Latex particle-encapsulated titania/polymer composite nanotubings: free-standing, one-dimensional package of colloidal particles†

Jianguo Huang‡ and Toyoki Kunitake*

Received (in Cambridge, UK) 2nd March 2005, Accepted 11th April 2005
First published as an Advance Article on the web 28th April 2005
DOI: 10.1039/b503125g

Latex nanoparticles were packed inside nanometer-thick titania/polymer composite nanotubules templated by porous alumina membrane, to give free-standing particle-in-tubing "micro-beanpods" after removal of the template membrane.

Organization of monodispersed colloidal particles like latex and silica microspheres into higher-order microstructures is attracting growing interest,[1,2] since it provides unique structures suitable for various advanced devices and functional materials such as photonic crystals[3] and porous polymers.[4] Low-dimensional colloidal aggregates are often generated by surface pattern-directed assembly. The substrates are usually pre-coated with certain organic layers as patterned by microcontact printing and lithographic techniques, and the particles are directed to assemble onto the surface pattern *via* electrostatic,[5] hydrophobic[5d] or hydrophilic interactions,[6] or *via* chemical bonding.[5f] Recently surface relief-patterned substrates (for example, silicon wafer with V-shaped or vertical wall grooves buried within the surface) were employed as templates to obtain ordered particle arrays *via* geometrically confined colloidal crystallization based on the parallel plate fluidic confinement technique,[7] microfluidic self-assembly,[8] spin-coating[9] or dip-coating[10] driven self-assembly, and directed evaporation induced self-assembly.[11] However, these colloidal particle arrays are fettered on the support substrate, and very little progress has been seen in fabricating free-standing one-dimensional colloidal aggregates.[7] We tackled this challenge by developing an efficient and versatile fabrication methodology for free-standing particle-in-nanotube "micro-beanpods", as described in Scheme 1.

Template synthesis with porous membranes is a well-known pathway for the preparation of nanotubular and nanofibrillar materials.[12] In the present work, titania/polymer nanocomposite tubules were obtained with nanometer precision by applying the surface sol–gel process on a porous alumina filtration membrane. The surface sol–gel process is composed of stepwise adsorption of metal alkoxides alone or by combination with polyhydroxyl compounds, such as polymers or small organic molecules. It is an efficient chemical method to prepare metal oxide/organic nanocomposite films with molecular precision.[13] This process is applicable to small surfaces of complex morphologies, since the resulting metal oxide films are extremely thin.[14] The pore walls of porous membranes can be employed as suitable substrates for such film deposition.[15]

The alumina filtration membrane employed (Whatman Anodisc 25, UK) is 60-μm-thick with nominal pore diameters of 100 nm, and cylindrical, monodisperse pores are arranged as a regular hexagonal array. The titania layer cannot be deposited directly onto the pore wall, because the alumina surface is negatively charged and is devoid of hydroxyl groups. Therefore, a positively charged PEI layer is first deposited onto the pore wall, and then a PAA layer is deposited to provide carboxyl groups and facilitate subsequent deposition of a titania layer. By repeating the titania/PVA deposition cycle, titania/polymer nanocomposite tubules spanning the whole thickness of the template membrane are uniformly formed (see ESI†).

