

# Surface properties of submicrometer silica spheres modified with aminopropyltriethoxysilane and phenyltriethoxysilane

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## Abstract

The surface of submicrometer silica spheres are modified with aminopropyl and phenyl groups through a one-step process. Various experimental techniques, i.e., scanning electron microscopy (SEM), quasi-elastic light scattering (QELS), differential scanning calorimetry (DSC), thermogravimetry (TG), zeta potential measurement, nitrogen sorption, and water vapor and organic dye adsorption are used to comprehensively characterize the pure (TEOS particles) and modified silica particles. The SEM micrographs of the particles demonstrate that the modified particles are spherical with uniform size and shape. The particles modified with aminopropyl groups (APTES particles) show the highest isoelectric point (IEP) and the highest weight loss at 780 °C because of the basic nature of aminopropyl groups and the higher reactivity of aminopropyltriethoxysilane. The particles modified with the phenyl groups (PhTES particles) show the lowest water vapor adsorption because their surface is more hydrophobic than that of TEOS and APTES particles. The organic dye (brilliant blue FCF or BBF) adsorption experiments demonstrate that the adsorption capacity of the particles increases greatly after acidification. This is caused by the protonation of silanol groups and amine groups on the particle surface, which presents an enhanced electrostatic attraction with BBF anions. The APTES particles exhibit the highest dye adsorption due to the hydrophobic attractions and the enhanced electrostatic attractions from aminopropyl groups.

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## 1. Introduction

Silica particles with uniform size and shape have applications in numerous areas including composite materials, photonics, thermal insulators, sensors, catalysts, adsorbents, pigments, detergents, cosmetics, pharmaceuticals, medical diagnostics, and immunoassays [1–4]. The functionalization of the silica particle surface can be used to enhance and/or control the overall properties of the particles for the desired applications. Nature of the functional groups on the particle surface usually plays a critical role in the surface properties of particles such as hydrophobicity and chemical reactivity [5].

Two protocols have been made available throughout the literature for the fabrication of the surface-modified spherical silica particles: (i) silanation of pure silica spheres with silane-coupling agents by refluxing in toluene (two-step method) [6]; (ii) preparation of organic/inorganic hybrid particles using organosilane precursors (one-step method) [3,7–10]. In the first method, water should be thoroughly removed before the surface modification step during which a poisonous solvent, i.e., toluene, is used. In the second method, it is not easy to control the particle size and shape and relatively large amount of organosilanes are needed. Since organosilanes are generally expensive, commercial and technological applications of the second method are limited.

In many applications of the surface-modified silica spheres, it is very important to control the monodispersity of particles

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[12–14]. In the preparation of photonic crystals, for instance, the monodispersity of the surface-modified particles is critical for a good assembly [11]. Although there have been many reports about the preparation of surface-modified silica particles, preparation of the particles with uniform shape, narrow size distribution, and different surface properties still remains to be a challenge. In addition, the effect of functional groups on the surface properties of the particles is not clearly understood. In this paper, a modified one-step process similar to that of Wang et al. [12,14] is used to prepare silica particles modified with aminopropyl and phenyl groups. Various experimental techniques are used to investigate the surface properties of the modified particles with an emphasis on the adsorption behaviors.

## 2. Experimental

### 2.1. Materials

Tetraethoxysilane (TEOS) and aminopropyltriethoxysilane (APTES) were obtained from Aldrich. Phenyltriethoxysilane (PhTES) was obtained from Gelest. Absolute ethanol and ammonia solution (28 wt% ammonia) were obtained from Duksan, Korea. All chemicals were used as received without further purification.

### 2.2. Preparation of the particles

Monodisperse silica spheres were prepared by the modified Stöber process [15]. Typical preparation is to rapidly mix two solutions at room temperature. The first solution was the mixture of 2.79 ml TEOS and 22.2 ml EtOH, and the second solution was the mixture of 0.638 ml 28 wt% ammonia, 6.8 ml deionized water, and 17.6 ml EtOH. Under stirring the first solution was added to the second solution, so the total volume of the solution was about 50 ml. The final composition was 0.25 M TEOS, 0.188 M NH<sub>3</sub>, 8 M H<sub>2</sub>O, and 13.6 M EtOH. A modified procedure from Wang et al. [12,14] without using any chloroform was then used to modify the particle surface. After 3.5 h of reaction,  $4.79 \times 10^{-4}$  mol of APTES or PhTES was injected into the stirred solution, and the reaction was allowed to continue for additional 19 h with stirring. For the preparation of pure silica spheres, the total reaction time was 22.5 h without addition of organosilane precursor.

