Functionalized self-assembled monolayers on mesoporous silica nanoparticles with high surface coverage

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Abstract
Mesoporous silica nanoparticles (MSNs) containing vinyl-, propyl-, isobutyl- and phenyl functionalized monolayers were reported. These functionalized MSNs were prepared via molecular self-assembly of organosilanes on the mesoporous supports. The relative surface coverage of the organic monolayers can reach up to 100% (about 5.06 silanes/nm²). These monolayer functionalize MSNs were analyzed by a number of techniques including transmission electron microscope, fourier transform infrared spectroscopy, X-ray diffraction pattern, cross-polarized Si29 MAS NMR spectroscopy, and nitrogen sorption measurement. The main elements (i.e., the number of absorbed water, the reactivity of organosilanes, and the stereochemistry of organosilane) that greatly affected the surface coverage and the quality of the organic functionalized monolayers on MSNs were fully discussed. The results show that the proper amount of physically absorbed water, the use of high active trichlorosilanes, and the functional groups with less steric hindrance are essential to generate MSNs with high surface coverage of monolayers.

Background
Periodic mesoporous silica materials have been intensively investigated over the last decade due to their ordered structure, large surface area, and well-defined pore size [1,2]. Mesoporous silica materials with different morphologies, such as spheres [3], fibers [4], films [5], and vesicles [6] have been developed. Very recently, small mesoporous silica nanoparticles (MSNs) have been receiving much attention [7-14]. Compared with bulk mesoporous silica (typical diameter of 500 nm to several micrometers), MSNs (diameters ranging from 50 to 500 nm) offer additional properties, such as fast mass transfer of molecules into or out of the pore systems, effective adhesion to the substrates, good suspension in solution, and easy permeability across cell membrane [15]. These features make MSNs excellent candidates for drug delivery vehicles [10], sensors [16], and catalyst supporter [17]. However, many applications require these materials to have special binding sites, stereochemical configuration, charge density or surface, and interface properties (such as wetting and adhesion) [18-20]. So, it is necessary to develop methods to modification of the large surface by organic functional groups to tailor the surface properties or to bind special targets, thus extending the use of MSNs to wide application [21,22].

So far, two main pathways are available for functionalization of MSNs with organic groups. One is the grafting method based on direct reaction between organosilane and surface silanols [23,24]. The limitation of this synthetic method is that the population of the organic groups would be limited to the original number of surface silanols and thus, a low surface coverage is obtained (<25%) [23-25]. Another approach for functionalization of MSNs is the one-pot synthesis method through co-condensation of tetraalkoxysilanes with terminal trialkoxyorganosilanes in the presence of structure-directing agents, leading to materials with organic residues anchored covalently to the pore walls [18,21]. Using this method, the organic MSNs with narrow particle size distribution in the range of about 40 to 150 nm could be synthesized, but this method leads to
disordered MSNs, and the content of organic functional-
ities in the modified silica phases does not normally ex-
cceed 40 mol% [18,21].

Molecular self-assembly of organosilanes has been
proven to be a powerful method to rationally engineer
the ceramic oxide surface properties [26-29]. In this
process, the organo-silanes are hydrolyzed to create the
corresponding hydroxysilanes on the polar oxide sur-
faces, and then, these hydroxysilanes absorb on the sur-
face via hydrogen bond. Aggregation of these hydrogen-
bound species, which driven by the attractive van der
Waals force between the pendant hydrocarbon chain
and cross-linking between neighboring silanes, as well as
condensation between the hydroxysilanes and the polar
oxide surface lead to a closely packed monolayers on the
oxide surface (Figure 1) [23]. Using this method, the
relative surface coverage of the monolayers can reach
100% [29]. So far, this method has been successfully ap-
plied for functionalizing the bulk mesoporous silicas
[20,30,31], but application of this method to produce the
monolayer functionalized MSNs with high coverage
failed. One possible reason is that the functional mole-
cules are very easy transferred out of the pores of MSNs
during functionalization process, leading to poor surface
coverage.

Here, we extent the self-assembled method toward the
generation of self-assembled monolayer functionalize
MSNs (SAM-MSNs) and show that the surface coverage
of the monolayers can be varied up to 100% within
MSNs, as well as retention of ordered structure. As
described in the following, various organic monolayers
could be assembled onto the porous walls of MSNs
using this general method.