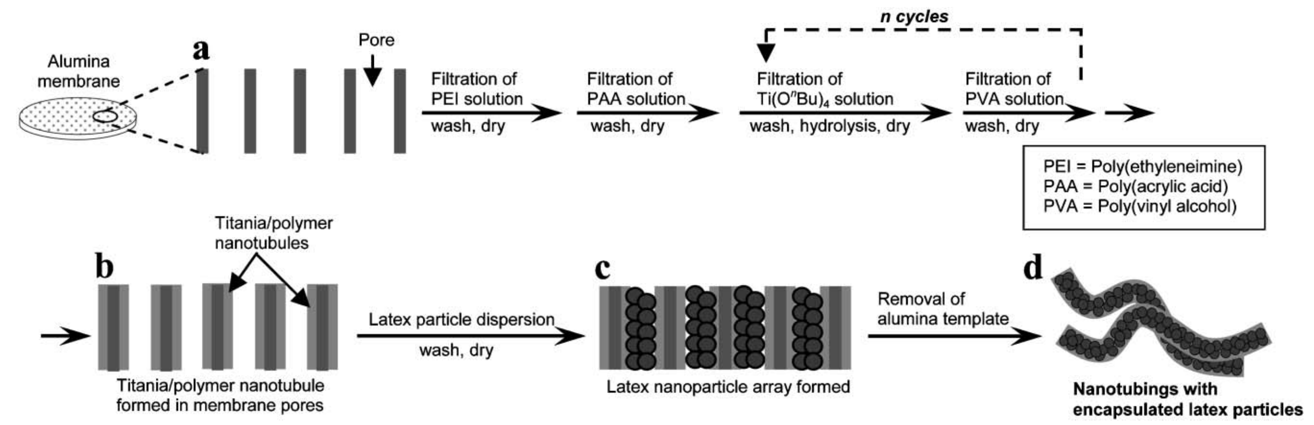
Fig. 1 shows morphologies of the obtained titania/polymer nanocomposite tubules. The wall of the tubule consists of one PEI layer, one PAA layer and ten cycles of titania/PVA bilayers (denoted as PEI/PAA/(titania/PVA)$_{10}$ hereafter); and has a uniform wall thickness of ~15 nm, as revealed by cross-sectional SEM observation (Fig. 1a). The wall thickness is adjustable by changing the number of titania/PVA deposition cycles. For example, the wall thickness of the PEI/PAA/(titania/PVA)$_5$ tubule is found to be ~8 nm. Highly aligned, close-packed tubing ensembles are retained after dissolution of the alumina template in strong alkali, as seen in Fig. 1b.§ The tubings are uniform without any macroscopic defects, and all are 60 μm long, in agreement with the thickness of the original alumina membrane template. The outside diameter of the tubing is found to be 200–250 nm, and is larger than the nominal pore diameter of the template membrane. This is because the actual pores are larger than the nominal diameter along most of the thickness of the template membrane, as shown by cross sectional SEM observation of a bare membrane. A similar observation has been made before.[16] Ultrasonication can disintegrate the ensemble to individual nanotubings, as seen from the TEM image of Fig. 1c. The released nanotubings are very flexible, and appear to have high mechanical strength, because they are not destroyed by long-time sonication. The tubings are uniform without any particle structures (Fig. 1c, Inset). The titania component is amorphous, in contrast with the crystalline nanoparticle-formed titania nanotubes that were prepared *via* conventional sol–gel template synthesis.[17]

The deposition also produces ultrathin titania/polymer composite films on the upper and lower surfaces of the alumina membrane without clogging the open ends of the pores. The surface films can hold the resultant nanotubings together in an aligned fashion after removal of the alumina template membrane. It is clear that the morphology of the alumina membrane is

---

† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b5/b503125g/

‡ *Present address*: National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan.
*kunitake@ruby.ocn.ne.jp



Scheme 1 Strategy for the fabrication of free-standing one-dimensional colloidal particle aggregates. The illustration shows the procedure of latex nanoparticle encapsulation in titania/polymer composite nanotubings templated by porous alumina membrane.

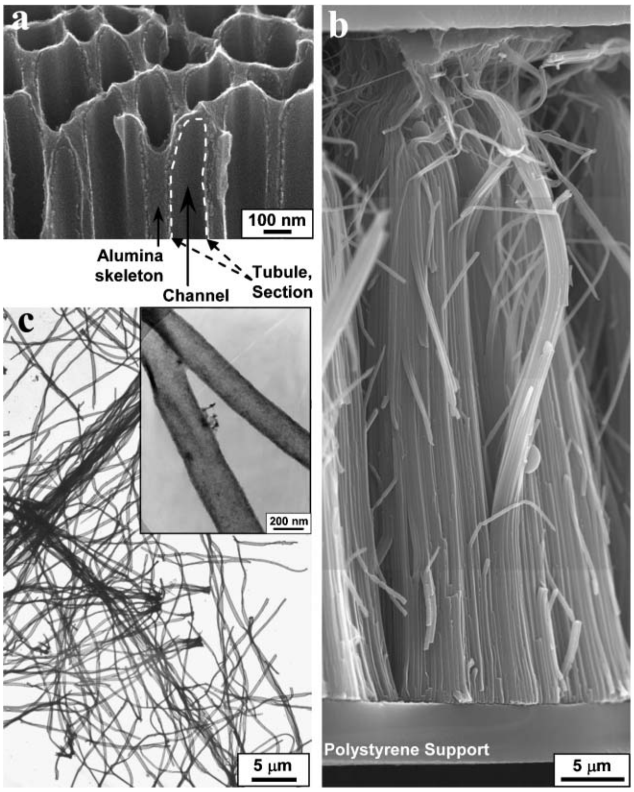


Fig. 1 Nanocomposite PEI/PAA/(titania/PVA)$_{10}$ tubings templated by porous alumina membrane. (a) Cross sectional field emission scanning electron micrograph (FE-SEM) image of the alumina membrane with as-deposited titania/polymer nanocomposite tubules inside the pores. (b) FE-SEM full side view of the titania/polymer nanotubing arrays obtained after dissolving away the alumina membrane template. (c) Transmission electron micrograph (TEM) of the titania/polymer nanotubings. The inset shows a TEM image of two individual tubings at high magnification.

