

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/6821425>

# First Isolation of Individual Silicate Platelets from Clay Exfoliation and Their Unique Self-Assembly into Fibrous Arrays

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · OCTOBER 2006

Impact Factor: 3.3 · DOI: 10.1021/jp0636773 · Source: PubMed

---

CITATIONS

48

---

READS

22

4 AUTHORS, INCLUDING:



Jiang-Jen Lin

National Taiwan University

211 PUBLICATIONS 3,029 CITATIONS

SEE PROFILE



Ming-Li Chiang

National Taiwan University

21 PUBLICATIONS 230 CITATIONS

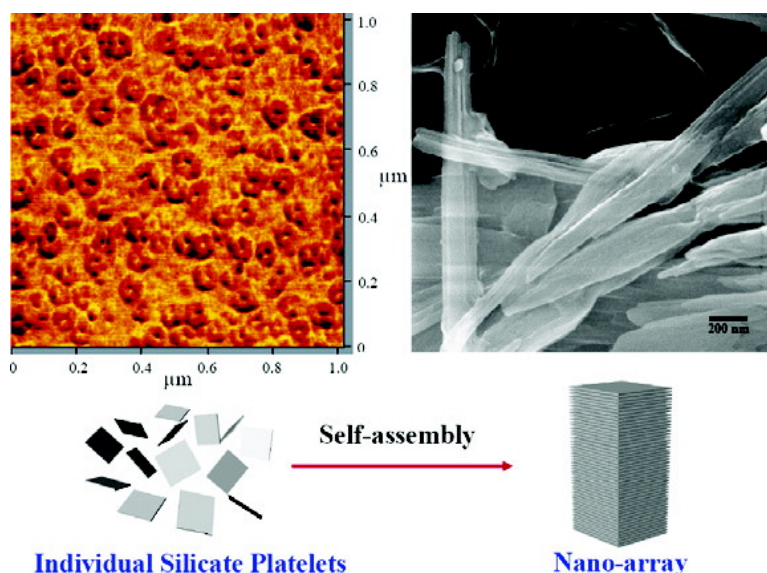
SEE PROFILE

## First Isolation of Individual Silicate Platelets from Clay Exfoliation and Their Unique Self-Assembly into Fibrous Arrays

Jiang-Jen Lin, Chien-Chia Chu, Ming-Li Chiang, and Wei-Cheng Tsai

*J. Phys. Chem. B*, **2006**, 110 (37), 18115-18120 • DOI: 10.1021/jp0636773

Downloaded from <http://pubs.acs.org> on December 28, 2008



### More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 5 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



**ACS Publications**  
High quality. High impact.

The Journal of Physical Chemistry B is published by the American Chemical Society,  
1155 Sixteenth Street N.W., Washington, DC 20036

# First Isolation of Individual Silicate Platelets from Clay Exfoliation and Their Unique Self-Assembly into Fibrous Arrays

Jiang-Jen Lin,\* Chien-Chia Chu, Ming-Li Chiang, and Wei-Cheng Tsai

*Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan*

*Received: June 13, 2006; In Final Form: August 15, 2006*

Thin silicate platelets in a dimension of approximately  $80 \times 80 \times 1 \text{ nm}^3$  are isolated for the first time by a newly developed process involving one-step exfoliation of natural montmorillonite clay and toluene/aqueous NaOH extraction. The platelets are observed to be polygon shape by transmission electron microscopy (TEM) and round bent-leaf shape by dynamic force microscopy (DFM). Individual platelets possessing high-aspect-ratio dimension and ionic character are able to self-assemble into microscale fiber bundles after water evaporation. The self-stacking mechanism indicated strong face-to-face ionic charge stacking propensity in triggering a vertical growth. Regularity of fibrous bundles in an average  $5 \mu\text{m}$  length has been observed.

## Introduction

Studies have shown that inorganic materials of the 1–100 nm scale may behave as quantum dots in electron movement,<sup>1</sup> and consequently give rise to unconventional physical properties.<sup>2–4</sup> A great deal of effort has been made to prepare nanomaterials for industrial applications including inorganic/polymer nanocomposites,<sup>5–9</sup> optoelectronic devices,<sup>10</sup> biomedical materials,<sup>11,12</sup> and so on. However, the isolation and manipulation of nanomaterials in such a scale still remains a challenge, mainly due to their strong tendency for bulk aggregation. For example, the naturally occurring smectite clays are widely reported for their wide applications in polymer/silicate nanocomposites,<sup>13–16</sup> but generally found the difficulties of dispersing these silicate platelets in the homogeneous state. The attracting ionic force between the layered silicate surface anions and the counter metal cations is intensive because of the high-aspect-ratio dimension of approximately  $100 \times 100 \times 1 \text{ nm}^3$  for each platelet.<sup>17</sup> To develop a process of exfoliating the layered silicates and manipulating the randomized platelets is desired for effectively utilizing these materials.

