One-dimensional metal hydroxide nanomaterials with macroscopically controlled orientation and aggregation: fascinating surface hydroxyl groups on anisotropic structures for functionalities

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This review briefly describes recent advances on the fabrication methods affording macroscopically controlled orientation and aggregation of one-dimensional (1D) metal hydroxide nanomaterials and the structuralization-driven functional applications. A special attention is focused on the functionalization based on two approaches: 1) superhydrophobic adhesive surface, and monolithic cation-exchangers and photocatalysts by controlled orientation and aggregation of titanate nanotubes, 2) a supported catalyst, electrothermal sensor and switchable fluorescence film by the structuralization of metal organic framework (MOF) derived from orientation/aggregation-controlled copper hydroxide nanotubes/nanobelts.

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1. Introduction

Nanomaterials have been used in a wide range of fields including electrical, optical, environmental and pharmaceutical applications due to the unique properties such as a large specific surface area and quantum effect in contrast to bulk materials. Among various morphologies of nanomaterials, one-dimensional (1D) nanomaterials have attracted attentions for potential applications including electronics, optoelectronics and advanced coatings due to their anisotropic physical and chemical properties derived from their structural anisotropy. The performance of the materials is closely related to not only their size and shape but also macroscopic aggregation states (positioning the 1D nanomaterials at the desired places) and orientation of individuals.

Metal hydroxides, constructed by a reaction between hydroxide anions and metal cations in basic aqueous media, are mostly obtained as crystalline nanomaterials with 1D or 2D structures, of which crystal structures are composed of a stacking of single metal hydroxide layers by hydrogen bonding or intercalating cation/anion species (Fig. 1). Metal hydroxides exhibit unique features: 1) aligned and abundant hydroxyl groups on their surfaces, 2) low lattice enthalpy compared to metal oxides, and 3) a layered structure capable of ion-exchange, which are different from metal oxides. Although these unique features allow metal hydroxide nanomaterials to be utilized in a variety of applications, especially as catalysts, adsorbents and ion-exchangeable materials, fascinating applications derived from the above-mentioned nature of metal hydroxides have not been fully explored yet. For instance, to our best knowledge, an efficient use of their aligned hydroxyl groups on their surfaces have not been studied. A control of macroscopic orientation and aggregation of metal hydroxide nanomaterials will open up the possible utilization of metal hydroxide nanomaterials for specific applications, as demonstrated in other 1D nanomaterials such as carbon nanotube and others. In this review, fabrication methods affording macroscopic orientation and aggregation of 1D metal hydroxide nanomaterials and their functional applications achieved by utilizing the features of 1D metal hydroxides are overviewed with an emphasis on the author’s works (Fig. 2). The functionalization was achieved by two approaches: 1) controlled orientation and aggregation of 1D titanate nanotubes, 2) the structuralization of other functional materials, metal organic framework (MOF), derived from orientation/aggregation-controlled copper hydroxide nanotubes/nanobelts. The two different approaches are briefly reviewed in the following sections.

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2. Controlling orientation and aggregation of titanate nanotube

2.1 Titanate nanotube

A titanate nanotube (TNT) is a tubular 1D nanomaterial with 5–10 nm in diameter and tens to several hundreds of nanometers in length. The crystal structure of TNT is known to be a lepidocrocite-type structure composed of layered titanate containing cations in the interlayer, which is same as gamma-type metal (oxy)hydroxide such as γ-AlOOH, γ-FeOOH, and Cu(OH)2. Owing to the characters such as the layered structure capable of cation-exchange, physicochemical properties similar to titania, high aspect ratio, and the large specific surface area originated from the tubular morphology, TNT is considered as a promising material for (photo)catalysts, hydrogen and Li ion storages, electrodes for Li ion batteries and solar cells, and light and electron emitters. TNTs are usually obtained as powders via a hydrothermal treatment (e.g., at 150 °C for 24 h) of crystalline TiO2 powders with 10 M NaOH aqueous solution where homogeneous TiO2 dissolution and TNT nucleation processes are generally out of control in a reaction solution, resulting in hairball-like secondary particles constituted of entangled TNTs with a lack of macroscopic orientation and aggregation. Due to the TNT formation process based on homogeneous nucleation, controlling macroscopic orientation and aggregation of TNTs is rather difficult in the reported approaches.