completely and precisely copied by titania/polymer composite films in our procedure. SEM observations confirm that there are open pores on both surfaces of an alumina membrane after deposition of titania/polymer multilayers. The tubular pores were used to direct assembly of colloidal particles in the tube interior. We filled a dispersion of polystyrene latex nanoparticles into the multilayer-modified pores by suction filtration.¶ The surface of the latex nanoparticle is modified with carboxyl groups, and the innermost layer of the nanocomposite tubule is composed of titania. The binding of carboxyl groups with the titania layer[13] is effectively employed for immobilization of latex nanoparticles onto the inner wall of the tubule.

Fig. 2 shows PEI/PAA/(titania/PVA)$_5$/titania nanotubules that encapsulated 100 nm-latex particles. A large number of the latex nanoparticles are retained in the pores of a cleaved alumina membrane, as shown by the SEM image displayed in Fig. 2a. The pores are not fully filled with latex particles in this image. Some particles are apparently lost when the membrane is cleaved for cross sectional SEM observation. Such particle-in-channel structure is observed along the whole length of all the pores. After removal of the alumina membrane template, particle-in-tubing "micro-beanpods" are obtained, as clearly recognized by TEM. Fig. 2b shows bundles of flexible titania/polymer nanotubings with the immobilized latex nanoparticles, which are held by the surface thin films. The length of the tubing is the same as the thickness of the original alumina membrane template (60 μm). TEM images of the individual tubing show that the "micro-beanpods" are very flexible (Fig. 2c). The latex nanoparticles are densely-packed inside the nanometer-thick tubing as an essentially ordered one-dimensional array (Fig. 2e). The outside diameter of the tubing is estimated to be *ca.* 200 nm, and this is smaller than that of the nanotubing without nanoparticles (200–250 nm, inset of Fig. 1c). Apparently, the nanocomposite lining shrinks onto latex particles during removal of the alumina template, since the tubing wall is extremely thin ($\sim$8 nm) and flexible. This observation is similar to the shrinkage of the titania shell upon removal of the inner latex core.[18] The latex nanoparticles are immobilized onto the inner wall of the tubings *via* the coordination between the carboxyl group on the particle and the titanium atom of the innermost tubing layer, as schematically illustrated in Fig. 2f. Therefore, the latex particle arrays in the "micro-beanpods" are much more stable than those fabricated using surface relief patterns. It is clear that the one-dimensional colloidal particle array exists without any support from the conventional solid substrate.

The current method used to fabricate one-dimensional free-standing colloidal particle arrays is facile and versatile. The chemical composition of the wrapping nanotubing and