Conventionally, the process for utilizing montmorillonite clay required a stepwise process, intercalation and exfoliation. The layered silicates can be organically modified in two categories, the intercalated<sup>5–8</sup> and the exfoliated,<sup>18–20</sup> depending on the degree of interlayer space expansion. In an intercalated structure, the silicate platelets maintain their original layered structure but are embedded with organics in the gallery. This is conventionally achieved by using low-molecular-weight quaternary ammonium surfactants which allow the intercalation of layered silicates with a gallery space in the range  $20\text{--}40 \text{ \AA}$ <sup>5–8</sup> compared to the pristine  $12 \text{ \AA}$ . The silicate platelets still maintain a layered structure (averaged 8–10 layers in each unit)<sup>17</sup> but are alternatively embedded with organic intercalants. In the exfoliated form, each individual silicate platelet is randomly dispersed in organic polymers through in situ monomer polymerization or polymer blending. However, incomplete exfoliation is frequently en-

countered due to the difficulty for overcoming the intensive ionic attraction between the neighboring platelets.

Previously, we synthesized exfoliating agents from the Mannich reaction of poly(oxyalkylene)-diamine with *p*-cresol and formaldehyde. The synthesized amine-terminating Mannich oligomers (AMO) or polyamines, consisting of several POP segments and multiple amine functionalities, were used to exfoliate the hydrophilic clays.<sup>21</sup> By partially converting into quaternary salts, the polyamines underwent an effective ionic exchange reaction and rendered  $\text{Na}^+$ -MMT into exfoliation. The subsequent NaOH extraction from toluene allowed the polyamine exfoliating agents to be recycled in the organic phase and led to the isolation of individual platelets in water suspension. Previously, we have demonstrated the randomized silicate platelets are effective for improving the physical properties in an epoxy system.<sup>22,23</sup> Here, we further report the characterization of the random platelets, their fundamental properties of ionic characteristics and high-aspect-ratio shape, and also a unique self-aligning nature during the water-evaporating process.

## Experimental Section

**Materials.** Sodium montmorillonite ( $\text{Na}^+$ -MMT), a sodium form of smectite aluminosilicates, was obtained from Nanocor Co. The naturally occurring clays have a generic structure of 2:1 layered silicate/aluminum oxides with two tetrahedron sheets sandwiching an edge-shared octahedral sheet. The commercially available clay, aggregated at an average size of  $0.1\text{--}2.0 \mu\text{m}$ , has exchangeable  $\text{Na}^+$  counterions with a cationic exchange capacity (CEC) of  $\sim 120 \text{ mequiv/100 g}$  and average 8–10 sheets in a primary stack. The size of individual platelets in the MMT primary stack is polydispersed in dimension, estimated to be  $80\text{--}100 \text{ nm}$  and  $\sim 1 \text{ nm}$  in thickness.<sup>24</sup> The individual silicate platelets were obtained from delaminating the above layered mineral through a newly developed exfoliation process and subsequent extraction with sodium hydroxide in our research group.<sup>21,24</sup>

**Exfoliation of  $\text{Na}^+$ -MMT with the Agents Prepared from Mannich Condensation of Poly(oxypropylene)-diamine, *p*-**

\* Corresponding author. Fax: +886-2-3366-5237. E-mail: jianglin@ntu.edu.tw.

**Cresol, and Formaldehyde.** The typical procedures for preparing the polyamine exfoliating agents involve the use of poly(oxypropylene)-diamine of various molecular weights ( $M_w$ ). The diamine with a molecular weight of 2000 g/mol (abbreviated as POP2000) is a poly(propylene glycol)-bis(2-aminopropyl ether) with a structure of 33 oxypropylene units and two terminal primary amines. The typical experimental procedures for preparing the Mannich polyamines are described. To a 1 L round-bottomed flask, equipped with a mechanical stirrer, a thermometer, a heating mantle, and a Dean–Stark trap, was added *p*-cresol (6.8 g, 63 mmol), POP2000 (189 g, 95 mmol), and toluene (100 mL). The mixtures were heated to 110 °C with stirring, followed by adding formalin (3.8 g, 127 mmol) in a dropwise manner. After completing the formalin addition, the reactor was heated to 130–140 °C for 3 h and then to 160–170 °C for 1 h. During the process, the generated water was removed slowly through a Dean–Stark trap. The prepared polyamines are amine-terminated and POP2000-segmented Mannich oligomers (AMO) and subsequently used for the clay exfoliation.