The particles were then separated by centrifugation, washed with ethanol, and then with deionized water. Sonication was used to redisperse the particles in the desired solvents, and centrifugation was used for solid–liquid separation. The isolated particles were easily redispersed by sonication once transferred into water, and used for QELS and zeta potential measurement. For thermoanalyses, N<sub>2</sub> sorption, and water vapor and dye adsorption experiments, particles were dried at 25 °C for three days.

### 2.3. Characterization of the particles

Scanning electron microscopy (SEM) of the particles was carried out using a JEOL 6300 SEM instrument. The sample

was prepared by dispensing drops of an aqueous suspension of particles onto a glass plate. This was allowed to dry at room temperature and was then coated with a thin Pt film.

A Nano ZS Zetasizer (Malvern Instruments Ltd.) was used to determine the particle size and zeta potential of the particles. Aqueous suspensions with  $1.0 \times 10^{-3}$  M KCl at different pH were used for zeta potential determination, and the relationship between zeta potential and pH was used to determine the IEP of the particles.

Thermoanalyses of the dried particles were conducted on a TA 5200 apparatus in N<sub>2</sub> with a heating rate of 10 °C min<sup>-1</sup>. The adsorption/desorption isotherms of nitrogen at 77 K were measured with a Micromeritics ASAP 2020 apparatus. Prior to the measurements, the particles were degassed for 2 h at 120 °C. The specific surface area was calculated from the BET equation.

### 2.4. Water vapor and organic dye adsorption

A material adsorbing a smaller amount of water vapor is known to be more hydrophobic [16]. Thus, in this study, water vapor adsorption was used as one of the method to compare the hydrophobicity of the particles. After drying at 80 °C to a constant weight, the particles were allowed to adsorb water vapor in a closed container containing liquid water at 25 °C for 85 h. During experiments, it was ensured that the particles were not in direct contact with the liquid water. The amount of water vapor adsorbed was estimated by weighing the particles before and after water vapor adsorption and expressed in the mass of water vapor adsorbed per unit area of particles (mg m<sup>-2</sup>).

For the dye adsorption experiments, brilliant blue FCF (BBF, Junsei Chemical Co., Ltd.) was used as an adsorbate. BBF is classified as a triphenylmethane dye with a CI number of 42090. The dried particles were used for the adsorption experiments. For the acidification of the particles, 0.1 g of the particles was mixed with 10 ml 1 M HCl solution. After acidification for one day, particles were separated by centrifugation, and then thoroughly washed with deionized water. In the adsorption experiments, 0.1 g of the dried particles were mixed with 10 ml aqueous solution containing 3.08 μM BBF and 0.001 M HCl. After three days, the mixture was separated by centrifugation. The concentration of BBF in the supernatant was determined by a T6 UV–visible spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China) at 630 nm. The amount of BBF adsorbed onto the particles (nmol m<sup>-2</sup>) was calculated by the following relationship:

$$q = \frac{V(C_0 - C)}{mS}, \quad (1)$$

where  $C_0$  and  $C$  are the initial and the residual BBF concentration in solution (nmol l<sup>-1</sup>),  $V$  the solution volume (l),  $m$  the particle mass (g), and  $S$  the determined BET surface area of the particles (m<sup>2</sup> g<sup>-1</sup>), respectively.

### 3. Results and discussion

#### 3.1. Preparation of the modified particles

If pure organosilanes were used, it was difficult to obtain particles with uniform size and shape, and in some cases no particles were formed. Although it was possible to prepare organic/inorganic hybrid particles using the mixture of TEOS and organosilane, the shape and size of the particles were not easy to control. Thus, we first prepared silica particles with uniform size and shape using TEOS. After 3.5 h of reaction, APTES or PhTES was added into the reaction mixture for surface mod-

