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子計劃一:奈米發光膠粒合成與粒間作用研究(2/2)

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計畫主持人： 韋文誠

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奈米光粒子合成能隙晶體結構製作與應用
子計劃一：奈米發光膠粒合成與粒間作用研究

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I. 中文摘要

本研究第二年主要工作是合成具有核殼結構單徑二氧化矽/二氧化鈦及鋦酸鍶螢光粒子，並探討顆粒之間作用行為，及分析顆粒對於光閘晶體之光學性質的影響。實驗使用粒徑均一之二氧化矽顆粒,在強電性斥力下自組成光閘晶體。再利用反應控制,以溶膠凝膠法生成的奈米二氧化鈦顆粒覆蓋於二氧化矽顆粒表面，創造出核殼結構的光閘晶體。鋦酸鍶則由硝酸前導溶液反應析出而得。顆粒及組合物之微結構主要利用各種電子顯微鏡進行分析觀察。並以反射光譜分析儀量測其光學性質的變化。組合測試中加入高分子界面劑(PMAA-NH_4, PDAAE or PVP)，藉由表面電性的量測，了解高分子電解質之功能。此外,藉由反射光譜分析儀的量測可知由二氧化矽/二氧化鈦核殼結構所組成的光閘晶體能有效濾除 500nm 反射峰，只保留 600nm 處的反射峰，使反射峰的範圍窄化。

關鍵詞：溶膠凝膠法、二氧化矽、二氧化鈦、鋦酸鍶、自我組成、單徑、光閘晶體、

Abstract
The objectives of this study are to synthesize SiO_2 core/TiO_2 shell and luminescence $SrIn_2O_4$ spherical particles, to understand the interparticle forces, and to assemble photonic crystals so to reveal the band gap properties. Nano-sized and homogeneous TiO_2 was prepared from the reaction of Ti alkoxide (TBOT) with the water provided by the esterification of butanol and acetic acid. $SrIn_2O_4$ was synthesis from nitrate solution. The configurations of the SiO_2/TiO_2 particles and the microstructure of assembly were characterized by SEM, AFM, and TEM. In addition, the PBG crystals were measured by reflective spectrometer and the particles by ζ-meter, respectively. With the addition of three polymers PMAA-NH_4, DAAE, and PVP dispersive role was investigated. The silica/titania core-shell structure could filter the visible light near 500 nm, and sharper the 600 nm spectrum comparing to that of the PBG crystal assembled by mono-silica particles.

Keywords: **s**ol-gel method, SiO_2, TiO_2, $SrIn_2O_4$ self-assembly, mono-size, PBG crystal,

II. Motivation and Objective

The synthesis of submicron mono-dispersive oxide particles starting from TEOS (tetraethyl orthosilicate) has been studied in the past project. Particle ripening and coalescence were the major growth mechanism after the nucleation of silica species after hydrolysis and condensation of TEOS. Essentially, the method reported by Stöber *et al*[1] is the most essential work on the synthesis of submicron mono-dispersive silica particles in diameter from 0.05 to 2.0 μm. Various processing parameters were used by Bowen *et al.*[2] and the others demonstrating the possibility of size changing by the bath temperatures (-20℃~80 ℃).

In recent years there has been renewal of interest in silica spherical particles because of their self-assembly property like natural opal to form photonic bandgap crystals (PBG crystals).[3] One of the main aims of PBG technology is the fabrication of three- dimensional (3-D) PBG in the visible and infrared (IR) region of the

electromagnetic spectrum. Colloidal process was utilized to carry the synthesized particles, then organized or self- assembled to an ordered 3-D structure.

TiO_2 particles could be synthesized by sol-gel method as well.[4] The material shows interesting optical (refractive index is 2.52-2.71), dielectric constant (DC 31-114), and colloidal properties (iso-electric point, iep = pH 4-6), which are different from silica powders (refractive index is 1.44-1.46; DC is 4.3-8.5; iep is pH 3-4).[5,6] In addition to those, the bandgap energy of TiO_2 is about 3.2 eV. Exposure on the UV light, TiO_2, one of photocatalysts, forms two carriers, electrons and holes, which introduce either reduction or oxidation reactions, respectively.

On the use of colloidal process to coat the other nano-materials on the surface of silica spheres changes the stability of the particles dispersed in the suspension. The mixture of two oxides may show a combinative colloidal properties.[7] but also changes the behavior of the PBG crystals. The purpose of this paper is to synthesize the SiO_2 core/TiO_2 shell particles and observe the microstructure of those particles and how core-shell structure affects the optic behavior of PBG crystal.

