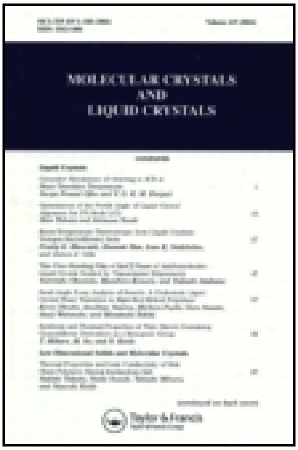

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Surface Functionalization of Silica Particles with Phthalocyanine

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Surface Functionalization of Silica Particles with Phthalocyanine

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Phthalocyanine moieties have been introduced onto mesoporous sphere-shaped silica particles prepared by the controlled hydrolysis of tetraethyl orthosilicate followed by surface modification with 3-aminopropylsilane by sol–gel process. Particles from sol–gel process were of size ranging from 190 to 500 nm. The surface modification reaction with amino groups was accomplished with a content of 1.2 mmol/g. Salt linkage was successfully formed between amino group on the silica surface and sulfonate group in phthalocyanine moieties by investigation of energy dispersive spectroscopy.

Keywords: functionalized silica spheres; phthalocyanine; surface modification

1. INTRODUCTION

Aminotrialkoxysilanes have received a great deal of attention in the fields of industry not only as coupling agents but surface modification in sol–gel system [1–3]. These materials are studied as the starting compounds or intermediates for a new way of preparing hybrid compounds with applications in sensors and electronics due to robust backbone with silane network structure [4–6].

Sol–gel reaction of organoalkoxysilane is represented by following equations.

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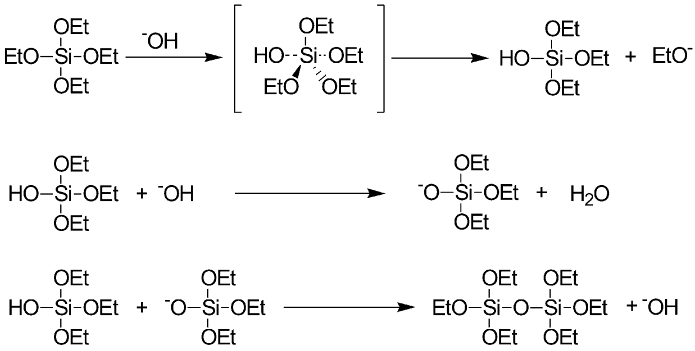


Sol–gel method is widely applied to prepare oxide particles with various properties such as large-pore gel spheres and small particles with high density. Though the technical conditions for obtaining uniform silica particles were found, a general agreement on the processes responsible for the particle formation and growth, final monodispersity, particle size and shape has not yet emerged [7,8].

Surface modification of silica particle with aminoalkylsilane is known as convenient and simple method for functionalization of silica particles [9,10]. Because of its basicity and nucleophilicity of amino groups organosilane compounds are attractive as coupling agents for sol–gel chemistry. The amino group, however, may act as a basic catalyst for the sol–gel polymerization of alkoxysilanes and may perturb the sol–gel process. Silica particles are particularly suitable for the realization of sensors as they are photochemically and photophysically inert.

We, herein, are reporting the first example of optical material obtained by surface functionalization with phthalocyanine of silica particle. To attain this goal, we prepared silica particles which have amino-modified surfaces. Copper phthalocyanine was incorporated onto the surface via salt linkage formation. Preparation methods and amino group functionalization of silica particles with sphere shape as well as phthalocyanine modification will be discussed in detail.

2. EXPERIMENTAL

2.1. Synthesis of Silica Particle Using Tetraethyl Orthosilicate (TEOS)

A 1 L glass resin kettle was charged with 115 mL of methanol and 85 mL of ammonium hydroxide as a reaction medium and catalyst,

TABLE 1 Reaction Conditions and Mean Particle Sizes of Silica Particles

Particle no.	TEOS in feed (mL/MeOH mL)	Mean particle size (standard deviation) (nm)
1	40/400	390 (60)
2	21.5/418.5	350 (50)
3	14/426	190 (30)
4	20/200 (20/200[a])	470 (60)

[a] APS in feed (mL/MeOH mL).

respectively. Appropriate amount of TEOS in methanol solution was added into the kettle dropwise (Table 1). The reaction was carried out for 3 hr at room temperature with stirring speed of 500 rpm. After the reaction, the particles obtained were isolated by ultracentrifugation and the supernatant solution was discarded. The particles were washed with deionized water several times to remove residual catalyst. The product particles were air-dried and dried *in vacuo* at 100°C for 2 days.

