

## Facile Modification of Surface of Silica Particles with Organosilanepolyol and Their Characterization

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The surface modification of silica particles (SPs) was systematically conducted by the treatment of 0.1-10 wt % phenylsilanetriol (PST) on the basis of SPs used through two step processes: 1) the PST coating of SPs *via* evaporation under reduced pressure and 2) their thermal condensation leading to Si-O-Si bond formation *via* heating at 130 °C. The evaluation of the modified SPs was conducted by the simple floating test on water and the measurement of the contact angle (CA) of water droplet on the 2-dimensional layer of modified SPs on slide glass. When PST was used about 2 wt % or above on the basis of SPs (about average size: 50 nm) used, the modified SPs were fully floated on the water and all dispersed into upper organic solvent layer after a shaking with the mixture of the water and benzene, indicating that the modified SPs have hydrophobic properties. The modified SPs were characterized by <sup>29</sup>Si MAS NMR and physicochemical properties including SEM, TEM, BET, adsorption/desorption isotherms, etc. were measured and compared each other in details. This research demonstrates that the organosilanetriol is a good modifier applicable for the surface modification of inorganic oxide particles using a low amount of modifier on the basis of oxide particles used.

**Key Words :** Surface modification, Phenylsilanetriol, Organoalkoxysilane, Hydrophobicity, Contact angle

### Introduction

Silica particles (SPs) are widely used as supports for heterogeneous catalysts<sup>1-3</sup> and for the removal of heavy metals<sup>4-6</sup> and as fillers for composites with organic polymers.<sup>7-9</sup> Originally SPs have lots of hydroxyl functionalities which are hydrophilic and reactive sites, and can be modified to alter functionalities on their surfaces.<sup>10,11</sup> Functional groups on the surface of modified SPs usually plays a critical role in the specific properties such as hydrophobicity, binding sites, and are chemically reactive.<sup>11-13</sup> The modification typically involves tailoring the surface properties of oxide particles and is accomplished by two general procedures: (i) silanization of pure silica spheres with alkoxy silane coupling agents by refluxing in solvent and then hybridization with organic polymers (two step processes)<sup>14</sup> and (ii) the direct preparation of organic/inorganic hybrid materials using a organosilane coupling agent (one step process).<sup>15</sup> From industrial point of view, especially, modified silica have been widely used for making inorganic-organic hybrid materials such as shoes and green tire.<sup>16</sup> Moreover, it can react with modifier to become hydrophobic and new reactive sites. For example, alkoxy silane is a good coupling agent for this purpose,<sup>11,17</sup> but it is not easy to find the optimum level of modifier for a well-uniformed modification on the surface of silica because two steps of its hydrolysis and condensation catalyzed by acid/base<sup>18,19</sup> occur almost coincidentally to give polymeric organosiloxane products through their self-condensation.<sup>20</sup> Although there have been many reports about the modification of silica particles (SPs) using alkoxy silanes, but not using their hydrolyzed products, silanepolyols. In a

chemical modification, the exposed hydroxyl groups on the surface of silica particles are the key reactive sites<sup>11</sup> and can interact easily with other polar moieties, in particular, like organosilanepolyol through strong hydrogen-bonded interaction. As a basic study to make the modified SPs applicable to inorganic-organic hydrid materials, we chose phenylsilanetriol (PST) as a model modifier among organosilane-polyols, which is relatively stable in polar organic solvent at room temperature and can form a hydrogen-bond with hydroxyl groups on the surface, being a good candidate for the surface modification of inorganic oxide particles without catalyst. At first, monodispersed SPs ( $200 \pm 30$  nm diameter) were prepared by Stöber method and systematically modified by the treatment of 0.1-10 wt % PST on the basis of SPs used without catalyst.

Herein, we report a facile modification approach to silica particles (SPs) using PST and the evaluation of their surface modification in details.

### Experimental

**Chemicals and Materials.** Tetraethoxysilane (TEOS) and phenyltrimethoxysilane were obtained from Aldrich. The ammonia solution (28 wt % ammonia) and acetic acid (99.6%) were obtained from Junsei Chemical. HPLC graded absolute ethanol (99.9 + %) was obtained from SK Chemical and methanol (99.5%) from Dae Jung Chemical, respectively. All chemicals were used as received without further purification.

