

行政院國家科學委員會補助專題研究計畫成果報告

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嵌合化合物之固態化學(3/3)

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本成果報告包括以下應繳交之附件：

- 赴國外出差或研習心得報告一份
- 赴大陸地區出差或研習心得報告一份
- 出席國際學術會議心得報告及發表之論文各一份
- 國際合作研究計畫國外研究報告書一份

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A study of morphology of mesoporous silica SBA-15

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The mesoporous silica SBA-15 in various morphologies micrometer-sized fibers, millimeter-scaled ropes and microspheres have been conveniently prepared by controlling the chemical composition. For reducing the size of particles of the SBA-15 materials, a delayed agitation process was found to lead to nanometer-sized fibers. We propose that it generates numerous nucleation seeds at the interface of TEOS and surfactant water solution and leads to very small fibers. With a proper aging time of 20 minutes, silica nanotubes-bundles with diameter of about 100 nm were obtained. In addition to the normal mesopores, the SBA-15 silica nanotubes possess extra textural porosity.

1. INTRODUCTION

Micelle-templated mesoporous silica (MMS) [1,2] are of great interest to scientific community because of their tunable mesopore structures which lead to many applications such as catalyst supports, adsorbent, and solid templates. In applications of the mesoporous silica such as catalysis, its morphology is an important controlling factor [3,4]. When a silica source is combined with a surfactant, the self-assembly process is complicated involving surfactant self-assembly in solution, mesophases transformation, and silica speciation reactions. All the factors influence the morphology of the mesoporous materials obtained. This has been amply demonstrated in MCM-41 materials [5]. Tuning the chemical composition, using proper inorganic precursors or applying physical field have achieved morphology and size controls on the mesoporous materials [6-8].

Recently the highly ordered SBA-15 [2], synthesized by using triblock copolymer $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, was found to exhibit rich morphologies. [9,10] The acid-made SBA-15 particles appear to be softer (weaker surfactant/silicate interaction), stickier (more surface silanol), and resulting in richer morphologies. Furthermore, the interface between the insoluble organic TEOS and aqueous copolymer solution appears to offer a new way of morphological control through multiphase assembly [10].

Basically, the formation process of MMS materials follows the sequence: nucleation → assembling growth → aggregation. The particle size of MMS will be dependent on the number of nucleation seeds during and the aggregation capability of the surfactant-silica clusters. The more the nuclei, the smaller the particle sizes. On the other hand, a decrease of growth and aggregation would also help the formation of smaller particles (or fibers). Recently, Mann and coworkers devised a growth quenching procedure in the alkaline synthesis of MCM-41 to obtain nanoparticles of mesoporous silicas [11].

In this report, we present several methods of morphological control of the SBA-15. We tuned the TEOS/triblock copolymer ratios or added a proper amount of multivalent salts in the $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ -TEOS-HCl- H_2O reaction composites to increase the aggregating ability of the triblock copolymer-silica species nanocomposites. Thus, the SBA-15 mesoporous silicas in macro-scaled form (e.g. centimeter-sized sphere, millimeter-sized ropes and micrometer-sized fibers) were facily prepared. Moreover, a delayed-agitation procedure was conveniently used to create rich silica nucleation seeds at the interface between the TEOS and surfactant aqueous solution. These induced the formation of nanotubes and fine microparticles of the SBA-15 mesoporous silica.

2. MATERIALS AND METHODS

2.1. Materials

The tri-block copolymer is (ethylene oxide)₂₀-(propylene oxide)₇₀-(ethylene oxide)₂₀, ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$; P123) from Aldrich as the mesostructure-templating species. The silica source is tetraethylorthosilicate (TEOS; 98% from Acrôs), and hydrochloride (HCl, 37%) is from Acrôs. All chemical agents were used as received.

