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Electronic Supplementary Information

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

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Experimental Details

1. Deposition of Titania/Polymer Nanocomposite Tubings: The solutions used for film deposition are: PEI (average molecular weight 10,000), 2 mg ml$^{-1}$ in water; PAA (average MW 12,500), 1 mg ml$^{-1}$ in 1:1 (v/v) ethanol/water; titanium $n$-butoxide (Ti(O$^n$Bu)$_4$), 100 mM in 1:1 (v/v) toluene/ethanol; PVA (average MW 25,000), 5 mg ml$^{-1}$ in water. Milli-Q water is used in all related cases. All experiments are carried out at room temperature.

The typical synthesis procedure is given as follows: An alumina filtration membrane (Whatman Anodisc 25, UK) is placed in a suction filter and is cleaned by suction filtration of 40 ml ethanol, followed by drying with air flow prior to use. Twenty ml of aqueous PEI is added into a filter funnel, and the first 10 ml of the solution is slowly suction-filtered through the alumina membrane, and the solution is left stand for 30 min to achieve film deposition. Then, the remaining 10 ml is slowly suction-filtered through the membrane and the membrane is washed immediately by suction filtration of 40 ml water to remove excess reagents from the pores, and dried by air flow. A thin PEI layer is thus deposited on the membrane pore wall as well as on the membrane surface. A PAA layer is then deposited onto the resultant PEI film surface via a similar process, resulting in PEI/PAA bilayer. Ten ml of Ti(O$^n$Bu)$_4$ solution is then added into the funnel. After careful suction filtration of 5 ml of the solution, the remaining solution is allowed to stand for 3 min for adsorption of the titania precursor, and then all the solution is filtrated. The membrane is thoroughly washed immediately by suction filtration of two 20-ml portions of ethanol and 20 ml water, and dried with air flow. The membrane is now coated with PEI/PAA/titania trilayer, on which a PVA layer is successively deposited using the same method as that of PEI layer deposition. Tubules consisting of PEI/PAA/titania/PVA multilayer are formed inside the membrane pores. By repeating the titania/PVA deposition cycle $n$ times, PEI/PAA/(titania/PVA)$_n$ nanocomposite tubules are formed within each pore of the template membrane. The titania/polymer nanocomposite tubings are released by immersing the sample in 6 M KOH to dissolve away the template alumina.
2. Electron Microscopy. To prepare specimens suitable for SEM observation, a small (~0.2 cm$^2$) piece of the template membrane (with the titania/polymer tubule inside the pore) was fully covered with a thin film of polystyrene (MW 2,330) as support matrix. The membrane was then broken in the middle to create an exposed face, from which aqueous KOH can start dissolving the alumina template. A half part of the membrane (~0.1 cm$^2$) was immersed in 1.0 ml of 6 M KOH at room temperature for 1 h to ensure complete removal of alumina. The specimen was thoroughly washed with Milli-Q water and ethanol, and dried with nitrogen gas. The resultant specimen was still rigid due to fixation by the coated polystyrene layer. The FE-SEM observation was done on the exposed face. FE-SEM micrographs were obtained on a Hitachi S-5200 instrument at an acceleration voltage of 25.0 kV; the samples were sputtered with platinum to reduce charging.

To prepare the TEM specimens, a small (~0.1 cm$^2$) piece of titania/polymer nanotubule-deposited alumina membrane was immersed in 1.0 ml of 6 M KOH for 5 min to completely dissolve the alumina, followed by thorough washing with water and ethanol. A very flexible small piece possessing the size and shape of the original alumina membrane was obtained, which was then suspended in 1.0 ml ethanol by ultrasonication. The suspension was dropped on silicon oxide-coated 200 mesh gold grid (SPI, USA) for observation. The TEM micrographs were acquired on a JEOL JEM-2000 instrument operating at 100 kV accelerating voltage and 60 µA filament current.