**Modification of Silica with PST.** Monodispersed SPs with  $200 \pm 30$  nm diameter were prepared by a procedure

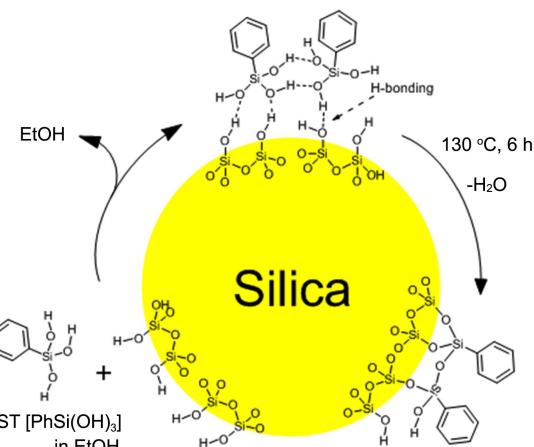
originally described by Stober *et al.*<sup>21</sup> and treated with phenylsilanetriol<sup>27</sup> as followsings: Into each suspension of SPs (0.5 g) dispersed in a 10 mL of absolute EtOH using ultrasonication for 10 min, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0 wt % of PSTs on the basis of the SPs used were added respectively. Then each suspension of mixture was stirred for 10 min, evaporated to remove off the volatiles under reduced pressure, then heated up to 130 °C under atmospheric pressure in oven and then stood for 6 h. Herein, a stacked 5.0 wt % PST ethanol solution was prepared and applied for the surface modification of SPs. Alternatively, phenyltrimethoxysilane (PTMS) was used as a modifier for the modification of SPs in place of PST. The modification procedure<sup>22</sup> was same except for the hydrolysis of PTMS. The hydrolysis of PTMS was conducted by adding 0.5 mL of aqueous ammonia solution (28 wt %) into the suspension of SPs (0.5 g) in methanol and stirred for 8 h.

**Array of Modified SPs on Slide Glasses.** Seven SPs modified with 0.1 wt % PST to 10 wt % and one untreated SPs were dispersed in benzene (2% wt/wt concentration) in each 25 mL vial, respectively. The apparatus was placed in a closed box to protect the experiment from air drafts. The temperature for the experiments was about 21 °C. The cleaned slide glasses were fixed with horizontal bar, which helps to get the dip-coated samples with the same withdrawing condition. Then 8 slide glasses were immersed vertically into the eight colloidal suspensions and slowly withdrawn up to air at a rate of 0.18 mm/min and dried to be SPs-coated layers on the glasses, respectively.

**Characterization.** The morphology of modified SPs was measured by scanning electron microscopy (SEM: HITACHI S-4100) and transmission electron microscopy (TEM: Philips CM30). <sup>29</sup>Si NMR data were obtained using Varian NMR 200 spectrometer at 4.7T at Larmor frequency of 79.49 MHz and spinning rate of 5 kHz by using 5 mm zirconia rotor. The data were acquired using a single pulse sequence with a pulse repetition delay of 100 s, an excitation pulse length of 1.5 μs, and field strength of 62.5 kHz. <sup>29</sup>Si NMR spectra were obtained with 2000 μs CP contact time, 5 s recycle delay, and proton excitation pulse length of 4 μs.

## Results and Discussion

**Modification of Silica with PST.** Silica particles (SPs) with 200 ± 30 nm diameter were prepared by a procedure described by Stober *et al.*,<sup>21</sup> and then modified with PST ranging from 0.1 wt % to 10.0 wt % based on the SPs used. A PST having three hydroxyl groups on the silicon atom is relatively stable itself for dehydrative condensation at room temperature and thus can readily make a hydrogen bonding interaction with hydroxyl groups on the surface of inorganic oxide particles. The procedure for the surface modification was carried out by two steps: 1) hydrogen-bonding formation of hydroxyl groups between SPs and PST through a evaporation of volatile solvent at the suspension mixture of SPs and PST in EtOH under reduced pressure and then 2) thermal condensation leading to Si-O-Si bond formation via



Scheme 1. Surface Modification of SPs with PST.

a heating up to 130 °C under an atmosphere of air and stood for 6 h. In the modification of SPs with organosilanetriol, the thermal energy only alter the hydrogen bonding of hydroxyls between SPs and PST into a Si-O-Si covalent bond that can modify the surface with organic functional group (Scheme 1).

