We introduce a biotemplating approach for creating highly entangled hollow TiO$_2$ nanoribbons by combining peptide assembly with an atomic layer deposition process. An aromatic peptide of diphenylalanine was readily assembled into a hierarchical organogel consisting of highly entangled nanoribbons. Unlike ordinary biomaterials, the peptide nanoribbon framework exhibited a high level of thermal stability, such that it may undergo the further functionalization process of vacuum deposition without significant damage to its nanoscale structure. A nanoscale layer of anatase TiO$_2$ was deposited on the nanoribbon framework by means of atomic layer deposition. After pyrolysis, a highly entangled nanotubular TiO$_2$ framework was created successfully. The highly entangled TiO$_2$ architecture exhibited UV-switchable wetting properties.

Introduction

Biotemplating utilizes naturally generated biomolecular structures as templates for functional materials. A broad spectrum of natural objects, ranging from nanoscale biomolecular assembly to microorganisms such as viruses or diatoms, have been used in the biotemplating process. Unlike synthetic template materials, biotemplates enable the construction of highly complicated hierarchical architectures through a mild, biocompatible process. The structures and functionalities of biotemplates can be intrinsically mutated from a molecular-scale by genetic engineering. In addition, naturally designed, highly specific biofunctionalities can be directly transferred to the final functional structures. Despite the numerous advantages, however, the development of a large-scale biotemplating process has rarely been achieved. This is mainly due to the low yield and low stability of biotemplates. In particular, the low thermal stability of biotemplates has limited the templating process to a wet-chemical process, which is generally considered to be disadvantageous for a large-scale fabrication process.

TiO$_2$ is a wide bandgap semiconductor with excellent photocatalytic activities. To its attractive properties, TiO$_2$ has been extensively used in various applications, including photocatalysis, sensors, and photovoltaics. In particular, nanotubular TiO$_2$, which has an extremely large surface area and a one-dimensional anisotropic geometry, has demonstrated remarkably enhanced photocatalytic and photovoltaic properties. To date, various approaches have been developed for the fabrication of nanotubular TiO$_2$, such as hydrothermal treatment, anodizing, seed growth, and sol-gel processes. However, most of the previous approaches require a multistep process and complicated chemistry.

Here we demonstrate a novel fabrication process for highly entangled hollow TiO$_2$ nanoribbons via templating of a peptide assembly. The organogel, which consists of a peptide nanoribbon framework, was readily assembled from an aromatic peptide of diphenylalanine. The peptide was introduced as the structural motif for the β-amyloid associated with Alzheimer’s disease. In contrast to the biomolecularly assembled structures that are usually used, nanoribbons constructed from highly ordered aromatic peptides exhibited remarkably high thermal stability, which allowed them to undergo a further functionalization process by means of atomic layer deposition (ALD) at a high temperature (140 °C to 160 °C). ALD is an advanced thin film deposition process that is applicable to arbitrarily shaped nonplanar substrates. This self-limiting deposition process, composed of sequential deposition of multi-component reactive species, provides atomic-scale control over film thickness and large-area uniformity. ALD was used to deposit a thin TiO$_2$ layer over a highly entangled 3-D peptide framework. After removal of the peptide template by pyrolysis, highly entangled hollow TiO$_2$ nanoribbons were prepared. Our approach represents a unique pathway towards combining biomolecular assembly with a vacuum deposition process—two processes that are usually considered incompatible with each other.

Experimental

Materials

A lyophilized form of the diphenylalanine was purchased from Bachem (Bubendorf, Switzerland) and used without further purification. Chloroform was purchased from Merck (Germany). Titanium tetra-isopropoxide [TTIP, Ti(OC$_3$H$_7$)$_4$] was purchased from Mecharonics (Korea) and used as received for ALD.
Preparation of hollow TiO2 networks

Peptide organogel was prepared by the dissolution of a predetermined amount of diphenylalanine into chloroform via sonication and subsequent cooling. Xerogel was prepared by spontaneous evaporation of chloroform at an ambient temperature. A thin layer of TiO2 was deposited on the xerogel by ALD (140 °C and 3 torr). TTIP was used as a precursor and ammonium (NH3) gas was used as a reactant. The TTIP, which was contained in a bubbler at 50 °C, was carried by an inert Ar gas stream. One deposition cycle of TiO2 consisted of four steps: (i) deposition of the TTIP precursor, (ii) a purge pulse of Ar, (iii) an injection of reactive NH3 gas, and (iv) another purge pulse of Ar. The flow rates were 50 sccm for the Ar purge and 25 sccm for the NH3 purge. During the deposition, 100 sccm of Ar gas was continuously supplied into the reactor as a carrier gas. Under these conditions, the saturated growth rate of the TiO2 layer was ~0.2 Å cycle-1. In a typical deposition process, 500 to 1000 cycles were required to generate a film with a thickness of 10 nm to 20 nm. The peptide template was removed by calcination at 400 °C for 1 h under air condition. The presence of carbon impurities was analyzed with a Carbon/Sulfur Determinator (model: ELTRA CS800, Germany).

