Large-Scale Fabrication of Copper-Ion-Coated Deoxyribonucleic Acid Hybrid Fibers by Ion Exchange and Self-Metallization

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ABSTRACT: It has been a challenge to achieve deoxyribonucleic acid (DNA) metallization and mass production with a high quality. The main aim of this study was to develop a large-scale production method of metal-ion-coated DNA hybrid fibers, which can be useful for the development of physical devices and sensors. Cetyltrimethylammonium-chloride-modified DNA molecules (CDNA) coated with metal ions through self-metallization exhibit enhanced optical and magnetic properties and thermal stability. In this paper, we present a simple synthesis route for Cu²⁺-coated CDNA hybrid fibers through ion exchange followed by self-metallization and analyze their structural and chemical composition (by X-ray diffraction (XRD), high-resolution field emission transmission electron microscopy (FETEM), and energy-dispersive X-ray spectroscopy (EDS)) and optical (by ultraviolet (UV)—visible absorption, Fourier transform infrared (FTIR), and X-ray photoelectron spectroscopies (XPS)), magnetic (by vibrating-sample magnetometry), and thermal (by a thermogravimetric analysis) characteristics. The XRD patterns, high-resolution FETEM images, and selected-area electron diffraction patterns confirmed the triclinic structure of Cu²⁺ in CDNA. The EDS results revealed the formation of Cu²⁺-coated CDNA fibers with a homogeneous distribution of Cu²⁺. The UV—vis, FTIR, and XPS spectra showed the electronic transition, interaction, and energy transfer between CDNA and Cu²⁺, respectively. The Cu²⁺-coated CDNA fibers exhibited a ferromagnetic nature owing to the presence of Cu²⁺. The magnetization of the Cu²⁺-coated CDNA fibers increased with the concentration of Cu²⁺ and decreased with the increase in temperature. Endothermic (absorbed heat) and exothermic (released heat) peaks in the differential thermal analysis curve were observed owing to the interaction of Cu²⁺ with the phosphate backbone.

1. INTRODUCTION

The development of flexible fibers with hybrid nanostructures consisting of organic and inorganic components is important for various applications in physical, chemical, and biological sciences, as well as materials engineering. The selection of organic and inorganic components is crucial to fabricate the hybrid nanostructures and utilize them for the development of novel devices and sensors. The main aim of this study was to develop a large-scale production method of unique hybrid nanostructures, which can be useful for the development of spintronic and optoelectronic devices and sensors. Naturally available biomolecules might be useful to replace the conventional inferior materials in various applications in both physical and biological sciences. Among the various biomolecules, deoxyribonucleic acid (DNA) molecules are promising owing to their intrinsic physical properties such as absorption at a specific target wavelength, transparency in the visible-light range, and biodegradable and flexible structure with efficient scaffold characteristics for the alignment of functional nanomaterials. DNA molecules modified with the cationic surfactant cetyltrimethylammonium chloride (CDNA) through an ion-exchange process can be dissolved in organic solvents and thus are intensively studied owing to the increased applicability of organic materials in target solvents. Among the various nanomaterials such as ions, nanoparticles, carbon-based materials, and proteins, metal ions (e.g., Cu²⁺) exhibit promising electrical, optical, and magnetic characteristics, which can be helpful in enhancing the DNA characteristics. Although thin films of metal-doped and lanthanide-ion-doped DNA duplexes have been fabricated, hybrid fibers of CDNA metallized with ions synthesized in a large-scale production in a powder form have been rarely discussed. Metal (e.g., Ag, Au, and Pd)-coated DNA nanowires fabricated by chemically derivatized and seeding growth methods were reported; however, the DNA metallization method was complex and the mass production of samples with a high quality was quite limited.

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fibers metallized with Cu$^{2+}$ are formed as core (CDNA)–shell (Cu$^{2+}$) structures by self-metallization, which can easily alter the electrical, optical, and magnetic characteristics of the samples.

In this study, we developed a novel simple methodology to synthesize CDNA fibers metallized with Cu$^{2+}$. The simple fabrication methodology is advantageous for the mass production of Cu$^{2+}$-coated CDNA hybrid fibers by ion-exchange and self-metallization processes. The synthesized Cu$^{2+}$-coated CDNA fibers were characterized by X-ray diffraction (XRD), high-resolution field-emission transmission electron microscopy (FETEM), and energy-dispersive X-ray spectroscopy (EDS) to analyze their crystal structures and chemical compositions with elemental mapping. In addition, ultraviolet (UV)–vis spectroscopy, Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and thermal analysis were carried out to evaluate the absorption characteristics, chemical interactions, spin states and chemical bondings, magnetic properties, and thermal properties of the Cu$^{2+}$-coated CDNA fibers, respectively.

2. EXPERIMENTAL METHODS

First, 3 g of DNA obtained by an enzyme isolation process (Marine Salmon P/No. DPO 1405787, GEM Corporation, Shiga, Japan) is dissolved in 1000 mL of deionized (DI) water followed by magnetic stirring (1000 rpm for 24 h at room temperature). Subsequently, 6 mL of cetyltrimethylammonium-chloride (Sigma-Aldrich, Seoul, Korea) is diluted in 1000 mL of DI water in another beaker followed by magnetic stirring. The diluted cetyltrimethylammonium-chloride solution is then slowly added into the DNA solution while stirring to achieve a homogeneous mixture of DNA and cetyltrimethylammonium-chloride. This process enables the attachment of the CTMA surfactant onto the surface of the DNA phosphate backbone through ion exchange, yielding a white precipitate of cetyltrimethylammonium-chloride. This process is further stirred for 5 h followed by filtering and washing with excess amount of DI water to remove the residues of cetyltrimethylammonium chloride and NaCl. Finally, white CDNA fibers are obtained by drying for 2 days at a temperature of 40 °C.