**Evaluation of Modified SPs.** In order to evaluate whether the surface of the SPs is well-modified, simple floating test on water has been taken with the ultrasonication for 1 min at first. The SPs treated with PST ranging from 0.1 wt % to 10.0 wt % based on the SPs used were compared with the untreated SPs in the floatability on water, respectively. The untreated SPs and less than 1 wt % PST-treated were precipitated down in water, particularly; the untreated SPs and 0.1 wt % PST-treated were precipitated immediately. The SPs modified with 0.2 wt % PST to 1 wt % were partially sunken, but 2.0 wt % of PST and above were fully floated on the water. Additionally, benzene solvent was added to each vial including the modified SPs and water, and then strongly shaken by hands. Two layers of water (lower) and organic solvent (upper) were separated, and one of both layers included all SPs as shown in Figure 1. In Figure 1, more than 2 wt % PST-treated SPs were dispersed into the upper benzene layer, while the SPs modified with 1.0 wt % below were positioned as suspension form in water layer. The suspension of modified SPs in each layer was stable for more than 1 week. The results showed that the modifier PST was required relatively a small amount of 2.0 wt % for the whole surface

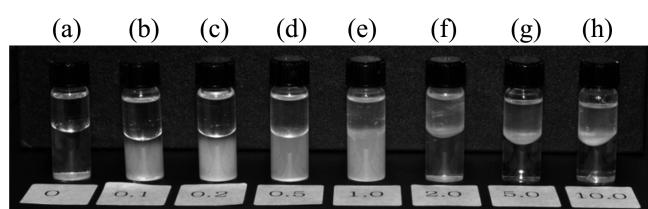
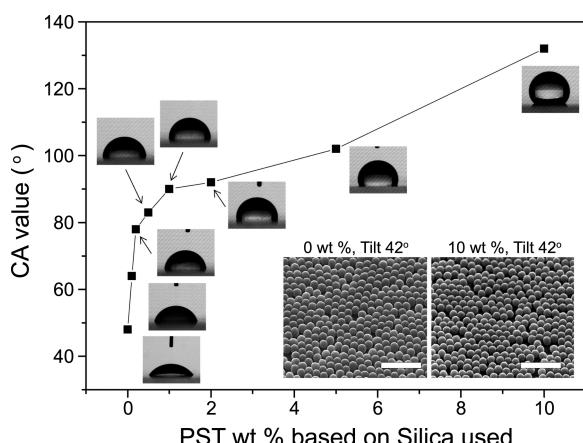


Figure 1. Vials containing SPs of (a) untreated and modified with (b) 0.1, (c) 0.2, (d) 0.5, (e) 1.0, (f) 2.0, (g) 5.0, and (h) 10.0 wt % of PST, respectively, in water (down layer) and benzene (up layer) solvent.

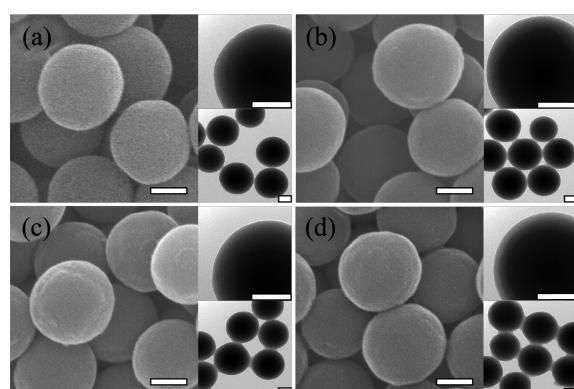


**Figure 2.** CAs of water droplets on the 2-dimensional SPs layers and SEM images of arrays of untreated and 10 wt % PST-modified SPs on glasses (each bar is 1  $\mu\text{m}$ ).

