

Fabrication of SiO_2 , Al_2O_3 , and TiO_2 Microcapsules with Hollow Core and Mesoporous Shell Structure

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Introduction

The hollow microcapsules have number of applications

- ❖ Catalysis*
- ❖ Chromatography*
- ❖ Protection of biologically active agents*
- ❖ Controlled and timed drug delivery system because of their high surface, big hollow structure, and compatibility with other materials*

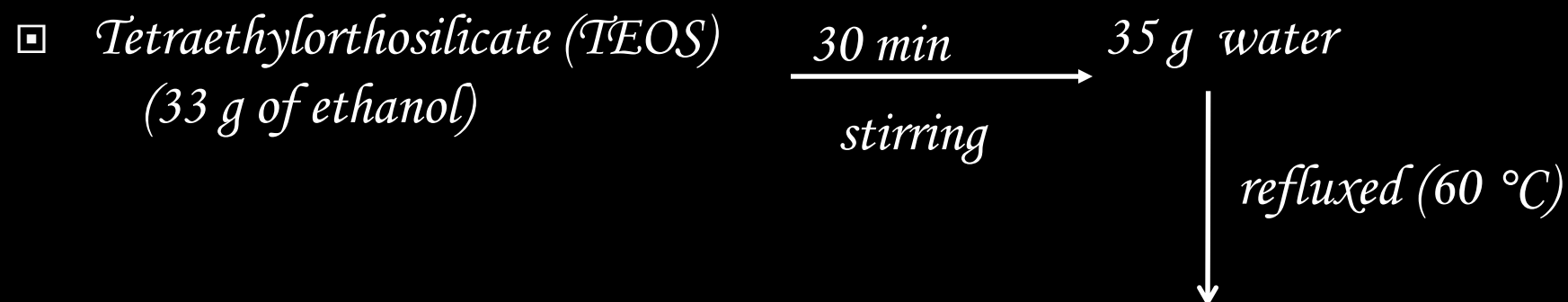
To fabricate the pure silica, alumina, and titania microcapsules with the hollow macroporous core and mesoporous shell structure.

Deposition of hydrophilic precursor sol containing surfactants in the hydrophobic solvents onto the polymer surfaces which are coated by ionic liquid (IL) salts.

Experimental Methods

Fabrication of Hollow Microcapsule with Mesoporous Shell.

Hollow SiO₂ microcapsule synthesis



HCl (1.25 g) dropwise mixture was vigorously stirred at 60 °C

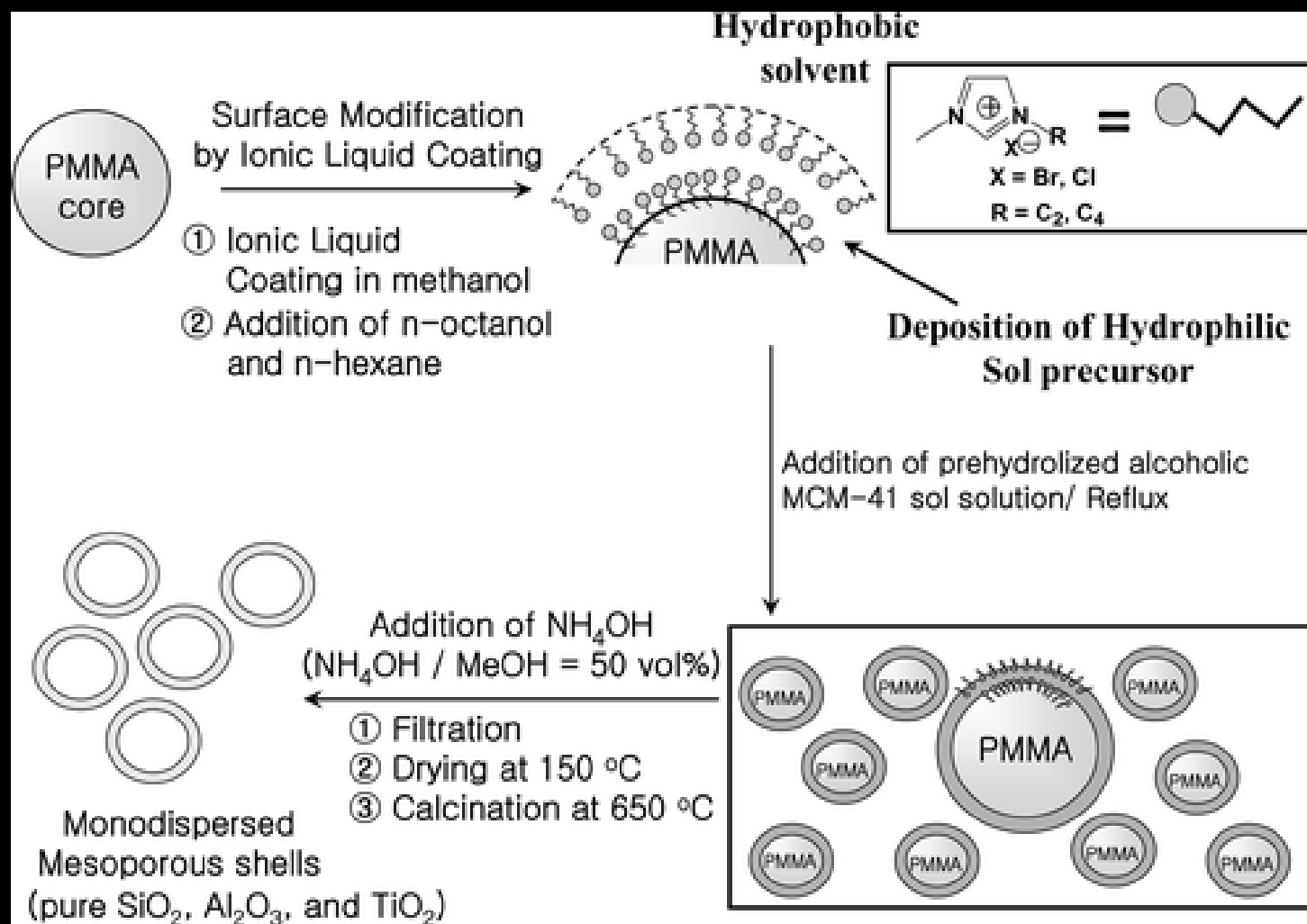
- *Mole ratio of TEOS:EtOH:H₂O:HCl was 1:3:8:5 in the mixture (solution A)*
- *Separately, the surfactant n-docsyltrimethylammonium chloride C22TMACl or C16 TMABr (8.75 g)was dissolved in 360 of ethanol (solution B)*
- *Solutions A and B were mixed for 2 h at 60 °C, the solvent was evaporated to reduce the total solution . (Silica sol prepared)*