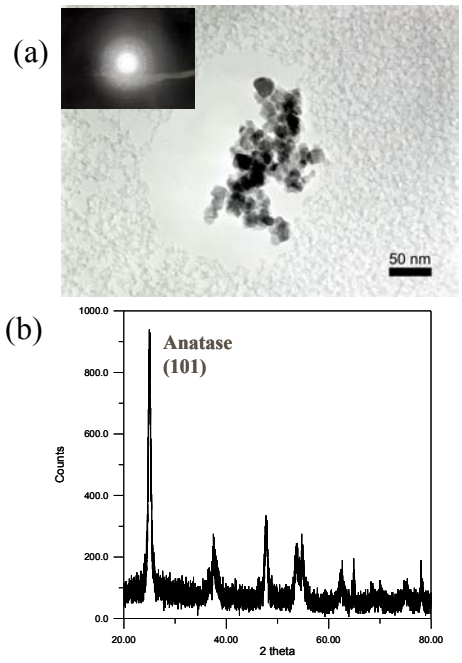

Fig. 1 (a) TEM macrograph and (b) XRD of nano TiO_2.

III. Result and Discussion

3-1 Synthesis of Nano-sized TiO_2

In order to reduce the reaction rate of TBOT, the synthesis of nano-sized TiO_2 used sol-gel method via the reaction of water which provided by the esterification of butanol and acetic acid. After drying and calcinations, the anatase phase is formed. Figs. 1(a) and 1(b) show the TEM macrograph and XRD result of TiO_2, respectively

3-2 Silica/titania Core-Shell Structure

Figs. 2 (a) and 2(b) are the SEM and the TEM of silica sediment. The packing structure of the sediment surface is in hexagonal closed packing (hcp). TEM result shows that more complicate packing structure of the silica sediment was observed and the more detail discussion of the packing structure was seen in our previous report,[8] which reported many kinds of defects on the surface of the SiO_2 package, such as the vacancies, faults, domain boundary, stacking faults, and the others. The main reasons for the formation of these defects are the force turbulence inducing different arrangement of SiO_2 particles during the sedimentation or packing. Those defects are related to the interparticle forces between the SiO_2 particles and the packed plane during the sedimentation. Other reasons, such as the thermal vibration of particles and the stress (capillary forces) induced during the drying, or/and sintering, should be well controlled.

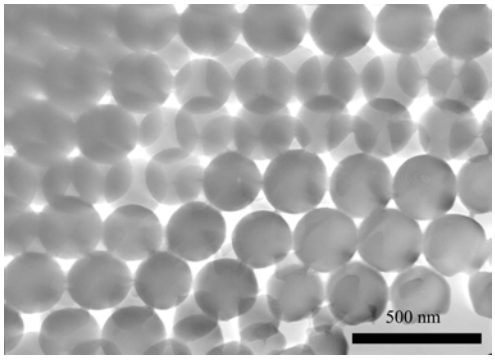

Fig. 2 (a) SEM and (b) TEM of self-assembled colloidal SiO_2 particles sintered at 950°C/2 h.

The synthesis method for core-shell

structure was conducted by immersed silica sediment in titania sol, then calcined amorphous titania to anatase phase. Fig. 3 is the TEM pictures of this sediment. The packing structures of Figs. 3(a) and 3(b) are cubic (fcc) and hcp, respectively. The surface of silica spheres are covered by a layer of nano-sized TiO_2 particles. The thickness of the TiO_2 layer is not uniform and about 10-30 nm that depended on the crystalline size of TiO_2.

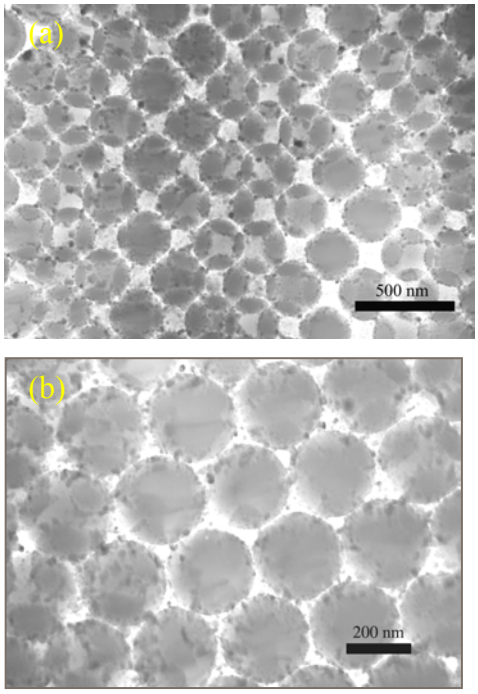

Fig. 3 TEM micrographs of the self-assembly colloidal silica/titania spheres sintered at 500°C