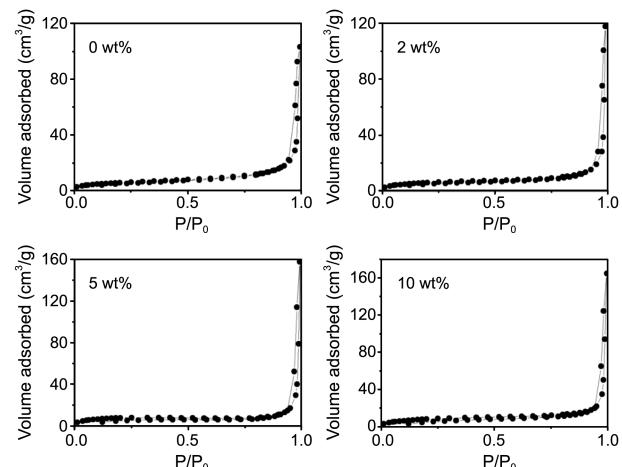
modification of SPs. These tests are simple and can be readily used for the evaluation of hydrophobic modification on the surface of inorganic oxide particles in laboratory and industrial field.

Alternatively, for evaluating their hydrophobicity, all modified SPs were arrayed to be 2-dimensional layers on the slide glasses using a dip-coating method, respectively. In these tests, all of samples were made under the same condition to have the uniformity of SPs' layer on glasses. The SEM images of two dimensional arrays of modified SPs on glasses were very similar to each other and even that of untreated SPs. Thus two images of untreated and 10 wt % PST-treated SPs among PST-treated are presented in Figure 2 (middle and right in bottom). In Figure 2, their layers were uniformly well-arrayed. On the basis of their uniformly layered images, the contact angles (CA) of water droplets on their layers were measured. The photographs of the CAs of water droplets on the SPs layers on glasses are shown in Figure 2. In Figure 2, their CAs increased drastically to 92° from 62° as the amount of modifier increased to 1 wt % from 0.1 wt % of PST and then to 132° at 10 wt % treatment, depending on the hydrophobicity of the modified SPs. Spirk *et al.* reported that the CAs of slide glasses modified with silanetriol increased with increasing the amount of modifier used.<sup>23</sup>

**Characterization of Modified SPs.** In order to look into



**Figure 3.** SEM (left) and TEM images (dark in right) of (a) untreated SPs, (b) 2.0 wt % PST modified, (c) 5.0 wt %, and (d) 10.0 wt % (all of scale bars indicate 60 nm).



**Figure 4.** Nitrogen adsorption/desorption isotherms of the untreated and modified SPs with 2.0, 5.0, and 10.0 wt % PST.

the surface morphologies of the modified SPs, the modified SPs derived from the treatments with 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 wt % of the PST were studied by SEM and TEM, and their representative images of the untreated (a) and modified SPs with 2.0 wt % PST-treated (b), 5.0 (c), and 10.0 (d) are shown in Figure 3. In Figure 3, the particle sizes of the modified SPs were almost unchanged and kept with the same spherical shapes until 1.0 wt %, then, the surface morphology has been slightly changed to be rougher at

**Table 1.** Physicochemical Data of Untreated and Modified SPs with 0.1–10 wt % PST

PST wt/wt% <sup>a</sup> (%)	mol	BET (S <sub>B</sub> /m <sup>2</sup> g <sup>-1</sup> )	Single point surface area <sup>b</sup> (m <sup>2</sup> /g)	Average pore volume <sup>c</sup> (V <sub>p</sub> /cm <sup>3</sup> g <sup>-1</sup> )	Porosity <sup>d</sup> , φ (%)	Apparent Density (g/mL)
0	-	21.8	20.1	0.04	9.0	1.7
0.2	$6.4 \times 10^{-6}$	20.7	19.3	0.04	8.0	1.6
0.5	$1.6 \times 10^{-5}$	22.1	20.3	0.04	8.8	1.8
1.0	$3.2 \times 10^{-5}$	23.3	21.6	0.04	8.8	1.7
2.0	$6.4 \times 10^{-5}$	23.4	21.4	0.05	9.1	1.8
5.0	$1.6 \times 10^{-4}$	30.5	28.5	0.05	9.2	1.7
10.0	$3.2 \times 10^{-4}$	32.9	28.7	0.05	10.7	1.8