Synthesis of Al_2O_3 and TiO_2 sols

- Synthesis of Al_2O_3 and TiO_2 sols containing C16TMACl surfactant, the acetic acid was used as hydrolyzing agent instead of HCl,
- Aluminum(III) chloride and titanium(IV) chloride was used as the precursors.
- In the preparation of TiO_2 sol, titanium(IV) chloride (TiCl_4)(6.8 g) and acetic acid (CH_3COOH 1 g) were put into the absolute methanol (MeOH ; 10 mL) and that solution was refluxed for 2 h.
- After addition of deionized water (3 g) the mixture was refluxed additionally for 2 h.
- The typical mole ratio of $\text{TiCl}_4:\text{MeOH}:\text{H}_2\text{O}:\text{CH}_3\text{COOH}$ was 1:8.7:4.7:0.5 in the mixture (solution C)
- Separately, C16TMABr (8.75 g) was dissolved in 25 mL of methanol (solution D)
- The mixture of solutions C and D was heated at 50 °C for 2 h under stirring.

- *PMMA surfaces were modified with ionic liquids such as butylmethylimidazolium bromide (BMIB) and ethyl-methylimidazolium bromide (EMIB)*
- *BMIB (1.5 g) or EMIB (1.5 g) was dissolved in 10 mL of methanol. After addition of PMMA particles (5 g) into that solution and stirring for 30 min, the solvent was removed under vacuum.*
- *The 1:3 volume ratio solution (50 mL) of n-octanol and n-hexane was added to PMMA spheres (10 g) coated with ionic liquid. n-Octanol was added to achieve good dispersion of IL-coated PMMA particles. BMIB or EMIB is soluble only in the water and methanol.*
- *Under the full dispersion of particles in the solution, the concentrated SiO₂ (or Al₂O₃, TiO₂) sol-solution (g) was added dropwise.*

- *The whole mixture was stirred at room temperature for 6 h, and it was refluxed additionally for 6h.*
- *As final step, the ammonia-water (2 mL) mixed in methanol (20 mL) was added to the suspension solution to solidify the mesoporous sol into the gel, and then the reaction mixture was kept under stirring. The collected composite particles were filtered, washed with various solvents, and dried at 150 °C for 12 h.*
- *The precursor PMMA polymer spheres were removed by direct calcination at 650 °C for 4h in air. The heating rate was maintained at 1 deg/min from the room temperature to 650 °C.*

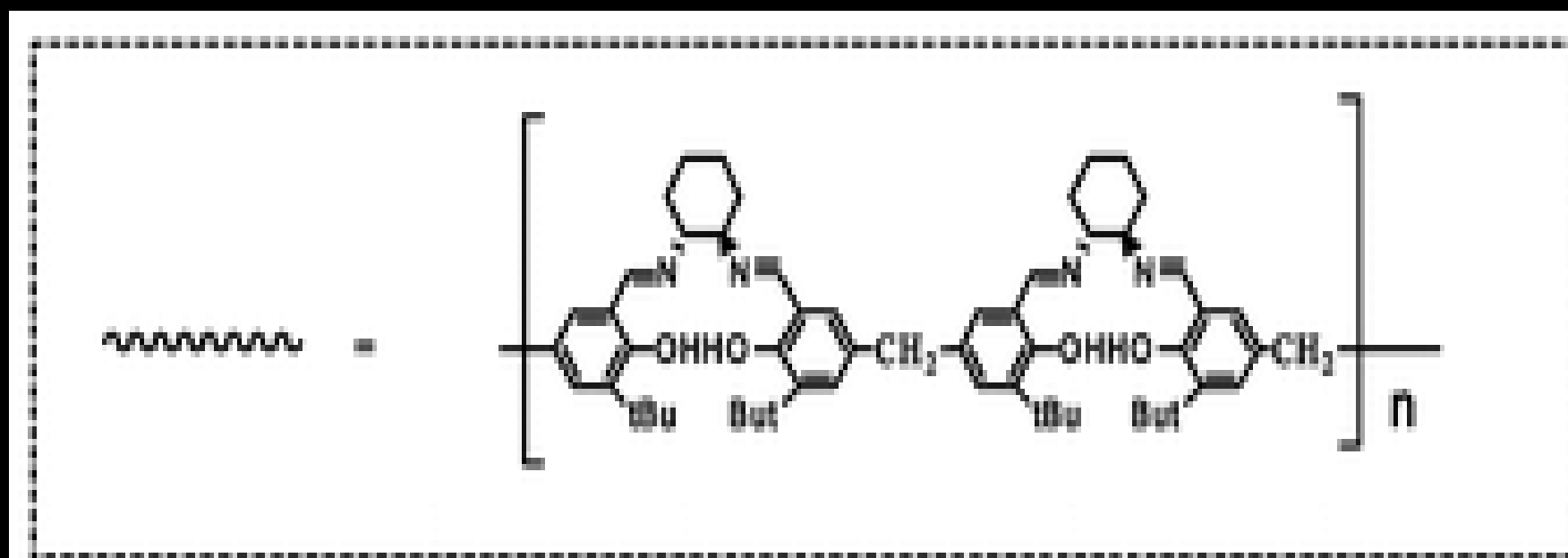
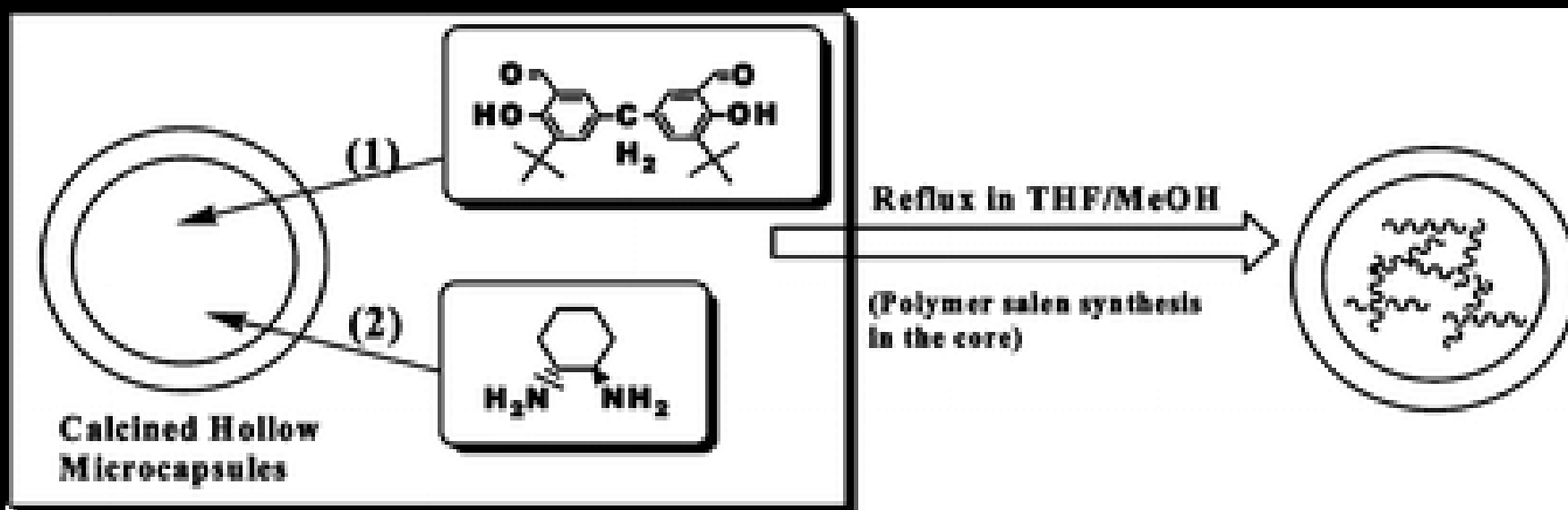


