

Silica Microcapsules and Microtubes Prepared from Rod-Like and Needle-Like Polyaniline Templates

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ABSTRACT: Rod-like or needle-like particles of polyanilinium *p*-toluene sulfonate have been used as templates for the formation of silica microcapsules or microtubes. Thus, an alkaline aqueous suspension of the needles was treated with tetraethyl orthosilicate to form silica-coated needles, which were subsequently calcined to remove the polyanilinium templates. The rod-like or needle-like polyaniline particles, their silica-coated derivatives and silica microcapsules or microtubes have been

characterized by thermogravimetric analysis, Fourier transformation infrared spectroscopy, scanning electron microscopy (SEM), field emission scanning electron microscopy (FE-SEM), and transmission electron microscopy. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 996–1004, 2010

Key words: conducting polymers; Polysilanes; Polysiloxanes; microstructure; flame retardance

INTRODUCTION

Silicate networks in the form of mesoporous silicas and silica nanotubes have been the subject of intense research interest, numerous template procedures having been developed for their syntheses. Silica microtubes consist of unique structures that have been reported using appropriate templates.^{1,2} Ideally, templates should be readily synthesized, have a well-defined morphology and be easily removable, most conveniently by calcination procedures which serve also to dehydrate any silanol network built around them. Silica microcapsules and microtubes produced in the present work were characterized to provide a close appraisal of properties which may be the basis for practical applications. Silica microcapsules commonly contained hollow silica microspheres and rod-like tubes. Structural features of silica microcapsules and microtubes, as judged to be similar to them of silica nanotubes, were of ordered and morphologically controlled structures with highly specific surface areas, broad spaces of cores and anisotropically physical and chemical properties.^{3,4} Template types used to pro-

duce silica nanotubes are usually divided into self assembly,⁵ biological substrates,⁶ organic crystals,⁷ nanoporous membranes,⁴ fiber-like oxides,^{3,8} and carbon nanotubes.⁹ We already reported the synthesis of needle-like polyanilines of 2–15 μm in diameter and 33–225 μm long, and rod-like polyanilines of around 5–10 μm in diameter, which were used as templates for silication with tetraethyl orthosilicate (TEOS).^{10,11} Polyanilines are known to have controllable and relatively high level of electrical conductivity, acceptable chemical stability, ease of monomer availability and synthesis, excellent environmental stability and electro-optical properties, and good corrosion resistance, and especially because the cost of their raw materials is low, polyanilines are relatively suitable for silication templates.^{12,13} Calcinations of silica-coated needle-like polyanilines successfully produced unique silica microtubes. Polyaniline/silica hybrids at a nanometer level had been prepared by the hydrolysis and condensation of TEOS,¹⁴ but polyaniline/silica hybrids at a micrometer level including rod-like or needle-like micro aggregates have seldom been reported. Hollow capsules or tubes could potentially minimize uncontrolled leakages of substances and improve their long-term storability, compared with uncapsuled carriers. Microtubes effectively encase a wide range of guest molecules, such as drugs, herbicides, cosmetic ingredients and diagnosis agents,^{15,16} and provide flexible structures based on changeable composition and unique surface properties like

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superhydrophobicity.¹⁷ Applications of the silica microtubes include biocatalyst support materials,¹⁸ core materials for biosensors and biomarkers,¹⁹ storage or delivery containers for biochemical substances,¹⁸ and optoelectric nanodevice materials.^{19,20}

In this work, the rod-like or needle-like polyanilines were silicated with TEOS and calcined at 450°C to produce the silica microcapsules or microtubes that might possess potential uses for aforementioned applications. The silica microcapsules and microtubes thus prepared were characterized with respect to experimental conditions employed by FTIR, TGA, SEM, FE-SEM or TEM. (See supporting information.)

EXPERIMENTAL PROCEDURE

Materials

Anilines (Samchun Chemical) were distilled under a reduced pressure before use. Ammonium peroxydisulfate (APS, Samchun Chemical), *p*-toluene sulfonic acid (*p*TSA, Samchun Chemical), aqueous ammonia (Samchun Chemical) and TEOS (Samchun Chemical) were used as received.

Synthesis of needle-like polyanilines

Needle-like particles of polyanilinium tosylates were prepared as described previously.^{10,11} Their conductivity ranged from 0.7 to 7 S/cm, and maximum aspect ratio was around 26 L/D. Average yield was 23–25 wt % at 0.5 APS/aniline molar ratio.

Synthesis of rod-like polyanilines

Rod-like polyanilines were prepared with about 0.5–1 hour APS addition at 0–15°C reaction temperature and other reaction conditions were the same as those of the needle-like polyanilines.^{10,11,21}

Silication of rod-like or needle-like polyanilines

Twenty gram of rod-like or needle-like polyanilines were thoroughly dispersed in a solution of 100 mL ethanol, 900 mL distilled water and 10 mL NH₃(aq) before adding 10 g TEOS to the mixture. Silica depositions were allowed to proceed at room temperature for 2 days, and then the solution was aged at 80°C for 2 day before the solids were collected by filtration, washed with distilled water and dried at 45°C under vacuum whose average recovery was 26 g. Silica-coated polyanilines were observed at a magnification of 1000× using a FE-SEM (Jeol, JSM 6701F).