<sup>a</sup>Based on 0.5 g of silica. <sup>b</sup>At the 0.12 of P/P<sub>0</sub>. <sup>c</sup>At the 0.97 of P/P<sub>0</sub>. <sup>d</sup>Followed equation,<sup>31</sup>  $\phi = V_p/(V_p + 0.455) \times 100$ .

higher weight % of PST. Their TEM images show all of the modified SPs do not have specific difference on the size or surface comparing with untreated SPs.

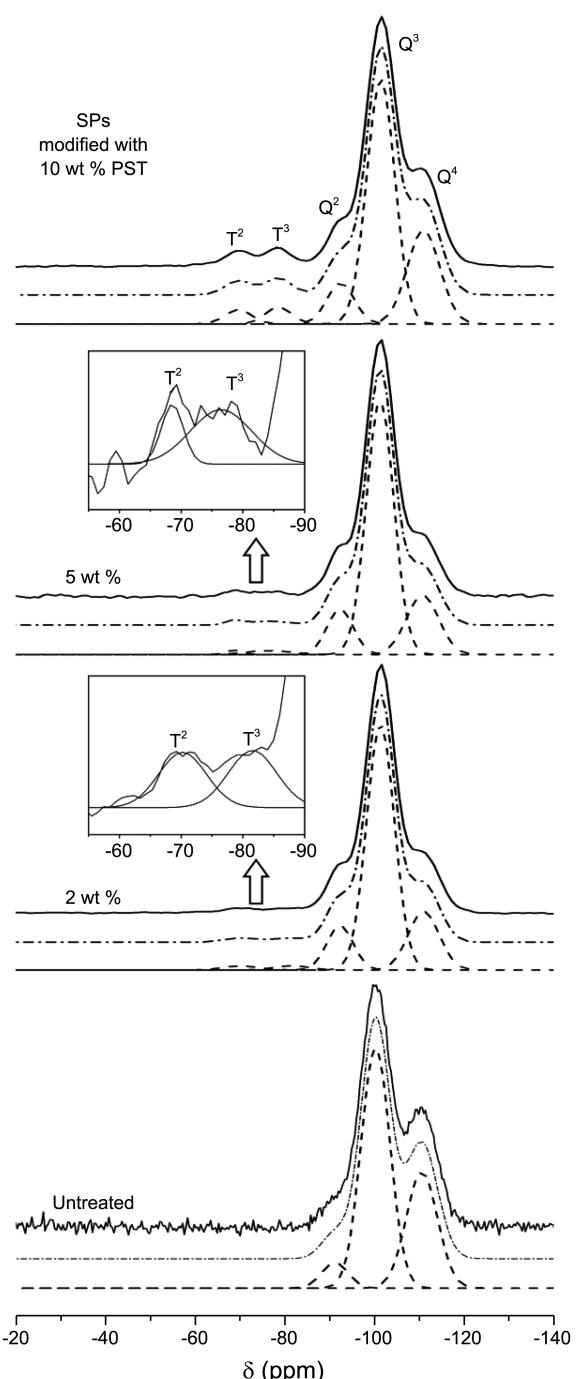
The nitrogen adsorption/desorption isotherms of the modified SPs at -196 °C are shown in Figure 4. The peak value of adsorbed volume obtained from the SPs modified with PST increases gradually to 165 cm<sup>3</sup>/g from 103 cm<sup>3</sup>/g as the amount of PST increases to 10 wt % from zero due to the formation of the surface layer. However, the types of hysteresis slope of the modified SPs are very similar to each other and even to that of the untreated SPs, their graphs are consistent with a typical type II isotherm of mesoporous solid with pore diameters in a range of 2-50 nm according to the IUPAC classification.<sup>23</sup> Also, it is the typical isotherm graph of the SPs synthesized by sol-gel method<sup>24,25</sup> that the representative nitrogen adsorption isotherms of the untreated SPs and the SPs modified with 2.0, 5.0, 10.0 wt % among them are shown in Figure 4.