2.2 Controlling orientation of titanate nanotubes for interfacial applications

The author and collaborators reported an alternative approach based on inhomogeneous nucleation of TNTs on
a precursory film to grow vertically-oriented TNTs on a substrate. A sol–gel derived amorphous TiO₂ film was used as a precursor for the TNT growth instead of the conventional powdery TiO₂, and a relatively milder hydrothermal condition, for example 110 °C in <1 M NaOH aqueous solution, was employed because the amorphous TiO₂ film exhibits higher solubility in a basic solution under hydrothermal conditions due to the low crystallinity and the existence of micro pores. The employment of the sol–gel derived amorphous TiO₂ film as a precursor and the relatively milder hydrothermal condition leaded to inhomogeneous nucleation of TNTs on the precursory TiO₂ film, resulting in oriented growth of TNTs perpendicularly to the entire surface of the precursory TiO₂ film [Figs. 3(a) and 3(b)]. As seen in the Fig. 3(b), the resultant TNTs has an inverse funnel shape, in which the tops of the nanosheets anchored on the precursory film surface are rolled-up to form nanotubes. In addition to the inhomogeneous nucleation approach affording the formation of the vertically-oriented TNTs, the use of the sol–gel derived amorphous TiO₂ film and the relatively milder hydrothermal condition can allow for the fabrication of vertically-oriented TNTs on a variety of substrates including silica glasses, plastics, and rubbers. Such semiconducting one-dimensional nanomaterials vertically-aligned on substrates are considered as promising electrodes for solar cells owing to a direct pathway for electron transfer from the point of injection to the electron sink with an improved electron transport and a higher charge collection efficiency.

The macroscopically oriented 1D nanostructures and the abundant surface hydroxyl groups on TNTs enable to fabricate functional interfaces. The as-synthesized vertically-oriented TNTs exhibited superhydrophilic surface with a contact angle (CA) of ~0° [Fig. 3(c)]. When surface hydrophobizing agents such as fluoroalkylsilane (FAS) and long-chain carboxylic acid, which reduce surface free energy, were grafted onto the TNTs by a chemical vapor deposition method, the surface showed superhydrophobicity (CA = 152°). The superhydrophobic surface also exhibited strong water adhesion: an 8 µL water droplet on the surface is strong enough to keep it anchored even while tilting the substrate 90 or 180° (superhydrophobic adhesive surface). The strong water adhesion was found to be originated from physically adsorbed water on remaining hydroxyl groups of TNTs. A considerable amount of unmodified surfaces remained due to higher density of surface hydroxyl groups than the grafting density of the hydrophobizing agents on TNTs. The physically adsorbed water plays a crucial role as a glue for the water droplet. This finding allowed for reversible and switchable water adhesion on the superhydrophobic adhesive surface by controlling adsorption/desorption of the physically adsorbed water on the TNTs. Desorption of physically adsorbed water on TNTs takes place by a gentle heat treatment beyond 80 °C, and re-adsorption...
(hydration) recovers in an ambient atmosphere without any structural change of TNTs. The contact angle reversibly changed from ~150° to ~137° by alternating mild heating (80°C, 30 min) and hydration (30 min in water) [Fig. 3(d)]. The change of contact angle enabled the surface repeatedly to catch and repel a falling water droplet (8 μL). Such a superhydrophobic adhesive surface is potentially used for small water droplet manipulation without any loss in a lab-on-a-chip, microfluidic devices and water/oil separation.\(^{14,15}\)