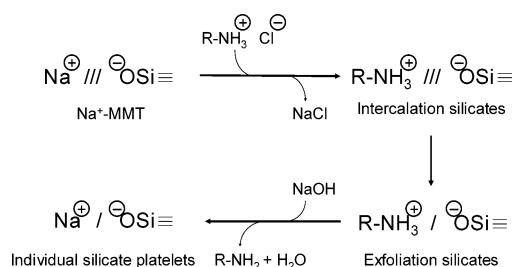
The exfoliation of  $\text{Na}^+$ -MMT with AMO was performed according to the procedures described previously.<sup>21</sup> The prepared AMO (57.5 g, 24 mmol) and 37 wt % aqueous hydrochloric acid (1.2 g, 12 mmol) were dissolved in 5 mL of deionized water to form polyamine salts and then mixed with  $\text{Na}^+$ -MMT (10 g), separately preswelled in 1 L of deionized water. The mixture was continuously stirred at 80–85 °C for an additional 5 h. The precipitate (AMO/MMT) was filtered, collected, and washed thoroughly with the water/ethanol mixture several times.

**Sodium Hydroxide Extraction and the Isolation of Random Silicate Platelets.** One equivalent amount of aqueous sodium hydroxide (10 wt %, 3.7 g) was added to the prepared AMO/MMT (54 g) suspension in ethanol at 60 °C and extracted by agitating the slurry with water/toluene. After allowing the solution to settle, it separated into two layers. The upper layer containing mostly toluene and AMO was removed. The bottom water phase was extracted with toluene for three times to remove organics, concentrated by using a rotary evaporator and characterized by thermogravimetric analysis (TGA), transmission electron microscopy (TEM), dynamic force microscopy (DFM), and pH analyses.

**Self-Assembly of Silicate Platelets Piling into Fibrous Arrays.** The silicate platelet suspension of 1 wt % was thinly coated in a glass slide or beaker and subjected to 80 °C evaporation in an oven for 4 h; a solid powder was obtained. The bulk sample of self-assembly was prepared from a platelet water suspension of 6 wt % in a beaker and dried under 80 °C for 8 h.

**Analysis and Characterization.** The basal spacing ( $n = 1$ ) was assigned from the apparent peak or calculated according to the Bragg's equation ( $n\lambda = 2d \sin \theta$ ) through the observed peaks of  $n = 2, 3$ , etc. Thermogravimetric analysis (TGA) was performed on a Seiko SII model SSC/5200, with the samples heating from 50 to 850 °C at 10 °C/min in air. Transmission electronic microscopy (TEM) was performed on a Zeiss EM 902A instrument operated at 80 kV. Scanning electron microscopy (SEM) and field emission SEM (FE-SEM) were performed on a Topcon scanning electron microscope (model ABT-150a) at an accelerating voltage of 20 kV and on a JEOL-6500 microscope at an accelerating voltage of 15 kV, respectively. Dynamic force microscopy (DFM) was performed on a Seiko SPI3800N instrument, series SPA-400, Seiko Instrument Inc. (cantilever type, SI-DF20;  $f = 139$  kHz; spring constant, 16 N/m; coating, Al). A ZetaPlus zetameter (Brookhaven Instru-

## SCHEME 1: Conceptual Description of Preparing Silicate Platelets



ment Corp., NJ) was used for characterizing the ionic property of the clays. The zeta potentials of the  $\text{Na}^+$ -MMT starting material and silicate platelets in aqueous suspension of 0.01 wt % concentration were measured in the pH range from 2 to 11. The background pH buffer solution from 2 to 4 was adjusted by  $\text{H}_3\text{PO}_4$  and  $\text{KH}_2\text{PO}_4$ , from 5 to 8 by  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ , and from 9 to 11 by  $\text{Na}_2\text{HPO}_4$  and  $\text{Na}_3\text{PO}_4$ , in each case at a concentration of 0.1–0.2 M. After the silicate addition, the suspension pH was further adjusted to the desired value by adding 0.5 M NaOH or HCl. The zeta potential was measured in the solution with an ionic strength of 0.2. The same instrument (ZetaPlus, Brookhaven) was used to estimate the average particle size in diameter of the silicate platelets. The readings of 100 nm for silicate platelets and 850 nm for  $\text{Na}^+$ -MMT were obtained.

## Results and Discussion

**Isolation and Characterization of Randomized Silicate Platelets in Water Suspension.** In our previous work,<sup>21</sup> the layered silicate clay was completely exfoliated into individual silicate platelets dispersed in the intercalating polyamines. The isolation of the organic-free silicate platelets is possibly performed by adding aqueous NaOH to convert the amine salts into amines which can be subsequently removed by toluene extraction. The overall process involves the direct exfoliation and two ionic exchange steps to generate silicate platelets in a random form (Scheme 1). The sodium ions in  $\text{Na}^+$ -MMT were replaced by the organic salts during the exfoliating process and re-established themselves onto the surface of individual silicate platelets. In the first step, the exfoliated silicates of chemical structure consisting of the oligomeric quaternary ammonium cations and the tethered silicate platelet ion pairs have been generated. The hybrid of hydrophilic silicate platelets and hydrophobic AMO-polyamine can be finely dispersed in toluene, measured to have an averaged 250 nm in diameter by using a laser particle analyzer. It formed an emulsion in the toluene/water mixing. With the addition of NaOH to this emulsion, the replacement of organic ammonium salts with sodium ions led to the immediate pH increase from 7.5 to 9.0. Simultaneously, the original emulsion of the polyamine/silicate hybrid in toluene/water was demulsified into two separate phases. The toluene organic phase dissolved the polyamine exfoliating agents and the silicates in the water phase. After a repetitive toluene extraction, the sodium silicate platelets in the water phase had over 95 wt % purity and contamination of organics in less than 5 wt %, measured by TGA.