Formation of silica microcapsules or microtubes

Precipitates obtained as above were calcined at 450°C for 1 to 4 h or 500 and 550°C for 4 h using an

electric furnace (YJ-880DP Series, UConTec). Yields for calcined silica-coated polyanilines were around 7–10 wt %. The wall thickness and length of silica microtubes were observed at a magnification of 1000× and 4000× by using a SEM (Hitachi S-3700N), FE-SEM (Jeol, JSM 6701F) and TEM (Hitachi H-7600).

Ultramicrotomy on TEM specimens for cross-section observations

Needle-like polyanilines were placed on a mould, which was filled with an epoxy resin (Epoxy 812 embedding kit) and then heated at 60°C for 2 days in a vacuum oven. Trimming an embedded specimen was carried out using a specially designed glass knife. Specimens were trimmed on the mount of an ultramicrotome (Leica ultracut UCT) to produce four large facets. Sectioning the trimmed samples was done in distilled water using a diamond knife whereby the thickness of sections was controlled to be 100 nm. The diamond knife had a cavity filled with distilled water whose level was carefully adjusted with a syringe. A hair or glass fiber tool was used to guide the sections toward a grid held in a tweezer and the sections were picked up on the copper grids and dried after extra water was removed from the grids using a facial tissue.

TGA measurements

Thermogravimetry of both polyaniline particles and silica-coated derivatives was performed for the rod-like and needle-like aggregates using a TGA (TA Instruments, Q50 Hi-Res TGA 2950) at 20°C/min heating rate up to 800°C under nitrogen.

Brunauer-Emmett-Teller (BET) surface area and pore characteristics

Specimens were degassed at 250°C for 1 h before nitrogen gas absorption. The method of Barrett-Joyner-Halenda was performed using a surface area and pore size analyzer (Quantachrome Autosorb-1) to measure BET surface areas, pore volumes and pore sizes.

FTIR measurements

FTIR spectra for the needle-like polyanilines and silica microtubes were measured by a gas chromatograph-interfaced FTIR system (FTS-2000 & 3900).

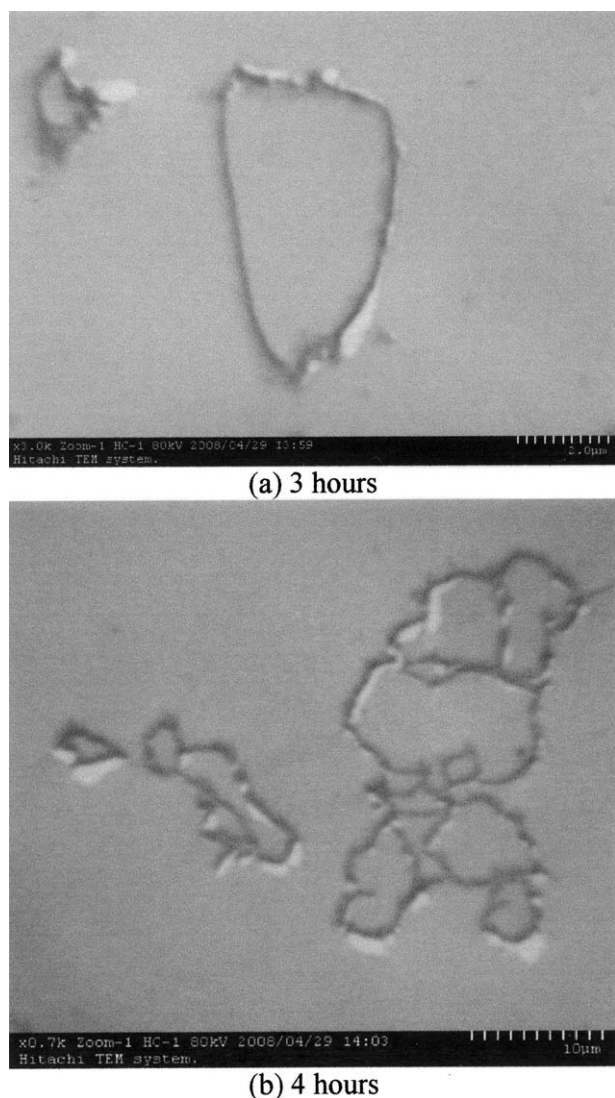


Figure 1 TEM images for the cross-sections of needle-like polyanilines prepared with various APS addition times.

