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Sensor Application of Submicro-Sized Silica Particle Functionalized with Hydroxyphenylbenzoxazole

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Submicro-sized uniform silica particles were prepared by low-temperature sol–gel process using tetraethoxy silane (TEOS). The silica particle was sized about 560 nm and was homogeneously sphere-shaped. The surface of silica particle was functionalized with hydroxyphenylbenzoxazole for a response to phosphate-nerve gases such as Sarin, Soman, and Tubun. Fluorescence spectra of suspension of the functionalized silica particle were significantly changed by exposure to nerve gas model compound, which showed fluorescence quenching.

Keywords: benzoxazole; luminescence; sensors; silica spheres

INTRODUCTION

Functionalized silica have been attracted for their potential applications such as organic–inorganic hybrid, encapsulation of enzymes, catalytic antibodies, other proteins, sensors, organometallic catalysts and colloidal crystals due to their mild preparation condition [1–9]. Most popular and practical approach for preparing organic–inorganic hybrids is achieved by sol–gel reaction [10–13]. The sol–gel process with its abnormally mild processing characteristics can be used to prepare pure and well-controlled functional organic–inorganic hybrid materials. The process involves the hydrolysis of metal alkoxides,

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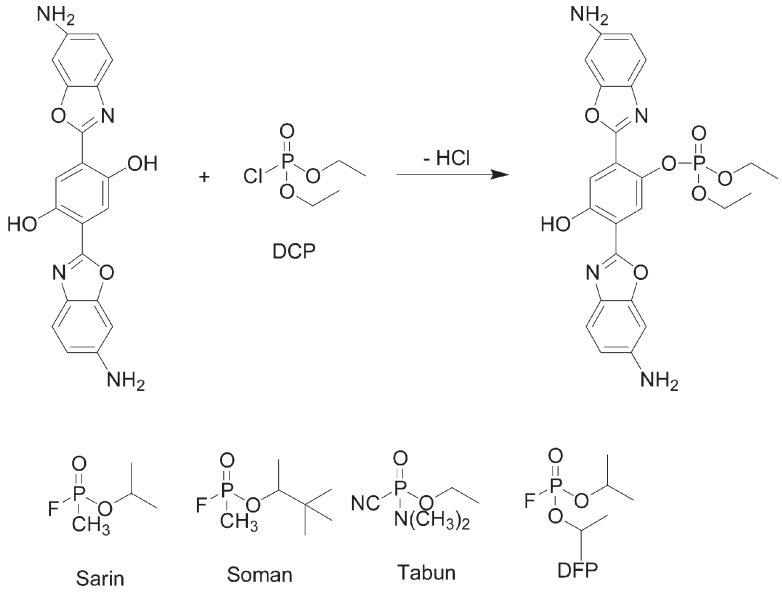
followed by a condensation reaction to produce metal oxides. Silicon alkoxide, e.g., TEOS and tetramethyl orthosilicate (TMOS), and the silica are the most widely used metal alkoxides.

Highly toxic volatile organophosphonate compound such as Sarin, Soman, and Tubun have rapid and fatal effects to mammalian life and are the basis of chemical weapons that are well known as nerve gas [14–17]. A leading principle in nerve gas sensing is connected to develop methods that respond to the general reactivity that provides the basis of their toxicity. The action mechanism of nerve agents is related to the reaction with a hydroxyl group to form a phosphate ester at the catalytic site of acetylcholinesterase. It is well-known that the hydroxyl groups can be easily reacted with phosphate group of nerve gases. We attempted to the hydroxyl groups in hydroxyphenylbenzoxazole as a probe group for nerve gases and expected the optical property change of hydroxyphenylbenzoxazole in terms of UV and fluorescence spectroscopy (Scheme 1). Compared to nerve gas compounds, compounds such as diisopropylfluorophosphate (DFP) and diethylchlorophosphate (DCP) have similar reactivity, but they have weaker efficacy than typical nerve agents. Therefore, they are good model compounds for the design of detector.



SCHEME 1 Reaction with nerve gas sensing and nerve gas moiety.

In this study, 2,5-bis(5-aminobenzoxazol-2-yl)benzene-1,4-diol was synthesized for surface functionalization of silica particle, which was expected as a hybrid material for sensing derivative of nerve gases. The hydroxyphenylbenzoxazole was introduced on the surface of silica particles successfully and the organic–inorganic hybrid materials have the ability of detecting model compound of nerve gas in fluorescence spectroscopy.

