are potential candidates for various application including catalysis [21], molecular sieving [22], ion exchange [23], drug delivery [24], etc. From the application point of view, the practicability of such porous granules increases manifolds if it can be made hollow too. Such hollow granules can be realized in a facile way through spray drying [10,15,16,25–30,36–38].

It is worth mentioning that the technique of spray drying provides efficient control over the external morphology and hollowness. The drying temperature vis-a-vis the rate of drying plays an important role in this regard. In case of slower drying rate the nano-particles find enough time to diffuse to the core of the drying droplet thereby resulting in an isotropically jammed granule. On the other hand if drying rate is faster, the nano-particles get jammed near to the air-water interface forming shell with hollow core [6,10,15,25–34]. In addition, temperature gradient across the core and shell in a drying droplet induces directional motion of the nano-particles, commonly known as 'thermophoresis' [30,35–38], which contribute to gradual shell thickening. Such shell may buckle under pressure imbalance when the remaining water from the core tries to evaporate through the porous shell and results doughnut shaped granules instead of spherical ones. The above phenomenon regarding the control of shape and hollowness by tuning the drying temperature has been discussed extensively in our recent work [30].

In this paper we have investigated the applicability of such nano-structured porous micro-granules as sorbent [39–41] of cationic dye [42], Methylene Blue (MB). One of the motivations behind this work is that, unlike individual nano-particles, these nano-structured micro-capsules can settle faster after sorption allowing the easy decantation of supernatant. We have investigated the dependence of sorption on the morphology and internal structure of spray dried nano-structured silica micro-capsules. It is worth mentioning that MB is widely used in various industrial techniques such as, printing industry, dyeing of cotton, leather, etc, redox indicator and also has medicinal uses at low concentration. However, MB is a water-soluble, harmful waste material at large concentration, which is required to be removed from the waste before discharge into the environment [43–49]. Sorption is one of the most investigated techniques for dye removal mainly due to its simplicity and high level of effectiveness [50–52]. Hence, a low-cost and efficient method of sorption of MB is an area of growing interest. It has been demonstrated by UV–vis [53] spectroscopy that almost 70% of the dye molecules get sorbed by the granules within two hours, which increases to ~94% by 24 h. To confirm the dye absorption by the granules, we have used scattering techniques and thermal analysis.

2. Experimental technique

2.1. Preparation of micro-capsules

The synthesis technique of the samples is elaborated in our earlier work [30]. In short, the nano-structured silica micro-capsules were formed by evaporation induced assembly of colloidal silica nano-particles using spray-drying technique. The particle size distribution for the colloidal nano-silica is depicted in Fig. SI 1. The morphology of the granules was tuned by controlling the drying temperature (110–180 °C). The morphology of the granules synthesized at 110 °C are spherical and the morphology gradually shifts towards doughnuts with increasing hollowness as drying temperature increases. The granules will be denoted by G-110, G-130, G-160 and G-180 corresponding to their different drying temperatures, 110 °C, 130 °C, 160 °C and 180 °C. Fig. 1(a) shows schematically the method of synthesis by spray drying.

2.2. Absorption spectral analysis by UV–vis

Absorption of dye molecules by the synthesized granules was measured by spectral analysis using JASCO V-650 UV–vis spectrophotometer. Blank measurement was performed using pure water, and then absorbance measurements were carried out for 50 ppm Methylene Blue (MB) dye solution. Subsequently, in-situ measurement of sorption of MB molecules by the powder granules was started after adding 0.1 g of the powder granules to the 50 ppm MB solution. The wavelength range of 400–900 nm was accessed during experiments. Sorption data were collected at every ten minute interval up to 2 h and again after 24 h. In-situ measurement was started at time t = 0, when the powder granules were just added to the dye solution. It should be noted that the absorption due to silica in this wavelength range is negligible [54]. Thus, the change in absorbance recorded by the spectrophotometer will be due to (i) removal of MB from the light path or (ii) due to the change in local concentration of MB as a result of sorption by the silica micro-capsules. In addition, sorption of Rhodamine- B dye was also performed.

2.3. Structural characterization

The morphology of the assembled granules was examined using field-emission scanning electron microscope (FE-SEM, Carl Zeiss Auriga). Further, in order to understand quantitatively the correlation of the nano-silica particles and to confirm dye sorption in the granules, small angle X-ray scattering (SAXS) experiments were performed before and after sorption. The scattered intensities were measured as a function of wave vector transfer $q = \frac{4\pi \sin\theta}{\lambda}$ where 2θ is the scattering angle and λ is the wavelength of the radiation used (0.154 nm) using a laboratory SAXS instrument. The accessible q range was ~ 0.1–2.0 nm^{-1}.

2.4. Thermal analysis

Thermo-gravimetric Analysis (TGA) and Differential Thermal-Analysis (DTA) of the dye-incorporated-granules were carried out using Netzsch Thermo-balance (Model No.: STA 409 PC Luxx) coupled to Bruker FTIR system (Model No.: Tensor 27) via a heated Teflon capillary (1 m long, 2 mm inner diameter) in air atmosphere.