2.2. Synthesis

The micrometer-sized fibrous mesoporous SBA-15 silicas were prepared according to the typical synthetic process reported by Stucky *et al.* [2]. 1.0 g triblock copolymers P123 and 9.44 g of 37% aqueous hydrochloride acid were dissolved in 30.0 g water to form a clear solution. Then 2.30 g TEOS was added to that solution under stirring condition then further stirred for 5-24 hr at the 40 °C. The gel chemical compositions in molar ratio is 1.0 P123:(64-160) TEOS: 555 HCl: 11584 H_2O . We differ from ref.[2] mainly in that higher acid concentration is used here.

The millimeter-sized silica ropes were prepared according to the above procedure and same composition except for an extra addition of (2.0-4.0)g of Na_2SO_4 or Na_3PO_4 .

With the same synthetic procedure, the centimeter-sized mesoporous SBA-15 silica sphere was obtained from a higher TEOS content system with TEOS/ $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ weight ratio in the range of 3.5 to 5.0 under a stirring rate of about 500 rpm.

For the preparation of SBA-15 silica nanotubes, a *delayed-agitation procedure* was performed. In this process, the TEOS was added into the surfactant-acid aqueous solution without agitation, and that two-phase solution (TEOS is on the upper layer) then stood statically for equal or longer than 20 minutes. After stirring the reaction mixture at high speed, a white precipitate was suddenly formed. The gel solution was further stirred for 18-24 hr. The chemical composition are the same as that for silica fiber (TEOS/ $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ weight ratio = 2.30). While using the composition for macrosphere formation (TEOS/ $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ weight

ratio = 4.0), microparticles were formed instead.

After filtration, washing with water and drying at room temperature, we recovered the SBA-15 mesoporous silica products. The surfactant templates were completely removed after calcination.

2.3. Measurements

X-ray powder diffraction (XRD) patterns were recorded on Wiggler-A beamline ($\lambda = 0.1326$ nm) of the Taiwan Synchrotron radiation research center at Hsinchu, Taiwan. N_2 adsorption-desorption isotherms were obtained at 77 K on a Micromeritics ASAP 2010 apparatus. Before the analysis, the calcined samples were outgases at 250°C for about 6 h under 10^{-3} torr condition. The pore size distribution was obtained from the analysis of the adsorption branch by using the BJH (Barrett-Joyner-Halenda) method. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were taken on the Hitachi S-800 and H-7100 with the operating voltages of 20 and 100 keV, respectively.

3. RESULTS AND DISCUSSION

Figure 1 shows several representative SEM, TEM and optical microscope images for SBA-15 mesoporous silicas synthesized from different reaction composites. Using the reaction composites similar to that of typical one [2], the micrometer-sized silica fibers were obtained and the length is in tens micrometers (Fig. 1A). Under higher magnification (Fig. 1B), one can clearly find the fibers are nodular which seems to be formed from sticking linearly many sub-micron particles. The nodular shape is different from the rope-like domain observed in ref. [2] where $[HCl] \sim 2.0$ M. This could be ascribed to the higher acidity ($[HCl] \sim 2.5$ M) in our synthesis composites. However, stirring is also an important factor.

With the addition of a proper amount of Na_2SO_4 or Na_3PO_4 , the fibrous mesoporous SBA-15 products in millimeter size were obtained, and the longer one is about 0.5 mm (Fig. 1C). Under a higher magnification (Fig. 1D), one can clearly see the morphology is rope-like and the SBA-15 ropes consist of fibers of micron diameter. Using microtome TEM technique to examine the nanostructures of the fibers (Fig. 1E), it is shown the SBA-15 nanochannels are well ordered and aligned with the direction of fibers. Therefore, the millimeter-sized SBA-15 silica ropes is regarded as a hierarchical structure similar to the silica ropes synthesized by this laboratory from C_{18} TMAB-TEOS- HNO_3 - H_2O composite [12,13]. Thus, we suggest that the addition of the multivalent salts promoted the elongation of the $EO_{20}PO_{70}EO_{20}$ -silica micelles. The long micelles are then shear-aligned into the millimeter-sized SBA-15 silica ropes. In contrast, the addition of univalent salts ($NaCl$, $NaBr$ or $NaNO_3$) did not help the formation of millimeter-sized silica ropes. The above explanation is further corroborated by a recent study of the effects of salts on the micellization of pluronic solution. [14] Pandit et al. [14] reported that salt solutions help the elongation of the micelles of Pluronic copolymers by increasing the hydrophobic domain. The power of the micelle formation is in the order: $Na_3PO_4 > Na_2SO_4 > NaCl$, with $NaCl$ solution being the least almost as effective as pure water.

