Functionalization of Cage Like Mesoporous Silica with Very Large Pore for Protein Adsorption

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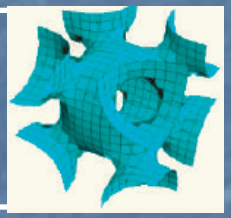
Introduction

Mesoporous silicas **:narrow pore size distribution, tuneable pore size and the possibility to modify surface characteristics, promising applications as supports for bio-molecule adsorption.However, used only for small biomolecular adsorption separation due to the pore size limitation (<10nm).**

In 2005, a *cage like structure* mesoporous material [1] : pore cavity size up to 27 nm and the entrance size up to 16 nm was synthesized (*the largest* pore size confirmed)
In addition, *Surface modification* of mesoporus silica (*functionalization*) using organosilanes is very important : improve the adsorption properties of the silica
(Cage-like silica picture is adapted from [3])

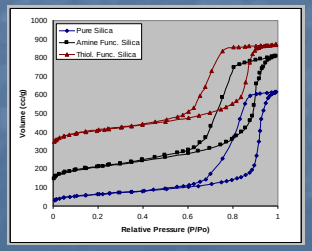


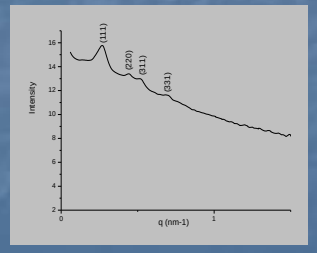
Experimental

Synthesis of Mesoporous Silica
The synthesis of mesoporous silica follows the LP-FDU-12 method [1,2]
a. Stirring/Synthesis : 1 gr F127 + 5 gr KCl + 60 ml of 2 M HCl + 1.2 gr TMB + 4.16 gr TEOS (15 C,24 hr).
b. Hydrothermal treatment 72 hrs (3 days)
c. Extraction with 250 ml of ethanol and 2 ml of HCl at 60 C, three times for 6 hr each.

Synthesis of Amine Functionalized Mesoporous Silica
The basic process is the same with NF LP-FDU. The difference is when added TEOS in the solution, certain amount of functional organosilane (APTES, VTMS,MPTMS,PTMS) also added to the solution.

Characterization





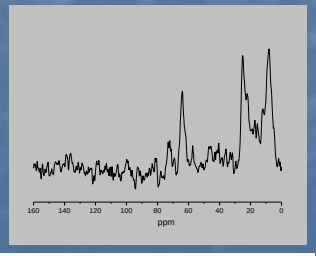


Figure 1. Type IV N2 adsorption-desorption isotherm of pure silica and functionalized Silica (1), SAXS spectra of pure silica (2) and 13C NMR analysis of Amine functionalized Silica(3)

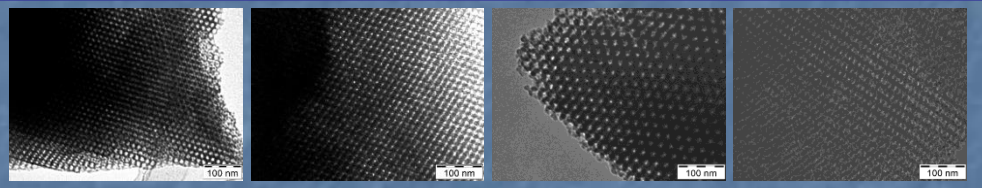


Figure 3. TEM Images of VTMS (1,2) and APTES (3,4).

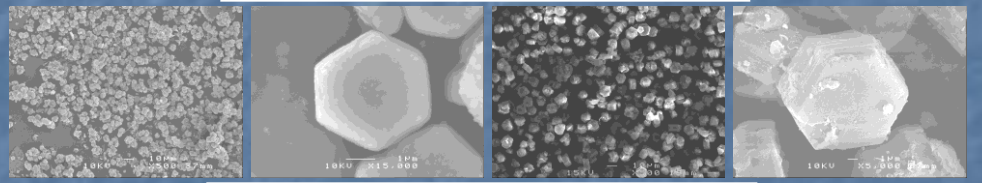
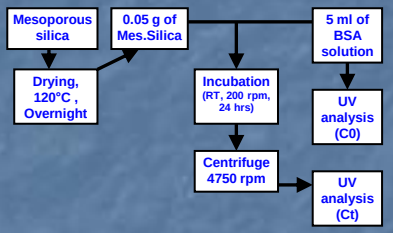


Figure 4. SEM Images of Pure Silica (1,2) and APTES (3,4).