2.2. Amine Functionalization onto Silica Surface

1 g of silica particles were mixed with 120 mL of a 5 vol% of 3-aminopropyltriethoxy silane (APS) in toluene. The reaction mixture was stirred for 24 hr at room temperature. After the surface modification, the silica was centrifuged and washed with toluene and ethanol several times. The washed powder were air-dried and then vacuum-dried at 100°C for 2 days.

2.3. Preparation of Silica Particle Covered with TEOS and APS Mixture

115 mL of methanol as a reaction medium and 85 mL of ammonium hydroxide as a catalyst were put into 1 L glass resin kettle followed by dropwise addition of TEOS in methanol (TEOS 20 mL and MeOH 200 mL). Then APS in methanol (APS 20 ml and MeOH 200 mL) was added dropwise. The reaction was carried out for 3 hr at room temperature. The resulting particles were separated by centrifugation and the supernatant was discarded. The collected particles were washed with deionized water several times to remove residual catalysts. The washed powder were air-dried and then vacuum-dried at 100°C for 2 days.

2.4. Copper-Phthalocyanine onto the Surface of Silica Particle

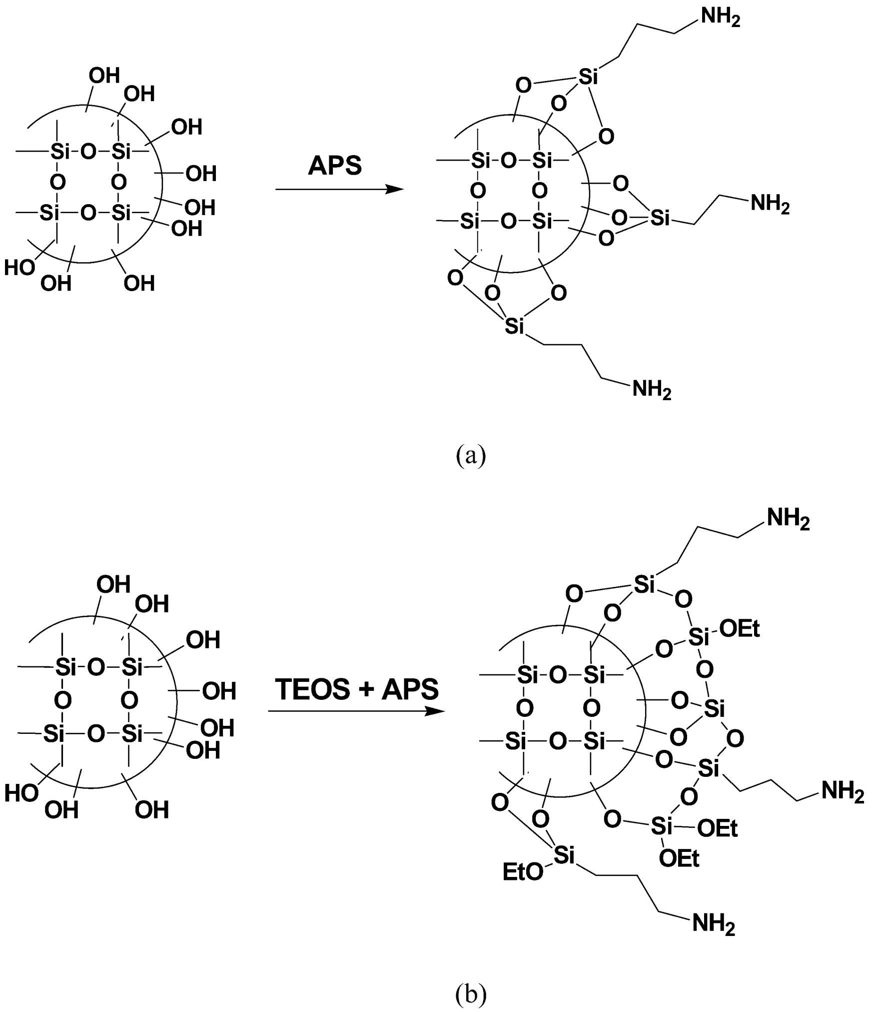
0.5 g of silica particle that have amino groups in surface was dispersed in deionized water. 0.5 mL of HCl was dropped into this dispersed solution and stirred for 10 min. Then the solution of $CuPc(SO_3^-Na^+)_4$ (copper(II) phthalocyanine tetrasulfonic acid, tetrasodium salt) in deionized water was added dropwise into dispersed solution and stirred for 12 h at room temperature. The particles were separated by centrifugation and washed with deionized water until supernatant was colorless. Then the particle was vacuum-dried at 80°C for 2 days.