RESULTS AND DISCUSSION

Morphology of rod-like and needle-like polyaniline templates

In aqueous media acidified with *p*TSA, aniline undergoes oxidation by APS to give seemingly crystalline polyanilinium tosylates which adopt various forms depending upon the conditions of oxidation reactions. Gradual additions of oxidants over several hours at a temperature near 15°C produce the needle-like particles used in the present experiments. When anilines were mixed with *p*TSA as an emulsifier, *p*TSA commonly built needle-like cores on which anilines were absorbed by creating an interface layer between the needle-like *p*TSA cores and water. Anilines were easily aligned along the interface in an aqueous medium at room temperature due to their hydrophilicity. At an early report,¹¹ we believed that the needle-like anilium-dopant com-

plexes were composed of alternating two layers of anilines and dopants, but it is sure that anilines were assembled along the interface between *p*TSA cores and water forming the needle-like anilinium tosylates. When APS was added fast and/or a reaction temperature was relatively high or low, the needle-like anilinium complexes were commonly broken during polymerization. In contrast, when APS was added very slowly and the reaction temperature was as high as 15°C, the needle-like anilinium tosylates were not broken until the polymerization ended. Figure 1(a) shows the cross-section of a needle-like polyaniline embedded in an epoxy resin, prepared with 15°C reaction time and 3 h APS addition time. Anilines, gathered on the interface of *p*TSA, were polymerized by APS added very slowly to prepare a polyaniline layer of average 0.3 µm thick and 8 µm in diameter (a dark line) surrounding a needle-like *p*TSA core. The 3 h APS addition time extensively produced a single-walled polyaniline aggregate, which were effectively combined each other by causing significantly transverse growth on the needle-like polyanilines at the 4 h APS addition time [Fig. 1(b)]. Spherical polyanilines are of average 8 µm in diameter from which the needle-like aggregates grew up. Rod-like polyanilines were prepared at 0.5–1 hour APS addition time, potentially developed into needle-like ones by a longer APS addition time. The needle-like polyanilines were prepared at the 3 h APS addition time whose single-walled needle-like structures were responsible for high conductivity and aspect ratio, such as average 2 S/cm and maximum 26 L/D. The multiwalled needle-like polyanilines grown by transverse growth of the combination of single-wall needle-like aggregates were prepared with 5 h APS addition time.

Silication of rod-like or needle-like polyanilines

*p*TSA, dissolved in water, naturally forms micelles and absorbs anilines on its micelle surfaces due to its amphiphilicity. Because anilines don't substantially permeate the micelles, anilines are commonly attached on the micelle surfaces by inverse emulsion process to form anilium-*p*TSA complexes as unique shapes such as needle-like aggregates, which were then polymerized by APS along their own needle-like shapes. TEOS added was possibly attached on the surface of polyanilines by surface interaction phenomena (Fig. 2).²² In a calcination process, final silica network structures, revealed by removal of polyaniline shells, substantially depend on calcination temperatures and annealing times.

Hydrogen atoms in amine groups of polyanilines vulnerably interact with ethoxy groups of TEOS to create secondary bonds, potentially hydrogen bonds, at an aqueous solution where ethoxy groups could

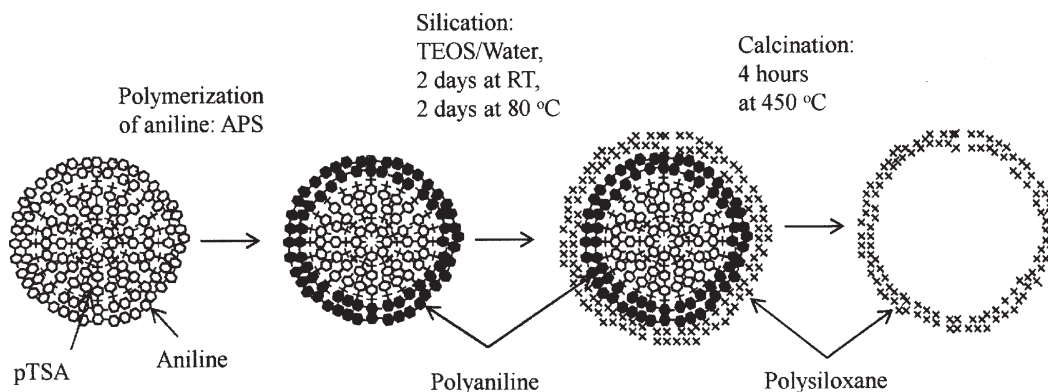


Figure 2 Schematic diagram for formation of hollow silica particle.

be easily hydrolyzed and replaced by hydroxyl groups, as depicted in Figure 3.²³ On the other hand, the other ethoxy groups of TEOS could simply create cross-linking networks by condensation reactions between adjacent ethoxy groups. Silica coating was generally performed by Stöber growth process including hydrolysis of TEOS in NH_3 /alcohol and condensation of SiO_2 on polyaniline aggregate surfaces. Figure 4(a,b) shows the FE-SEM images of the needle-like polyanilines prepared at 15°C reaction temperature and 5 h APS addition time and the silica-coated needle-like polyanilines containing free silica particles on the surfaces. Coating with TESO basically produced rough surfaces on the needle-like polyanilines. A multilayer deposition of polymer electrolytes was reported to potentially induce smooth and uniform surface coatings of TEOS on polystyrene beads.¹⁵