BSA adsorption



Sample	Cavity (nm)	Entrance (nm)	Zeta (mv)	Qm (mg/g)
Pure silica	279	108	- 9.56	36.14
Vinyl CH=Ch2	274	115	-5.79	50.93
Phenyl C6H5	194	105	-5.22	30.45
Thiol -SH	193	90	-0.312	6.19
Amine NH2	254	108	29.3	132.57

Conclusion

1. Pure silica and Organic functionalized cage-like mesoporous silica with an order structure and large pore size have been synthesized

2. Amine functionalization improved the adsorption properties of pure silica through creating strong electrostatic interactions

3. Amine mesoporous silica attained the highest BSA adsorption amount

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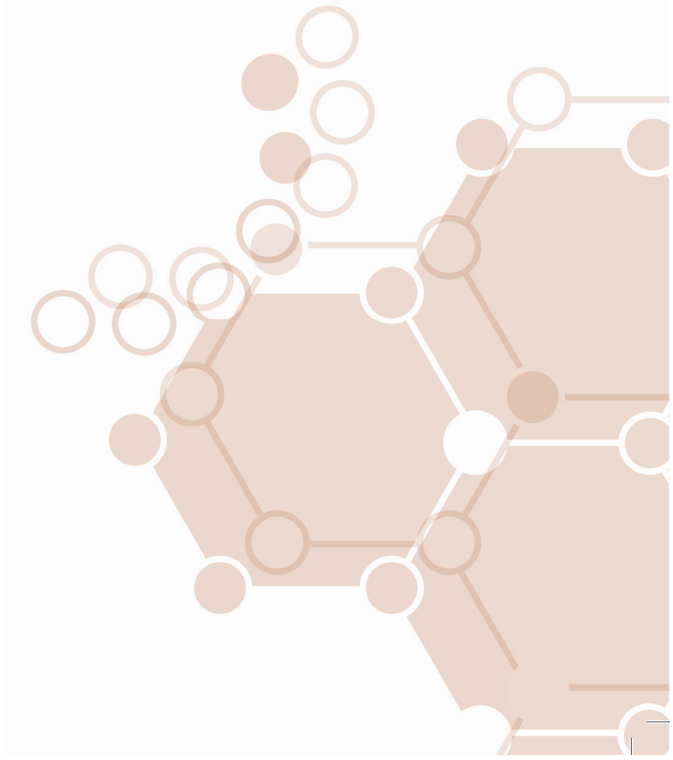

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There has been ever increasing attention and effort in mesoporous material synthesis since discovery of a new family of mesoporous silicas- M41S by Mobil researcher in 1992 [1]. Mesoporous silicas have many advantages such as narrow pore size distribution, tuneable pore size and the possibility to modify surface characteristics, which makes them promising applications as supports for bio-molecule adsorption [2]. However, these materials can so far only be used for small biomolecular adsorption separation due to the pore size limitation (<10nm). In 2005, a cage like structure mesoporous material with pore cavity size up to 27 nm and the entrance size up to 16 nm was successfully synthesized and reported as the largest pore size confirmed [4].

The structure of cage like materials is basically a large cavity with many entrance pores. Comparing to 1D channel system like MCM-41, the 3D pore system shows superiority in terms of mass diffusion or mass transfer [5-7]. The possibility of pore blocking inside the 3D is much smaller than that in 1D channel pores [7]. This advantage stimulates many researches in using the 3D mesostructure in biomolecules adsorption and enzyme immobilization [7]. In addition, surface modification of mesoporus silica through functionalization using organosilanes is very important. Such modification can improve the adsorption properties of the silica [8-9]

In this paper we report the functionalization of large pore mesoporous silica with cage like structure using a co-condensation method. (Mercaptopropyl)-trimethoxysilane and 3-Aminopropyl)triethoxysilane were used as sources of amine and thiol organosilane. In order to create a very large pore, low temperature synthesis and high hydrothermal temperature methods were used.

The synthesis of the functionalized mesoporous silica follows the method reported in the literature except using the mixture of TEOS and organosilane as precursor [4,5]. N_2 adsorption-desorption isotherm for

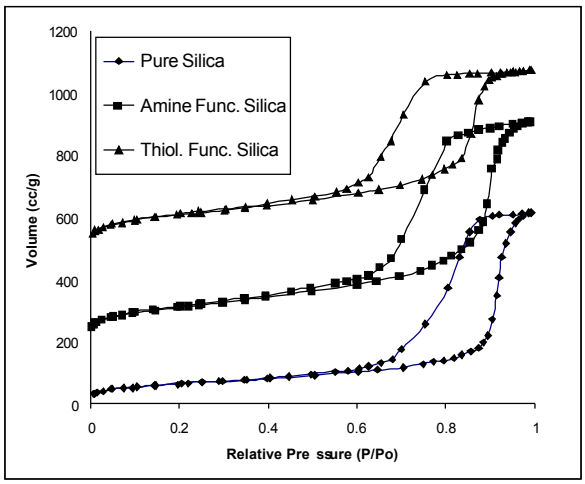

Figure 1. N_2 adsorption-desorption isotherms of pure silica, amine functionalized silica and thiol functionalized silica. The isotherms are offset vertically by 100 and 300 cm^3 STP g^{-1}