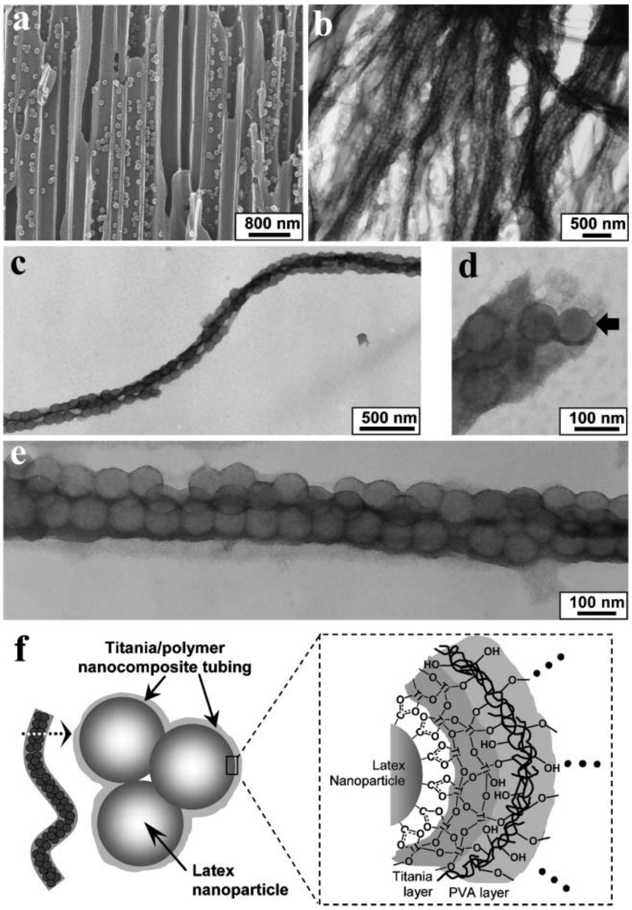


Fig. 2 Latex nanoparticle-encapsulated PEI/PAA/(titania/PVA)$_5$/titania nanocomposite tubings. (a) Cross sectional FE-SEM image of an alumina membrane with as-deposited titania/polymer composite tubules immobilized with latex particles. (b) TEM image of latex particle-encapsulated polymer/titania nanotubing arrays obtained after removing the alumina template. (c), (d) and (e), TEM images of individual free-standing latex particle-encapsulated nanotubings at varied magnifications. (d) shows an opening of one single nanotubing which was broken in the middle, note that the two latex nanoparticles indicated by the arrow are partially embedded inside the tubing, and partially exposed. (f) Schematic illustration of the latex nanoparticle-encapsulated titania/polymer nanocomposite tubings (not to scale).

encapsulated colloidal particle can be varied as needed. The flexible "micro-beanpod" presents a new type of colloidal assembly. It should promote novel materials design with specified functionalities.

Jianguo Huang‡ and Toyoki Kunitake*
Topochemical Design Laboratory, Frontier Research System, The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama, 351-0198, Japan. E-mail: kunitake@ruby.ocn.ne.jp;
Fax: +81-48-464-6391; Tel: +81-48-467-9601

Notes and references

§ Because the nanotubes obtained after removal of the alumina template are flexible, we use the word "tubing" rather than "tubule" to describe the sample.

¶ Experimental method: An alumina filtration membrane is placed in a suction filter, and PEI/PAA/(titania/PVA)$_n$/titania nanotubules are firstly deposited (see ESI†). The innermost layer of this nanocomposite tubule is composed of titania. Twenty ml of an aqueous suspension of polystyrene latex (0.1 mg ml^{-1}; micromod$^{®}$-greenF COOH, particle size 100 nm) are added into the filter funnel, the first 10 ml of the suspension are slowly suction-filtered through the alumina membrane, and the suspension is allowed to stand for 30 min to achieve adsorption of latex nanoparticles onto the tubule inner wall. After the remaining 10 ml are slowly suction-filtered through the membrane, the membrane is washed immediately by suction filtration of 40 ml water and dried by air flow. The membrane pores are thus filled with latex nanoparticles. Free-standing nanotubings with stuffed latex nanoparticles are obtained after dissolving away the alumina template (Scheme 1).

1 Selected reviews: (*a*) Y. Xia, B. Gates, Y. Yin and Y. Lu, *Adv. Mater.*, 2000, **12**, 693; (*b*) A. Stein and R. C. Schroden, *Curr. Opin. Solid State Mater. Sci.*, 2001, **5**, 553; (*c*) Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim and H. Yan, *Adv. Mater.*, 2003, **15**, 353; (*d*) D. Wang and H. Möhwald, *J. Mater. Chem.*, 2004, **14**, 459.

2 (*a*) O. D. Velev, A. M. Lenhoff and E. W. Kaler, *Science*, 2000, **287**, 2240; (*b*) A. D. Dinsmore, M. F. Hsu, M. G. Nikolaides, M. Marquez, A. R. Bausch and D. A. Weitz1, *Science*, 2002, **298**, 1006.

3 (*a*) P. V. Braun and P. Wiltzius, *Nature*, 1999, **402**, 603; (*b*) E. Chomski and G. A. Ozin, *Adv. Mater.*, 2000, **12**, 1071; (*c*) N. Tétreault, H. Míguez, S. M. Yang, V. Kitaev and G. A. Ozin, *Adv. Mater.*, 2003, **15**, 1167; (*d*) Z. Zhong, Y. Yin, B. Gates and Y. Xia, *Adv. Mater.*, 2000, **12**, 206; (*e*) P. Jiang, J. F. Bertone and V. L. Colvin, *Science*, 2001, **291**, 453.

4 (*a*) S. A. Johnson, P. J. Ollivier and T. E. Mallouk, *Science*, 1999, **283**, 963; (*b*) J. H. Moon, S. Kim, G.-R. Yi, Y.-H. Lee and S.-M. Yang, *Langmuir*, 2004, **20**, 2033.

