Optical Nanosensor Design with Uniform Pore Geometry and Large Particle Morphology

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1. Synthesis of silica materials as supporters

1.1. Hexagonal P6mm (HOM-2) and cubic Pm3n (HOM-9) silica Monoliths

HOM-2 silica monoliths were synthesized by using direct templating method of lyotropic liquid crystalline phase of Brij 56. Typical conditions and procedure used in the synthesis of HOM-2 monoliths at a specific Brij 56 / TMOS ratio of 50 wt% in the microemulsion system were as follows. First, Brij 56 / TMOS was mixed in a 100-cm³ round flask and then shaking at 50 °C for 2 min until homogeneous. Then, 1 g of H₂O/HCl (pH= 1.3) was quickly added, thus forming a clear solution (i.e., homogenous). The mass ratio of Brij 56: TMOS: H₂O/HCl was 1: 2: 1. In the quaternary microemulsion system formed by addition of alkanes (C₁₂-alkane) with a Brij 56: dodecane ratios of 2: 1 to the hexagonal phase domains at Brij 56/TMOS of 50 wt%, the HOM-9 materials were synthesized through the phase transition of hexagonal P6mm- cubic Pm3n. The methanol produced from this hydrolysis of TMOS was removed in vacuo at 40 ºC. As the hydrolysis/condensation reactions continued during the evacuation, the liquid viscosity of the material increased, and the resulting optical gel-like material acquired the shape and size of the reaction vessel. After a 10 minute evacuation, the translucent glassy monoliths were collected and kept at 40 ºC for 16 h. The surfactant was removed by calcination at 450 ºC (1 h under nitrogen and 6 h under oxygen).

1.2. Hexagonal silica powder (SBA-15)

SBA-15 silica powder was fabricated as previously reported. However, 8 g of Pluronic P123 (EO₂₀PO₇₀EO₂₀) copolymer was first dissolved in 250 ml of 1.9 M HCl at 40 ºC, and then 16 g of tetraethoxysilane (TEOS) were added with continuous stirring to the previous solution. The initial molar ratio was 1.0 TEOS: 0.018 P123: 6.2 HCl: 181 H₂O. The final solution was transferred to a closed polyethylene flask and aged at 40 ºC for 24 hours and then at 85 ºC for 48 hours. The white precipitate was recovered by filtration and dried at 60 ºC. The surfactant moiety was removed by calcinations under air at 500 ºC for 6 hours.
**Figure S2.** XRD patterns (A, B, C) and N$_2$ adsorption/desorption isotherms at 77 K (D, E, F) of hexagonal HOM-2 monoliths (A, D), hexagonal SBA-15 powders (B, E), and cage cubic Pm3n HOM-9 monoliths (C, F), respectively, after calcination (a), after TMAC functionalization (b) and after PR incorporated silica-TMAC materials. Representative TEM images of functionalized TMAC/SBA-15 (G) and TMAC/HOM-9 carriers (H) recorded along the (H) [210] direction.

**Table S2.** Specific textural parameters of 2D and 3D mesoporous silica powders (SBA) and monoliths (HOM) after surface modification by TMAC ligands moieties.

<table>
<thead>
<tr>
<th>Supported Silica Materials</th>
<th>Treatment Conditions</th>
<th>*Unit-lattice (a)</th>
<th>Surface area ($S_{BET}$)</th>
<th>Pore volume ($V_p$)</th>
<th>Pore size (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(nm)</td>
<td>m$^2$/g</td>
<td>cm$^3$/g</td>
<td>nm</td>
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### Table 1

<table>
<thead>
<tr>
<th>Structure</th>
<th>Material</th>
<th>Unit Lattice Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexagonal P6mm</td>
<td>Calcined SBA-15</td>
<td>10.2</td>
</tr>
<tr>
<td>Powders</td>
<td>SBA-15/TMAC</td>
<td>10.0</td>
</tr>
<tr>
<td>Hexagonal P6mm</td>
<td>Calcined HOM-2</td>
<td>5.2</td>
</tr>
<tr>
<td>Monoliths</td>
<td>HOM-2/TMAC</td>
<td>5.1</td>
</tr>
<tr>
<td>Cubic Pm3n</td>
<td>Calcined HOM-9</td>
<td>15.0</td>
</tr>
<tr>
<td>Monoliths</td>
<td>HOM-9/TMAC</td>
<td>14.9</td>
</tr>
</tbody>
</table>