all materials (Figure 1.) show the type IV isotherm which is typical of mesoporosus material. The cavity size and the entrance size of the samples can be calculated based on adsorption and desorption branch of adsorption isotherm, respectively, by applying the BdB model. The physical properties of the samples are given in Table 1. It can be seen that all samples have very large cavity between 20 – 30 nm. These samples also have large entrance sizes, high surface areas and large pore volumes.

Table 1. The physical properties of functionalized and unfunctionalized mesoporous silicas

Sample	Surface area (m^2/g)	Pore Volume (cm^3/g)	Cavity size (nm)	Entrance size (nm)
Pure silica	228.8	0.9518	27.9	10.8
Amine func. silica	403.2	1.0950	25.4	10.8
Thiol func.Silica	393.7	0.8836	19.3	9.0

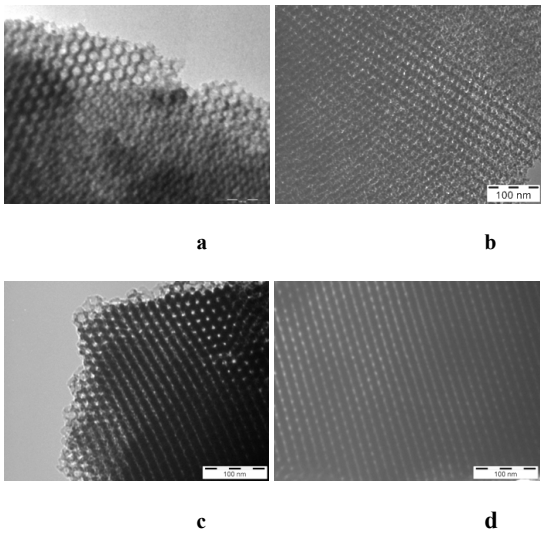

Figure 2. TEM images of (a –b) amine functionalized silic a and (c-d) thiol functionalized silica.

The TEM images of functionalized mesoporous silica (Figure 2.) show that the samples have large pore and order pore structure. The successful synthesis of high order large pore mesoporous silica is due to the low temperature method and the addition of inorganic salt [4].

All samples were used as adsorbent in BSA (Bovine serum albumin) adsorption. The amine functionalized mesoporous silica shows very high adsorption capacity. It is almost four times higher compared with unfunctionalized mesoporous silica (pure silica) (figure 3.). It is believed that the amine on the surface is able to promote strong electrostatic interactions with BSA. The adsorption of BSA was conducted at the pH of 4.7. At this pH, amine functionalized silica is positively charged while pure silica is negatively charged.

BSA adsorption on SBA-15 t ype of mesoporous silica with pore size between 5.1 and 5.6 nm has been reported before. The results showed a very low amount of BSA adsorbed [8], which suggests that Bovine serum albumin was not adsorbed on the internal surface. The pore size was too small for BSA to diffuse through [8]. In our study, BSA was adsorbed on the internal surface. This result is further confirmed by comparing BSA adsorption on mesoporosus silica or as-synthesized mesoporous silica, respectively. The results show that the large cavity size (20-30nm) and entrance size (9- 11 nm) of the FDU 12 type mesoporous silica synthesized in this work can facilitate BSA adsorption in internal pores. BSA with the dimension of 4x4x14 nm can diffuse through the pore cavity easiliy.

In summary, functionalized large pore mesoporous silicas with ordered structure were synthesized using low synthesis temperature and high hydrothermal temperature method. The large cavity and entrance size of the materials improved the BSA diffusion and adsorption into the cavity. The amine functionalized mesoporous silicas show much improved protein adsorption property co mpared with the unfunctionalized one.

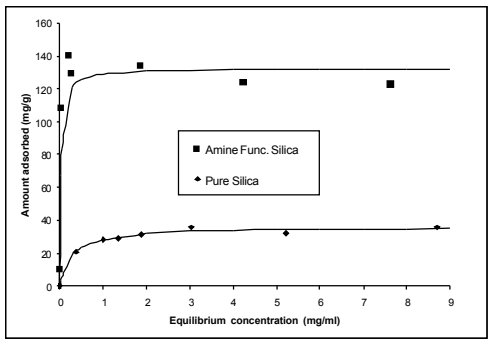

Figure 3. Adsorption isotherm curves of BSA of Amine functionalized silica and pure silica. The solid line are fitting results of the Langmuir equation.

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