Figure 5(a) shows the TGA curves for the rod-like polyanilines, silica-coated rod-like polyanilines and silica microcapsules, and Figure 5(b) exhibits the TGA curves for the needle-like polyanilines, silica-coated needle-like polyanilines and silica microtubes. The difference between the decomposition temperature (T_d) of the needle-like polyanilines and that of the silica-coated needle-like polyanilines was about 10°C, but the difference between the T_d of the rod-

like polyaniline and that of silica-coated rod-like polyaniline was so large as 30°C whose characteristics are also listed in Table I. The rod-like polyanilines

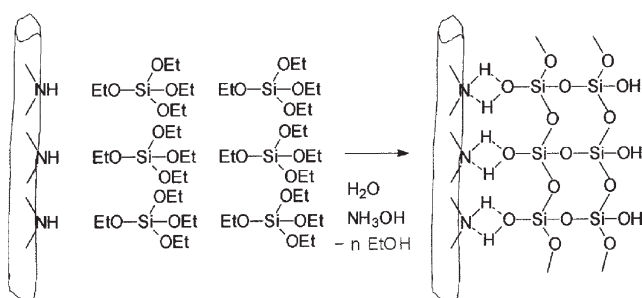
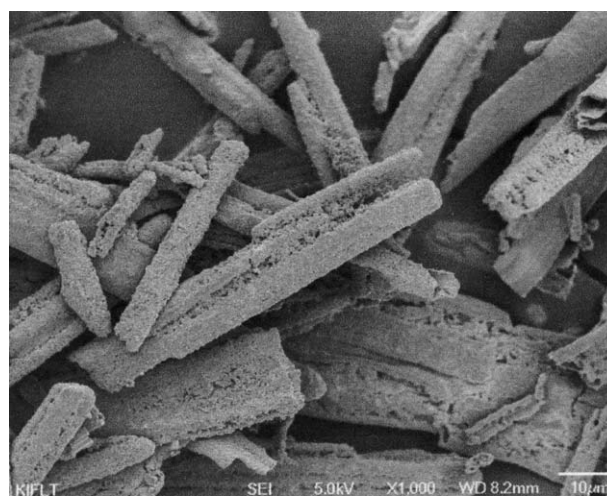
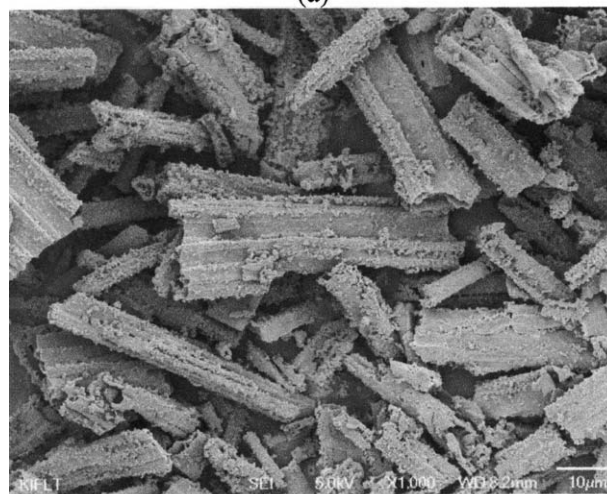


Figure 3 Silication on the surface of needle-like polyanilines by TEOS.²³



(a)



(b)

Figure 4 FE-SEM images of (a) needle-like polyanilines, prepared with 5 h APS addition time, and (b) silica-coated needle-like polyanilines.

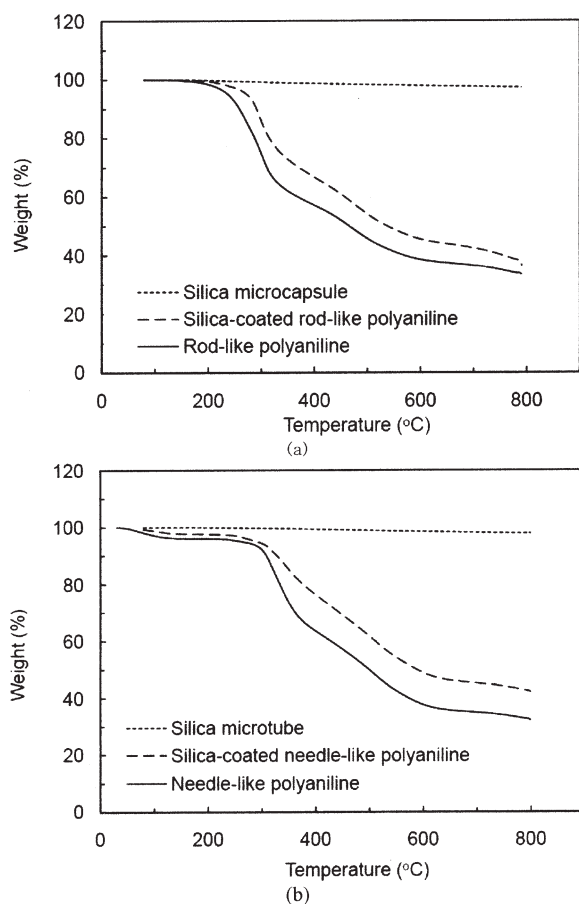


Figure 5 TGA thermograms of (a) rod-like polyanilines (0.5 hour APS addition time) and their derivatives, (b) needle-like polyanilines (4 hours APS addition time) and their derivatives.