Some physicochemical data of the untreated and the modified SPs are summarized in Table 1.

In Table 1, the specific surface areas of the SPs at the data of BET increase steeply up to 32.9 m<sup>2</sup>/g from 21.8 m<sup>2</sup>/g and the single point surface areas at the 0.12 of P/P<sub>0</sub> increase in the same trend observed in BET measurement. Moreover, the average pore volume and porosity increase slightly depending on the amount of modifier used. The apparent density of the SPs is rarely changed, suggesting that the amount of modifier on the surface influence rarely the density of the SPs due to the relatively low amount of the modifier with relation to the SPs used.

In order to characterize the chemical structure of the surface of the modified SPs, solid-state <sup>29</sup>Si NMR was used. <sup>29</sup>Si MAS NMR data of the untreated SPs, 2 wt % PST modified and 5 wt % are plotted in Figure 5. In Figure 5, three broad peaks around -92, -101 and -110 ppm are the typical signals of Q<sup>2</sup>, Q<sup>3</sup> and Q<sup>4</sup> types of silica, respectively,<sup>26</sup> and new two small peaks appeared at -78 and -69 ppm from the SPs modified with 2 wt % PST, which are assigned to T<sup>3</sup> and T<sup>2</sup> species<sup>27,28</sup> made from the condensation of PST modifier. The relative peak-area of Q<sup>2</sup>, Q<sup>3</sup> and Q<sup>4</sup> units of the untreated SPs was 5.98:61.62:32.40, as summarized in Table 2.

In this table, untreated SPs were mostly composed of isolated silanol groups (Q<sup>3</sup>), SiO<sub>4</sub> without silanol groups (Q<sup>4</sup>), and minor groups of germinal silanols (Q<sup>2</sup>). The intensity of T groups was appeared at 2 wt % with quite little peak area due to the low amount of modifier and was increased as the concentration of PST modifier increased; however, <sup>29</sup>Si MAS NMR spectra obtained from the SPs below 1 wt % PST shows no T type signals that <sup>29</sup>Si NMR spectra was not a powerful tool for characterizing the surface of SPs modified with quite low amount of modifier used in our NMR experimental conditions. On the basis of T<sup>m</sup> signals in the <sup>29</sup>Si MAS NMR data, the relative peak area of Q<sup>n</sup> and T<sup>m</sup> NMR signals allows the quantitative assessment of the incorporation degree of the organic moiety. As shown in Table 2,  $\Sigma T^m / (\Sigma T^m + \Sigma Q^n)$  are in close agreement with



**Figure 5.** <sup>29</sup>Si MAS NMR spectra of SPs. The lines of —, ---, -·- represent the experimental spectra, sum of the respective deconvoluted peaks, and respective deconvolution peaks, respectively.

those expected based on the added modifier. In this experimental, Q<sup>3</sup> was significantly acquired even in a case of 10 wt % that it may be detected in an inner part of silanol in SPs and those tendency can also be observed by the case of surface modification using organoalkoxysilane to as-prepared SPs.<sup>29</sup>

**Theoretical Estimation of the Optimum Amount of Modifier in Hydrophobic Modification of Surface.** It is important that the number of hydroxyl-containing silicon atoms on the surface of SPs can be counted in order to

**Table 2.** Relative Peak Area of T<sup>m</sup> and Q<sup>n</sup> Groups Obtained from <sup>29</sup>Si MAS NMR Spectra

	T <sup>2</sup> (%)	T <sup>3</sup> (%)	Q <sup>2</sup> (%)	Q <sup>3</sup> (%)	Q <sup>4</sup> (%)	$\Sigma T^m / (\Sigma T^m + \Sigma Q^n)$
10	3.17	3.72	9.44	57.88	25.79	0.07
5	1.39	1.46	11.53	67.64	17.97	0.03
2	0.65	1.65	11.51	67.68	18.52	0.02
Untreated	-	-	5.98	61.62	32.40	-