EXPERIMENTAL

Reagents and Measurements

TEOS were purchased from Samchen Chemical and ammonium hydroxide was used as catalyst for the sol–gel reaction. 2,4-Diaminophenol dihydrochloride and 2,5-dihydroxyterephthalic acid were purchased from Acros and Aldrich, respectively. Toluene 2,4-diisocyanate (TDI) and DCP were obtained from Junsei and Aldrich, respectively. Polyphosphoric acid (PPA), DMF, and toluene were used without further purification.

UV-Visible spectra were recorded on a Perkin Elmer Lambda 35 spectrometer. Steady-state fluorescence measurement was carried out using a Perkin Elmer LS 45 spectrofluorimeter. The photographs of scanning electron microscopy were taken using Topcon SM-500.

Preparation of Silica Particles

Submicro-sized uniformed silica particle were synthesized by low-temperature sol–gel process with TEOS. TEOS (20 ml) was added into ethanol (200 ml) solution mixed with distilled water (10 ml) and ammonium hydroxide (40 ml). The solution was stirred for 14 h at room temperature, and then the particles were separated by centrifugation. The silica particles were washed with ethanol and distilled water several times. After washing, silica particles were dried in vacuum oven at 100°C for 24 h, then were heated at 600°C for 5 h in a furnace.

Synthesis of 2,5-Bis(5-aminobenzoxazol-2-yl) benzene-1,4-diol 1

2,5-dihydroxyterephthalic acid (2.02 g, 10 mmol), P_2O_5 (8.51 g, 60 mmol) and 2,4-diaminophenol hydrochloride (5.03 g, 25 mmol) were added into 500 ml 3-neck round flask, then PPA (100 ml) was added into the flask. The mixture was heated to 130°C and stirred for 3 h under inert gas state, then the temperature was increased at 150°C.

After 16 h, the temperature was arrived at 180°C and stirred for 3 h, then the mixture was kept at 210°C for 48 h. It was cooled to room temperature and carried into the ice-water bath, then pH of solution was adjusted about 7 by adding sodium hydroxide. The precipitates were separated by centrifuge and dried in vacuum oven at 50°C for 12 h. The solid was vacuum-sublimed at 330°C and whitish yellow solid was washed by DMF, then was dried in vacuum oven at 50°C for 12 h.

Functionalization of Silica Particle

The silica particles (2 g) were dispersed in toluene (150 ml) in 250 ml 3-neck round flask. The dispersion was heated to 50°C, then triethylamine was added as catalyst. TDI was added into dispersion and the mixture was stirred for 5 h. Functionalized silica particles were separated by centrifugation and washed with toluene and ethanol and were vacuum dried at 70°C for 24 h.

Incorporation of 1 on the Surface of Silica Particle

Isocyanate-functionalized silica particles (0.8 g) were added into **1** solution in DMF at 250 ml 3-neck round flask. The mixture was heated to 45°C and stirred under inert gas state. After 4 h, silica particles were separated by centrifugation and washed with DMF until the washing solution became colorless, then the particle was vacuum dried at 80°C for 24 h.

RESULTS AND DISCUSSION

Submicro-sized silica particles were prepared by low-temperature sol–gel reaction. Average size of these particles was measured about 560 nm and the standard deviation is 20 nm and the particle was sphere-shaped (Fig. 1).

The isocyanate group was introduced on the surface of silica particle and confirmed with TGA analysis (Fig. 2(a)) and FT-IR spectroscopy (Fig. 2(b)). The weight of silica particle was not changed along the heating period, on the other hand, the weight of isocyanate-functionalized silica particle decreased about 7.6 wt% at around 320°C, but the weight was maintained above 320°C in TGA thermogram. The stretching hands of Si–O–Si bond, aromatic C=C bond and isocyanate were observed at 1100 cm^{-1}, 1700 ~ 1500 cm^{-1} and 2270 cm^{-1}, respectively.