2.5. Characterization

Scanning electron microscope (SEM, Topcon SM-500) was used to investigate the shape of particles at an accelerating voltage of 20 kV after gold coating. Thermogravimetric analysis (TGA) was performed with a Perkin Elmer TGA 7 equipped with a TGA 7/3 instrument controller at a heating rate of 20°C/min under nitrogen. IR spectra were taken with a Magna IR 560 Fourier transform infrared (FT-IR) spectrometer. Particle size and its distribution were measured with image analysis software program Scope Eye (TDI Package) based on SEM photographs. The content of amino group of the silica particles was determined by consumption of HCl [11]. In a typical procedure, into a 100 mL flask, 0.1 g silica particle and 20 mL of 0.144 mol/L aqueous HCl solution were charged, and the mixture was stirred at room temperature for 24 hr and centrifuged. Then the filtrate was back-titrated with aqueous NaOH by using phenolphthalein as an indicator. Then the amount of terminal amino groups per 1.0 g silica particle was calculated.

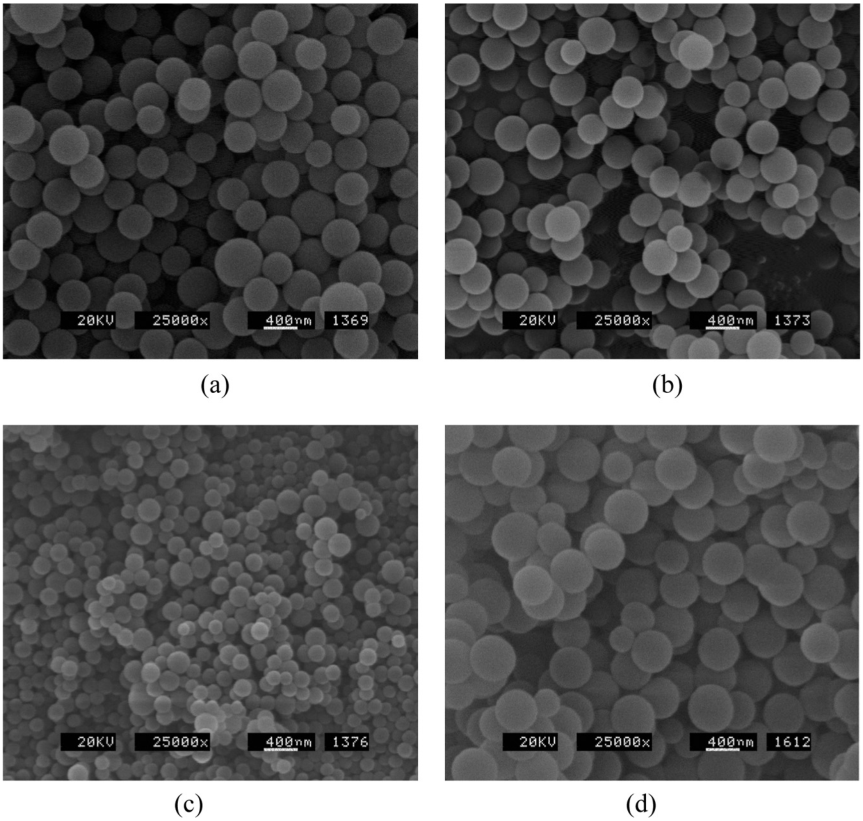
3. RESULTS AND DISCUSSION

Physical and chemical structures of silica surfaces are of considerable difference each other according to their preparation methods [12]. They can be crystalline, as in crystalline quartz, or amorphous, as in fused silica. They can be hydrophobic if prepared when the surface structures are mainly composed of siloxane Si–O–Si groups, while they can be hydrophilic when the surface structures have silanol Si–OH groups. Hydrophobic silica can be made into hydrophilic by hydroxylation the siloxane groups into silanol groups. When silica is exposed to water for an extended time, its hydroxylation occurs to produce polymeric chains of $Si(OH)_2-O-Si(OH)_2-OH$ groups, which can be linked up in many different ways to form a three-dimensional network or silica gel. The chemistry and chemical reactions of silica surfaces in aqueous solutions are generally considered within the above framework. Therefore mesoporous silica samples were prepared in the presence of alcohols resulting in completely amorphous silica xerogels where polymeric chains formed a three dimensional network with hydroxyl groups present at the surface.



SCHEME 1 Preparation of silica particles functionalized with amino groups (a) Method I: silica particles **1**, **2**, and **3**; (b) Method II: particle **4**.