degraded around 240°C, and the needle-like polyanilines showed better thermal stability ($T_d = 290^\circ\text{C}$) than the rod-like polyanilines. It is sure because the crystallinity of the needle-like polyanilines is higher than that of the rod-like polyanilines similar to that of the spherical polyanilines.¹⁰ The silica-coated rod-like and needle-like polyanilines started to degrade around 270 and 300°C, and their decomposition almost ended about 600°C. Coating with TEOS obviously improved thermal stability of the rod-like and needle-like polyanilines. The tar content of the rod-like polyanilines was almost the same 33% as that of the needle-like polyanilines, and the tar contents of the silica-coated rod-like and silica-coated needle-like polyanilines were 38 and 43 wt %, respectively. Therefore, the weight of the silica coating layer was about 5 wt % for the silica-coated rod-like polyanilines and 10 wt % for the silica-coated needle-like polyanilines in this work. However, the silica microcapsules and microtubes didn't show a significant change in weight and thermally very stable up to 800°C, and their tar contents were 97 and 98%, respectively.

Calcination of silica-coated polyanilines

The color of silica microtubes was changed according to the amount of residual polyanilines inside the silica microtubes. An optimum calcination temperature and annealing time were 450°C and 4 h in this work, potentially depending on the volume of specimens and thickness of coated silica layers because a large amount of specimens and thick silica layers tend to block heat flow toward the polyaniline layers. The spherical polyanilines occasionally contain the rod-like aggregates (shorter in length than the needle-like polyanilines) commonly prepared with relatively high reaction temperatures such as 10–15°C during polymerization [Fig. 6(a)].^{10,11} Figure 6(b) shows the surface of the silica-coated rod-like polyanilines, which were calcined at 450°C calcinations temperature for 4 h annealing time and thus transformed to the silica microcapsules composed of hollow silica spheres and silica rod-like tubes [Fig. 6(c)]. The silica microcapsules were easily prepared at the 450°C calcinations temperature and 4 h annealing time compared with the silica microtubes because small pore volumes of the silica microcapsules are more effective to resist an excessive heat flow causing silica wall collapse than large ones of the silica microtubes.

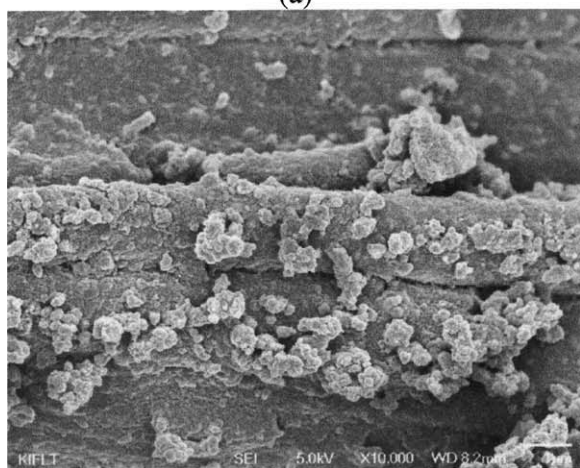
Table II lists the BET characteristics for the silica microcapsules and microtubes. The BET surface area, pore volume and pore size for the silica microcapsules were 792 m²/g, 0.77 cm³/g, and 388 nm and those for the silica microtubes were 487 m²/g, 1.05 cm³/g, and 862 nm. Because the silica microcapsules contained various pore sizes of hollow spheres and capsules per unit weight, the BET surface area of the silica microcapsules was higher than that of silica microtubes. The pore volume of the silica microcapsules was smaller than that of the silica microtubes because the pore size and length of the silica microcapsules were smaller than those of silica microtubes. The BET surface area is generally inversely proportional to the pore size. For instance, a high BET surface area of 980 m²/g for 180 nm pore size of silica gels has been reported.²⁴ The silica microcapsules and microtubes with a large BET surface area could also give potential applications to

TABLE I
TGA Characteristics for Rod-Like and Needle-Like Polyanilines and their Derivatives

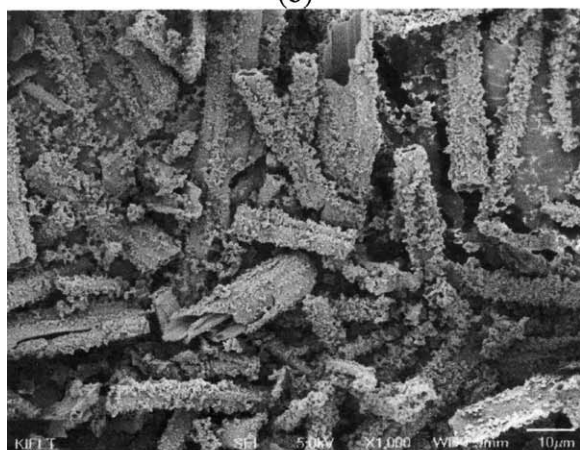
Materials	T_d (°C)	Tar (%)
Rod-like polyaniline	240	33
Silica-coated rod-like polyaniline	270	38
Silica microcapsule	None	97
Needle-like polyaniline	290	33
Silica-coated needle-like polyaniline	300	43
Silica microtube	None	98