**Methods**

The organosilanes (vinyl-trichlorsilan, propyl-trichlor-
silan, isobutyl-trichlorosilane, and phenyl-trichloril-silan)
were purchased from Sigma-Aldrich Corporation, St.
Louis, MO, USA. Other reagents were purchased from
Shanghai Zhenxin Reagents Factory, Jiading, Shanghai.
Toluene was dried over 10 Å molecular sieves for 10 days
and then refluxed over Na for 10 h. Ultrapure water
($\sigma = 18.2 \ M\Omega \ cm$) was degassed and decarbonated with
argon.

Surface analysis of samples was performed on a Micro-
meritics ASAP 2010 analyzer (GA, USA) at the
temperature of liquid nitrogen. The surface areas were
calculated by the Brunauer-Emmett-Teller (BET) and
pore size distribution was measured by Barrett-Joyner-
Halenda (BJH) methods. Samples were outgassed at
100°C for 12 h before analysis. The pore volume was
taken at a relative pressure of 0.99. Cross-polarized solid
state $^{29}$Si NMR experiments were recorded on Bruker
DSX 300 NMR (Bruker Optik Gmbh, Ettlingen, Germany).
The following experimental parameters were used: 4.0
KHz spinning frequency, 45° pulse width of 2.4 ls, 30 s
recycle delay, and 360 scans. Fourier transform infra-
red spectroscopy (FTIR) spectra were obtained using a
Bruker Vertex70 spectrophotometer using KBr pellets.
The transmission electron microscope (TEM) images
were obtained from JEOL 2100 operating at 200 kV
(Akishima, Tokyo, Japan). The samples were prepared
by evaporation of a drop of sample solution on a grid
at room temperature.

For preparation of organic monolayer functionalized
MSNs, MSNs were first prepared according to a
reported method [32,33]. Typically, 1 g of cetyltrimethy-
laumenium bromide (CTAB) was dissolved in a solution
of 480 mL water and 3.5 mL of 2 M NaOH. Mesitylene
(7.0 mL) was then added to the solution. The mixture
was stirred vigorously at 80°C for 2 h, following which
tetraethyl orthosilicate (TEOS) (5.0 mL) was added
dropwise. The reaction mixture was stirred for further
2 h at 80°C. The resulting precipitate was collected by
filtration, washed with methanol, and dried under a vacuum at 100°C for 24 h. The surfactant templates and mesitylene were extracted from the samples using HCl/methanol solution. A suspension of 1.0 g of the as-synthesized MSNs was stirred for 6 h at 50°C in 100 mL methanol with 0.75 mL concentrated hydrochloric acid. The template-removed product was then collected via filtration and dried under vacuum at 100°C for 12 h.

The procedure for functionalization of MSNs with organic monolayers was described as follows: 1 g of MSNs (1095 m² of surface area) was suspended in 50 mL of dried toluene. To this mixture was added 0.33 mL of water (18.22 mmol, corresponding to 1 × 10¹⁹ water molecules/m², just equal to twice the number of silanol groups present on a fully hydroxylated silica surface).¹⁹

The suspension was stirred vigorously for 3 h at room temperature to allow the water to disperse through the mesoporous matrix. Then organic trichlorosilans (9.11 mmol, corresponding to 5 × 10¹⁸ water molecules/m² just equal to the number of silanol groups present on a fully hydroxylated silica surface) were added via syringes, and the mixture was stirred for 12 h at room temperature under N₂. The produces were collected by filtration, washed with plenty of 2-propanol, and dried under a vacuum.

Results and discussion
To synthesize the SAM-MSNs, the MSNs were first prepared. MSNs were synthesized in CTAB/OH, TEOS, and mesitylene solution, which have been reported previously [32,33]. As shown in the Figure 2, MSNs have a particle diameter of 100 to 200 nm and composed of

Figure 2 The TEM of MSN (a), Vi-SAM-MSNs (b), Pr-SAM-MSNs (c), Is-SAM-MSNs (d), and Ph-SAM-MSNs (e).
ordered hexagonal array of mesoporous channels. The nitrogen surface sorption analysis of MSNs gave the BET surface area of 1.095 m$^2$/g$^{-1}$ and the pore size of 6.5 nm.

