



# A facile method for preparing thiocyanato-functionalized porous silica nanospheres



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## ABSTRACT

In this study, we present a facile method to prepare thiocyanato-functionalized porous silica nanospheres. Thiocyanato functionalized silica shells were coated on positively charged cetyltrimethylammonium bromide (CTAB) micelles via hydrolysis and condensation of (3-thiocyanatopropyl)triethoxysilane (TCPTES), the CTAB cores were removed subsequently to form thiocyanato-functionalized porous silica nanospheres. We demonstrate that the contents of the thiocyanato groups within the functionalized porous silica nanosphere frameworks gradually diminished as a function of hydrothermal treatment time at 100 °C until complete removal, confirmed by TGA and FTIR spectra. The data indicate that extended operation at relatively elevated temperatures may lead to the decomposition of the thiocyanato functional groups. In addition, at a lower CTAB concentration (0.0009 M), non-porous thiocyanato functionalized silica nanospheres were formed. However, increasing the CTAB concentration to 0.01 M resulted in porous nanospheres inferring that a CTAB concentration threshold is needed to form thiocyanato-functionalized porous silica nanospheres.

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## Introduction

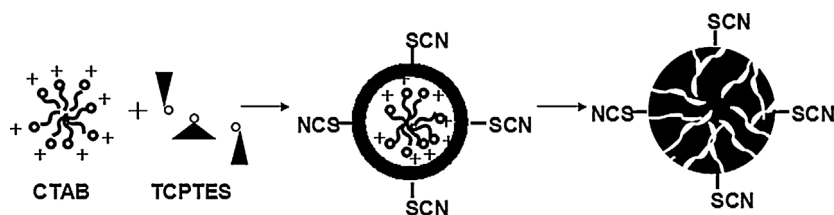
The design and synthesis of organic/inorganic hybrid silica materials are especially attractive in recent decades, because they combine the versatility of the organic chemistry with the advantage of inorganic species (Meng et al., 2009; Contessotto et al., 2009; Arkhireeva, Hay, & Manzano, 2005; Sharma, Das, & Maitra, 2004). Among the various hybrid silica materials, silica nanospheres with porous structures are particularly noteworthy because of their low density, low toxicity, high biocompatibility, large specific surface areas, and excellent thermal and mechanical stability, and thus have been widely applied in the fields of catalysis, separation/adsorption, biomedicine, and controlled drug release (Deng & Marlow, 2012; Teng, Wang, Li, & Zhang, 2011; Yang, Liu, Li, Liu, & Yang, 2011; Trilla, Cattoen, Blanc, Man, & Pleixats, 2011; Sasidharan et al., 2011).

There are two common functionalization strategies that can be adopted when functionalizing porous silica spheres: post-synthetic grafting of functional siloxanes and in situ co-condensation (Burkett, Sims, & Mann, 1996; Lim, Blanford, & Stein, 1997;

Anwander et al., 2000; Yao et al., 2005; Wei et al., 2005; Choi et al., 2005; Lin et al., 2009; Zarabadi-Poor, Badieli, Fahlman, Arab, & Ziarani, 2011; Han, Chen, Wang, Gao, & Che, 2011; Vathyam et al., 2011; Liu, Yan, Zhang, Yang, & Bai, 2012). In the former method, organic functional groups are directly grafted onto the surface of porous silica materials. It may lead to a nonhomogeneous distribution of the organic groups within the pores and a lower degree of occupation. In extreme cases (e.g., with very bulky grafting species), complete closure of the pores can be caused (pore blocking). Compared with the post-synthetic grafting method, co-condensation synthesis involves the simultaneous condensation of corresponding silica and organosiloxane precursors, which can result in a decrease in the long-range order with increasing (R'O)<sub>3</sub>SiR concentration in the reaction mixture. For this reason, optimizing control of the added functional siloxane is necessary for facile preparation of organic-functionalized porous silica materials when using one silica precursor only.

In this study, we adopted a simple one-step method using (3-thiocyanatopropyl)triethoxysilane (TCPTES) as the sole precursor and the cationic surface active agent, cetyltrimethylammonium bromide (CTAB), as a template to synthesize thiocyanato-functionalized porous silica nanospheres under alkaline conditions. The porous structure and the size of the spherical particles can be tailored as a function of hydrothermal treatment time and CTAB

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**Scheme 1.** The schematic diagram of the formation mechanism of thiocyanato-functionalized porous silica nanospheres.