(a)



(b)



(c)

Figure 6 FE-SEM images for (a) rod-like polyanilines prepared with 10°C reaction temperature and 0.5 hour APS addition time, (b) silica-coated rod-like polyanilines, and (c) silica microcapsules calcined at 450°C for 4 h.

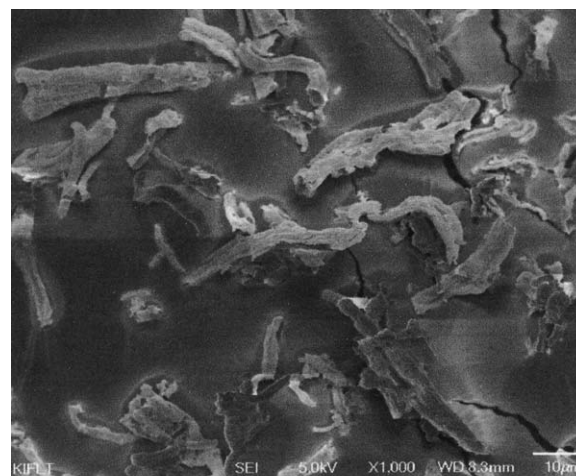
adhesives, abrasive resistance paints, chromatography, waste removal²⁵ and heat resistance electorodes.²⁶

The formation of silica microtubes was significantly affected by the calcination temperatures, such

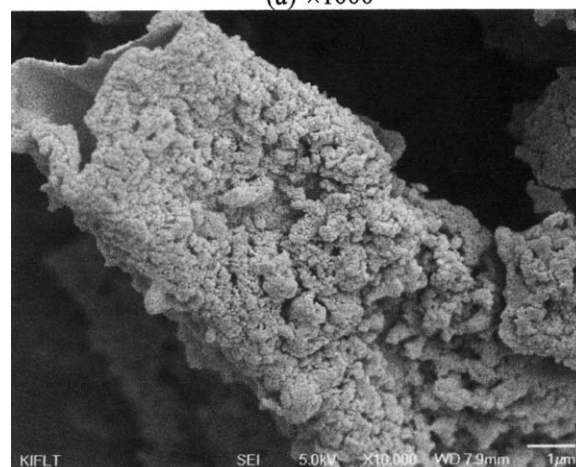
TABLE II
BET Data for Silica Microcapsules and Microtubes

Materials	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
Silica microcapsule	792	0.77	388
Silica microtube	487	1.05	862

as 450, 500 and 550°C, rather than by the annealing times at the calcinations temperatures, because the decomposition of the silica-coated needle-like polyanilines continued even near the calcinations temperatures, starting from 300°C and ended at 600°C. At the 500°C calcination temperature, many silica microtubes started to be collapsed [Fig. 7(a)], and more silica microtubes were eventually collapsed at 550°C, regardless of the annealing time. The FE-SEM image for a silica microtube, produced at 500°C calcinations temperature and 4 h annealing time, clearly shows a hollow core pattern with silica walls



(a) ×1000



(b) ×10000

Figure 7 FE-SEM image for (a) collapsed silica microtubes and (b) a silica microtube, calcined at 500°C calcinations temperature and 4 h annealing time.

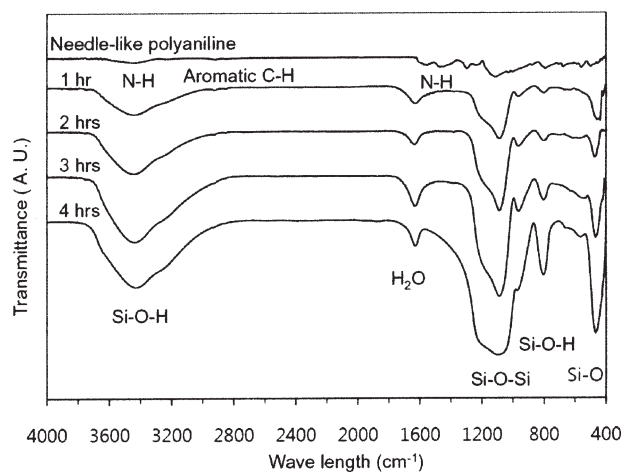


Figure 8 FTIR spectra for needle-like polyanilines and silica microtubes calcined at 450°C for 1–4 hours annealing times.

[Fig. 7(b)]. Thick silica layers and small pore sizes of silica microtubes possibly increase a minimum calcination temperature to cause collapse of silica walls.