SAM-MSNs were synthesized via deposition of organic monolayers on the pore walls of MSNs. First, the surface of MSNs was prehydrated with two monolayers worth of water, followed by treatment with one monolayer worth of organosilanes (based on the available surface area). The organosilanes (vinyl-trichlorosilan, propyl-trichlorosilan, isobutyl-trichlorosilan, and phenyl-trichlorosilan) then underwent hydrolysis and became covalently attached to the substrate and cross-linked to one another, generating SAM-MSNs with different organic groups (denoted Vi-SAM-MSNs, Pr-SAM-MSNs, Is-SAM-MSNs, and Ph-SAM-MSNs, respectively).

The surface coverage of the functional groups could be estimated by gravimetric analysis [20,31]. Based on the weight change (W%) after functionalization, the surface area (SA, 1095 m$^2$/g), the molecular weight ($M_n$) of the functional groups [OH-Si-(O)-R], and the assumption of 5 × 10$^{18}$ silanols per square meter on a fully hydroxylated silica surface [20,31], surface coverage ($X$) can be calculated from

$$X = \left( \frac{(W\% / M_n) \times 6.02 \times 10^{23}}{(SA \times 5 \times 10^{18})} \right)$$

This gravimetric method of estimating surface coverage is felt to be accurate within ±10% [31]. It should be mentioned that when this gravimetric method was used to determine the surface coverage, the byproducts (e.g., residual polysiloxanes) trapped within the nano-pores should be excluded. Since only two monolayers worth of water and one monolayer worth of organosilanes (based on the available surface area) were used in preparation of SAM-MSNs, few byproducts within the pores could be expected. This assumption was also confirmed by TEM and BET results, which will be discussed below. The surface coverage could also be calculated from solid state $^29$Si NMR spectroscopy, but this method is less accurate than the gravimetric method because of the signal-to-noise limitation of the solid state $^29$Si NMR spectroscopy (accurate within ±15%) [20,31]. Table 1 indicated that the surface coverage was varied from 37% to 100% depending on different organosilanes used.

Figure 2 shows the TEM of MSNs and the SAM-MSN samples with different functional groups. It could be found that both MSNs and SAM-MSN samples were comprised of MCM-41-type, hexagonal array of mesoporous channels, suggesting the functionalization of MSNs with organic monolayer did not destruct the order hexagonal array of mesoporous channels. From TEM pictures, no free non-porous silica particles were observed in all SAM-MSN samples. This result confirmed that all organic functional groups were anchored on the surface of MSNs. The TEM images also show that the pores are still open even though the 100% of full surface was covered by functional groups (Figure 2b).

Table 1 Properties of different self-assembled monolayer functionalize mesoporous silica nanoparticles (SAM-MAN)

| Sample          | Functional molecules | Weight changes after functionalization | Coverage (%) | BET surface area (m$^2$/g) | BJH pore size (nm) | Pore volume (cm$^3$/g) |
|-----------------|----------------------|----------------------------------------|--------------|----------------------------|-------------------|-----------------------|
| MSN             | 0                    | 0                                      | 1,095        | 6.5                        | 2.0               |                       |
| Vi-SAM-MSN      | vinyl-trichlorosilan | 81                                     | 101          | 438                        | 4.79              | 0.5                   |
| Pr-SAM-MSN      | propyl-trichlorosilan| 62                                     | 65           | 489                        | 4.63              | 0.63                  |
| Is-SAM-MSN      | isobutyl-MSN         | 40                                     | 37           | 582                        | 5.31              | 0.94                  |
| Ph-SAM-MSN      | phenyl-trichlorosilan| 100                                    | 80           | 480                        | 4.71              | 0.56                  |
in Table 1. The BET surface area of the functionalized MSNs was about half the value of the pure MSN. The decrease in the surface areas is reasonable because the mass of MSNs increased significantly (by 60% to approximately 100%) after functionalization. The functionalization of MSNs also results in the reduction of pore volume and shrinkage of the BJH pore diameter (Table 1), which was ascribed to the lining of pore wall with the organic functional groups. The BET characterization shows that all SAM-MSNs show type IV sorption isotherms. These isotherm characterizations are consistent with the fact that the functional groups were grafted onto the pore walls, and few free polysiloxanes were trapped in the pores (Figure 5) [36,37].

