Facile and Stable Dispersion of Carbon Nanotubes into a Hydrogel Composed of a Low Molecular-weight Gelator Bearing a Tautomeric Dye Group

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It was found that single-walled carbon nanotubes are stably dispersed into a low molecular-weight hydrogel (β-D-glucopyranoside–azonaphthol conjugate). From absorption and fluorescence spectral observations and microscopic images, it was shown that this gelator tends to orientate on the surface of SWNTs and specifically emits fluorescence light.

Organogels are thermoreversible, viscoelastic materials consisting of low molecular-weight compounds self-assembled primarily according to the 1-D motif and then into complex 3-D structures.[1] Multiple noncovalent interactions such as hydrogen bonding, donor–acceptor, and hydrophobic interactions between the organogel building blocks are responsible for the gel-forming process. Although many examples of gelators for organic solvents have been reported in the literature, a fewer studies on gelators for water (hydrogelators) have been presented so far.[2] The development of strong, thermoreversible hydrogelators can lead to new useful materials, particularly in relation to biochemical and pharmaceutical purposes, for drug delivery, wound healing, tissue engineering processes, etc.[3] In our group we have synthesized and studied a variety of sugar-based compounds that are able to gelate water, organic solvents, or both.[4,5] We, as well as others, have noticed that hydrophobic interactions, for example in the form of aromatic π–π stacking, are indispensable for the formation of oriented aggregates in water and are most probably the initial driving force for the self-assembly process.[1,2] This characteristic of the gel system has brought about one idea to us that the gelator bearing an aromatic π-group may be capable of dispersing single-walled carbon nanotubes (SWNTs) into the medium, because it is known that several π-group-containing compounds are useful to stably disperse SWNTs into organic solvents.[6,7] Recently, we developed new sugar-based gelators bearing an azonaphthol moiety, which serves not only as an aggregative functional group but also as a probe for the microscopic solvent polarity: from a UV–vis spectral change induced by the azo–hydrazone tautomerism, the microenvironmental polarity in the fibrous gelator aggregates can be estimated.[8] Therefore, if this gelator disperses
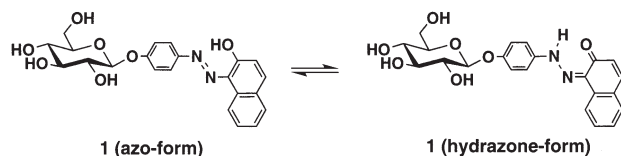
SWNTs by the interaction between the π-group in the gelator and the π-surface of SWNTs, one can readily detect the interaction by spectroscopic methods. Thus, the motivation of this study is related to two factors, facile and stable dispersion of SWNTs into the aqueous solution containing a hydrogelator and spectro-

scopic detection of the SWNTs–gelator composite. Here, we used a β-D-glucopyranoside–azonaphthol conjugate (**1**) which is known to show the highest gelation ability for water among several conjugates tested previously.[8]

Gelator **1** (0.26 mg) was dissolved in a mixed solvent of water (0.240 dm^3) and ethanol (6.0 × 10^{-2} dm^3) and the mixture was heated at reflux temperature to dissolve **1**. When the solution was cooled to room temperature, we obtained a red-colored gel. The sol-gel phase-transition temperature (T_{gel}) estimated by a tube-inversion method was 57 °C.[9] When SWNTs (0.08 mg: length 1–3 μm)[9] were added to this solution at reflux temperature, we obtained a dark red-colored gel which had the T_{gel} value at 66 °C. This gel existed stably at least for 3 months without the precipitation of SWNTs. When the same treatment was operated in the absence of **1**, we obtained the SWNTs precipitate and a clear aqueous supernatant solution. These results indicate that the hydrogel of **1** can stably disperse SWNTs and the gel stability is enhanced by addition of SWNTs.
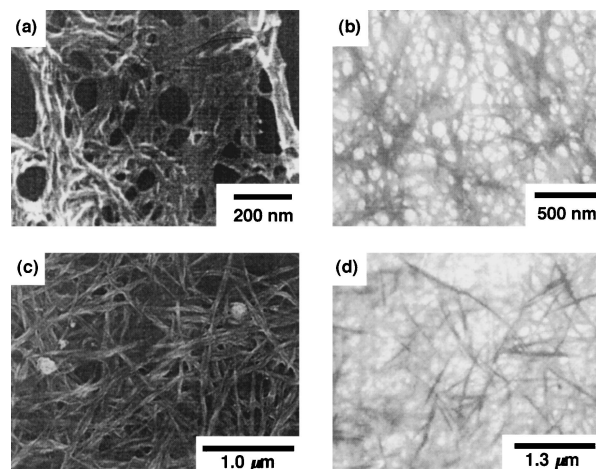

Figure 1. (a), (c) SEM and (b), (d) TEM (without staining) images of the xerogels obtained from (a), (b) the aqueous gel of **1** (2.0 × 10^{-3} mol dm^{-3}) and the aqueous gel of **1** (2.0 × 10^{-3} mol dm^{-3}) + SWNTs (0.1 mg mL^{-1}).