Scheme 1: Schematic Illustration for the Synthesis of Mesoporous Microcapsules

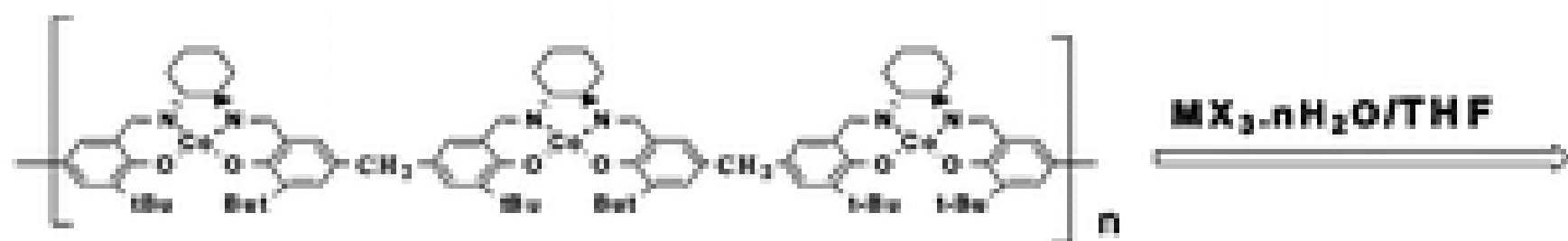
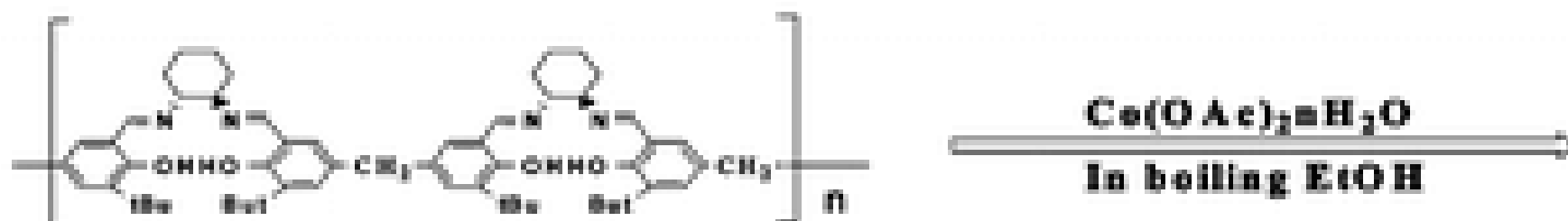
Catalyst Preparation

- The polymeric salen ligand was synthesized in the cores of microcapsules by using dimeric dialdehyde derivative, which was reported by Jacobs et al.
- The polymeric salen ligand entrapped in void cores of mesoporous silica shell (μm) was obtained by the condensation reaction between dimeric dialdehyde derivative and 2-diaminocyclohexane in boiling $\text{CH}_3\text{OH}/\text{THF}$
- Dimeric dialdehyde dissolved in THF at high concentration was absorbed into the mesoporous silica microcapsules, and the solvent was evaporated under vacuum.
- Then, the 1,2-diaminocyclohexane in THF was introduced similarly.
- The powder samples were refluxed in the mixed THF/methanol solution for 3 h, and collected after subsequent filtration.

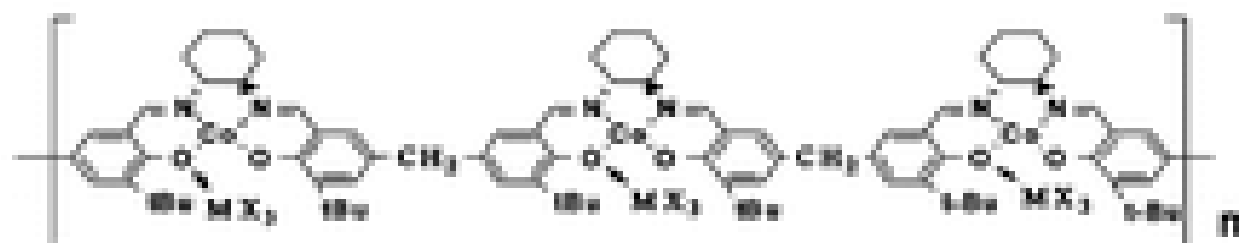
- Cobalt insertion into the polymeric salen ligand was accomplished by adding solution of $\text{Co}(\text{OAc})_4 \cdot \text{H}_2\text{O}$ in 50 mL of 1:3 MeOH/toluene to the salen containing silica microcapsules with stirring at 80 °C. The microcapsules turned red
- Filtered and rinsed sequentially with methanol, methylene chloride (MC) tetrahydrofuran (THF) and toluene and then dried under vacuum to yield the pink powder.
- To solution of hydrated aluminum, gallium, and indium chloride in THF was added the precatalyst cobalt (R,R)-salen containing microcapsule, then the mixture was stirred in open atmosphere at room temperature.
- After subsequent treatment, the color of the microcapsule catalyst changed from red to dark olive green. The final catalyst solid was collected after washing with MC and THF. Catalyst washed with MC and THF.