The isolation of individual platelets was evidenced by the direct observation of their TEM images on a copper grid. The silicate platelet suspension of different concentrations was air-dried on a TEM grid. The platelets are shown to be well-dispersed and have a polygon or circular shape, with an estimated diameter of 80–100 nm (Figure 1a,b). However, the



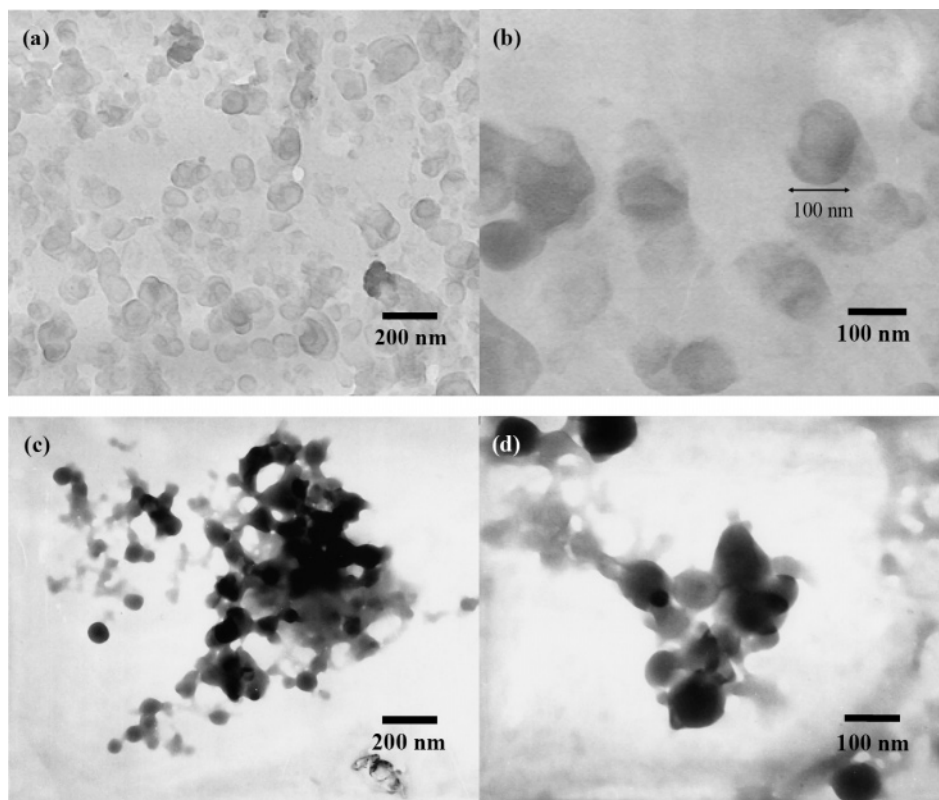


Figure 1. TEM of silicate platelets.

