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Fabrication of Fluorescent One-dimensional-nanocomposites through One-pot Self-assembling Polymerization on Nano-helical Silica

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This paper presents a new class of one-dimensional nanostructures exhibiting remarkable fluorescent solvatochromism. This is fabricated through the self-assembling polymerization of 2,6-dihydroxyanthracene with a small crosslinker on the surface of silica helices obtained from a sol-gel reaction with tetraethoxysilane in the presence of the gemini surfactant-derived chiral assembly.

Keywords: Fluorescent solvatochromism |
Helical self-assembly | Nanocomposite

One-dimensional (1D) nanomaterials have received significant attention owing to their peculiar dimensional restriction, physicochemical and optical properties, and various applications such as in optoelectronic devices,¹ photovoltaics,² solar cells,³ and photonics.⁴ Such 1D nanomaterials have been provided as helical self-assemblies,^{5,6} nanofibers,⁷ nanorods,⁸ and nanotubes⁹ and, therefore, they have frequently been fabricated using a bottom-up approach based on a self-assembling technique such as supramolecular chiral self-assembly,^{10–12} polymer electrospinning,¹³ and block building through crystallization.¹⁴ Owing to their enhanced features such as a high specific surface area, mechanical properties, and chiral optical properties, they play an important role in a wide range of applications.^{4b,4c,15} The most challenging aspect is to introduce optical properties into these 1D nanostructures, one of the most convenient methodologies of which can be consolidated through a fabrication using the adsorption or grafting of fluorescent components such as organic dyes¹⁶ and quantum dots¹⁷ on the surfaces. However, these types of fluorescent 1D nanomaterials still face certain problems, such as a lack of stability from an elution or a disassociation, and quenching from a highly dense immobilization, among others. To overcome these problems, some better systems should be newly developed.

In this paper, we introduce a new and facile approach (Figure 1) for the creation of fluorescent 1D nanomaterials based on fluorescent polymer-deposition through their direct polymerization, which may overcome the limitation of quenching and a loss in photochemical properties. Other advantages include the use of an organic monomer, absence of heavy metals, and good solubility in various solvents.

In this study, we selected twisted nanoribbons as the 1D nanomaterials, which were delivered from a simple combination of a non-chiral gemini surfactant and chiral tartrate anion (16-2-16 aggregates, as shown in Figure 1A) because this new class of 1D nanomaterial demonstrates distinct advantages in well-controlled helical structures in terms of diameter and pitch¹⁸ and good applicability for materialization through a sol-gel tran-

scription method.¹⁹ 1D nanosilica having a helical morphology was prepared via a sol-gel reaction of tetraethoxysilane (TEOS) on 16-2-16 aggregates as a template, and the removal of the template and unreacted TEOS was achieved through sufficient washing with 2-propanol and ethanol. Figures 2b and 2c show transmission electron microscopy (TEM) images of the nanosilica obtained, of which the diameter and helical pitch were determined to be 30 and 69 nm (Table 1), respectively. The other parameters (Table 1) include a width and thickness of 29 and 15 nm, respectively, which were measured based on the scheme shown in the TEM image of Table 1.

The fluorescent polymer deposition on the nanosilica helices was carried out as follows: 2,6-dihydroxyanthracene (2,6-DHA) was used as the main monomer for fluorescent functionalization (Figure 1B). This approach was inspired based on the fact that the polymerization of 1,5-dihydroxynaphthalene through cross-linking with 1,3,5-trimethyl-1,3,5-triazinane (TMTA) produces black polymers from a ring extension reaction leading to carbon-like structures,²⁰ whereas the corresponding 2,6-isomer provides colored and fluorescent polymers.²¹ Based on these findings, the hybridization of 1D helical nanosilica with a fluorescent polymer was achieved. The nanosilica and 2,6-DHA (1 mM) were mixed at a 1:1 weight ratio in ethanol. TMTA was added to the mixture, and polymerization was then conducted at 150 °C for 5 min using a microwave reactor. The product was collected through centrifugation, purified with ethanol, and washed several times until the supernatant became colorless despite the initial reddish color of the supernatant. The thermo-gravimetric analysis indicated that the weight loss of the polymer-deposited nanosilica at 900 °C was approximately 18 wt %, and the elemental analysis proved that the carbon and nitrogen contents were 14.4 wt % and 1.42 wt % respectively.