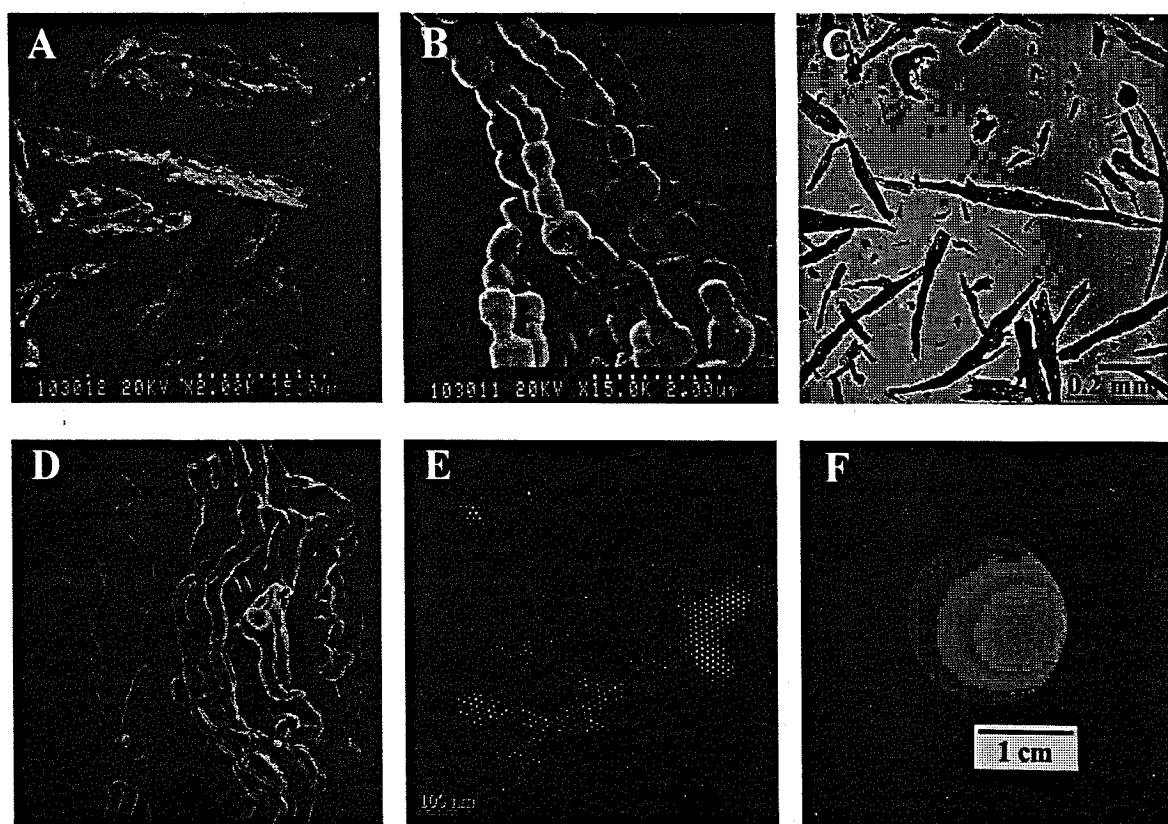


Figure 1. The SEM, TEM and optical microscope images of the SBA-15 mesoporous silicas, synthesized from different reaction composition, in various morphologies: A. The SEM micrograph of micrometer-sized fibers (TEOS/ $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ weight ratio = 2.30); B. SEM micrograph of sample A in higher magnification; C. The optical micrograph of millimeter-sized silica ropes (TEOS/ Na_2SO_4 / $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ weight ratios = 2.30/2.0/1.0); D. SEM micrograph of sample C in higher magnification; E. Microtome TEM micrograph of sample C.; F. Photograph of the centimeter-sized sphere (TEOS/ $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ weight ratio = 4.0).

To examine the effect of aggregation, one may use more TEOS at high acidity to promote the cross condensation between surfaces of silica particles. When the TEOS/ $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ weight ratio was adjusted into the higher range of 3.5-5.0, we saw the silica- $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ particles mutually aggregated together during the reaction process and then a centimeter-sized sphere was formed (Fig. 1F). We found the sphere has interestingly high elastic property and mechanical stability [15]. In strong acidic condition, the larger silica oligomers have greater binding strength with $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ micelles and stronger aggregation capability. However, further increasing the TEOS/ $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ weight ratio higher than 7.0, most of TEOS were hydrolyzed and formed the template-free amorphous silicas in acidic condition [16]. The macro-sphere was no longer produced at such high TEOS content.

Besides the compositional adjustments on the cooperation assembly of the silica- $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ composites, controlling the number of the nucleating seeds in the gel solution is also an essential determining factor on the morphology of the mesoporous materials. According to previous reports [17,18], the silica nuclei can be progressively created at the

interface of the hydrophobic TEOS and aqueous surfactant solution via a surfactant-catalyzed hydrolysis of TEOS. Based on this concept, we performed a delayed-agitation method to induce more nucleation seeds in the synthesis of SBA-15 mesoporous silicas. It is hoped that the growth and aggregation processes will be retarded relatively because of transport limitation. In Fig. 2A, we see bundles of nanotubes of SBA-15 were obtained after the two-phase reaction mixture stood statically for a 20-minute and then followed by a sudden stirring at high speed.