2.3 Controlling aggregation of titanate nanotubes for monolithic cation-exchanger and photocatalyst

TNT is one of potential candidate materials for solid catalysts, cation exchangers, and adsorbents for environmental toxic ions due to their high surface area,\(^{8}\) strong Bronsted acidity,\(^{16}\) cation exchange capability\(^{17}\) and photocatalytic activity.\(^{18}\) Although TNTs are usually obtained in a powder form, bulk-shaped (monolithic) TNTs on the centimeter scale are usually preferred in practical applications such as catalysts, adsorbents, and hydrogen and Li\(^+\) storage materials from a view point of handling, recovery, separation, and recycling. However, green pellets prepared by mechanical pressing of powdery TNTs are usually dense, resulting in an insufficient number of active sites to the surfaces of bulk materials because of the absence of flow channels inside the bulk materials for the rapid diffusion of adsorbate.\(^{19}\) Hierarchically porous TNTs monoliths are preferable in these applications. The author and collaborators reported the fabrication of hierarchically porous TNT-based monoliths by interconnecting individual TNTs with titania nanoparticles (Fig. 4).\(^{20}\) A condensed aqueous emulsion of TiO\(_2\) nanoparticles was employed as precursors, which yielded TNT secondary particles and intervening TNT bridges within small cavities between the TNT secondary particles during the conversion from TiO\(_2\) to TNT.\(^{21}\) The TNT bridges promote the formation of three-dimensional TNT frameworks [Figs. 4(c) and 4(d)]. The dense and entangled TNTs formed in small cavities resulted in other more sparse TNT areas. The TNT density variation generated continuous macropores as seen in Figs. 4(b) and 4(c). The resulting monolith has both nanotubes derived from the nanotubular structure and macropores with a broad distribution from 10 nm to 10 μm in diameter. It was found that the macro porosity is adjustable by simply varying the concentration of titania emulsions: smaller concentration of the emulsion resulted in larger porosity. The monolith has potential as a Li\(^+\) storage material, an adsorbent for environmental toxic ions, and a reusable photocatalytic monolith owing to the hierarchical architecture, and cation-exchangeable and photocatalytic activities of TNT. A Li\(^+\) adsorption investigation showed that the monolith exhibited a faster rate and a higher capacity of Li\(^+\) exchange than a dense TNT pellet [Fig. 4(e)]. The monolith is also useable as a recyclable photocatalytic monolith [Fig. 4(f)]. The photocatalytic activity was found to be enhanced by partially converting TNTs into SrTiO\(_3\) nanoparticles where SrTiO\(_3\) nanoparticles have a close contact with TNTs.\(^{22}\)

