Boehmite Nanofibers as a Dispersant for Nanotubes in an Aqueous Sol

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Abstract

By exploiting the dispersibility and rigidity of boehmite nanofibers (BNFs) with a high aspect ratio of 4 nm in diameter and several micrometers in length, multiwall-carbon nanotubes (MWCNTs) were successfully dispersed in aqueous solutions. In these sols, the MWCNTs were dispersed at a ratio of about 5–8% relative to BNFs. Self-standing BNF–nanotube films were also obtained by filtering these dispersions and showing their functionality. These films can be expected to be applied to sensing materials.

Text

One-dimensional materials such as nanofibers, nanotubes, and nanowires have received a great deal of attention in the field of nanotechnology.[1] Depending on their composition, these materials can exhibit interesting properties that are not found in bulk materials owing to their specific shape, which consists of a high aspect ratio and a narrow diameter composed of a limited number of molecules. Because of their unique
characteristics, these materials have been the subject of extensive research motivated by not only fundamental scientific interest but also the potential practical applications such as electronic materials, sensors, and fillers for composite materials.[2-7] Nanofibers and nanotubes can be produced by various methods, such as electrospinning, decomposition of biological materials, and hydrothermal treatment.[8-11] A common problem encountered while handling these materials is aggregation. Similar to the case of quantum dots and nanoparticles, which readily form secondary particles and lose their interesting physical properties, nanofibers and nanotubes are susceptible to bundle formation. One solution for maintaining the unique functions of nanofibers and nanotubes in macroscale is to disperse them in liquids or polymers, which necessitates the use of dispersants and surface modification, although the optimal method must be determined for each material. For example, various techniques have been proposed for the dispersion of carbon nanotubes in a liquid, such as surface oxidation, polymer coating, and the use of surfactants or an appropriate dispersion medium.[12-18] Each of these methods for dispersing one-dimensional materials has both advantages and disadvantages, and the most appropriate choice can depend on the specific application.

Our group has studied porous materials by using (pseudo)boehmite nanofibers (BNFs) composed of aluminum oxide hydroxide (AlOOH), which has a high aspect ratio of 4 nm in diameter and several micrometers in length.[19-22] Nanofibers prepared by the solvothermal method can be stably dispersed in concentrated aqueous acetic acid for several months.[23, 24] However, when a base or phosphoric acid is added under appropriate conditions, the nanofibers form a three-dimensional network without bundling, and the dispersed sol becomes a gel. By supercritical drying of the wet gel obtained from this reaction, ultralow-bulk-density transparent porous monoliths
(aerogels of 5 mg cm$^{-3}$ or less) can be obtained, which have potential applications as optical materials.[21] By dispersing functional materials such as fluorescent molecules or nanoparticles in the gel before freeze-drying, a transparent monolith (cryogel) containing the functional material dispersed in the nanofiber network can also be obtained.[19, 22] These materials are expected to apply to the fabrication of sensing materials. As the nanofiber dispersion sol is fluid, it is also possible to disperse the functional material using ultrasonication. However, because the BNFs themselves are rigid materials, they are expected to hinder the aggregation of the functional material. In particular, when the functional material is also a one-dimensional material, the movement in the dispersion is mostly restricted. Indeed, the addition of multi-walled carbon nanotubes (MWCNT) to a BNF dispersion was found to afford a relatively stable dispersion. The results of this study demonstrate the applicability of already dispersed one-dimensional materials as dispersants.

To investigate the dispersibility several BNF dispersions with different concentrations were prepared, and MWCNTs were then added and dispersed by sonication. The obtained BNF–MWCNT sols remained black even after ultracentrifugation at 10,000 ×g for 5 minutes, which indicated that the MWCNTs were still dispersed (Figure 1). In contrast, when the MWCNTs were added to water or aqueous acetic acid, ultracentrifugation resulted in pelletization of the MWCNTs and the formation of a colorless and transparent supernatant. These results confirmed that the presence of BNF affected the dispersion state of the MWCNTs under aqueous conditions. Table 1 shows the MWCNT concentrations in the supernatants obtained after ultracentrifugation of BNF–MWCNT dispersions containing various BNF concentrations. MWCNTs were dispersed at a weight ratio of 5–8% relative to BNF. A
lower BNF concentration in the dispersion resulted in a reduction in the amount of dispersible MWCNT and an increase in the error. Figure 1c shows transmission electron microscopy (TEM) images obtained after casting the obtained BNF–MWCNT dispersion on a grid. The MWCNTs were kept in the dispersed state by multiple BNFs, and no noticeable aggregation was observed. Interestingly, the addition of the MWCNTs was found to lead to a change in the viscosity relative to the BNF dispersion. In the system with the highest viscosity (sample X2.5 in Table 1), the viscosity decreased from 76 Pa s to 49 Pa s. This reduction was ascribed to the homogeneous dispersion of the MWCNTs between the BNFs, which weakened the hydrogen-bonding interactions. From these results, it is considered that the dispersed MWCNTs became physically entangled between the rigid BNFs in the dispersed state. Even when this BNF–MWCNT dispersion was allowed to stand for one month, almost no change in the dispersion state was observed.
Figure 1  a) Schematic diagram showing the dispersion of MWCNTs by BNFs. b) Photograph of BNF–MWCNT dispersion X5. The left sample, which shows a fivefold dilution of X5, became translucent and slight precipitation occurred over time. c) TEM images after casting the obtained BNF–MWCNT dispersion on a grid, showing the dispersion of the MWCNTs between multiple BNFs.