***Scheme 2:** Synthetic Procedure of Chiral Cobalt Polymer Salen in the Core of Mesoporous Silica Microcapsules (μm)*



Polymer (Salen)Co (A)



Polymer (Salen) Catalyst (1)-(3)

MX₃ ; (1) = AlCl₃
 (2) = GaCl₃
 (3) = InCl₃

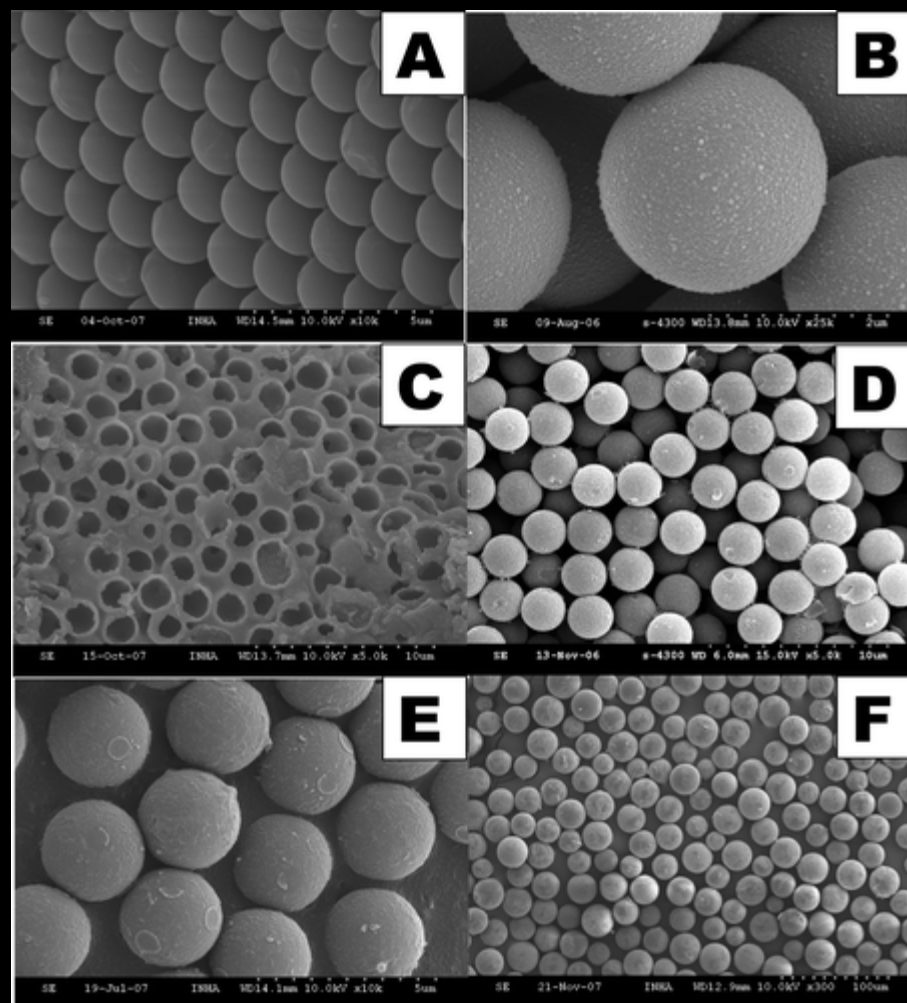


Figure 1. Characterization of microcapsules having hollow core with mesoporous shell: SEM images of parent 2 μm PMMA spheres (A) hollow spherical SiO_2 particles with the core diameter of 2 μm (B) the broken SiO_2 shells (C) hollow Al_2O_3 particles (D) 2 μm TiO_2 microbeads (E) and those of hollow SiO_2 microparticles with core diameter of 25 μm (F)