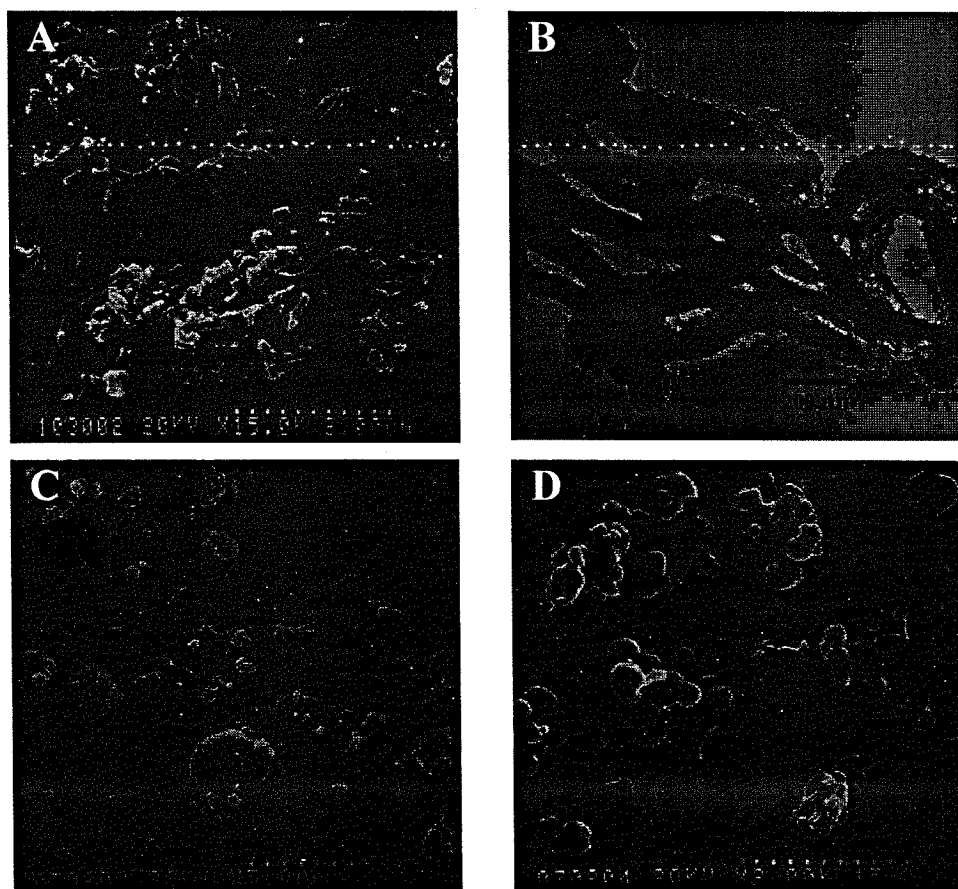


Figure 2. The SEM and TEM micrographs of the SBA-15 mesoporous silicas prepared by the delayed-agitation process. A. The SEM micrograph of SBA-15 nanotubes (TEOS/EO₂₀PO₇₀EO₂₀ weight ratio = 2.3; aging time = 20 min); B. TEM micrograph of sample A.; C. The SEM micrograph of microparticles (aging time = 1 hr); D. The SEM image of microparticles (TEOS/EO₂₀PO₇₀EO₂₀ weight ratio = 4.0; aging time = 20 min).

The TEM micrograph shows nanotubes consisting of about ten nanochannels with the diameter at about 100 nm (Fig. 2B). To our knowledge, this may be the smallest dimension SBA-15 silica ever made. Prolonging the aging time of the reaction mixture to about 1.0 hr, the SBA-15 product is in inhomogeneous microparticles instead of the nanotubes (Fig. 2C).

To explain the above results, we propose that the nucleation seeds of the SBA-15 be continuously generated at the interface of TEOS-EO₂₀PO₇₀EO₂₀ solution. In the early nucleation stage, the number of nucleation seeds would increase with the aging time. However,

the nucleation seeds would also aggregate with each other or grow into larger ones. Thus aging-time control crucially determines the homogeneity and the particle dimension of the final SBA-15 products. From many tests on aging-time, we found 20-minute aging can produce the smallest silica nanotube-bundle.