Characterization of the morphology

The morphology of the peptide xerogel and TiO2 nanoribbon framework was analyzed by means of a field emission scanning electron microscope (FESEM; Hitachi S-4800 SEM, Japan). An osmium coating was applied to enhance the scattering contrast and electric conductivity. A high-resolution transmission electron microscope (HRTEM; JEOL JEM-2100F, Japan) was used to characterize the crystalline morphology of the TiO2 nanoribbons. To prepare a specimen for the HRTEM investigation, we dispersed the calcinated TiO2 sample in ethanol by means of sonication. One drop of the suspension was added to a carbon film supported copper grid and the grid was air dried. The crystal structure of the nanotubes was characterized by means of powder XRD with Cu Kα radiation on a D/Max 2500 X-ray diffractometer (Rikagu, Japan).

Characterization of the gelation behavior and surface properties

Dynamic rheological properties were measured with the aid of an advanced rheometric expansion system (ARES; Rheometric Scientific™) under an oscillatory strain of 5% (cone-and-plate geometry, 50 mm in diameter, a cone angle of 0.04 radians, and a gap of 0.05 mm). The contact angle of the water on the TiO2 framework was measured with a Phoenix150 contact angle analyzer (Surface Electro Optics Co., Korea). The TiO2 framework was irradiated with UV (6 mW cm-2 at 254 nm) or purged with O2 gas in darkness to before the contact angle was measured.

Results and discussion

The overall process of creating hollow TiO2 nanoribbons is schematically described in Fig. 1. Firstly, organogel was prepared by sonication diphenylalanine in chloroform and leaving it to cool under ambient conditions. Upon cooling of the sonicated sample, the diphenylalanine spontaneously assembled into an organogel, forming opaque aggregates. Xerogel was readily prepared from the organogel under ambient conditions due to the high volatility of chloroform. The peptide framework of the xerogel was coated with a thin continuous layer of TiO2 by means of ALD. A deposition cycle consisted of the following successive steps, which were repeated until the TiO2 layer reached a desired thickness: (i) TTIP deposition, (ii) an Ar gas purge, (iii) NH3 gas exposure, and (iv) Ar gas purge of NH3 gas. The deposition temperature was 140 °C, where each deposition cycle generated an average deposition thickness of ~0.2 Å. After the deposition, the peptide template was calcined at a high temperature such that the remaining TiO2 networks were composed of highly entangled hollow tubular nanoribbons.

The organogelation behavior of diphenylalanine is presented in Fig. 2. The gelation behavior was examined by the fluidity of the prepared mixture. Fig. 2(a) summarizes the gelation behavior as a function of peptide concentration. At a concentration less than 0.3 mg mL-1 (0.96 mM), the peptide mixture formed a transparent solution. Light-scattering measurements failed to detect any aggregates in the solution. Gelation occurred above the critical concentration of 0.3 mg mL-1. In the concentration range from 0.3 mg mL-1 to 4 mg mL-1 (12.8 mM), an opaque self-supporting structure floating in the organic solvent was observed. This structure is an unpercolated gel that exhibits viscous fluidity with an excessive chloroform solvent. Since the critical concentration of 0.3 mg mL-1 was extremely low, diphenylalanine was classified as a supergelator. 21 At a concentration higher than 4 mg mL-1, a percolated gel was formed. The gel network extended over the entire sample, preventing the gel from exhibiting any fluidity when the glass vial was turned upside down. At the saturation concentration of 4 mg mL-1, one diphenylalanine molecule immobilizes an average of 1000 chloroform molecules, indicating that about 99.7% of the gel volume was occupied by chloroform. Upon heating, the prepared organogel did not show any thermal transition up to 100 °C.
above which the chloroform completely evaporated. Further heating revealed that the major thermal degradation of the peptide nanoribbon framework occurred above 300 °C, demonstrating the remarkably high thermal stability of the self-assembled structure consisting of aromatic diphenylalanine. (ESI† Fig. S1.)