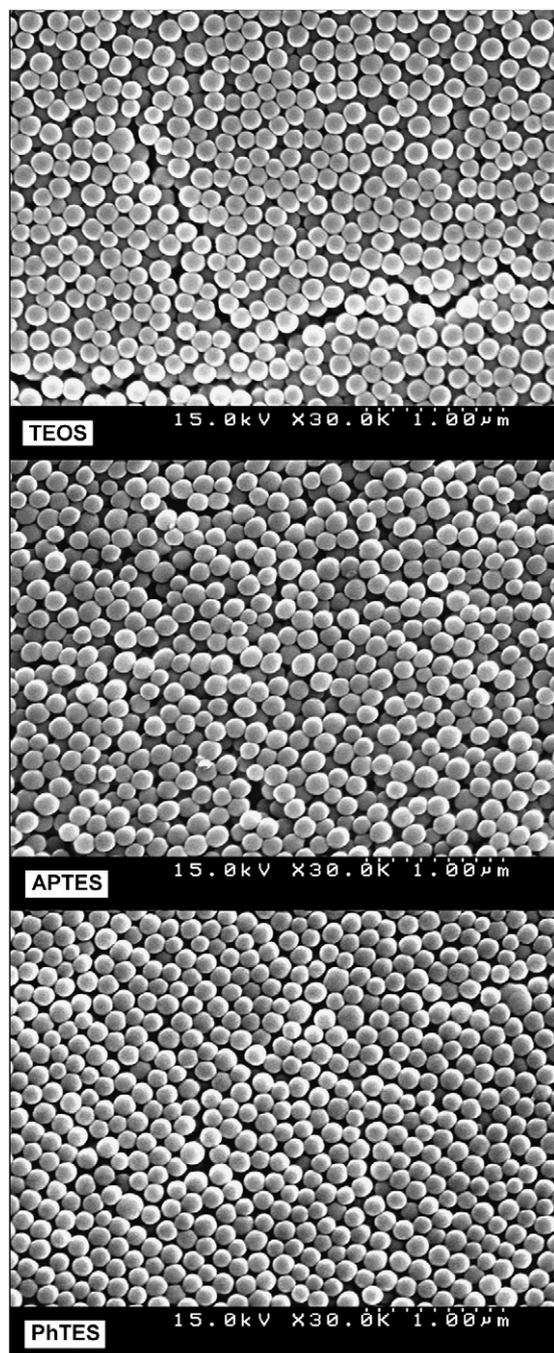


Fig. 1. SEM micrographs of the particles.

ification. The ethoxy groups of the organosilane were readily hydrolyzed and reacted with silanol groups on the silica particle surface. The size of the modified particles could be easily controlled by using “mother” pure silica particles of different size. Using this method, it is easy to prepare uniform particles with different size and surface properties.

#### 3.2. Particle shape and size

SEM micrographs of the prepared particles are shown in Fig. 1, which demonstrates that the modified particles are spherical with uniform size and shape. The final particle size determined by both QELS and SEM is compared in Table 1. The QELS method always gives larger size than SEM method as reported by Costa et al. [17]. Before the addition of the organosilane, the size of the silica particles was 132 nm from QELS. It is clear that the size of both pure silica particles (without further addition of organosilane) and the modified particles increased.

#### 3.3. Thermoanalyses and surface area measurement

DSC thermograms and TG curves of the particles are given in Figs. 2 and 3, respectively. The total weight loss of the particles at 180 and 780 °C is also listed in Table 2. All the particles have the DSC and TG curves of the same shape. The weight loss below 180 °C is due to ethanol and water evaporation, corresponding to an endothermic DSC peak around 115 °C. A further weight decrease between 180 and 780 °C is related to organic group decomposition and silanol group condensation (dehydroxylation), which corresponds to a weak and broad

Table 1  
Average particle size determined by QELS and SEM

Particle type <sup>a</sup>	Average size (nm)	
	QELS	SEM
TEOS	164	149
APTES	171	150
PhTES	167	135

<sup>a</sup> TEOS stands for the unmodified particles. The other symbols stand for the particles modified with the corresponding organosilanes.