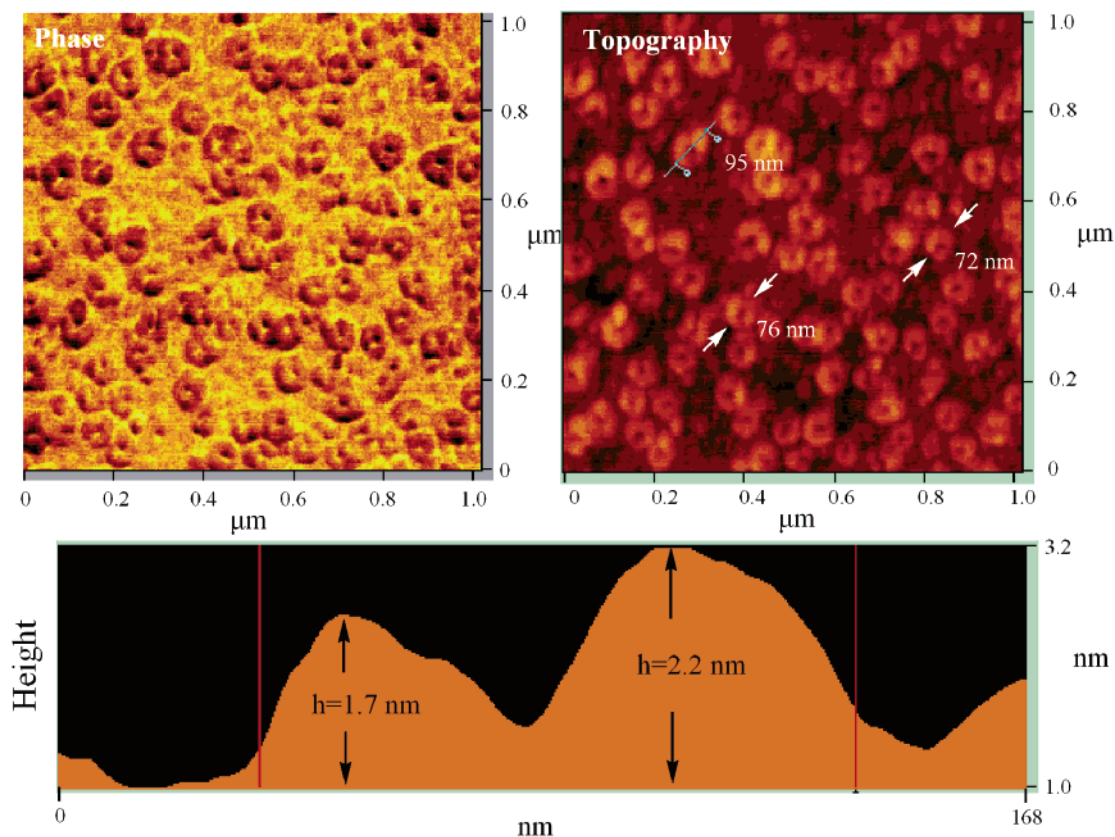
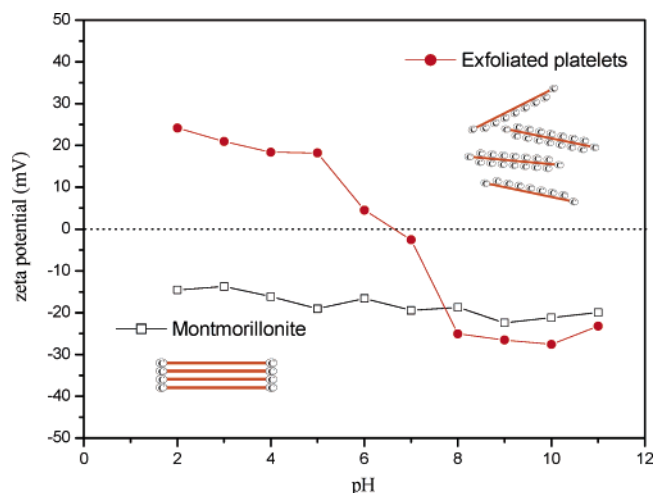


Figure 2. DFM of silicate platelets.

polygonal platelets are observed to be in an aggregated form when the TEM micrograph was prepared from a higher water suspension concentration, 1.0 wt % instead of 0.1 wt % (Figure 1c,d). The isolation of pure silicate platelets in water allows the first time observation for the shape of an individual platelet.

In the literature,<sup>18,20</sup> Na<sup>+</sup>-MMT is generally exfoliated in the polymer-surrounded matrix and hence only possibly observed in the shape of interlayer lines from the side view.

Different from the TEM imaging, the DFM analyses allow the measurement of platelet thickness. By using the topographic