Fig. 2b shows dynamic mechanical spectra of the peptide organogel, which contains 8 mg mL⁻¹ of diphenylalanine. In the frequency range that was explored, the storage modulus (G') was always higher than the loss modulus (G''), exhibiting the typical elastic behavior of a percolated gel network. The complex viscosity (n*) showed a shear thinning behavior, as is frequently observed in structured fluids. Fig. 2c shows a SEM image of the xerogel prepared from an organogel that contained 2 mg mL⁻¹ of peptide. The rapid evaporation of volatile chloroform resulted in xerogel frameworks with large surface areas. As shown in Fig. 2d, linear and flat nanoribbons were observed as the framework of the organogel. The nanoribbons did not show any branching or cross-linking, suggesting that the entangled gel morphology relies on the physical interaction among the nanoribbons. The nanoribbons had an average length of hundreds of micrometres and an average width of hundreds of nanometres. Consequently, their extremely large aspect ratio was of the order of 1 × 10².

Fig. 3a and 3b show SEM images of TiO₂-deposited xerogel before and after the calcinations of the peptide template. The morphology that consisted of the highly entangled nanoribbons was well preserved during the ALD process performed at 140 °C and the subsequent calcination at 400 °C. The content of the residual carbon in final TiO₂ structures was less than 0.5 wt%. The cross-sectional morphology of a TiO₂ nanoribbon after calcination, which is shown in Fig. 3c, reveals, as expected, that the nanoribbon has a hollow tubular morphology. Fig. 3d presents a powder X-ray diffraction (XRD) spectrum of TiO₂ nanoribbons with four well-resolved diffraction peaks. Those peaks are typical diffraction peaks from the (101), (004), (200), and (211) crystalline lattice planes of the anatase TiO₂ phase (PDF No. 21-1272). An average crystallite size of 9.8 nm was calculated using the Scherrer equation:
where $L$ is the crystallite size and $B(2\theta)$ is the line width.

Fig. 4a shows a transmission electron microscopy (TEM) image of an isolated hollow TiO$_2$ nanoribbon. The sidewall was very smooth with a thickness of about 10 nm. The image shows a nanoribbon with an open end, though nanoribbons with either an open or closed end were observed (ESI† Fig. S2). The crystal lattice fringes extended over the entire sample, demonstrating the highly crystallinity of the TiO$_2$ nanostructure. As indicated in Fig. 4b, the crystalline lattice spacing of 3.52 Å is distinct. This corresponds to the (101) lattice plane of a tetragonal anatase TiO$_2$ crystal. Fig. 4c shows the Fourier transformation of a TEM image; the result is consistent with a typical electron diffraction pattern for anatase TiO$_2$ (ESI† Fig. S3).

The prepared TiO$_2$ nanoribbon network exhibited reversible photo-switching of the surface tension. Fig. 5 shows the influence of UV radiation ($\lambda = 254$ nm; intensity: 6 mW cm$^{-2}$; radiation time: 40 min) on the water contact angle over the hollow TiO$_2$ network. As shown in Fig. 5a, the prepared organogel network can be completely wetted by a water droplet. By contrast, the as-prepared TiO$_2$ nanoribbon network showed a high water contact angle of approximately 87° due to the hydrophobic surface property of TiO$_2$. The contact angle could be remarkably reduced to 35° after UV irradiation. This is attributed to an increase in the hydrophilic surface functionalities caused by the UV radiation. When the UV-radiated sample was stored in a dark O$_2$ atmosphere for 1 h, the contact angle recovered its high value. The reversible switching of the surface property is a well-known property of anatase TiO$_2$. The extremely thin TiO$_2$ wall of the hollow nanoribbon network exhibited a macroscopically detectable wettability change with UV radiation.

Conclusions

We demonstrated a novel approach for the fabrication of highly entangled hollow TiO$_2$ nanoribbons using a biotemplating process. Our approach takes advantage of the rapid, straightforward self-assembly of an aromatic peptide molecule into nanoribbons, which are physically cross-linked to form an organogel network. The remarkably high thermal stability of the aromatic peptide assembly allowed for the direct deposition of a nanoscale TiO$_2$ layer on the peptide xerogel network through an ALD process. Owing to the ultrafine thickness tunability of ALD process and the easy calcination of biomolecular templates, highly entangled hollow anatase TiO$_2$ nanoribbons that replicate the peptide organogel morphology could be readily produced. The highly crystalline anatase TiO$_2$ nanostructure is potentially useful for various advanced applications in photochemistry and optoelectronics.

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