In order to show further the effect of increasing nucleation seeds on the SBA-15 particle size, the delayed-agitation process was also applied to the composites for centimeter-sized sphere as well. One could obviously find the SBA-15 morphology transformed into the microparticles (Fig. 2D) instead of the macro-sphere (Fig. 1 F). The size reducing also occurred in the system for silica fibers or ropes.

Fig. 3A shows the XRD patterns of the as-synthesized mesoporous SBA-15 aforementioned in different morphologies and dimensions. All of the SBA-15 samples possess distinct 2-3 peaks indexed to the well-ordered hexagonal structure. The almost identical d-spacings of 8.8 nm for these samples reflect the same reaction temperature of 40 °C and similar composition [2]. When examining their N₂ adsorption isotherms (Fig. 3B), it is clear that all samples have a sharp capillary condensation at $P/P_0 \sim 0.60$ - 0.70 corresponding to pore sizes around 6.0 nm. The BET surface areas of these samples are about of 450-550 m²/g.

However, the adsorption behavior of the SBA-15 silica nanotubes is worth mentioning. In that sample, there exists further increase of N₂ condensation at $P/P_0 > 0.9$ (indicated by an arrow in Fig. 3B), which is attributed to the filling of textural pores [3]. The textural porosity results from the aggregation of the small-sized bundles (sample IV). The samples with larger domain (sample I, II, III) show little or no textural porosity.