*Unit-lattice constant (a_{P6mm} = \frac{2d_{100}}{\sqrt{3}}, and a_{Pm3n} = \frac{d_{210}}{\sqrt{5}})*

TG-DTA curves of incorporated TMAC hexagonal silica monoliths (HOM-2/TMAC) were shown in Fig. S3. The TG profile shows the gradual decrease in the weight of HOM-2/TMAC; however, the total weight loss was about 15% between 200 and 700 °C. Two broad exothermic peaks were observed at 320 and 520 °C in the DTA curve. These results indicated the TMAC fragments were decomposed between 200 and 700 °C.\[31\] In addition, TG analysis provided evidence that the weight loss of the TMAC with the mesoporous silicas, namely, free-standing supporters was decreased in the order HOM-9 (1.7 mmol/g) > HOM-2 (1.5 mmol/g) > SBA-15 (1.4 mmol/g), in agreement with the adsorption capacity of the loaded organic moieties of these materials (see Table 1).
Figure S3. TG and DTA analyses of functionalized TMAC/HOM-2 hexagonal silica monoliths.

S4

The FTIR spectra of HOM-9 and HOM-modified TMAC (Fig. S4) revealed that the TMAC and PR organic moieties were functionalized the HOM monoliths. With all samples, the appearance of a broad absorption band in the 3000-3500 cm\(^{-1}\) region indicated the presence of Si-OH asymmetric stretching. In addition, two strong bands at 1100 and 960 cm\(^{-1}\) were assigned to Si-O-Si and Si-OH stretching vibrations, respectively.\(^{[32,33]}\) The silica-modified TMAC showed additional absorption bands at 2960 and 1400 cm\(^{-1}\), which were due to the aliphatic C-H and the stronger C-N bonds, respectively.\(^{[32]}\) There is no significant change in the absorption bands with the loading of PR probe molecules or even after the metal ion binding, indicating the stability of the silica-functionalized organic moieties onto the pore surfaces without potential leaching out during the naked-eye detection even with introducing a high-concentration of detected metal ions. The FTIR results were consistent with EDS X-ray microanalysis of each element. However, the composition contents of HOM-TMAC-PR (sensor) were estimated by recording EDS X-ray microanalysis of each element (C, N, O, Si and S contents of 9.01, 6.78, 53.3, 30.14, and 0.76 mass\%, respectively). The data, in general, indicated the successful functionalized of TMAC with the silica carriers; however, the high concentration of nitrogen and sulfur compared to carbon within HOM-TMAC-PR could be due to some un-reacted functionalities with the probe moieties, in consistent with the adsorption amounts (Q) of the PR-probe molecule (see Table 1).
S5

Furthermore, $^{29}$Si NMR spectroscopy was used to investigate the successful tuning of the silica surfaces by charged molecule (TMAC) and by probe moiety (PR) through the elucidation of the molecular environment in the silica materials.\textsuperscript{[34]} First, $^{29}$Si NMR spectrum of the hexagonal HOM-2 monoliths (Fig. S5a) showed three overlapping signals (Q\textsubscript{n} peaks), which are representative to pure silica framework matrices. These peaks were characteristics of silanediol (OH)\textsubscript{2}Si(OSi)\textsubscript{2} (Q\textsubscript{2}), silanol (OH)Si(OSi)\textsubscript{3} (Q\textsubscript{3}), and siloxane Si(OSi)\textsubscript{4} (Q\textsubscript{4}) groups which appeared at -91, -101, -110 ppm, respectively.\textsuperscript{[34]} Second, $^{29}$Si NMR spectra, for example Fig. S5b, of silica-TMAC ligand show signals representative of various silicon environments of the T\textsubscript{n} and Q\textsubscript{n} silane moieties; however, T\textsubscript{n} peaks are representative of silicon matrix directly bounded to organic species. Figure S5b shows that in addition to Q\textsubscript{2}, Q\textsubscript{3}, and Q\textsubscript{4}, three different signals were observed at -53, -61, -71 ppm, which correspond to three different environments for siloxane group in functionalized monolayers of T\textsubscript{1} [R-Si(OH)\textsubscript{2}(OSi)\textsubscript{3}], T\textsubscript{2} [R-Si(OH)\textsubscript{2}(OSi)\textsubscript{3}], and T\textsubscript{3} [R-Si(OSiO)]. This result indicated that the silicon atom in the siloxane matrix was directly bounded organic groups of TMAC molecule, as consistent with elemental analysis (C, H, and N) data. It is also important to note that the increase of the intense peak of the siloxane groups (Q\textsubscript{4}) with the incorporation of the TMAC ligand or even PR indicated the Si-OH sites (silanediol and silanol groups) of the silica pore wall underwent condensation reaction with the organosilane coupling agent, forming covalent linkage to the silica frameworks.