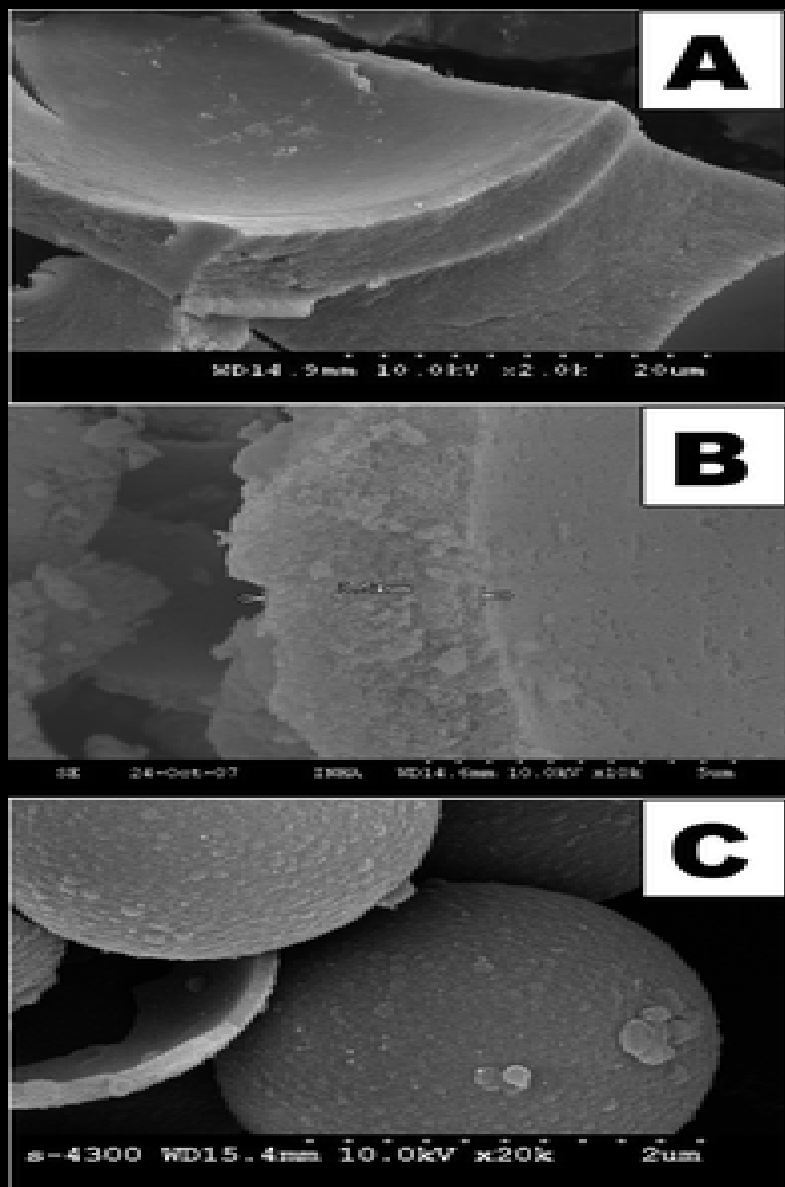


Figure 2: SEM images of the broken shell of mesoporous silica microspheres: at 2 μm thickness and mean diameter of 50 μm (A and (B) and at 0.15 μm thickness and mean diameter of 2 μm (C).

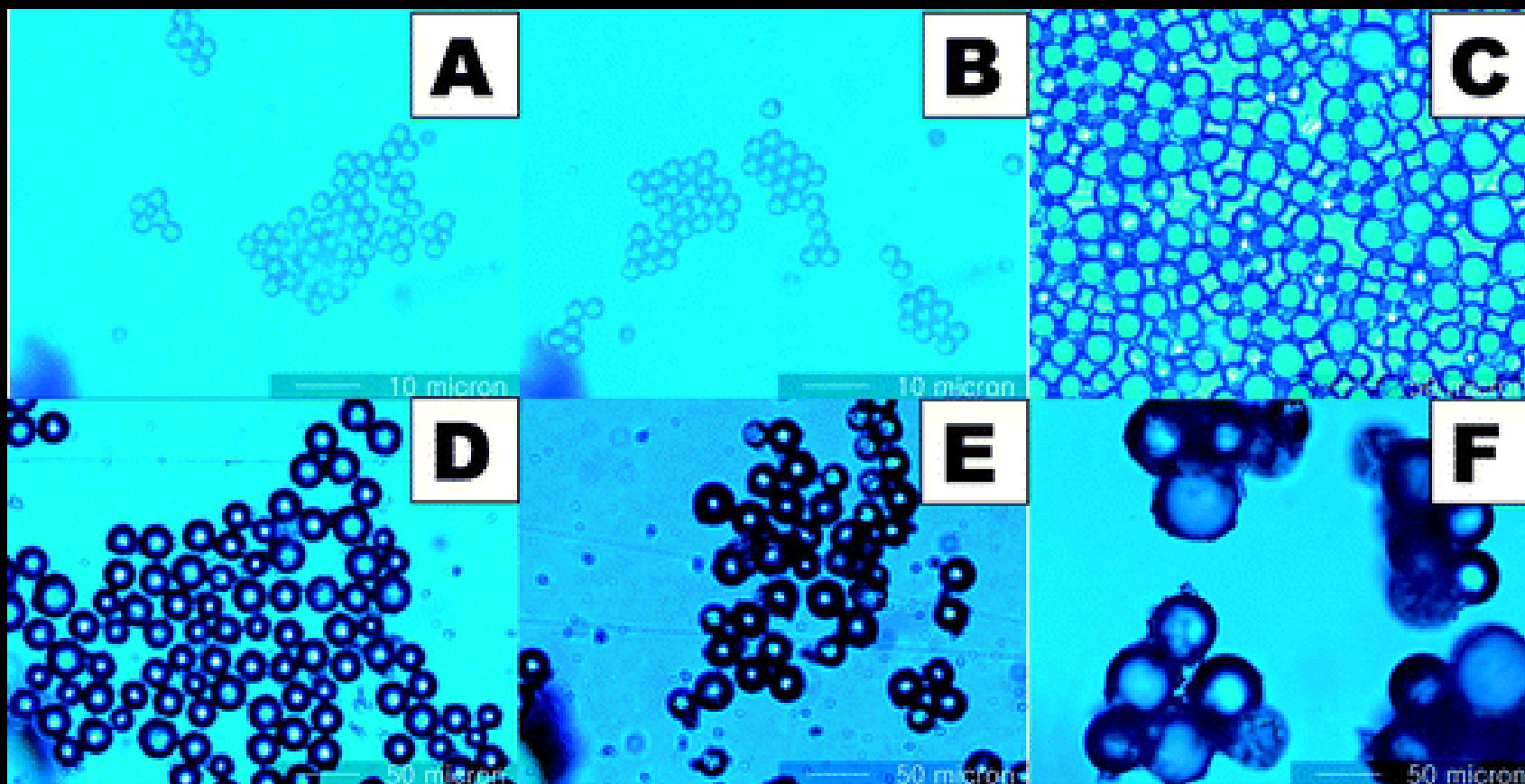


Figure 3. Optical microscope photographs of various hollow-type microcapsules: (A) pure PMMA polymer particles used as template core (mean particle size 2 μm) (B) calcined pure silica microcapsules (mean particle size 2 μm) (C) pure PMMA template core (mean particle size 25 μm) (D) calcined silica microcapsules (mean particle size 25 μm) (E) calcined pure titania microcapsules (mean particle size 25 μm) and (F) calcined silica microcapsules (mean particle size 60 μm)