It was confirmed that the 1D morphology with a helical form was maintained after the polymerization process. Similar procedures were performed using water or a mixture of water and THF, although the helical structures collapsed in these solvent systems. This is probably caused by the alkaline behavior of the TMTA, where the pH of the solvent system was between 8.5 and 9.0, thereby leading to a hydrolysis of the Si-O bonds. Based on these fundamental results, we used ethanol without water as a solvent to perform polymerization. Ethanol was considered as the best solvent for the stability of helical nanosilica.

The color of the product obtained was brownish green (Figure 2d) after drying, and the TEM images show only a helical morphology (Figure 2e) similar to the original nanosilica helices. Therefore, the change in color from white to brownish green can be explained by the coloration of the nanosilica.

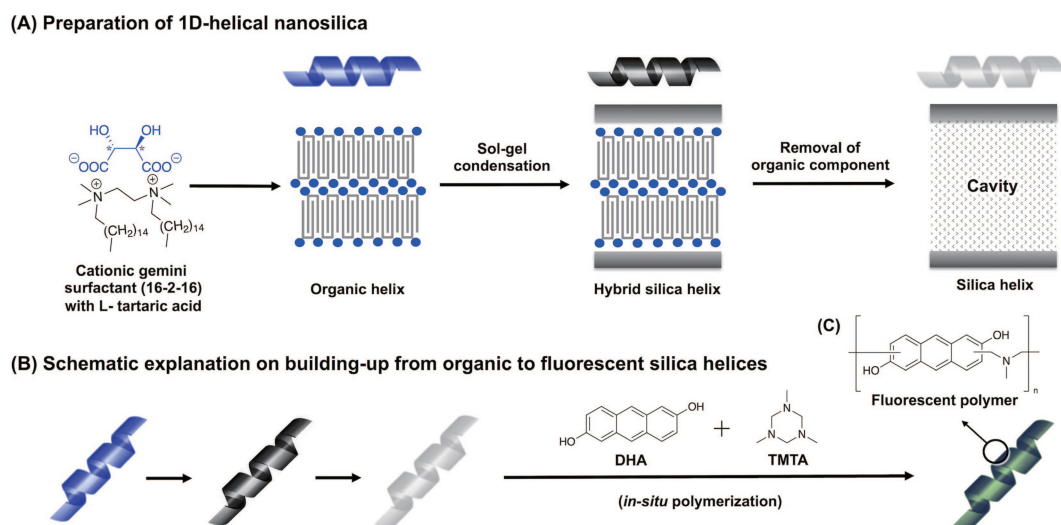


Figure 1. Schematic illustration showing the preparation processes of (A) 1D-nanosilica helix and (B) its following polymer deposition with (C) estimated chemical structure of the fluorescent polymer.