To confirm the grafting of the organosiloxanes onto the pore walls of MSNs, the samples were analyzed by solid state $^{29}$Si NMR and FTIR. The $^{29}$Si NMR spectra (Figure 6 and Table 2) show the presence of two additional peaks, T$^2$ and T$^3$ [$T^2 = R-Si-(OSi)_2(OH)$, $T^3 = RSi-(OSi)_3$, $R =$ organic groups] in the functionalized MSNs. These peaks are ascribed to the resonances of the incorporated organosiloxanes in the functionalized MSNs. FTIR spectra further confirmed the functional groups grafted onto MSNs (Figure 7). The peaks around 2,800 to 2,970 cm$^{-1}$, which were assigned to the aliphatic C-H vibrations, were observed in the Pr- (2,960, 2,930, 2,873 cm$^{-1}$) and Is- (2,963, 2,939, 2,866 cm$^{-1}$) SAM-MAN samples. The alkene C-H vibration (3,067 cm$^{-1}$) and C = C stretching vibration (1,570, 1,607 cm$^{-1}$) were observed in the Vi-SAM-MSN sample. The aromatic C-H (3,075, 3,055 cm$^{-1}$) and ring C = C (1,590, 1,432 cm$^{-1}$) stretching vibrations were clearly observed in Ph-SAM-MSN sample.

The surface coverage and the quality of the organic functionalized monolayers on MSNs are greatly affected by three facts: the number of absorbed water, reactivity of organosilanes, and the stereochemistry of organosilane. The organic molecules could be anchored onto the mesoporous silica surface through ‘direct silanation’ mechanism, but the population of the organic

![Figure 4](http://www.nanoscalereslett.com/content/7/1/334) Nitrogen sorption isotherm (a and b) and BJH pore size distribution of different SAM-MSNs.

![Figure 5](http://www.nanoscalereslett.com/content/7/1/334) Schematic drawing of the self-assembled monolayer structure within a mesopore. The red, blue, green, and white spheres indicate the oxygen, silicon, carbon, and hydrogen atom, respectively.
groups would be limited to the number of surface silanols, resulting in a low surface coverage (only 22% of full surface coverage was observed when MSNs reacted with vinyl-trichlorosilan). A proper amount of physically absorbed water is of utmost importance to build the functionalized monolayers on MSNs. This absorbed water provides a hydrated interface to hydrolyze organosilanes, which is one of the critical first steps in the deposition of the monolayers. It was found that only two monolayers worth of water (based on the available surface area) is enough to hydrolyze organosilanes and deposition of functional monolayers. However, excess of water should be avoided because the presence of free water would lead to polymerization of organosilanes in a solution.

The use of trichlorosilanes as functional molecules is necessary for the preparation of SAM-MSNs with high surface coverage. A low surface coverage was obtained (about 20%) when trialkoxyorganosilanes were used for deposited monolayers on the MSNs surface, whereas a high surface coverage was possible when trialkoxyorganosilanes was used to functionalize the bulk mesoporous silica. The reason for this different behavior might be that the functional molecules are very easy to be transferred out of the pores of MSNs during the functionalization process. So, a functional molecule with a higher activity is essential to be hydrolyzed and deposited on the pore walls of MSNs. Trichlorosilanes show higher active toward the absorbed water than trialkoxyorganosilanes. Especially, the hydrolysis of trichlorosilanes generates HCl which can greatly enhance the condensation reaction between neighboring silanes, as well as between the hydroxysilanes and the polar oxide surface, leading to closely packed monolayers on the oxide surface.

The stereochemistry of organosilane is another element that significantly affects the surface coverage of the organic functionalized monolayers on SMNs. The vinyl and phenyl-based organosilanes with a short alkane chain generated SAM-MSNs with high surface coverage (100% and 80%, respectively), whereas a relatively low surface coverage (approximately 65%) was obtained when the propyl-based organosilane with a longer alkane chain was used. Isobutyl-trichlorosilane generated the lowest surface coverage (37%). The reason might be that the side methyl groups blocked the condensation reaction between neighboring silanes, resulting in less functional molecules deposition on the MSN surface.

Conclusions

The SAM-MSNs were synthesized, and the relative surface coverage of the organic monolayers can reach up to 100%. It was found that an appropriate level interfacial hydration, the use of trichlorosilanes as functional molecules, and the functional groups with less steric hindrance are essential to generate MSNs with high surface coverage of monolayers. The functional monolayers provide special attributes (such as binding sites, stereocemical configuration, and special interface properties) for mesoporous silica surface. We believed that the combination of unique structure of MSNs and functionalized monolayers can extend the use of MSNs to a wide array of applications (such as adsorption, sensing, catalysis, and drug delivery) and also benefit the
development of new generation of sophisticated functional nanocomposites.

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