2,5-Bis(5-aminobenzoxazol-2-yl)benzene-1,4-diol **1** was synthesized by reaction using 2,5-dihydroxyterephthalic acid and 2,4-diaminophenol

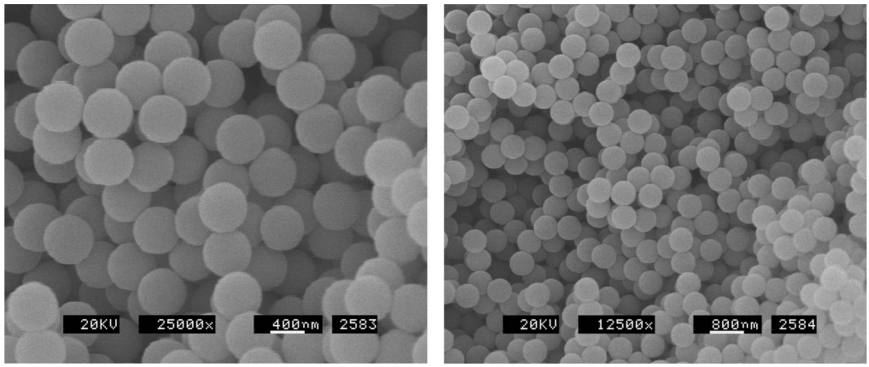


FIGURE 1 SEM photographs of submicro-sized uniform silica particle.

hydrochloride in PPA and P_2O_5 used as dehydrating agents (Scheme 2). The whitish yellow solid was obtained after sublimation. In the UV spectra of **1** in DMF solution, the maximum wavelength appeared at 342 nm and 423 nm, and lower wavelength showed a red shift and higher wavelength shifted to blue wavelength resulted from electron perturbation upon addition of DCP solution (Fig. 3(a)). In PL spectra of **1** in DMF, the wavelength and fluorescence intensity were changed by addition of DCP solution. When excited at 423 nm (Fig. 3(b)), the emission intensity was significantly enhanced with saturation. Hereby, we greatly expected that compound **1** can be applied to sensor material by DCP because it has large change of color in fluorescence. Therefore, in order to introduce on the surface of silica particle, the reaction was carried out between isocyanate group in silica and diamino groups in **1** in DMF. The silica particle functionalized with **1** was investigated in toluene suspension. The silica particles were dispersed in toluene and change of fluorescence spectra were observed by addition of DCP solution. Fluorescence intensities decreased upon addition of DCP solution (Fig. 4) without changes in emission wavelength.

In solution state compound **1** is free to rotate to form planar structure. Thus it is presumed that some extent of π–π stacking occurred among themselves and this resulted in the low intensity of fluorescence. When DCP was added into the solution, a hydroxyl group in **1** would react with DCP and that this led to deterioration of intermolecular interaction. Therefore, the fluorescence intensity would certainly increase with two distinctive emission maxima (normal Stokes shift maximum and large Stokes shift maximum due to ESIPT (excited state intramolecular proton transfer)). On the contrary, when the

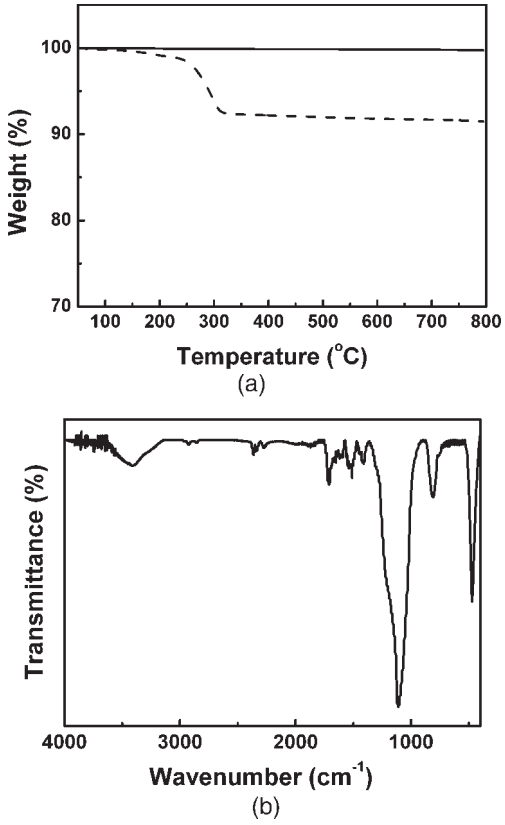
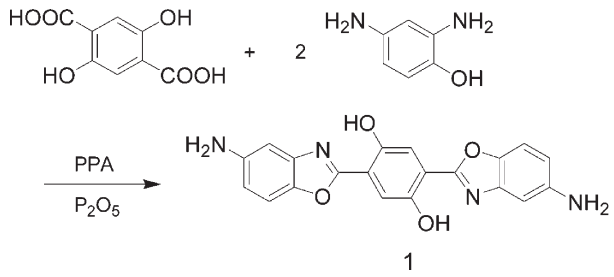