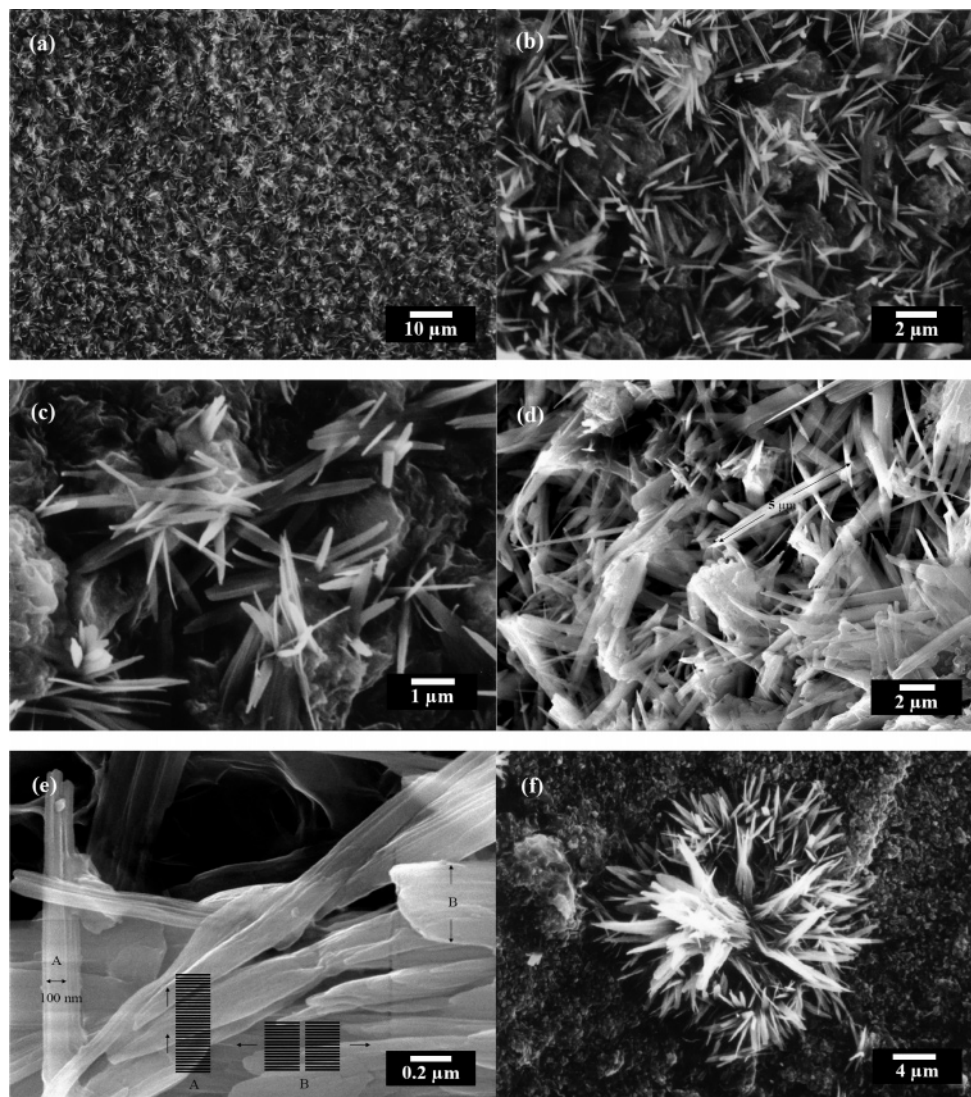
**Figure 3.** Zeta potentials of silicate platelets.

image, we further observed a unique morphology of bent-leaf shapes of these thin platelets on a polyethersulfone substrate after the water evaporation (Figure 2). The topographical contrast displays the uniformity of its structure with an average of 2 nm thickness for the bent structure, consisting of the side view of TEM micrograms. The bent-shape platelets were likely caused by different rates of the drying process on each thin

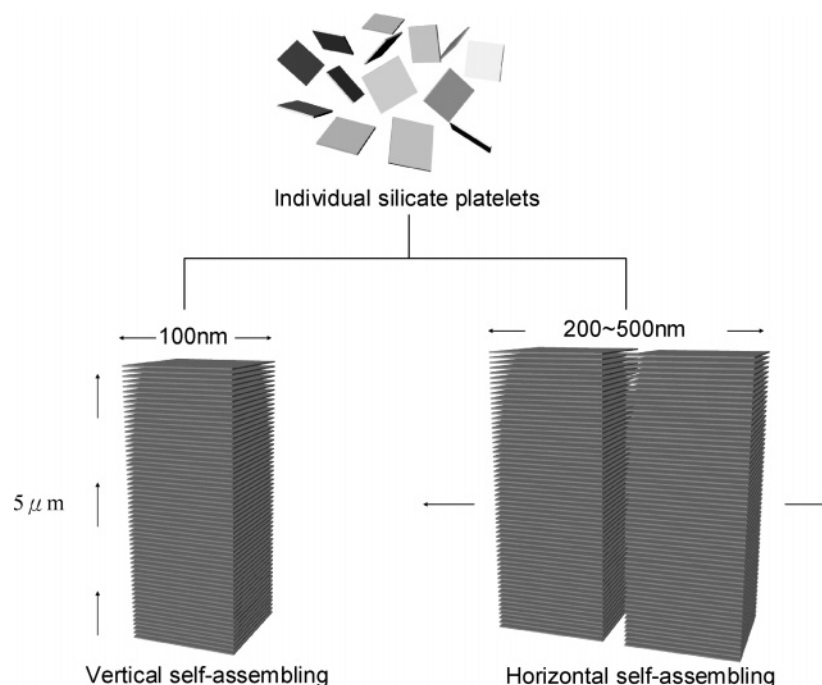
platelet. During the drying process, the rim of individual circular platelets is lifted up to form a cuplike morphology, observed like a core-shell vesicle shape under DFM.