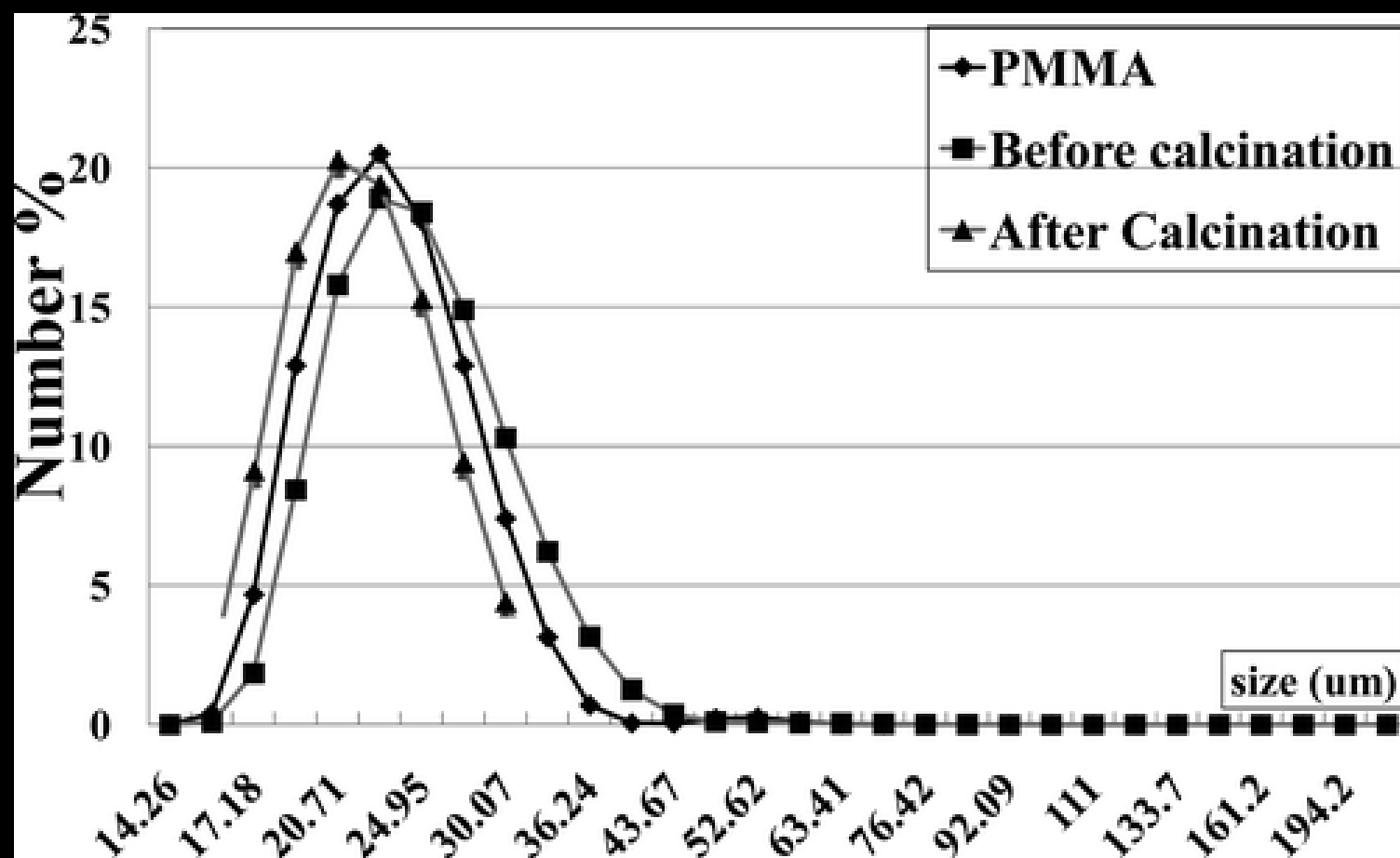


Figure 4 Particle size distribution curves for ♦ PMMA spheres used as a template; ■ as-synthesized composite coated by silica sol (after drying at 150 °C); ▲ and silica particles obtained after calcination at 650 °C.

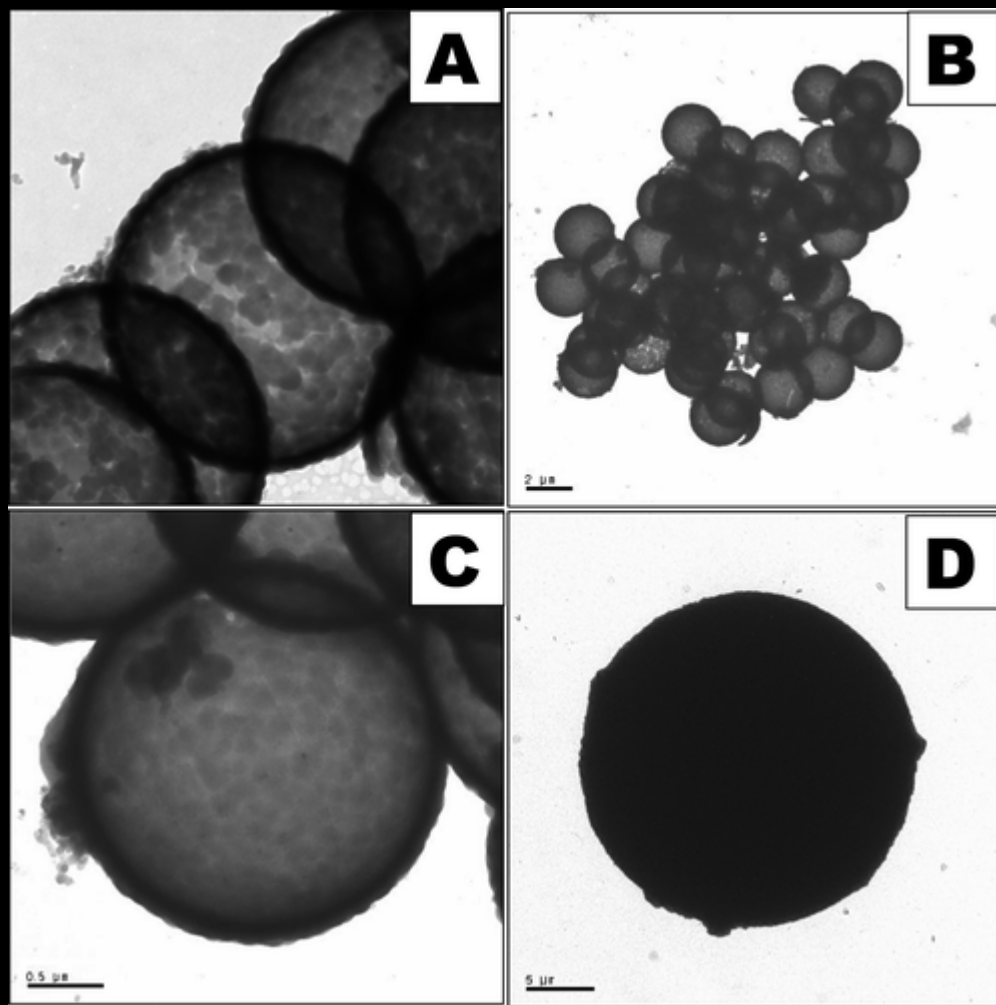


Figure 5. TEM images of calcined hollow shell-type mesoporous silica spheres: at 0.15 μm thickness and mean diameter of μm (A and B) mesoporous alumina microspheres (C) and thick silica particles having mean diameter of 25 μm (D)