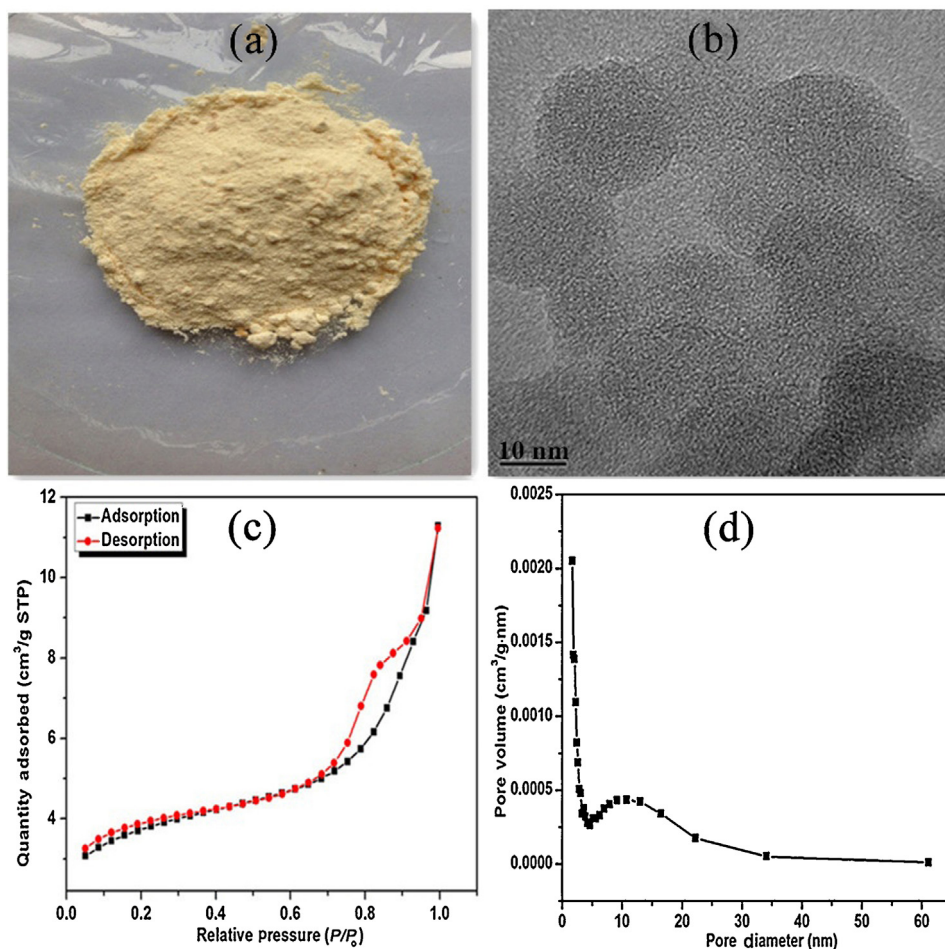
concentration. It is well known that surfactant molecules form micelles of uniform size (typically in the range from several to several tens of nanometers) and well-defined shape, e.g., spherical or lamellar (Mandal & Kruk, 2011). The micelles can further aggregate forming lyotropic liquid crystal structures, such as cylinders or spheres. The reports of a new surfactant-templating mechanism in the 1990s led to a new family of porous silicas, referred to as mesoporous silicas, with excellent long-range ordering (Beck et al., 1992; Kresge, Leonowicz, Roth, Vartuli, & Beck, 1992; Inagaki, Fukushima, & Kuroda, 1993; Zhao, Huo, Feng, Chmelka, & Stucky, 1998). Extending the one-step method of utilizing a sole functional siloxane – in this case TCPTES – in the absence of a silica source to generate alternative functionalized porous silica nanospheres may provide a general method to allow the direct synthesis of tailored functionality to the nanospheres. To the best of our knowledge, the current work on the one-step synthesis of organic-functionalized porous silica nanospheres can effectively avoid the drawbacks

of the above-mentioned post-modification and co-condensation strategies. Beyond that, the key point of this method lies in that the organic functional groups exist in the entire silica network including the inner core and outer shell. Furthermore, compared with the former two methods, the one-step method offers a higher and more uniform surface coverage of functional groups and better control of the surface properties of the resultant materials.

## Experimental

### Reagents and materials

TCPTES was purchased from Aladdin (purity 98%, Shanghai, China). Ethanol (95%), HCl (38%), and  $\text{NH}_3 \cdot \text{H}_2\text{O}$  solutions (28 wt%), CTAB (99%) were all purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Water (resistivity:



**Fig. 1.** (a) Optical photograph and (b) TEM micrograph of thiocyanato-functionalized porous silica nanospheres with 0-h hydrothermal treatment; (c) the nitrogen adsorption-desorption isotherm and (d) corresponding pore size distribution curve. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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