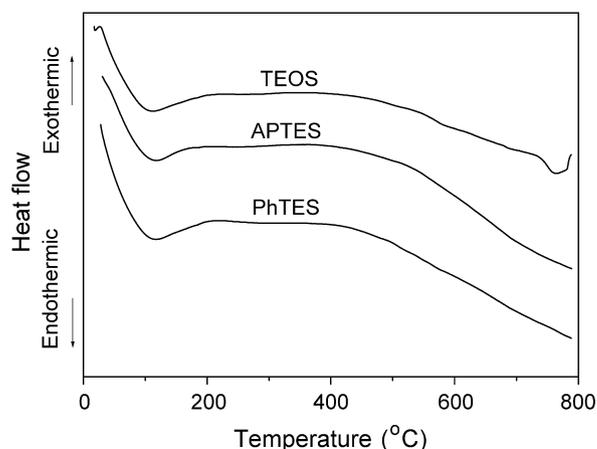


Fig. 2. DSC thermograms of the particles. The curves have been shifted in the vertical direction to make them distinguishable.

exothermic DSC peak around 200–500 °C. Although there is no obvious difference in the weight loss at 180 °C, at 780 °C the APTES particles exhibit a higher weight loss than TEOS and PhTES particles. Since aminopropyltriethoxysilane can act as a base catalyst in the surface modification reaction, it is possible that the extent of surface modification reaction is higher, resulting in a higher weight loss at 780 °C from the decomposition of aminopropyl groups.

Nitrogen adsorption/desorption isotherms of the particles are shown in Fig. 4. All the particles show isotherms of type II, typical of nonporous solids, with type H1 hysteresis loops that are often obtained with materials consisting of agglomerates or compacts of approximately uniform spheres [18]. The calculated and determined BET surface areas of the particles are compared in Table 2. Assuming nonporous particles, the spe-

cific surface area ( $\text{m}^2 \text{g}^{-1}$ ) of the particles can be calculated based on the SEM particle size by the following equation:

$$S_{\text{cal}} = \frac{6000}{\rho d}, \quad (2)$$

where  $d$  is the average particle diameter (nm) from SEM images, and  $\rho$  is the density of the particles, which was taken as  $2.08 \text{ g cm}^{-3}$  [19]. Although the BET surface areas are larger than the calculated values, these values are on the same magnitude, suggesting virtually nonporous nature of the particles. Hybrid particles prepared from tetraethoxysilane and vinyltriethoxysilane were also found to be nonporous [9].

### 3.4. Isoelectric point and water vapor adsorption

Fig. 5 shows the change in zeta potential of the particles with pH, from which the isoelectric point (IEP) was determined (Table 2). For the APTES particles, the effect of basic amine groups on the surface is reflected in the high zeta potential values, which also causes a considerable shift of IEP to higher pH value.

Water vapor adsorption of the particles is compared in Table 2. The PhTES particles show the lowest water vapor adsorption because of the hydrophobic nature of phenyl groups on the surface while APTES particles show the highest adsorption due to the amine groups, which can form hydrogen bonds with water molecules. Comparison of the water vapor adsorption results confirms a successful surface modification because the modified particles exhibit different surface hydrophobicity.

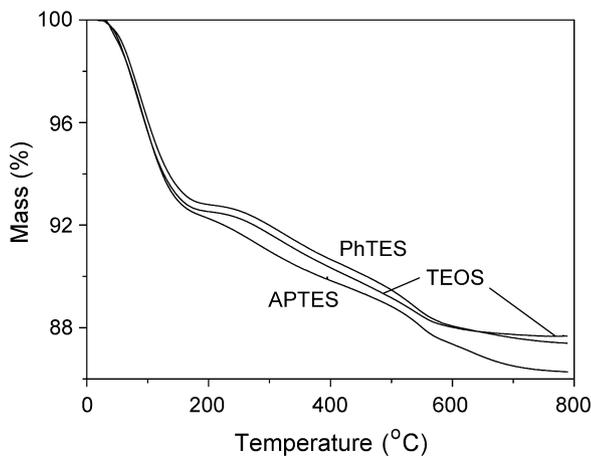


Fig. 3. TG curves of the particles.

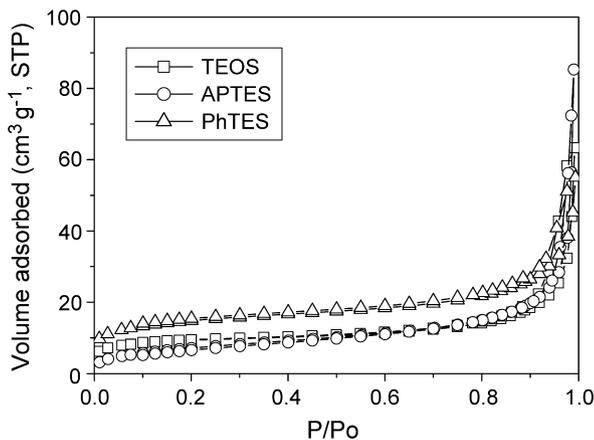


Fig. 4. N<sub>2</sub> adsorption/desorption isotherms of the particles.