The incorporation of terminal amino groups to silica to functionalize silica particle was achieved by the reaction with APS using two methods. One is related to the introduction of amino group by chemical modification of silica particle with APS as shown in Scheme 1(a) (Method I). Scheme 1(b) shows the surface functionalization using mixture of TEOS and APS due to the low reactivity of APS when used solely (Method II). However, according to titration for determination of amino group content in silica particles, 1.2 mmol/g of amino group was introduced into the particles regardless of preparation methods. The particle **4** from Method II was larger-sized than particles **1**, **2**, and **3** from Method I, of which reaction conditions and size are shown in Table 1. Figure 1 shows the SEM photograph of each particle with different reaction condition. Particles shown in



(a) (b)

(c) (d)

FIGURE 1 SEM photographs of silica particle **1** (a), **2** (b), **3** (c), and **4** (d).

Figure 1(a), (b), and (c) were prepared by Method I and particles in Figure 1(d) by Method II. Uniform and perfect sphere-type particles with no agglomeration were prepared according to hydrolysis and polycondensation reaction.

Incorporation of APS on silica network was confirmed by FT-IR and TGA. Compared to IR spectrum of silica particles, the APS-modified silica showed characteristic bands at 2955 cm^{-1} and 2880 cm^{-1} due to CH_2 absorption and 1640 cm^{-1} for amino band. This suggests that APS was successfully introduced onto the silica surface. Along with those characteristic bands of APS, OH bands around 3400 cm^{-1} was also observed because of the presence of Si–OH groups. TGA showed less than 10% weight loss for unmodified silica particle **1** at 800°C presumably due to loss of water, ethanol, and calcinations of remained ethoxy groups in the silica (Fig. 2(a)). After APS- surface modification of silica particle **1**, weight loss increased more than 5% resulted from the degradation of APS on the surface. After TGA, the sphere shape of silica particles remained the same with the initial shape which implies inherent thermal stability of silica materials.

Further functionalization of silica surface with copper-phthalocyanine was carried out via salt formation between sulfonate groups in phthalocyanine and ammonium groups in silica (Scheme 2). The presence of copper in the silica particle was mapped with EDS and is shown in Figure 3. It is thought that the phthalocyanines are uniformly distributed in the silica particles.

