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ORIGINAL ARTICLE

Tuning particle morphology of mesoporous silica nanoparticles for adsorption of dyes from aqueous solution

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Abstract Spherical and rod mesoporous silica nanoparticles with hexagonal mesostructure were prepared using the modified Stöber method. The morphology, size and internal pore structure can be controlled by simple changing of surfactant concentration and water:ethanol molar ratio. Monodispersed spheroid MCM-41 was obtained at 40 °C under basic conditions using cetyltrimethylammonium bromide (C_{16}TAB) as template. Obtained materials were characterized by X-ray diffraction (XRD), nitrogen physisorption (BET), transmission electron microscopy (TEM) and scanning electronic microscopy (SEM). The results reveal that the pore volume and surface area increase when the amount of C_{16}TAB increases whereas the pore diameter and particle size decrease. However, the use of ethanol as cosolvent led to an increase in the particles' size. Moreover, the addition of a 3-aminopropyltriethoxysilane greatly influenced the final particle shape. The material was effectively used for the removal of two fluorescent dyes (Hoechst 33342 and rhodamine 6g) from aqueous solution. Adsorption isotherm models, Langmuir, Freundlich and Temkin were used to simulate the equilibrium data. The Langmuir model was found to fit the experimental data better than others models.

1. Introduction

The design of mesoporous materials with simultaneous control of the morphology, particle size, and porosity was considered as a key parameter for their applications [1–4]. Since the discovery of mesoporous materials [5,6], MCM-41 has become the most popular type of the M-41S family of mesoporous silica materials [5–7]. The importance of these nanoparticles was shown not only in the scientific field [8–10], but also in various

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industrial applications [11–15]. Up to now a large variety of mesoporous silica with tunable mesostructural features have been developed for various uses in particular for biomedical field. For example, Li et al. [16] and Liberman et al. [17] have focused on the recent development of controllable drug delivery systems based on mesoporous silica nanoparticles. They reported that those materials can serve as efficient carriers for various therapeutic agents. In the same context, Hartono et al. [18] have synthesized mesoporous silica nanoparticles with a large pore functionalized with poly(2-dimethylaminoethyl acrylate). They have shown that the nanopores of the obtained material constitute a reservoir for the chloroquine to facilitate endosomal escape [18]. Schlipf et al. [19] have been investigated the diffusivity of lipids confined in mesoporous silica. These materials have also emerged as promising adsorbents for dye contamination which causes serious pollution to water resources. Nayab et al. [20] reported the synthesis of branched polyamine functionalized mesoporous Silica via a facile "grafting-to" approach as absorbent for water remediation.

The final shape and size of the internal structure of these materials were highly depending on reaction parameters such as solvent, temperature, pH, drying, stirring rates and surfactant/silica molar ratio [6,21–31]. The morphology was also controlled by the co-condensation of tetraethoxysilane and hydrophobic organoalkoxysilane. Zhang et al. [32] showed that it is possible to generate diverse morphologies such as rods or spheres, with controlled particle size using a series of alkyl substituted silanes with various functionalities. The first synthesis of spherical mesoporous silica particles was done via a modification of the Stöber process [33] as reported by Grün et al. [34]. So, micrometer and submicrometer-sized mesoporous spheres were synthesized by adding a freshly distilled silica precursor in an alcoholic solution of diluted surfactant under basic conditions. Lv et al. [35] synthesized monodispersed silica spheres using hexadecyl-trimethyl ammonium chloride as surfactant and triethanolamine (TEA) as base catalyst.

Recently, Wang et al. [36] reported simple synthesis of mesoporous silica with various morphologies (nanocubes, truncated nanocubes, microspheres and twisted nanorods) via a modified Stöber process by changing the amount of *n*-hexane and the ammonia water in the synthesis system. However, they have not changed a single parameter to achieve a precise morphology of the material. For example by increasing the amount of ammonia water and simultaneously reducing the amount of *n*-hexane, they obtained twisted silica rods. In this regard, we report in this work a facile synthesis of mesoporous silica nanoparticles with tunable morphology via sol gel process using C_{16}TAB as template and sodium hydroxide as catalyst. By simple modification of a single parameter, particle shape was changed from nanosphere to nanorod. The as-prepared mesoporous silica nanoparticles in aqueous media were used for the removal of rhodamine 6g and Hoechst 33342 from aqueous solution. A modelization of sorption data, using the Langmuir, Freundlich and Temkin adsorptions models, is also discussed.

2. Experimental

2.1. Chemicals

All chemicals were used as received without purification. Tetraethyl orthosilicate TEOS (99%), hexadecyltrimethylammonium bromide C_{16}TAB (99%), sodium hydroxide NaOH (98%), (3-aminopropyl)triethoxysilane APTES (99%), Hoechst 33342 (H33342) and rhodamine 6g (Rh 6g) were purchased from Sigma–Aldrich. H33342 and Rh 6g were used as probe for adsorption study (Table 1). Deionized water was used for all experiments.

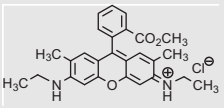
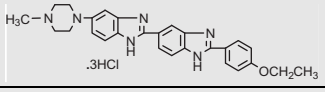
2.2. Synthesis of spheres silica nanoparticles

Mesostructured silica was synthesized under basic conditions using C_{16}TAB as surfactant micellar template, and TEOS as silica precursor. Typically, 0.05 g of C_{16}TAB was dissolved in 50 g of deionized water. The mixture was stirred for 3 h at room temperature, and then the temperature was raised to 40 °C. 575 µL of TEOS and 350 µL of NaOH (2 mol L^{-1}) was added sequentially and rapidly. A white precipitate was observed after 3 min of stirring at 600 rpm. The mixture was continuously stirred for an additional 2 h at 40 °C and 24 h at room temperature. The resulting solid was collected by centrifugation and washed with distilled water and ethanol. The template removal was performed using a conventional calcination by heating in air at 550 °C for 5 h with a heating rate of 1 °C min^{-1}.

2.3. Synthesis of rods silica nanoparticles

The rods silica was prepared using the previous procedure except that the TEOS and the appropriate amount of APTES were subsequently added to the solution at 40 °C under intensive stirring. The resulting white solid was collected by centrifugation and washed with distilled water and ethanol. The removal of the surfactant template was achieved by refluxing in 50 mL ethanol/1 mol L^{-1} HCl for 10 h.

Table 1 Physical and chemical properties of Hoechst 33342 and Rhodamine 6g.

Molecular name	Molecular formula	Molecular structure	Molecular weight (g mol^{-1})	Color	Solubility in water (mg mL^{-1})
Rhodamine 6g	$C_{28}H_{31}ClN_2O_3$		479.01	Red-brown	20
Hoechst 33342	$C_{27}H_{28}N_6O{\cdot}3HCl{\cdot}3H_2O$		561.93	Dark-Yellow	25