Figure S4. FTIR spectra of cgae silica monoliths (HOM-9) (a), functionalized TMAC/HOM-9 (b), cage nanosensors HOM-9/TMAC/PR (c), and the cage nanosensor after detection of Sb (III) ion.
Third, with the immobilization of PR-probe, one signal resonance of T₃ (Figure S5c) was the main component with negligible existence of T₂ dominate, indicating that the PR molecule was loaded closely to one another in functionalized monolayer.⁴³

![Figure S5](image_url)

**Figure S5.** $^{29}$Si NMR spectra of calcined hexagonal P6mm mesoporous silica (HOM-2) monoliths (a) functionalized TMAC/HOM-2 monoliths (b), and hexagonal nanosensors HOM-2/TMAC/PR monoliths (c).

### S6

**Key factors affecting on the optical sensing of Sb³⁺ ions**

The high performance of the sensors was dependent of key factors such as the amounts of support-based sensor, reaction temperature, and the pH value that led to possible naked-eye detection of Sb³⁺. Nonetheless, increase of temperature from 25 to 40 °C did not result in any significant change in the color reaction of the [Sb-PR]$^{3+}$ complex, the diffusion of the metal ions onto the monoliths or even powders materials and reaction response-time were substantially enhanced with the temperature.⁴⁴ Generally, visual detection was sensitive to the amount of material used and pH values. Herein, we carried out a series of experiments to systematically define and evaluate the relative importance of the pH value and the amount of sensor on the detection of Sb³⁺ ion.⁴⁴

1. **Effect of sensor amount**
In fact, high surface area and porosity, and the particle-size morphology of the materials are advantageous to allow high adsorption capacity of the chromophore probe in fast kinetic. The amount adsorbed of the probe has significant influence to create significant sensing system. Therefore, results show that the quality of the sensing system is also depended on the amount of solid support-probe used; however, the probe concentration substantially affects the sensitivity in ordinary spectrophotometric methods. The findings revealed that 4 mg of nanosensors was sufficient to present good color separation between the blank (sensor) and the detected sample even at low Sb$^{III}$ concentration (Figure S6a).

2. Effect of pH

During the naked-eye detection, the color change and the absorption intensity of the nanosensor was observed after introducing the Sb$^{III}$ ion into the framework matrices modified probe. The effect of the pH solution on the formation [Sb-PR]$^+$ complex was evident (Figure S6b). The pH response was studied by continuously monitoring the color and the [Sb-PR]$^+$ complex spectra after addition of Sb$^{III}$ analyte ion at different pH range of 1-11. Results show that the complexation of Sb$^{III}$ ion with PR-probe formed at wide pH of 1-5 range; however, the maximum color and spectra development were at pH value of 3.

![Figure S6](image-url)

**Figure S6.** Control conditions for efficient sensing systems of Sb$^{III}$ ion detection. Effect of HOM-2/TMAC/PR nanosensor amounts (a) and effect of pH (b) on optical absorbance spectra of [Sb-PR]$^+$ complex during the detection of Sb$^{III}$ concentration of [500 ppb] at 532 nm using hexagonal nanosensors.