5 (*a*) J. Tien, A. Terfort and G. M. Whitesides, *Langmuir*, 1997, **13**, 5349; (*b*) J. Aizenberg, P. V. Braun and P. Wiltzius, *Phys. Rev. Lett.*, 2000, **84**, 2997; (*c*) L. M. Demers and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 3069; (*d*) H. Zheng, I. Lee, M. F. Rubner and P. T. Hammond, *Adv. Mater.*, 2002, **14**, 569; (*e*) F. Hua, J. Shi, Y. Lvov and T. Cui, *Nano Lett.*, 2002, **2**, 1219; (*f*) Y. Masuda, M. Itoh, T. Yonezawa and K. Koumoto, *Langmuir*, 2002, **18**, 4155.

6 Z.-Z. Gu, A. Fujishima and O. Sato, *Angew. Chem., Int. Ed.*, 2002, **41**, 2068.

7 (*a*) Y. Yin, Y. Lu and Y. Xia, *J. Mater. Chem.*, 2001, **11**, 987; (*b*) Y. Yin, Y. Lu, B. Gates and Y. Xia, *J. Am. Chem. Soc.*, 2001, **123**, 8718; (*c*) Y. Yin and Y. Xia, *J. Am. Chem. Soc.*, 2003, **125**, 2048.

8 S. M. Yang and G. A. Ozin, *Chem. Commun.*, 2000, 2507.

9 (*a*) G. A. Ozin and S. M. Yang, *Adv. Funct. Mater.*, 2001, **11**, 95; (*b*) D. Xia, A. Biswas, D. Li and S. R. J. Brueck, *Adv. Mater.*, 2004, **16**, 1427; (*c*) D. Xia and S. R. J. Brueck, *Nano Lett.*, 2004, **4**, 1295.

10 (*a*) D.-G. Choi, H. K. Yu, S. G. Jang and S.-M. Yang, *Chem. Mater.*, 2003, **15**, 4169; (*b*) D.-G. Choi, S. G. Jang, H. K. Yu and S.-M. Yang, *Chem. Mater.*, 2004, **16**, 3410.

11 S. M. Yang, H. Míguez and G. A. Ozin, *Adv. Funct. Mater.*, 2002, **12**, 425.

12 Selected reviews: (*a*) C. R. Martin, *Science*, 1994, **266**, 1961; (*b*) C. R. Martin, *Acc. Chem. Res.*, 1995, **28**, 61; (*c*) A. Huczko, *Appl. Phys. A*, 2000, **70**, 365; (*d*) N. I. Kovtyukhova and T. E. Mallouk, *Chem. Eur. J.*, 2002, **8**, 4354.

13 (*a*) I. Ichinose, S.-W. Lee and T. Kunitake, in *Supramolecular Organization and Materials Design*, ed. W. Jones and C. N. R. Rao, Cambridge University Press, UK, 2002, pp. 172–213; (*b*) J. Huang, I. Ichinose and T. Kunitake, *Chem. Commun.*, 2002, 2070; (*c*) J. Huang, I. Ichinose, T. Kunitake and A. Nakao, *Langmuir*, 2002, **18**, 9048.

14 (*a*) J. Huang and T. Kunitake, *J. Am. Chem. Soc.*, 2003, **125**, 11834; highlighted; (*b*) R. A. Caruso, *Angew. Chem., Int. Ed.*, 2004, **43**, 2746; (*c*) J. Huang, T. Kunitake and S. Onoue, *Chem. Commun.*, 2004, 1008.

15 J. Huang and T. Kunitake, *Titania/polymer nanocomposite tubings: template synthesis and nanoparticle encapsulation*, in *Proceedings of the CSJ (The Chemical Society of Japan) 83rd Spring Meeting, Part I*, The Chemical Society of Japan, Tokyo, 2003, p. 513.

16 S. A. Miller, V. Y. Young and C. R. Martin, *J. Am. Chem. Soc.*, 2001, **123**, 12335.

17 (*a*) B. B. Lakshmi, C. J. Patrissi and C. R. Martin, *Chem. Mater.*, 1997, **9**, 2544; (*b*) S. M. Liu, L. M. Gan, L. H. Liu, W. D. Zhang and H. C. Zeng, *Chem. Mater.*, 2002, **14**, 1391.

18 S. Fujikawa and T. Kunitake, *Chem. Lett.*, 2002, 1134.