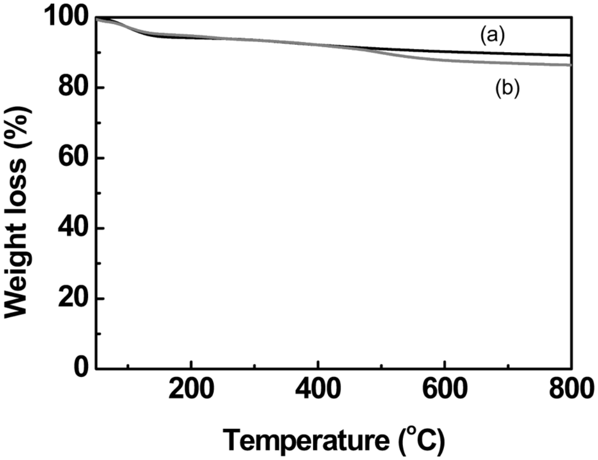
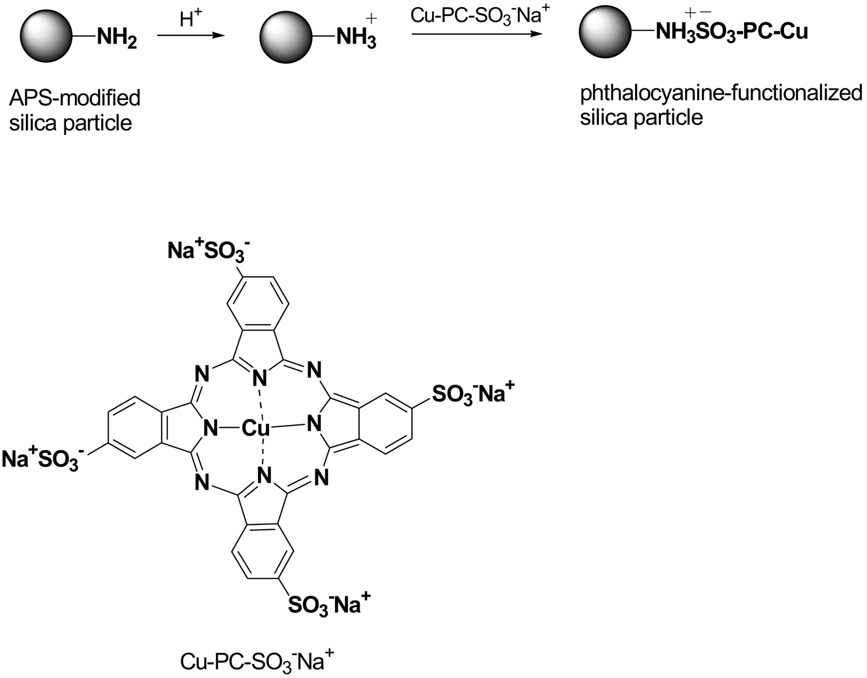


FIGURE 2 TGA thermogram of silica particle **1** (a), and amino-functionalized silica particle **1** (b).



SCHEME 2 Introduction of copper phthalocyanine onto the surface of amino-modified silica particle.

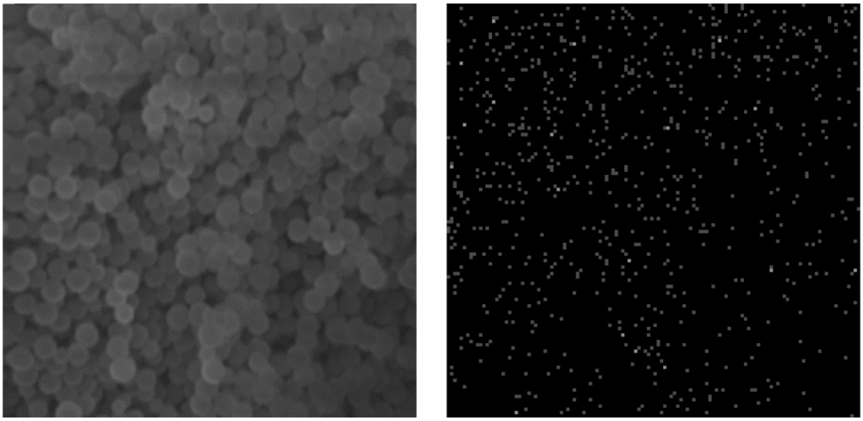


FIGURE 3 EDS mapping of sulfur element in silica particles.

4. CONCLUSION

Silica particle functionalized with amino group were prepared under a variety of reaction conditions to control particle size and amino group content. Sphere-shaped particles with various diameters ranging from 190 to 500 nm were obtained via hydrolysis and polycondensation reaction in the presence of base. Amino-functionalized silica particles will be used as an intermediate for sensory materials modification. Copper phthalocyanine was introduced to APS-modified silica particle to use as a sensory material for toxic gas, which is now under study.

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