**Physical Properties of the Silicate Platelets.** The high density of ionic charges on a thin platelet surface is expected to exhibit unusual properties. The calculation from 1.2 mequiv/g of CEC and 720 m<sup>2</sup>/g surface areas could amount to the numbers such as 20 000 ions per platelet, 0.9 nm<sup>2</sup> area per ion, and  $4 \times 10^{16}$  platelets per gram. The numbers of ionic charges on such a thin platelet imply that the material may possess an intensive tendency for attracting polar organics and water molecules. As a matter of fact, the platelet suspension in water at 3.0 wt % concentration becomes gelatinous. It was observed that the viscosity increases significantly when adding a few percentages of the silicate platelets into polar organic compounds such as ethylene glycol, poly(ethylene glycol) (PEG), and 1,4-butanediol. Presumably, the platelet surface ionic charges were solvated by the  $-(\text{CH}_2\text{CH}_2\text{O})_x-$  segments in a cross-link manner and rendered the amorphous PEG phase separation.

For the ionic behaviors, the randomized platelets were investigated by measuring their zeta potential under various pH values. As shown in Figure 3, the Na<sup>+</sup>-MMT suspension in water at a concentration of 0.01 wt % demonstrated the zeta potentials at a constant of approximately -18 mV over the pH range from 2 to 11. The zeta potential without an obvious change



**Figure 4.** SEM of self-aligned arrays.



**Figure 5.** Conceptual diagrams of self-aligned arrays.

for  $\text{Na}^+$ -MMT was also reported elsewhere.<sup>25,26</sup> However, other types of clays may have the properties of pH-dependent charges due to the presence of the amphoteric edges with  $\text{Al}-\text{OH}$  and  $\text{Si}-\text{OH}$  groups and permanent negative charges by isomorphous substitutions (e.g.,  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  or  $\text{Mg}^{2+}$  for  $\text{Al}^{3+}$ ).<sup>26,27</sup> When there is a low percentage of amphoteric edges<sup>26,28,29</sup> in total surface area, the clay may not have a pH-dependent zeta potential. With a significantly different charge behavior from  $\text{Na}^+$ -MMT, the zeta potentials of the exfoliated platelets exhibited an isoelectric point (IEP) at pH 6.4. The zeta potentials changed from 21 to  $-25$  mV in the range pH 5–8. It was noted that the platelets in 0.01 wt % suspension were finely dispersed at higher pH values than the IEP. An apparent coagulation occurred when the pH was below the IEP ( $\sim 6.4$ ). The phenomenon of pH-dependent zeta potential may be explained by the platelet surface containing the large number of newly exposed hydroxyl functionalities, which originally existed but were buried within the layered structure.

**Self-Assembly into Fibrous Arrays.** The random silicate platelets, with the nature of high-aspect-ratio geometric shape and intense ionic bridging characteristics, are expected to have a self-assembling ability. We observed a concentration-dependent effect for self-aligning during the water evaporation. By subjecting the 6 wt % silicate suspension to evaporation at  $80^\circ\text{C}$  until dryness, a solid lump of bulk silicates was obtained. The cross section of the internal surface was examined by SEM. At a low magnification (1000 times), the dissected surface is shown to have a uniform morphology of foreign flowerlike clusters over a large area (Figure 4a). Under the examination of a higher magnification (5000–10 000 times), the detailed structure is more like a bunch of fibrous bundles with an average fiber length up to several micrometers (Figure 4b,c). The detailed images of these bundles were also examined by using FE-SEM. The vivid pictures show irregular fibers (Figure 4d) and individual fiber bundles in  $\sim 100$  nm width and average bundles consisting of four to six single fibers (Figure 4e). In the inserted picture in Figure 4e, the proposed mechanism for the vertical and horizontal piling of silicate platelets into bundles is described. Two competing directions of vertical and horizontal

growths dictate the irregularity of individual fiber appearance and also their cluster shapes.

Further studies indicate that the self-assembling on a glass surface in low concentration is different from the arrays in bulk formed from a high concentration. At 1 wt % concentration, the piling may begin by the platelets adhering onto the glass wall as the nucleus and grow with less restriction in different directions. Influenced by a glass surface interaction, the morphologies are flexible fibers.<sup>24</sup> One example is the radiate- or bent-fiber clusters, as illustrated in Figure 4f, although the self-piling mechanism is similar to the bulk materials. The naturally occurring montmorillonite clays generally exist with a primary structure of only on average 8–10 platelets in a stack or approximately 10 nm in length. By comparison, the self-assembled stack from the individual silicate platelets can be grown up vertically to micrometers in length after water evaporation. The X-ray diffraction (XRD) measurement indicated the self-assembly had a regular  $18 \text{ \AA}$  basal spacing, which is reassembled from the individual platelets of featherless XRD pattern. Assuming the fiber bundles are composed of several fibers (100–500 nm in diameter for each), it can then be estimated that the fiber length in  $1 \mu\text{m}$  is piled up by approximately 500 platelets. An observed  $5 \mu\text{m}$  bundle could actually contain as many as 2500 platelets for each fiber in vertical length. The mechanism for the formation of microfiber bundles is attributed to two main parameters favoring the platelet piling, the intensive face-to-face ionic charges and the high-aspect-ratio of the thin platelets (Figure 5). Judged from the zeta potential of the random platelets, the platelet face contains a large number of hydroxyl functionalities which existed as negative charge forms at a pH larger than the IEP (6.4). Therefore, the platelet face-to-face alignment into lengthy fibers under the conditions of pH 9 is favored over any edge-to-face irregular aggregation.