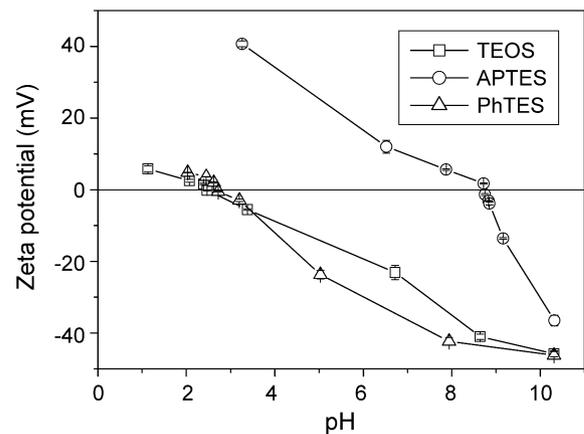


Fig. 5. The relationship between zeta potential and pH.

Table 2  
Comparison of weight loss, surface area, IEP, and water vapor adsorption of the particles

Particle type	Weight loss (%)		Surface area ( $\text{m}^2 \text{g}^{-1}$ )		IEP	Water vapor adsorption ( $\text{mg m}^{-2}$ )
	At 180 °C	At 780 °C	Determined	Calculated		
TEOS	7.4	12.3	32.7	19.4	2.45	11.4
APTES	7.6	13.7	26.4	19.2	8.73	13.8
PhTES	7.1	12.6	52.3	21.4	2.70	6.06

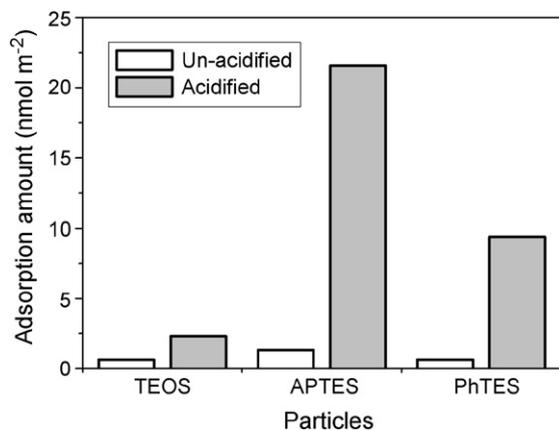


Fig. 6. Comparison of BBF adsorption by the particles.

### 3.5. Organic dye adsorption

To further compare the surface properties of the particles, two sets of organic dye (BBF) adsorption experiments were carried out. In the first set, the dried particles without acidification were used and the adsorption experiment was carried out once. In the second set of experiments, the particles after acidification were used. Since the adsorption capacity of the particles increased greatly after acidification, the adsorption experiment was carried out twice for the acidified particles. The results of dye adsorption experiments are compared in Fig. 6. The difference in the adsorption capacity of the particles is caused mainly by the interactions between BBF and the particle surface. The possible interactions between BBF and the surface of the acidified particles are schematically demonstrated in Fig. 7. There can be three types of interactions: (1) hydrogen bonding (not shown in Fig. 7); (2) electrostatic interaction; (3) hydrophobic interaction [20–26]. These interactions belong to noncovalent interactions, which have been reported to play an important role in molecular recognition [27]. Noncovalent interactions are known to act at distances of several angstroms or even tens of angstroms.

Even after surface modification the particles still have silanol groups on their surfaces. These silanol groups can form hydrogen bonds with sulfonate groups of BBF. These hydrogen bonds should help the adsorption of BBF.

The surface of pure silica becomes hydrated in an aqueous medium. A high degree of surface hydration leads to the formation of water layers at the interface. The thickness of this layer may reach 20 or more statistical monolayers, which may influence the rheological properties of concentrated suspensions [28]. In aqueous solutions, surface silanol groups and amine groups can be protonated or deprotonated depending on the solution pH, which results in the corresponding changes of the surface charge. At low pH (~3 in this study), for instance, the particles are protonated, i.e., positively charged.