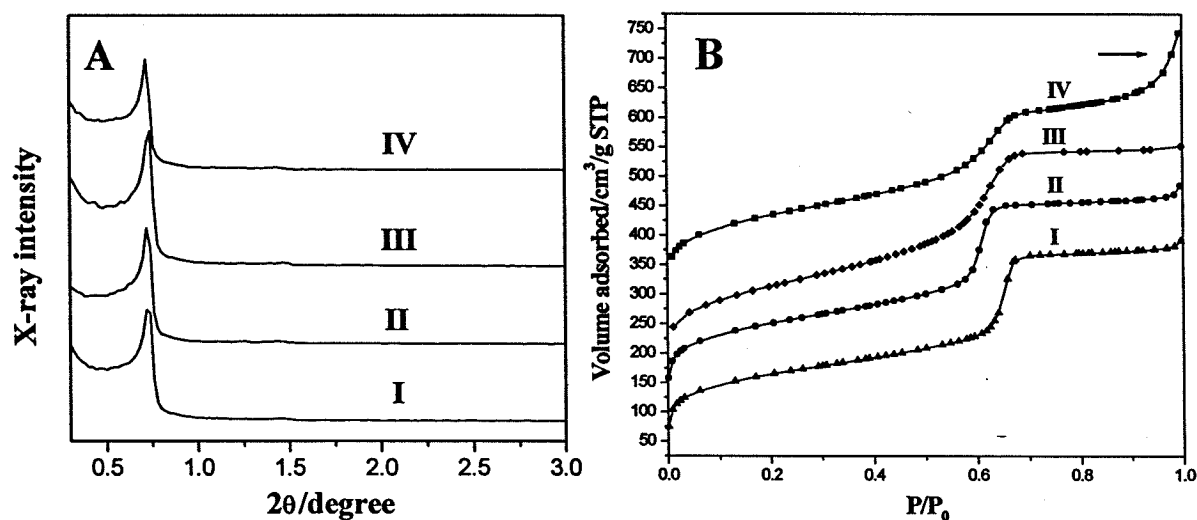


Figure 3. The XRD patterns and N₂-adsorption isotherms of the SBA-15 mesoporous silicas in various morphologies and dimensions. A. XRD patterns; B. N₂-adsorption isotherms. I. Micrometer-sized fiber; II. Millimeter-sized rope; III. Centimeter-sized sphere; IV. Nanotubes.

Besides of morphology control, we also used the post-synthesis hydrothermal treatment to tune the pore size and porosity of these SBA-15 mesoporous silicas [19]. After 100 °C hydrothermal treatment for one day, pore size (~ 7.5 nm), surface area (~ 650 m²/g) and porosity (~ 0.9 cm³/g) increased in all of the SBA-15 samples but the morphologies were still

preserved. Combining with the hydrothermal treatment, the SBA-15 mesoporous materials with desired morphologies, dimensions and porosity could be easily prepared for potential applications.

4. CONCLUSION

In conclusion, the controls of nucleation, growth and aggregation are shown to be fundamental factors in tailoring the morphologies of the mesoporous materials. Adjusting the chemical composition or performing the delayed-agitation process can help us conveniently obtain the SBA-15 mesoporous silicas in different morphologies and dimensions. It should be a versatile mesoporous material with potential applications in catalyst, separations, sensors, and nano-materials fabrications. Besides, the control of interfacial nucleation could help one to understand other sol-gel processes such as biomineralization or in designing better methods for creating new inorganic-organic nanocomposites.