## Conclusion

Individual silicate platelets are isolated by the process of sodium montmorillonite exfoliation and subsequent toluene/aqueous NaOH extraction. The polygon shape in 80–100 nm



diameter and the platelet thickness (1–3 nm) were observed by TEM and DFM, respectively. Of high-aspect-ratio dimension (approximately  $80 \times 80 \times 1 \text{ nm}^3$ ) and ionic character on platelet surfaces, the individual platelets are able to self-assemble into microscale fiber bundles and clusters. The transformation of naturally abundant clays into random platelets and the reassembling properties reveal the hidden characters of these thin layer mineral materials and their potential applications.

**Acknowledgment.** We acknowledge the financial support from National Science Council (NSC) of Taiwan and the assistants from the Regional Instruments Center at NCHU Analytical Electron Microscope.

## References and Notes

- (1) Wang, C.; Shim, M.; Sionnest, P. G. *Science* **2001**, *291*, 2390.
- (2) Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J. Mater. Res.* **1993**, *8*, 1179.
- (3) Porter, D.; Metcalfe, E.; Thomas, M. J. K. *Fire Mater.* **2000**, *24*, 45.
- (4) Fu, X.; Qutubuddin, S. *Polymer* **2001**, *42*, 807.
- (5) Zanetti, M.; Lomakin, S.; Camino, G. *Macromol. Mater. Eng.* **2000**, *279*, 1.
- (6) Giannelis, E. P. *Appl. Organomet. Chem.* **1998**, *12*, 675.
- (7) Giannelis, E. P. *Adv. Mater.* **1996**, *8*, 29.
- (8) Alexandre, M.; Dubois, P. *Mater. Sci. Eng.* **2000**, *28*, 1.
- (9) Ray, S. S.; Okamoto, M. *Prog. Polym. Sci.* **2003**, *28*, 1539.
- (10) Eckle, M.; Decher, G. *Nano Lett.* **2001**, *1*, 45.
- (11) Choy, J. H.; Kwak, S. Y.; Jeong, Y. J.; Park, J. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4041.
- (12) Cristofaro, A. D.; Violante, A. *Appl. Clay Sci.* **2001**, *19*, 59.
- (13) Pinnavaia, T. J. *Science* **1983**, *220*, 365.
- (14) Gilman, W. *Appl. Clay Sci.* **1999**, *15*, 31.
- (15) Hasegawa, N.; Okamoto, H.; Kawasumi, M.; Usuki, A. *J. Appl. Polym. Sci.* **1999**, *74*, 3359.
- (16) Pinnavaia, T. J.; Lan, T. U.S. Patent 5,801,214, 1998.
- (17) Usuki, A.; Hasegawa, N.; Kadoura, H.; Okamoto, T. *Nano Lett.* **2001**, *1*, 271.
- (18) Lin, J. J.; Chen, I. J.; Chu, C. C. *Polym. J.* **2003**, *35*, 411.
- (19) Wang, H.; Zhao, T.; Zhi, L.; Yan, Y.; Yu, Y. *Macromol. Rapid Commun.* **2002**, *23*, 44.
- (20) Choi, Y. S.; Choi, M. H.; Wang, K. H.; Kim, S. O.; Kim, Y. K.; Chung, I. J. *Macromolecules* **2001**, *34*, 8978.
- (21) Chu, C. C.; Chiang, M. L.; Tsai, C. M.; Lin, J. J. *Macromolecules* **2005**, *38*, 6240.
- (22) Jan, I. N.; Lee, T. M.; Chiou, K. C.; Lin, J. J. *Ind. Eng. Chem. Res.* **2005**, *44*, 2086.
- (23) Chu, C. C.; Lin, J. J.; Shiu, C. R.; Kwan, C. C. *Polym. J.* **2005**, *37*, 1.
- (24) Lin, J. J.; Chu, C. C.; Chou, C. C. *Adv. Mater.* **2005**, *17*, 301.
- (25) Heath, O.; Tadros, T. E. *J. Colloid Interface Sci.* **1983**, *93*, 307.
- (26) Liu, J.; Zhou, Z.; Xu, Z.; Masliyah, J. J. *Colloid Interface Sci.* **2002**, *252*, 409.
- (27) Olphen, H. V. *An Introduction to Clay Colloid Chemistry*; Wiley: New York, 1976.
- (28) Tombácz, E.; Szekeres, M. *Appl. Clay Sci.* **2004**, *27*, 75.
- (29) Lagaly G.; Ziesmer S. *Adv. Colloid Interface Sci.* **2003**, *100–102*, 105.