Figures 1a and 1b show SEM and TEM images of the xerogel prepared from the hydrogel of **1**, respectively. One can recognize a network structure composed of fibrillar bundles, characteristic of the structure for low molecular-weight gels. When SWNTs were added, the morphology changed to more straight fibers and a clearer light-and-shade contrast appeared in the TEM picture (Figure 1d). Since the length of the shaded bars is comparable with that of SWNTs (1–3 μm), one can propose that they are SWNTs (presumably, bundled ones) dispersed into the aqueous gel of **1**.

In a water–ethanol (80:20 v/v) mixed solution, **1** (2.0 ×

1 (azo-form)　　　　　　　　**1 (hydrazone-form)**

10^{-5} mol dm^{-3}) gave the absorption maxima at 416 nm (for azo form) and 500 nm (for hydrazone form). The excitation spectrum monitored at 560 nm (fluorescence maximum) gave the maximum peak at 520 nm, indicating that the emissive species is the hydrazone form of **1**.
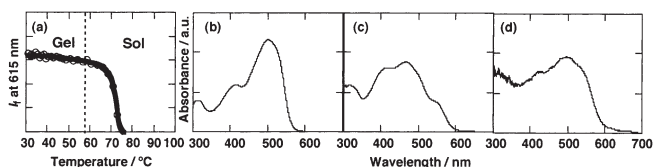

Figure 2. (a) Fluorescence intensity (I_f) at 615 nm plotted against the medium temperature : [**1**] = 2×10^{-3} mol dm^{-3}, water–ethanol (80:20 v/v), λ_{ex} = 467 nm and UV–vis absorption spectra of (b) **1** (2.0×10^{-5} mol dm^{-3}) in the sol phase, (c) **1** (2.0×10^{-3} mol dm^{-3}) in the gel phase, and (d) **1** (6.4×10^{-5} mol dm^{-3}) + SWNTs (0.028 mg dm^{-3}): this is the difference spectrum after offsetting the absorption of SWNTs.

Figure 2a shows the fluorescence intensity (I_f) at 615 nm plotted against the medium temperature. In the sol phase (>57 °C), the I_f is very weak but begins to increase near the T_{gel} (57 °C). Once the phase is converted to the gel phase, the I_f keeps the high, constant values. To our eyes, the gel formation is recognizable as emission of the red fluorescence. With these lines of information in mind, we carefully observed the sols with a confocal laser scanning microscope (CLSM). The dried samples for CLSM observations were prepared by casting a sol solution containing **1** (2.0×10^{-5} mol dm^{-3}) and SWNTs (0.10 mg dm^{-3}) on a glass plate. It is clearly seen from the CLSM images (see the Graphical Abstract[10]) that the fluorescence is observable at the spots where the presence of SWNTs is recognized by the light transmission image. The coincidence implies that **1** tends to aggregate, even below the critical gelation concentration, on the surface of SWNTs and emits the fluorescence.

Then, how is the azo–hydrazone tautomerism changed by the gel formation and the interaction with SWNTs ? As shown in Figure 2c, the fraction of hydrazone form is decreased in the gel phase, compared with that in the sol phase (Figure 2b). Since the fraction of hydrazone form is decreased in the apolar environment,[8] this trend implies that the gel phase is more apolar than the balk phase (i.e., water:ethanol = 80:20 v/v). The fluorescence intensity in the gel phase increased (Figure 2a) in spite of the decrease in the fraction of emissive hydrazone form. This means that the fluorescence intensity of hydrazone form is intensified in the gel phase by suppression of molecular freedom. The UV–vis spectrum obtained from a mixture of **1** and SWNTs (Figure 2d) in the sol phase shows that the azo/hydrazone ratio is almost same as that in the gel phase. In other words, the dye molecules arranged on the SWNTs surface report it to be a more apolar environment.

In conclusion, the present paper has demonstrated several novel observations for the gelator–SWNTs interaction: that is, (1) SWNTs are stably dispersed, (2) the gelators tend to orientate on the surface of SWNTs, (3) the gel stability is improved by addition of SWNTs, and (4) the microenvironment of the SWNTs surface can be monitored. We thus believe that the low molecular-weight hydrogel is a potential medium to sustain SWNTs and sometimes fragile physical property of hydrogels is improved by conjugation with stiff SWNT as a construction material.

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10 Conditions: cast membranes for the CLSM were prepared from the aqueous solution of **1** (2.0×10^{-5} mol dm^{-3}) and SWNTs (0.10 mg dm^{-3}), (a) fluorescence image, (b) light transmission image, and (c) (a) + (b). In spite of the reddish fluorescence from the **1** + SWNTs gel, the CLSM images show greenish fluorescence since the images were taken through the filter.