3. Controlling orientation and aggregation of Cu(OH)\(_2\) nanotubes/nanobelts

3.1 Cu(OH)\(_2\) nanotube/nanobelt as a scaffold for fabricating MOF architectures

Metal hydroxide has, in principle, lower lattice enthalpy than metal oxide,\(^{23}\) and also abundant hydroxyl groups on its surface, which makes it a promising precursor and scaffold for organic–inorganic hybrid materials. As one of fascinating organic–inorganic hybrid materials, MOFs also called porous coordination polymers constituted of metal ion connectors and organic linkers receive a considerable attention as a new class of molecular-scale microporous materials due to their tunable architectures and chemical functionalities.\(^{24,25}\) Due to these features, MOF attracts great interests for applications such as storage, separation and catalysis.\(^{26,27}\) In contrast, research interests for applications are now rapidly growing on MOF-based electrical/ optical devices including sensors, microelectronics, and transistors because their functionalities are designable in a molecular level.\(^{28}\) Positioning MOF crystals at desired locations and controlling an orientation have been highly desired to realize MOF-based devices.\(^{29}\) MOFs are usually synthesized by a solvothermal method from metal salt and organic linker. The author and collaborators have been developing a MOF fabrication method using metal hydroxide as a precursor and scaffold.\(^{30,31}\) Cu(OH)\(_2\) nanotubes/nanobelts are mostly employed as scaffolds and Cu\(^{2+}\) sources for the MOF synthesis because of the existence of a variety of fascinating Cu-based MOFs. The conversion from Cu(OH)\(_2\) into Cu-based MOF is conducted by simply soaking the Cu(OH)\(_2\) nanotubes/nanobelts into a solution containing organic linkers constituting the target Cu-based MOFs [Fig. 5(a)]. In this process, a direct reaction of Cu(OH)\(_2\) with the organic linkers takes place through an acid-base reaction. Owing to the high reactivity of Cu(OH)\(_2\) with the organic linkers originated from the low lattice enthalpy and the abundant reactive hydroxyl groups, this approach offers advantages such as short processing time and mild synthetic conditions (e.g., room temperature, mixed solvent of water and ethanol). The use of pre-deposited Cu(OH)\(_2\) nanotubes/nanobelts can also afford the fabrication of Cu-based MOFs on 3D architectures. Figures 5(b)–5(d) show Cu\(_2\)(BTC)\(_2\) (BTC = 1,3,5-benzenetricarboxylate) MOF patterns fabricated from pre-deposited Cu(OH)\(_2\) nanotube arrays.\(^{32}\) The Cu(OH)\(_2\) nanotube arrays were synthesized by surface oxidation of metallic copper patterns in a basic solution. The protocol also allows to homogeneously decorate a Cu mesh with the Cu\(_2\)(BTC)\(_2\) MOFs [Figs. 5(e) and 5(f)]. The MOF-decorated mesh is usable as a supported catalyst to accelerate the Friedländer reaction between 2-aminobenzophenones and acetylacetone [Fig. 5(g)]. The MOF films on a various substrates are also fabricated from Cu(OH)\(_2\) nanobelt films prepared by depositing a Cu(OH)\(_2\) nanobelt dispersion. The MOF films on conductive substrates can
be used for size-selective electrochemical sensing and non-enzymatic electrocatalysis of glucose.33)

3.2 Oriented Cu(OH)$_2$ nanobelts as scaffolds for fabricating MOF oriented films

An achievement of MOF films with macroscopically controlled crystallographic orientations has been required to enhance the sophisticated functionalities for practical applications. As one of promising methods, liquid phase epitaxy on surfaces functionalized with self-assembled monolayer has been used for oriented MOF films.34) However, a control of crystallographic orientation along all three axes in a macroscopic scale was not achieved; especially, in-plane orientation (a direction parallel to a substrate) is hardly controlled by reported methods for oriented MOF film. The author and collaborators have recently developed a novel method achieving MOF films with crystallographic orientation along all three axes in a centimetre-scale via heteroepitaxial growth of MOF on metal hydroxide.35) The key to success is the use of metal hydroxide as a scaffold and precursor [Figs. 6(a) and 6(b)]. As described above, metal hydroxide has aligned hydroxyl groups on the surface in atomic level, which differ from metal oxide and other materials. The surface