FIGURE 2 (a) TGA thermogram (solid: silica particle, dashed: isocyanate-functionalized silica particle) and (b) IR spectroscopy of silica particle functionalized with TDI.



SCHEME 2 Synthesis of 2,5-bis(5-aminobenzoxazol-2-yl)benzene-1,4-diol.

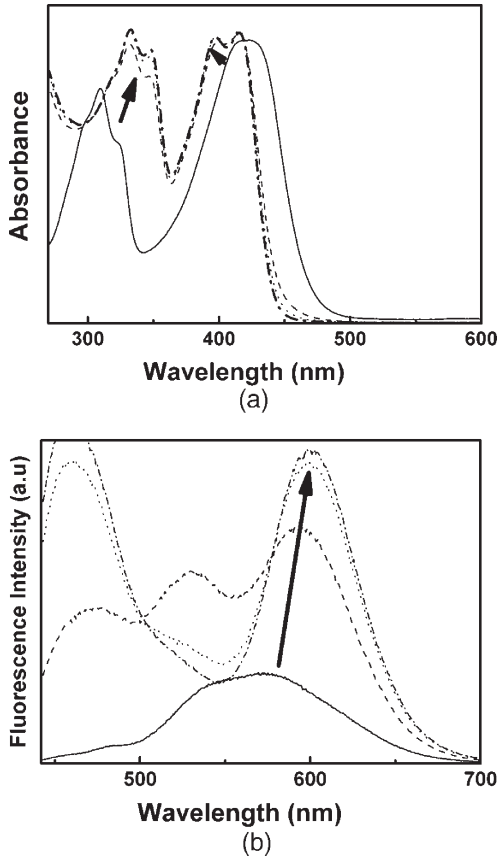


FIGURE 3 (a) UV and (b) fluorescence spectra of **1** in DMF (solid: 6.67×10^{-5} M of 1; dashed: 2.88×10^{-4} M; dotted: 5.74×10^{-4} M; dash dotted: 8.58×10^{-4} M of DCP).

benzoxazole molecules are attached to silica surface, there should be some limitation to get stable conformation on the surface of silica particle. Hence, the fluorescence quenching was induced on the surface.

CONCLUSION

We synthesized the silica particles using TEOS under basic catalyst condition by sol–gel method. The silica particles were uniformly sized about 560 nm and have sphere-like shape. Compound **1** was synthesized and the fluorescence color was bright yellow. UV and fluorescence spectroscopy of **1** was greatly changed by addition of model

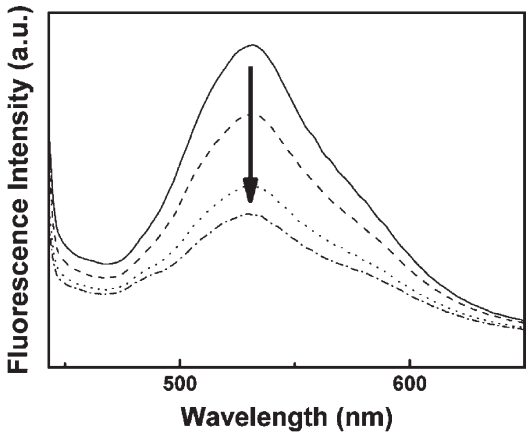


FIGURE 4 Fluorescence spectra of silica particle functionalized with **1** in DMF (solid: 5.70×10^{-2} wt% of silica particle; dashed: 1.60×10^{-10} M; dotted: 3.31×10^{-10} M; dash dotted: 5.13×10^{-10} M of DCP).

compound of nerve gases in DMF solution. Fluorescence of silica particle functionalized with **1** changed upon exposure to model compound of nerve gas in toluene solution.

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