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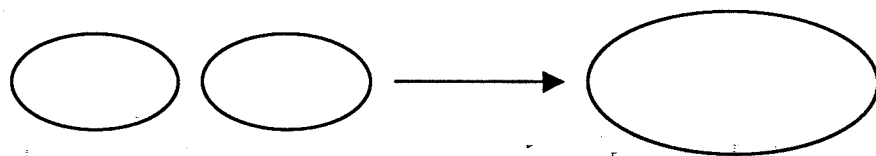
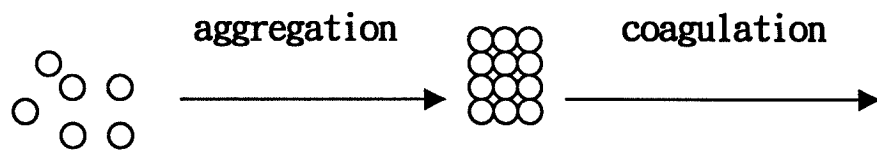
日本會議報告 5/11---12/11

牟中原

這次到日本一共參加三個會議，都是有關界面與膠體的領域。今年是日本化學會界面化學組成 25 週年。為了慶祝週年而擴大舉行國際界面化學研討會，於東京市谷私學會館舉行，時間是 11 月 5 日至 8 日。會議共有國際學者 80 人及日本學者 600 人參加，相當盛大，共分 5 個場次：1. 界面吸附 2. 奈米材料 3. 微胞及微乳液 4. 薄膜 5. 生物科學應用。除了演講，還有兩場次的壁報展有論文 300 篇。重要心得如下：

1. 法國 Pilemi 教授量得銀奈米粒子的超晶格排列之光譜發現平行與垂直極化的光譜不同。在平行極化，除了 2.8ev 外，在 3.5ev 還有一個峰。他說這是粒子間 dipole 作用所致。
2. 九州大學 Midome 博士以 YAGlaser 打溶液金奈米粒子發現可以將這些粒子沉積到表面上，而非極性的溶劑較有利沉積。
3. 大學發表在無界面活性劑條件下，水與油的乳液之穩定度，他們

發現



他們用 DSL 以及 FFEM 兩種技術來觀察這現象。我的問題則是鹽類效應如何？

東京會後即受 Prof. Shirahama 之邀到九州阿蘇火山風景區參加會後會 11 月 9—10 日「Amphiphile and Colloid Solution」，此會議由 Maeda 及 Artono 教授主持。此會議有 110 人參加，國際人士 14 人，我應邀作了一個演講。心得有：

1. Strey 教授可以合作量，我們有興趣系統的相圖。
2. Kaler 教授對我的工作有興趣，可以下次邀來台灣。
3. Kumamoto 大學研究群合成了很多有意思的多頭陽離子型界面活性劑。
4. Suighara 教授做了有意思的蛋白質脂肪管狀結構。
5. Craig 教授報告了微胞在固體 (SiO_2) 表面之緩慢吸附。

11 月 11 日到 12 日受邀訪問佐賀醫科大學參加「Physical Aspects of Amphiphil Colloids」會後會，由 Suezak 教授主持，我作了 45 分鐘報告。心得有：

1. Porte 教授以特殊的 telechelic 高分子與 microemulsion 作用而作出有磷彈性的系統。
2. Fleer 教授以理論說明 polymer brush 對 $\text{H}_2\text{O}/\text{Oil}$ 的吸附，此次會議多數為物理學家。

[International Symposium on the Science of Surfaces and Nanostructures]

會議報告

牟中原

此次參加在新加坡舉行之奈米材料會議，是新加坡國立大學物理系教授 Andrew Wee 與中研院物理所鄭天佐教授共同發起，10 月 22 日至 24 日共三天，參加國家有 15 國，台灣參加者有 10 人，全部作口頭報告。此次大會的主題包含表面物理、奈米顆粒、奈米化學及同步輻射的應用。會議期間，參觀了新加坡國立大學物理系及化學系，並有新加坡半日遊，造訪了新加坡光明禪寺、新加坡國立博物館、植物園。

會議議程如下：

此次會議得 Surface Review and Letters 同意，將刊登此次會議所發表的論文。會議的另一主要成果是促成台灣與新加坡雙邊學術交流，進行合作研究的計畫正在發展中。