3-3 Heterogeneous Aggregation

The aim of heterogeneous aggregates of two kinds of oxide particles in solution is to create the shell structure on SiO_2 particles. This method adjusts pH value of the solution, which is between the iep values of two oxides. At the pH, one oxide particle shows positive charge and the other is negative. Figs. 4 and 5 are the ζ-potential of the SiO_2 and TiO_2 particles versus pH of the aqueous and ethanol suspensions. In ethanol suspension, both particles carried less charge on the surface and the iep shift to basic side.

One TEM result of the heterogeneous aggregates of SiO_2 and TiO_2 particles at pH 3 in ethanol is shown in Fig.6. The particles show nano-TiO_2 coating but not uniform in thickness. This process needs further improvement.

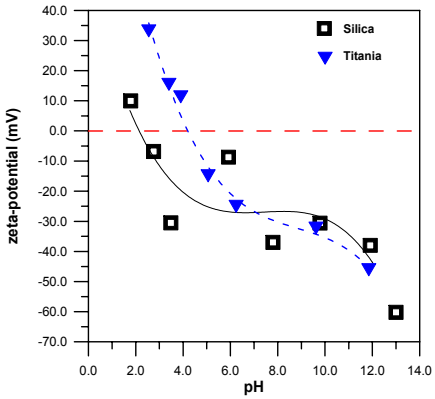

Fig. 4 Zeta potential of the silica and titania particles versus pH of the aqueous suspension.

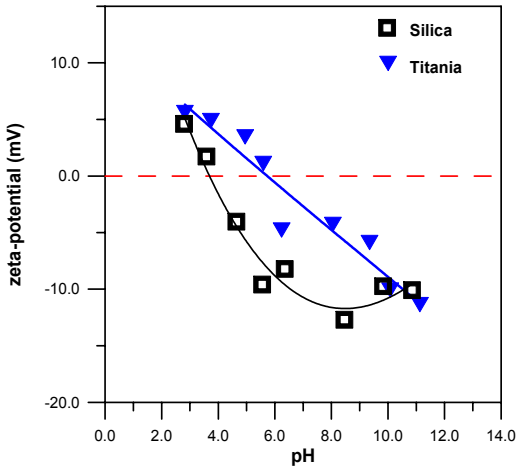

Fig. 5 Zeta potential of silica and titania particles versus pH of ethanol suspension.

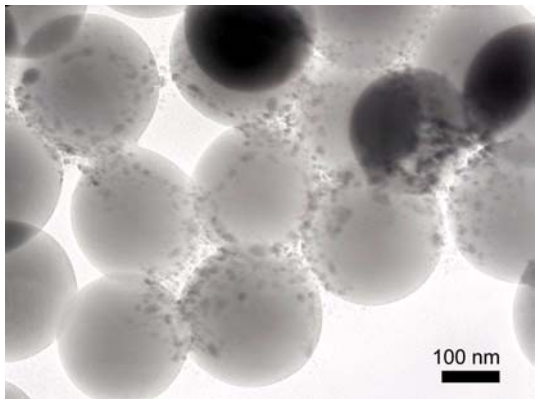

Fig. 6 TEM of colloidal silica/titania spheres by heterogeneous aggregation method.

3-4 Interparticle Force with Polymer Addition

In order to get a long-range stability, two polymer electrolytes were selected to disperse SiO_2 in aqueous solution. As the amount of dispersion increases, the ζ-potential of SiO_2 decreases due to the electrolyte concentration. (Fig. 7) PDAAE

and PMAA-NH_4 seem can't absorbed on SiO_2, but show steric effect between silica surface to stabilize the particles in the aqueous solution.