The BBF has sulfonate groups that can dissociate in aqueous solution. The dye molecule appears as a monovalent or divalent anion or in neutral form depending on the pH. Thus, we may expect that in weakly acidic solutions there exist electrostatic attractions between the positively-charged surface and the BBF anions, promoting the BBF adsorption. Since the surface

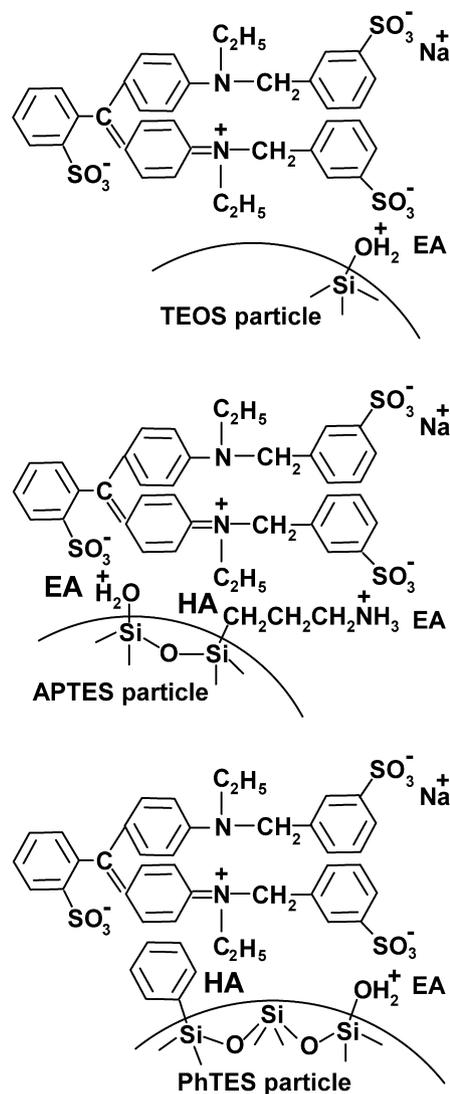


Fig. 7. Schematic diagrams for the adsorption of BBF by the acidified particles. EA represents electrostatic attraction; HA represents hydrophobic attraction.

silanol groups and amine groups are not fully protonated for unacidified particles, there exists a relatively weak electrostatic attraction between the particles and BBF anions, presenting a moderate adsorption capacity. After acidification, however, the surface silanol and amine groups are fully protonated and there exists a strong electrostatic attraction. This should promote the adsorption greatly, so the APTES particles show the highest adsorption capacity.

It has been demonstrated that the adsorption capacity of some organic dyes on hybrid gels is much higher than that on pure silica gels [21,23,25], suggesting that hydrophobic interactions between the surface organic groups of the hybrid gels and the organic dyes play an important role in adsorption. For the adsorption of BBF by the modified particles, there exists a hydrophobic attraction between BBF and the organic groups on the particles as demonstrated in Fig. 7. We may expect that hydrophobic attractions also play an important role in the adsorption of BBF by the modified particles, since the modified particles have a higher adsorption capacity than the pure silica particles. For the controlled release of dyes and drugs from

hybrid gels, hydrophobic attractions were also found to play an important role [29–31]. The hydrophobic attraction and the enhanced electrostatic attraction due to aminopropyl groups appear to be responsible for the highest adsorption capacity of APTES particles.

#### 4. Summary

Submicrometer silica spheres modified with aminopropyl and phenyl groups were prepared through a one-step process. A series of experimental techniques were used to characterize the modified particles comprehensively. The modified particles exhibited characteristic changes in the surface properties, especially IEP, water vapor and organic dye adsorption. The particles modified with aminopropyl groups showed the highest isoelectric point (IEP), weight loss at 780 °C, and water vapor and dye adsorption capacity. Acidification of particles greatly enhanced the organic dye adsorption because the protonation of the surface silanol and amine groups resulted in a strong electrostatic attraction between dye anions and the positively charged particle surface.

The method used in this study is a convenient and economical method to prepare uniform silica spheres with different surface properties. The knowledge gained from this study will be useful in the design of silica spheres with tailored size and surface properties.