<sup>a</sup>For each sample, the sum of the peak areas was adjusted to 100%

estimate theoretically the optimum amount of modifier for the monolayer modification of SPs in a molecular level. Chuang *et al.*,<sup>30</sup> reported that the distance between adjacent hydroxyl-containing silicon atoms on the surface of silica is almost 5 Å and the theoretical number of hydroxyl-containing silicon atoms on the surface of silica are four per square nanometer. On the basis of surface area (BET of untreated SPs: 21.8 m<sup>2</sup>/g) (Table 1), the optimum amount of the modifier is roughly calculated to be needed more than 2.3 wt % if the modifier covers a hydroxyl-containing silicon atom on the untreated SPs by one to one. In this study, however, the amount of PST making for the hydrophobic SPs was 2 wt % lower than theoretical 2.3 wt %. It seems like that PST can block slightly more than a hydroxyl-silicon atom on the surface of the SPs. Alternatively, when phenyltrimethoxysilane (PTMS) was compared with the PST modifier. The modification procedure<sup>28</sup> was the same as above except for an additional hydrolysis step of PTMS for 8 h. On a full floatability on water, PTMS was used above 5 wt % on the basis of SPs used and for making a full SPs-dispersed suspension in non-polar solvent, requiring about 2.5 times of PST mole used. These results suggested that PTMS is not better modifier than PST in an aspect of usage of modifier.

### Conclusions

The surface modification of SPs with 0.1-10.0 wt % of PST, which is stable intermediate formed from the hydrolysis of PTMS, has been studied with catalyst-free and only thermal treatment. The SPs treated with 2 wt % PST and more was to be fully hydrophobic in the floating test. CAs of water droplets on the 2-dimensional layers of modified SPs on the slide glasses increased as the amount of PST used increased. 2 wt % of PST used for the hydrophobic modification of SPs is a little lower than the theoretical amount of 2.3 wt % for covering all hydroxyl-silicon atoms at the surface of SPs. The surface roughness, surface area, and size distributions were rarely changed even though the amount of modifier used increases to 2.0 wt %. But some aggregates of the SPs with were observed at 5.0 wt % and 10.0 wt % PST treatments. For evaluating the surface modification of inorganic oxide particles, especially floating test and contact angle test were strong and easy tools. In this research, it was demonstrated that the hydroxyl groups on the surface of inorganic oxide can be effectively modified with organosilanepolyol to be hydrophobic and to generate new functionality.