Table 1  Concentrations of the BNF dispersions and the concentration of each component in the supernatants obtained from ultracentrifugation of the resulting BNF–MWCNT dispersions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BNF concentration in sol [wt %]</th>
<th>CNT concentration in sol [wt %]</th>
<th>Weight ratio of CNT to BNF [wt. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X2.5</td>
<td>2.7</td>
<td>0.21</td>
<td>7.8</td>
</tr>
<tr>
<td>X5</td>
<td>1.3</td>
<td>0.094</td>
<td>7.2</td>
</tr>
<tr>
<td>X10</td>
<td>0.64</td>
<td>0.034</td>
<td>5.3</td>
</tr>
</tbody>
</table>
In a similar manner to paper, the structure of which consists of intertwined cellulose fibers, one-dimensional materials such as nanofibers, nanotubes, and nanowires are known to be capable of forming films upon removal of the solvent by filtration and evaporation. With respect to BNFs, Kodaira et al. fabricated free-standing films with visible-light reflectivity and thermally insulating properties by preparing nanofiber bundles under appropriate conditions and subsequently depositing them.\[25\] In the case of the BNF–MWCNT dispersion, it was possible to prepare a black self-supporting film by vacuum filtration through a polycarbonate membrane filter (Figure 2). Scanning electron microscopy (SEM) images confirmed that this film had a structure in which the BNFs and MWCNTs were arranged in layers. As BNFs are composed of aluminum oxide hydroxide and act as an insulator, the obtained film exhibited only the low electrical conductivity of the MWCNTs. Instead of MWCNTs, polydiacetylene nanotubes (PDANTs), which have been reported as a vapochromic material,\[26-28\] could also be dispersed with the BNTs to prepare a similar film. Although PDANTs themselves can be dispersed in water or alcohols, the resulting composite films were stable to immersion in these solvents. This observation indicated that the PDANTs in the film were successfully confined in a dispersed state with the BNFs. As with the BNF–MWCNT film, the PDANT–MWCNT film was also found to have a structure in which the nanofibers formed overlapping layers. Exposure of this composite film to water or 2-propanol vapor revealed that it had vapochromic properties (Figure 3, Movies S1 and S2). Although the color change was small and different from that which occurs for pure PDANTs, the basic functionality remained even after film formation. Therefore, the use of BNF as a dispersant/carrier is expected to be a
promising method for fabricating functional films when additional one-dimensional materials with unique functionalities are synthesized in the future.

Figure 2  a) Photograph of BNF–MWCNT (X5) and BNF–PDANT films formed by vacuum filtration. Cross-sectional SEM images of b) the BNF–MWCNT film and c) the BNF–PDANT film.

Figure 3  Vapochromic behavior of a BNF–PDANT film upon exposure to water vapor. See also Movies S1 and S2.
As in the case of the BNF dispersion, the dispersed state of the BNF–MWCNT and BNF–PDANT gels was also maintained upon increasing the pH by adding a base to the binary dispersions. However, when these wet gels were subjected to supercritical drying, considerable shrinkage occurred, and the reproducibility of the obtained aerogels was low. This was because the addition of the nanotubes reduced the bonding between the BNFs and the networks became non-uniform. At present, the formation of monoliths based on BNF composites remains difficult.

In summary, MWCNTs were successfully dispersed in aqueous solution by exploiting the dispersibility and rigidity of BNFs. In these dispersions, the MWCNTs were dispersed at a ratio of about 5–8% relative to BNF. Self-standing BNF–nanotube films were also obtained by filtering these dispersions, allowing the introduction of functionalities such as chromic properties depending on the type of dispersed nanotubes. These dispersions can potentially be applied in the fabrication of functional films and used as inks and fillers. Unlike existing methods such as chemical modification, the application of this method to one-dimensional materials such as single-walled carbon nanotubes, which are susceptible to bundle formation, remains challenging, and further research is required. In future work, the described method for physically creating a dispersed state by utilizing the geometric properties of a one-dimensional material is expected to lead to the development of new dispersants.

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BNF+MWCNT dispersion