The N–H stretching vibration for the needle-like polyanilines appeared at 3450 cm^{-1} and 1400–1600 cm^{-1} (Fig. 8). Aromatic C–H vibration at 2900–3000 cm^{-1} for the needle-like polyanilines still remained even after the silica-coated needle-like polyanilines were calcined for 1 or 2 h annealing time. Aromatic C–H vibration, slightly observed for silica microtubes prepared with 3 h annealing time, completely disappeared for those prepared with 4 h annealing time. The OH stretching of the framework Si–OH is related to the peak at 3456 cm^{-1} and the symmetric stretching vibration of Si–OH headgroups appeared at 965 cm^{-1} . The peaks around 800 and 1150 cm^{-1} are assigned to symmetric and asymmetric vibrations of the Si–O–Si. The peak at 460 cm^{-1} is attributed to the Si–O bending mode. The peak at 1646 cm^{-1} is due to the bending mode of water.² The peaks at 965, 800 and 460 cm^{-1} increased as the annealing time increased on a basis of the peak at 1150 cm^{-1} .

Even though the 450°C calcination temperature changed many silica-coated needle-like aggregates into silica microtubes, insufficiently calcined silica microtubes were sometimes produced by such a short annealing time and a relatively large volume of specimens. Various colors of silica microtubes occurred due to the thickness of residual polyaniline layers produced by various annealing times. As calcined at 450°C for 1 to 4 h annealing time, the silica-coated needle-like polyanilines were gradually transformed into silica microtubes whose colors were changed from black for 1 h [Fig. 9(a)] through purple for 2 h [Fig. 9(b)] and gray for 3 h [Fig. 9(c)] to white for 4 h annealing time [Fig. 9(d)]. Figure 10

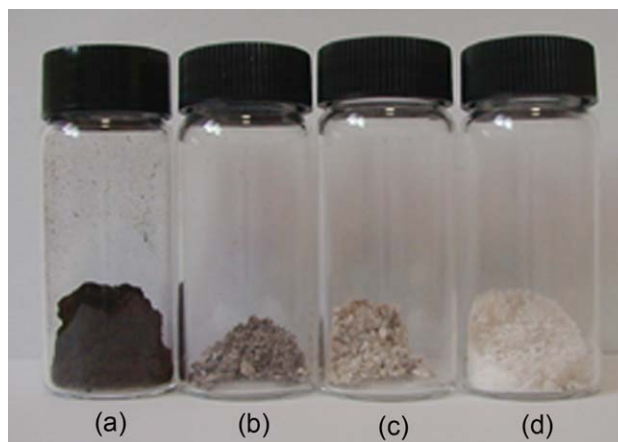


Figure 9 Silica microtubes calcined at 450°C for various annealing times: (a) 1 h (black), (b) 2 h (purple), (c) 3 h (gray), (d) 4 h (white). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

shows a SEM image of the black-colored silica microtubes calcined at the 450°C temperature for the 1 h annealing time. Almost all silica microtubes were translucent because of their hollow cores, so that other microtubes behind top microtubes were slightly reflected. The size of the silica microtubes was 2–15 μm in diameter, 33–225 μm long and 0.1–0.2 μm thick.

Figure 11 shows TEM images of the silica microtubes produced at the 450°C calcinations temperature for 1 to 4 h annealing time. The silica microtubes took different colors according to the calcination time. The calcination for the 1 h annealing time produced the black silica microtubes holding thick polyaniline layers on the templates [Fig. 11(a)]. The purple silica microtubes were produced

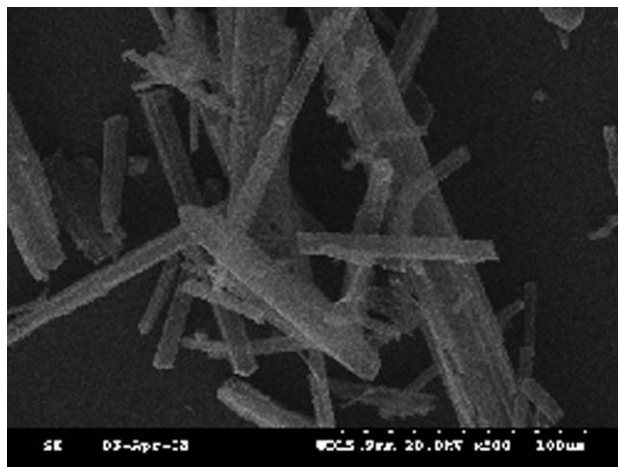


Figure 10 SEM image of silica microtubes produced from silica-coated needle-like polyanilines (4 hours APS addition time) calcined at 450°C for 1 h annealing time.