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### References

- Minakata, S.; Komatsu, M. *Chem. Rev.* **2009**, *109*, 711.
- (a) Zhang, W.; Jiang, P.; Zhang, P.; Zheng, J.; Li, H. *Bull. Korean Chem. Soc.* **2012**, *33*, 4015. (b) Shu-wen, G.; Li-jun, L.; Qian, Z.; Liang-yin, W. *Bull. Korean Chem. Soc.* **2012**, *33*, 1279.
- Bharali, P.; Thrimurthulu, G.; Katta, L.; Reddy, B. M. *J. Ind. Eng. Chem.* **2012**, *18*, 1128.
- Min, B. K.; Santra, A. K.; Goodman, D. W. *Catal. Today* **2003**, *85*, 113.
- (a) Lim, C. W.; Song, K.; Kim, S. H. *J. Ind. Eng. Chem.* **2012**, *18*, 24. (b) He, C.; Zhang, X.; Gao, S.; Chen, J.; Hao, Z. *J. Ind. Eng. Chem.* **2012**, *18*, 1598.
- (a) Boudjahem, A.-G.; Redjel, A.; Mokrane, T. *J. Ind. Eng. Chem.* **2012**, *18*, 303. (b) Lee, H. W.; Cho, H. J.; Yim, J.-H.; Kim, J. M.; Sohn, J. M.; Yoo, K.-S.; Kim, S.-S.; Park Y.-K. *J. Ind. Eng. Chem.* **2011**, *17*, 504.
- Yantasee, W.; Rutledge, R. D.; Chouyyok, W. *ACS Appl. Mater. Interfaces* **2010**, *2*, 2749.
- (a) Hwang, S.; Hsu, P. J. *J. Ind. Eng. Chem.* **2013**, *19*, 1377. (b) Quang, D. V.; Kim, J. K.; Sarawade, P. B.; Tuan, D. H.; Kim, H. T. *J. Ind. Eng. Chem.* **2012**, *18*, 87.
- Al-bishri, H. M.; Abdel-Fattah, T. M.; Mahmoud, M. E. *J. Ind. Eng. Chem.* **2012**, *18*, 1252.
- Ichimura, K.; Funabiki, A.; Aoki, K.-I.; Akiyama, H. *Langmuir* **2008**, *24*, 6470.
- Trewyn, B. G.; Slowing, I. I.; Giri, S.; Chen, H.-T.; Lin, V. S.-Y. *Acc. Chem. Rec.* **2007**, *40*, 846.
- Kim, D.-J.; Hwang, H.-Y.; Jung, S.-B.; Nam, S.-Y. *J. Ind. Eng. Chem.* **2012**, *18*, 744.
- Lee, B.; Koo, S. *J. Ind. Eng. Chem.* **2012**, *18*, 1191.
- Raghavan, S. R.; Walls, H. J.; Khan, S. A. *Langmuir* **2000**, *16*, 7920.
- Lee, Y.-G.; Park, C.-Y.; Song, K.-H.; Kim, S.-S.; Oh, S.-G. *J. Ind. Eng. Chem.* **2012**, *18*, 744.
- (a) Choi, S.-S.; Kim, J.-C. *J. Ind. Eng. Chem.* **2012**, *18*, 1166. (b) Hilonga, A.; Kim, J. K.; Sarawade, P. B.; Quang, D. V.; Shao, G. N.; Elineenma, G.; Kim, H. T. *J. Ind. Eng. Chem.* **2012**, *18*, 1841.
- Sabzi, M.; Mirabedini, S. M.; Zohuriaan-Mehr, J.; Atai, M. *Prog. Org. Coat.* **2009**, *65*, 222.
- Wu, Z.; Xiang, H.; Kim, T.; Chun, M-C.; Lee, K. *J. Colloid. Interface Sci.* **2006**, *304*, 119.
- Lee, Y.-G.; Park, J.-H.; Oh, C.; Oh, S.-G.; Kim, Y. C. *Langmuir* **2007**, *23*, 10875.
- Matsoukas, T.; Gulari, E. *J. Colloid Interface Sci.* **1989**, *132*, 13.
- Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.
- Chen, G.; Zhou, S.; Gu, G.; Yang, H.; Wu, L. *J. Colloid Interface Sci.* **2005**, *281*, 339.
- Rouquerol, J.; Avnir, D.; Fairbridge, C. W.; Everett, D. H.; Haynes,

- J. H.; Pernicone, N.; Ramsay, J. D. F.; Sing, K. S. W.; Unger, K. K. *Pure Appl. Chem.* **1994**, *66*, 1739.
24. Pu, H.; Zhang, X.; Yuan, J.; Yang, Z. *J. Colloid Interface Sci.* **2009**, *331*, 389.
25. Thomassen, L. C. J.; Aerts, A.; Rabolli, V.; Lison, D.; Gonzalez, L.; Kirsch-Volders, M.; Napierska, D.; Hoet, P. H.; Kirschhock, C. E. A.; Martens, J. A. *Langmuir* **2009**, *26*, 328.
26. Kim, S. H.; Han, O. H.; Kim, J. K.; Lee, K. H. *Bull. Korean Chem. Soc.* **2011**, *32*, 3644.
27. van Blaaderen, A.; Vrij, A. *J. Colloid Interface Sci.* **1993**, *156*, 1.
28. Kao, H.-M.; Liao, C.-H.; Hung, T.-T.; Pan, Y.-C.; Chiang, A. S. T. *Chem. Mater.* **2008**, *20*, 2412.
29. Wang, M.; Chen, C.; Ma, J.; Xu, J. *J. Mater. Chem.* **2011**, *21*, 6962.
30. Maciel, G. E. *J. Am. Chem. Soc.* **1996**, *118*, 401.
31. Sankaraiah, S.; Lee, J. M.; Kim, J. H.; Choi, S. W. *Macromolecules* **2008**, *41*, 6195.