Fig. 4. Hierarchically porous TNT-based monolith: (a) Optical image of the centimeter-scale monolith. (b, c) SEM images showing the macropores and framework constructed of interconnected and entangled TNTs. TNT secondary particles were bridged by entangled TNTs. (d) Transmission electron microscope (TEM) image showing the tubular TNT structure. (e) Lithium-proton ion exchange capability of hierarchically porous TNT-based monolith, dense pellet and blank. Reproduced from Ref. 20 with permission from American Chemical Society. (f) Photocatalytic degradation (First-order reaction kinetics for the rhodamine B (RhB) degradation) by the TNT-based (TNT/TiO$_2$) monolith and the TNT-based monolith partially converted to SrTiO$_3$ (STO/TNT/TiO$_2$ monolith). Blank (WPC. WOP) indicates bank data collected with photocatalyst without photoirradiation, and Blank (WOCP. WPI) indicates data collected without photocatalyst with photodissipation. Reproduced from Ref. 22 with permission from The Ceramic Society of Japan.
hydroxyl groups are able to be directly reacted with carboxylic acid-based organic linkers through an acid-base reaction, possibly resulting in the aligned organic linker layers on the surface of metal hydroxide. Given that MOFs are constructed via a modular synthetic approach we hypothesized that an epitaxially aligned MOF would be synthesized if the dimensions of the organic linkers were analogous to the lattice parameter (or a whole number multiple) of the metal hydroxide: heteroepitaxial growth takes place in case the regularity of the organic linkers of MOF is consistent with that of hydroxyl groups of metal hydroxide [Fig. 6(c)]. By consulting a database, it was found that Cu$_2$(BDC)$_2$ (BDC: 1,4-benzenedicarboxylate) possesses lattice parameters ($a$ and $b$ axes) that closely match those of Cu(OH)$_2$: P4$_{2}$(c and a axes): $a = 10.61$ Å, $b = 5.80$ Å, $c = 10.61$ Å in Cu$_2$(BDC)$_2$; and Cmc21 space group, $a = 2.95$ Å, $b = 10.59$ Å, $c = 5.26$ Å in Cu(OH)$_2$. Thus, we predicted that the $a$ and $b$ axis of the MOF would align with the $c$ and $a$ axis of a Cu(OH)$_2$ substrate, respectively. An oriented Cu(OH)$_2$ nanobelt film is employed as a “pseudo single crystal film” because the synthesis of large single crystal Cu(OH)$_2$ is almost impossible due to the rapid crystallization [Fig. 6(d)]. Figures 6(e) and 6(f) exhibit the Cu$_2$(BDC)$_2$ MOFs grown on the pseudo single crystal film of Cu(OH)$_2$. The scanning electron microscope (SEM) images clearly show that the plate Cu$_2$(BDC)$_2$ crystals aligned in the same direction orthogonal to the nanobelts. The crystallographic orientation along all three axes in a centimetre-scale was confirmed by X-ray diffraction investigations. The macroscopically oriented MOF films are capable of introducing functional molecules into their micropores for generating anisotropic physical properties. The MOF films accommodating organic dye molecules exhibited the switchable fluorescence ‘ON’ or ‘OFF’ by changing the orientation of the substrate with respect to the polarization direction of the incident light [Figs. 6(g)–6(i)]. The result confirmed that the oriented MOF film can afford a macroscopic alignment of functional molecules in a same direction. By applying liquid phase epitaxy on the oriented MOF films, the precise alignment of multiple layers of MOF films, MOF-on-MOF films, over macroscopic length scales can be fabricated, providing a new toolbox for multifunctional microporous coatings.36

4. Summary

Recent advances on the fabrication methods affording macroscopically controlled orientation and aggregation of 1D metal hydroxide nanomaterials and the structuralization-driven applications were overviewsed with an emphasis on the author’s works. The fabrication of vertically-oriented TNTs led to superhydrophobic adhesive surfaces. By
utilizing water adsorption/desorption characters on the TNTs, the switchable wettability on the superhydrophobic adhesive surfaces was achieved. Hierarchically porous TNT-based monoliths were fabricated by interconnecting individual TNTs, which are demonstrated to be usable as reusable cation-exchanging and photocatalytic monoliths. Metal hydroxide can be also a promising scaffold and precursor for positioning MOF crystals at desired locations and controlling an orientation owing to low lattice enthalpy and aligned and abundant reactive hydroxyl groups originated from the nature of metal hydroxide. To our best knowledge, heteroepitaxial growth of MOF on metal hydroxide is a first report fruitfully utilizing the aligned hydroxyl groups on metal hydroxide in atomic level. The fruitful use of the aligned hydroxyl groups is expected to be extended to the other organic–inorganic hybrid materials, organics, and inorganics.

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