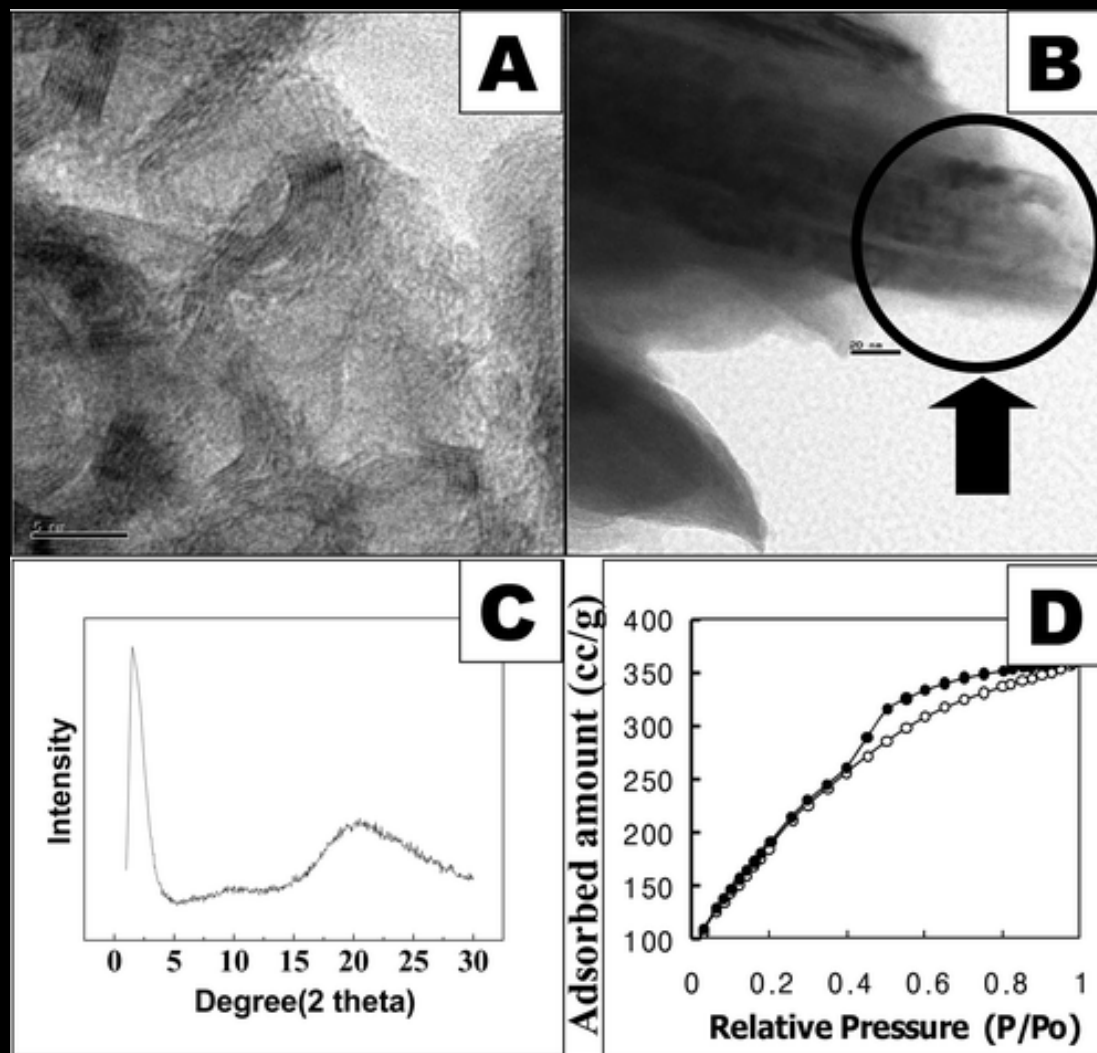


Figure 6. Mesoporous structures of 2 and 30 μm silica microbeads: high-magnification TEM image of silica shell with 0.15 μm thickness (A) and that at 2 μm thickness (B); XRD diffractogram (C); and nitrogen adsorption/desorption isotherm (D).