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#### References

- [1] K. Nozawa, H. Gailhanou, L. Raison, P. Panizza, H. Ushiki, E. Sellier, J.P. Delville, M.H. Delville, *Langmuir* 21 (2005) 1516.
- [2] S.-Y. Kim, E. Kim, S.-S. Kim, W. Kim, *J. Colloid Interface Sci.* 292 (2005) 93.
- [3] C.R. Miller, R. Vogel, P.P.T. Surawski, K.S. Jack, S.R. Corrie, M. Trau, *Langmuir* 21 (2005) 9733.
- [4] M. Marquez, B.P. Grady, I. Robb, *Colloids Surf. A* 266 (2005) 18.
- [5] A. Arkhireeva, J.N. Hay, W. Oware, *J. Non-Cryst. Solids* 351 (2005) 1688.
- [6] A.G. Howard, N.H. Khdary, *Analyst* 130 (2005) 1432.
- [7] A. Arkhireeva, J.N. Hay, J.M. Lane, M. Manzano, H. Masters, W. Oware, S.J. Shaw, *J. Sol–Gel Sci. Technol.* 31 (2004) 31.
- [8] P.M. Chevalier, D.L. Ou, *J. Sol–Gel Sci. Technol.* 26 (2003) 597.
- [9] Y.S. Li, B. Li, N.Y. Han, B.J. Xu, *J. Chromatogr. A* 1021 (2003) 183.
- [10] J.Y. Choi, C.H. Kim, D.K. Kim, *J. Am. Ceram. Soc.* 81 (1998) 1184.
- [11] S. Wong, V. Kitaev, G.A. Ozin, *J. Am. Chem. Soc.* 125 (2003) 15589.
- [12] W. Wang, B. Gu, L. Liang, W.A. Hamilton, *J. Phys. Chem. B* 107 (2003) 12113.
- [13] W. Wang, B. Gu, L. Liang, W.A. Hamilton, *J. Phys. Chem. B* 107 (2003) 3400.
- [14] W. Wang, B. Gu, *J. Phys. Chem. B* 109 (2005) 22175.
- [15] W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.* 26 (1968) 62.
- [16] X.S. Zhao, G.Q. Lu, X. Hu, *Microporous Mesoporous Mater.* 41 (2000) 37.
- [17] C.A.R. Costa, C.A.P. Leite, F. Galembeck, *J. Phys. Chem. B* 107 (2003) 4747.
- [18] K.M.S. Khalil, A.A. Elsamahy, M.S. Elanany, *J. Colloid Interface Sci.* 249 (2002) 359.
- [19] M. Kobayashi, M. Skarba, P. Galletto, D. Cakara, M. Borkovec, *J. Colloid Interface Sci.* 292 (2005) 139.
- [20] Z. Wu, I.-S. Ahn, Y. Lin, L. Huang, X. Lan, K. Lee, *Compos. Interfaces* 11 (2004) 205.
- [21] Z. Wu, I.-S. Ahn, C.-H. Lee, J.-H. Kim, Y.G. Shul, K. Lee, *Colloids Surf. A* 240 (2004) 157.
- [22] Z. Wu, J. Wu, H. Xiang, M.-S. Chun, K. Lee, *Colloids Surf. A* 279 (2006) 167.
- [23] Z. Wu, H. Joo, I.-S. Ahn, S. Haam, J.-H. Kim, K. Lee, *Chem. Eng. J.* 102 (2004) 277.
- [24] Z. Wu, H. Joo, K. Lee, *Chem. Eng. J.* 112 (2005) 227.
- [25] Z. Wu, K. Lee, *Chem. Res. Chin. Univ.* 20 (2004) 185.
- [26] L. You, Z. Wu, T. Kim, K. Lee, *J. Colloid Interface Sci.* 300 (2006) 526.
- [27] K. Muller-Dethlefs, P. Hobza, *Chem. Rev.* 100 (2000) 143.
- [28] V.V. Turov, I.F. Mironyuk, *Colloids Surf. A* 134 (1998) 257.
- [29] Z. Wu, H. Joo, I.-S. Ahn, J.-H. Kim, C.-K. Kim, K. Lee, *J. Non-Cryst. Solids* 342 (2004) 46.
- [30] Y. Jiang, Z. Wu, L. You, H. Xiang, *Colloids Surf. B* 49 (2006) 55.
- [31] Z. Wu, H. Joo, T.G. Lee, K. Lee, *J. Controlled Release* 104 (2005) 497.