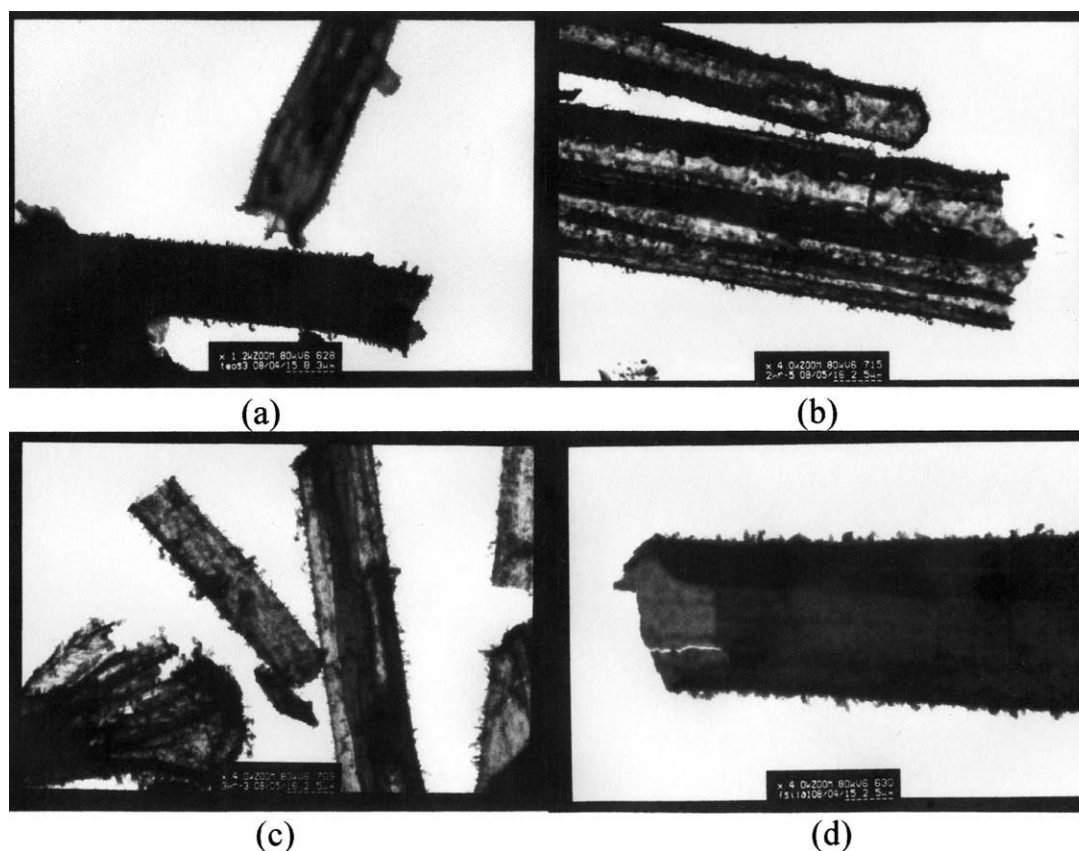


Figure 11 TEM images of silica microtubes produced by the calcination at 450°C for various annealing times. The lengths of scale bars are (a) 8.3 μm and (b), (c) and (d) 2.5 μm .

by the 2 h annealing time [Fig. 11(b)], and the 3 h annealing time prepared the gray silica microtubes including a small amount of partially purple particles [Fig. 11(c)]. The white silica microtubes were produced by the 4 h annealing time [Fig. 11(d)]. An optimum calcination temperature and annealing time to produce silica microtubes were actually different with specimen volumes for calcinations because of a furnace capacity. A larger volume of specimens possibly protected more inner specimens from heat wave in a furnace and thus the inner specimens were less calcined. A thick silica layer of the silica-coated needle-like polyanilines could also increase a minimum calcination temperature or annealing time to cause the collapse of silica microtubes. Silica microtubes could be potentially used as fillers for superhydrophobic coating, insulating coating of electricity wires, ant flame retardant coating, fast adhesives and reinforcement composites.

CONCLUSION

The rod-like polyaniline aggregates were synthesized from anilinium *p*TSA complexes at 2°C reac-

tion temperature with 0.5 hour APS addition time and the needle-like polyaniline aggregates were prepared at 15°C reaction temperature with 3 to 5 h APS addition times by oxidative polymerization. The rod-like or needle-like polyanilines were composed of *p*TSA cylindrical cores surrounded by polyaniline outer layers. TEOS was reacted on the rod-like or needle-like polyanilines in water/alcohol/ NH_3 and then silica-coated polyanilines were aged at 80°C in an oven. The optimum calcination temperature and annealing time were 450°C and 4 h in this work, possibly varied according to the volume of specimens and thickness of silica layers. The weight percents of the silica coating layers were about 5 wt % for the silica-coated rod-like polyanilines and 10 wt % for the silica-coated needle-like polyanilines. The decomposition temperature for the silica-coated needle-like polyanilines was higher than that of the silicate rod-like polyanilines, but the BET surface area of the silica microcapsules was higher than that of the silica microtubes. The size of silica microtubes was 2–15 μm in diameter, 33–225 μm long and 0.1–0.2 μm wall-thick. Various colored silica microtubes were prepared by the calcinations at 450°C for 1 to 4 h annealing times.

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