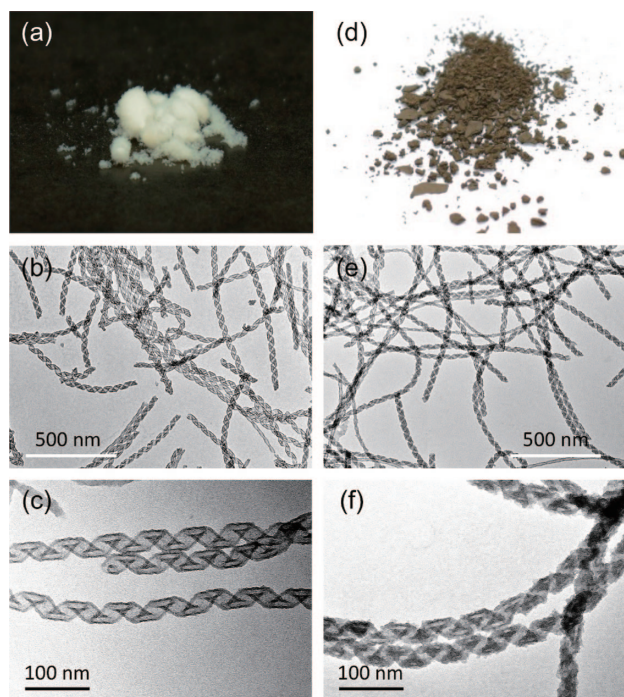


Figure 2. (a) White powders from bare silica helices and (b–c) their TEM images. (d) Brownish greenish powders from the polymer-deposited silica helices and (e–f) their TEM images.

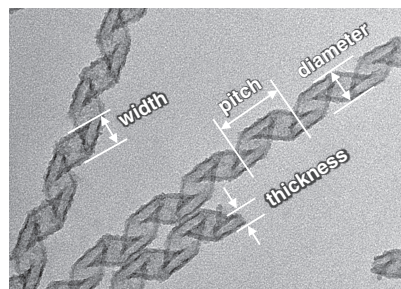
By comparing their detailed morphologies before and after polymerization, the diameter, width, and thickness of the product slightly increased in the original silica, whereas there was no significant change in the helical pitch, as shown in Table 1.

The mechanisms of polymer deposition on the silica are yet to be determined because 2,6-DHA has four reactive sites at the next positions (1-, 3-, 5- and 7-positions) of the phenolic carbon, although it is estimated that two distinct mechanisms may be

Table 1. Comparison of the measured parameters on silica helices before and after polymerization.

Parameters ^a	Bare silica		Polymer-deposited silica		Difference ^c (nm)
	Size (nm)	SD ^b	Size (nm)	SD ^b	
Diameter	30	1.2	34	1.0	4
Pitch	69	1.3	68	1.1	~ 0
Width	29	1.3	33	1.4	4
Thickness	15	0.6	17	1.1	2

^a Each parameter was determined according to the following TEM image. ^b Standard deviations were calculated from at least 10 nano-helices. ^c Determined by the difference between the average parameters of the polymer-deposited silica and the bare silica.



possible: first, through direct polymerization on the silica surface, and second, through a deposition of the produced oligomers onto a silica surface. Both processes likely occur competitively through a weak interaction between the Si-OH and nitrogen atoms of a crosslinker.

An elemental analysis promotes further discussion regarding this problem. The estimated chemical structure of the polymer is shown in Figure 1C. If the polymerization involves a one-to-one addition reaction based on the estimated structure (Figure 1C), the C/N value should be 14.58 based on C₁₄H₁₀O₂ and CH₂N(CH₃)CH₂ from 2,6-DHA and TMTA; however, the

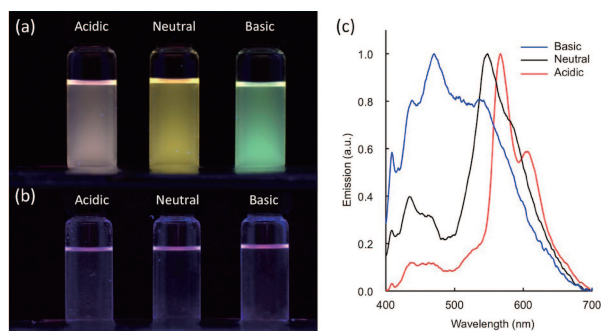


Figure 3. (a) Emission colors of the polymer-silica hybrids and (b) the bare silica helices in aqueous media with different pH under UV-lamp excited at 365 nm. (c) Normalized emission spectra of the polymer-silica hybrid with different pH levels excited at 365 nm. Concentration of silica: 0.25 mg ml^{-1} . The sample pH was adjusted to be pH 2, pH 7 and pH 11 using 0.1 M HCl and 0.1 M NaOH.

observed C/N value was 10.15 in the polymer-silica hybrid, where the C and N contents were 14.42% and 1.42%, respectively. This increase in the N content suggests multiple introductions of $\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2$ on the anthracene moiety leading to the promotion of crosslinking structures.