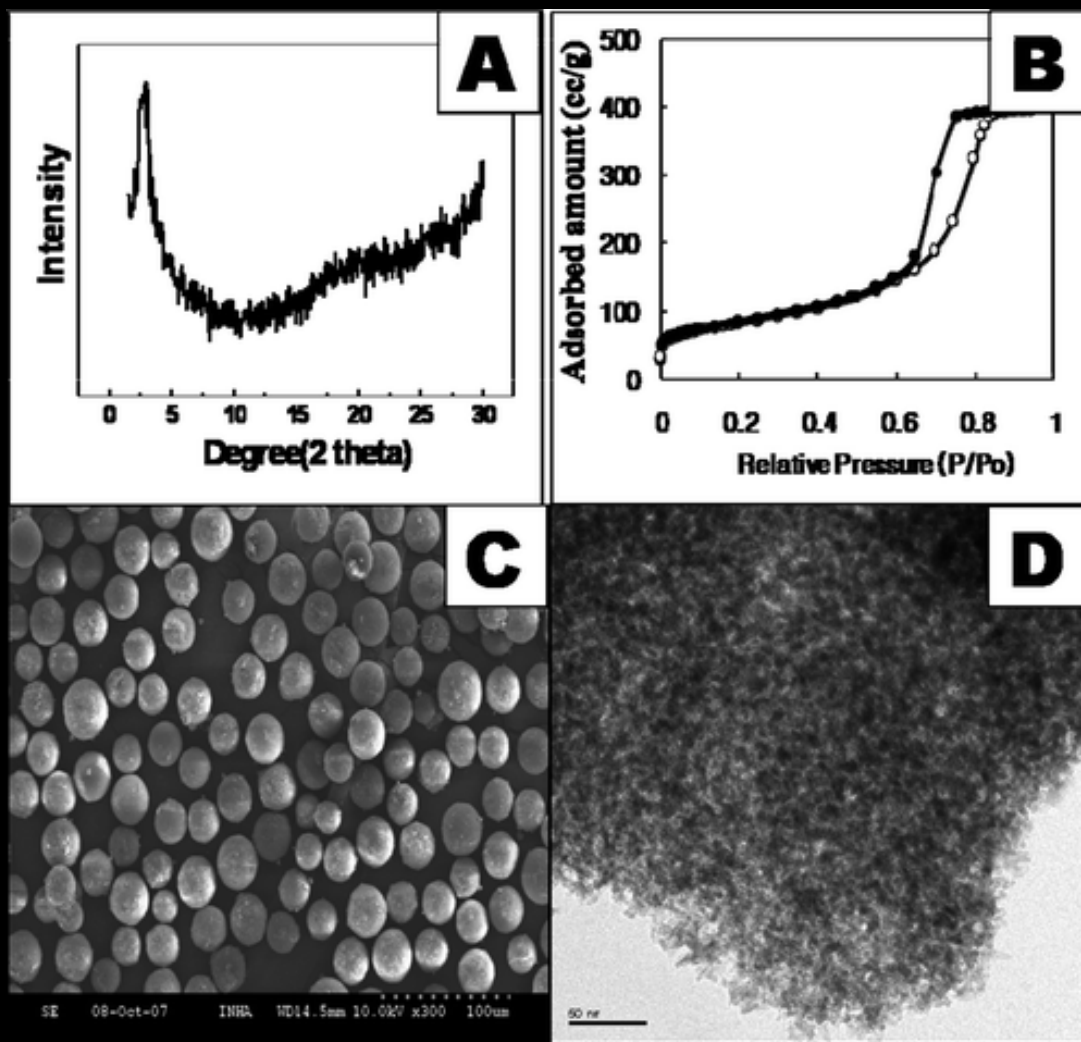
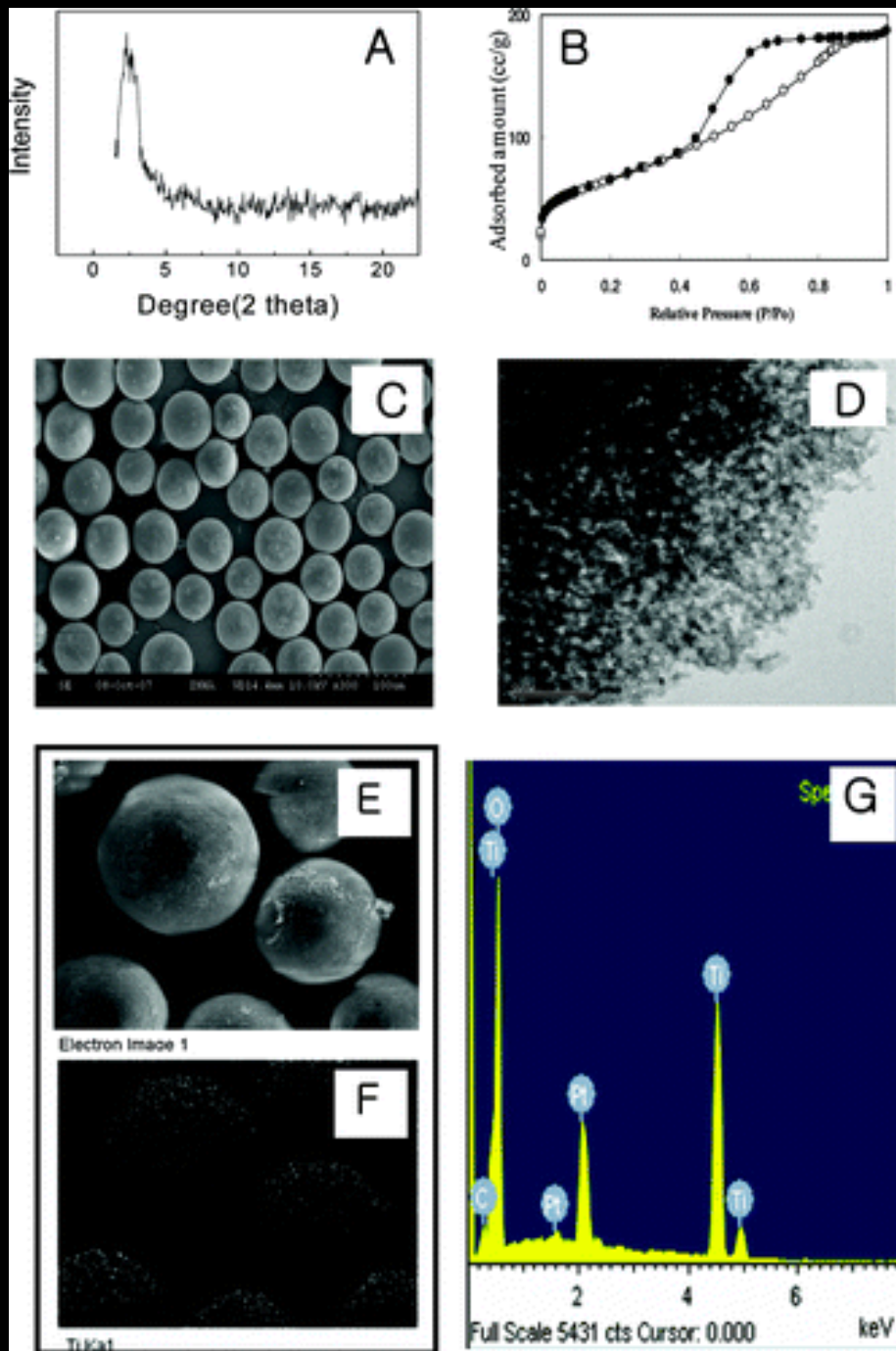


Figure 7. Characterization of Al_2O_3 microcapsules having hollow core with mesoporous shell: XRD diffractogram (A), nitrogen adsorption/desorption isotherm (B), SEM images of hollow Al_2O_3 particles with core diameter of $25\ \mu\text{m}$ (C), TEM image (D)



*Figure 8. Characterization of TiO_2 microcapsules having hollow core with mesoporous shell:
(A) XRD diffractogram*

(B) Nitrogen adsorption/desorption isotherm

(C) SEM images of hollow TiO_2 particles with core diameter of 35 μm

(D) High-magnification TEM image

Summary

- *Pure SiO_2 , Al_2O_3 , and TiO_2 microcapsules having a hollow core with a mesoporous shell were synthesized using PMMA polymer spheres after modification of their surfaces with IL.*
- *Newly synthesized microcapsules have bimodal pore systems of uniform and tunable hollow macroscopic cores with mesopores in the shells, they would have a wide range of applications, including as adsorbents, chromatographic packing materials, catalysts, and advanced storage materials in the controlled drug delivery system.*
- *Efforts are underway to elucidate other significant applications of these materials in the catalytic systems.*

THANK YOU!!!