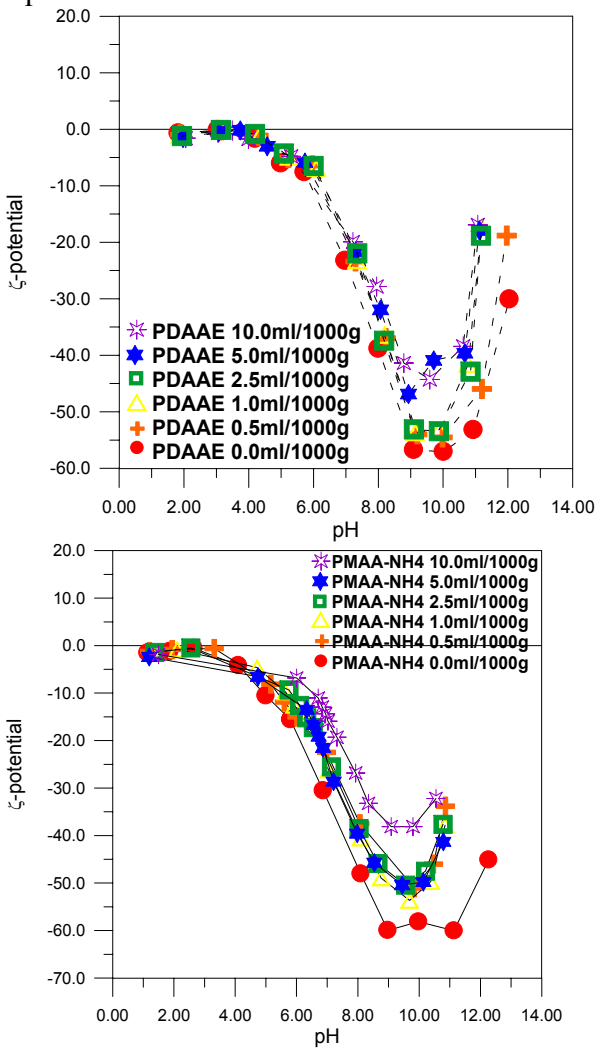

Fig. 7 ζ-potential of SiO_2 powder in aqueous solution with (a) PDAAE (b) PMAA-NH_4 in a concentration of 5 wt% SiO_2 powder.

3-5 Optical Properties of PBG crystal

With a thin layer coating of 30 nm anatase phase, the sediment reflects different spectra from the original one. The PBG crystals of silica/ titania core-shell structure could filter the visible light and the reflective spectra is mainly at 600 nm, which is sharper than that in the PBG crystal of mono-silica particles. (Fig. 8)

3-6 Synthesis of $SrIn_2O_4$

One example is shown in Fig. 9 with elongated shape (aspect ratio is 6)

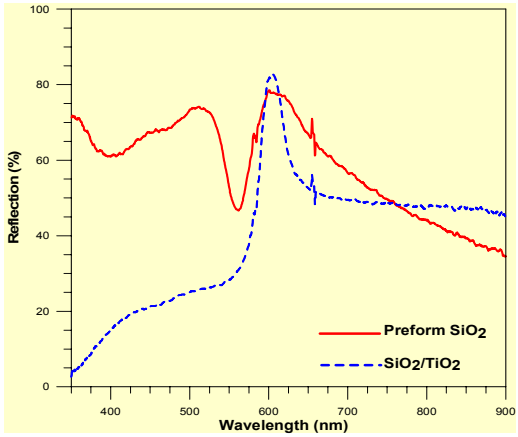

Fig. 8 Reflective spectra of the silica and silica/titania PBG crystals observed at reflective angle 0° with fixed angle 0° of the incident light. ……

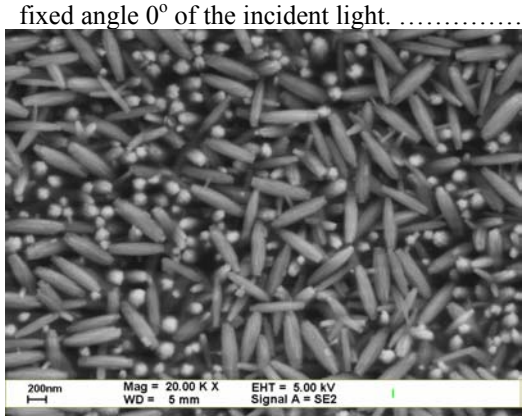

Fig. 9 $SrIn_2O_4$ crystals in elongated shape

IV. Self-Evaluation

Most of the planned objectives are achieved, except the measurement of interparticle force.

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