A ζ -potential analysis provides additional information on the surface structure. The bare silica helices exhibited $+14 \pm 1.5$ and -25 ± 2.5 mV at pH 4 and 8.5, respectively, which could be explained by the presence of Si^+OH and SiO^- . In contrast, the distinct increases in these values were observed to be $+21.4 \pm 1.9$ and -48.0 ± 2.0 mV at pH 4.0 and 8.5 through the introduction of the anthracene-derived polymer. These results strongly suggest the co-existence of additional basic and acidic sources from $\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2$ and the phenolic OH groups of the surface polymer.

The versatility of the polymer-silica hybrids can be emphasized by their unique fluorescent (FL) property. Figures 3a and 3b show a comparison of the fluorescent colors in aqueous dispersion states excited at 365 nm between the polymer-silica hybrids and bare silica. The distinct difference demonstrates that the deposited-organic component on the silica is not due to the monomer adsorption; however, the pH-dependent Stokes shift in the polymer-silica hybrid agrees with the pH-dependent change of the dissociation states between phenolic OH and O^- on the anthracene moiety in the polymer layer.

The uniqueness of the FL property can also be emphasized based on the solvent dependency. As shown in Figure 4, good dispersity in various organic solvents was observed, indicating an effective hydrophobicity from the deposited-polymer, and a distinct fluorescent solvatochromism²² was observed. This is one of the characteristic phenomena of a 2,6-DHA-derived polymer, and it was estimated that the fluorescent solvatochromism is induced through the “on-off” switch in the intramolecular hydrogen bonding interaction between $\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2$ from the crosslinker and phenolic OH groups from the anthracene moiety: the estimated interaction mechanism is proposed in Figure 4C, where the state I can be formed in acidic or polar solvents such as DMSO, but the state II based on intramolecular hydrogen bonding interaction is formed in a non-polar solvent such as toluene. In a basic condition, the phenolic anion state generated

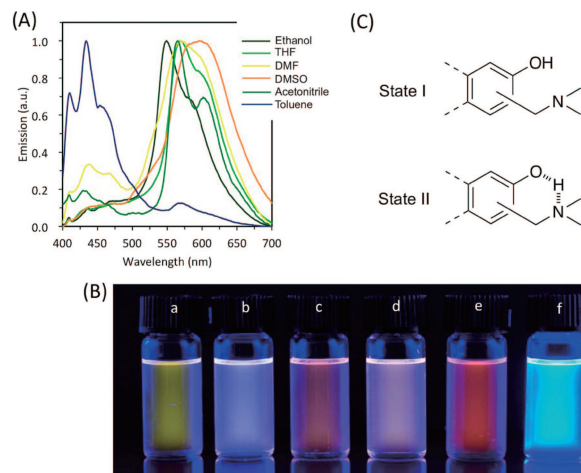


Figure 4. Solvent-dependent changes in (A) the fluorescent spectra and (B) the luminescent color in the polymer-silica hybrid dispersed in various organic media: (a) ethanol, (b) tetrahydrofuran, (c) dimethyl-formamide, (d) dimethylsulfoxide, (e) acetonitrile, and (f) toluene, under a UV-lamp excited at 365 nm. (C) Estimated mechanism on the fluorescent solvatochromism in the polymer component.

is probably similar to that in the state II. Detailed discussion will be presented in a future report with further investigation.

In conclusion, we established a new and facile method for creating fluorescent 1D nanomaterials composed of silica helices as a core with fluorescent polymer as a shell. The obtained 1D nanosilica hybrids showed (1) an amphiphilic property, leading to good dispersity in aqueous systems with a wide range of pH, (2) good dispersity in various organic solvents owing to an enhancement in hydrophobicity, and (3) a fluorescent property with remarkable solvatochromism. These advantages will expand the possible applications of 1D nanomaterials.

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