For the CDNA solution, 0.5 g of CDNA fibers is dissolved in 50 mL of methanol, followed by magnetic stirring at 1000 rpm for 24 h at room temperature to obtain the final solution with 1 wt % of CDNA. To prepare a copper-ion (Cu$^{2+}$) solution (1 M), an appropriate quantity of copper nitrate [Cu(NO$_3$)$_2$] powder (Sigma Aldrich, Seoul, Korea) is dissolved in methanol by vortexing. For the Cu$^{2+}$-coated CDNA (denoted as Cu-CDNA), proper amounts of Cu$^{2+}$ solution (0, 5, 7, 10, 12, and 15 mM) are slowly added dropwise into the DNA solution while stirring. Consequently, the Cu$^{2+}$ ions are attached onto the surface of the DNA phosphate backbone through self-metallization. The solution containing the fibers is further stirred for 3 h, followed by incubation at 50 °C for 2 days for drying, yielding the Cu-CDNA fibers.

A high-power powder XRD (D8 Advance, Bruker, MA) is used to analyze the structural characteristics of the Cu-CDNA fibers. High-resolution FETEM (JEM-2100F, JEOL, Tokyo, Japan) operated at 200 kV is used for imaging and selected-area electron diffraction (SAED) of the Cu-CDNA fibers. The state-of-the-art EDS (Oxford Instruments 80 TLE detector system, Abingdon, U.K.) equipped with the FETEM enabled an efficient and fast elemental mapping of the Cu-CDNA fibers at the nanoscale. A UV–vis–near-infrared spectrophotometer (V-670, JASCO, Tokyo, Japan) is employed to analyze the optical absorption of the Cu-CDNA fibers in the wavelength range of 200–900 nm. A FTIR spectrometer (TENSOR 27, Detector: MIR-ATR (ZnSe), Bruker Inc., MA) is employed to analyze the chemical interactions between Cu$^{2+}$ and CDNA fibers in the wavenumber range of 600–3700 cm$^{-1}$. XPS (ESCALAB 250Xi, Thermo Scientific, Winsted, U.K.) is used to analyze the spin state, composition, and charge transfer associated with the binding energy of the Cu-CDNA fibers. The XPS spectrum is acquired using an Al K$_\alpha$ X-ray source in the binding energy range up to 1350 eV.

VSM (PPMS-9, Quantum Design, CA) is used to analyze the magnetic characteristics, i.e., the magnetic field (H)-dependent magnetization (M) and temperature (T)-dependent M of the Cu-CDNA fibers. Thermal analyses (TG/DTA7300 Seiko Instruments, Chiba, Japan) including a thermogravimetric analysis (TGA), differential thermogravimetry (DTG), and differential thermal analysis (DTA) are carried out to characterize the thermal properties of the Cu-CDNA fibers.

3. RESULTS AND DISCUSSION

Schematics and photographs of the DNA fibers, CDNA fibers prepared through the ion-exchange process, and Cu$^{2+}$-coated CDNA fibers prepared through self-metallization are shown in Figure 1. During the self-metallization, the positively charged Cu$^{2+}$ ions were coordinated on the DNA phosphate backbone group through the electrostatic interaction followed by formation of a polycrystalline structure. Finally, CDNA fibers metallized with Cu$^{2+}$ were formed as core–shell structures. The synthesis of the CDNA fibers metallized with Cu$^{2+}$ was explained in detail in experimental methods.

XRD was carried out to analyze the characteristic crystal structure of the Cu$^{2+}$-coated CDNA fibers (Figure 2a). The diffraction pattern of the pristine CDNA fibers showed a broad peak at 2θ of 20°. The characteristic diffraction peaks of the Cu$^{2+}$-coated CDNA fibers at 2θ of 16.5, 19.4, 20.6, 21.8, 22.7, 23.8, 24.9, and 25.6° corresponded to the (021), (221), (201), (220), (130), (222), (022), (112), and (221) planes, respectively, which mostly matched with those of the triclinic copper phosphate (Joint Committee on Powder Diffraction Standards (JCPDS) card no. 52–1346). The triclinic phase of copper phosphate was an indirect evidence of the Cu$^{2+}$ binding on the DNA phosphate backbone. The diffraction peak intensity

Figure 1. Schematics and photographs of (a) DNA fibers, (b) CDNA fibers obtained through the ion-exchange process, and (c) Cu$^{2+}$-coated CDNA fibers obtained through self-metallization.

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increased with [Cu$^{2+}$] on CDNA owing to the increased relative amount of Cu$^{2+}$ on the CDNA fiber.

Figure 2b–d shows the typical high-resolution FETEM images and SAED pattern of the Cu$^{2+}$-coated CDNA fibers having 10 mM of Cu$^{2+}$ (denoted as Cu (10)-CDNA) to verify the crystalline structure of the sample. Relatively thinner and thicker CDNA bundles coated with Cu$^{2+}$ (inset) are observed in Figure 2b. The magnified FETEM image shows the highly crystalline structure of the sample with an interplanar lattice spacing of 0.39 nm, which corresponds to the (222) planes of copper phosphate in the Cu$^{2+}$-coated CDNA fibers. The copper phosphate was well-crystallized on the Cu$^{2+}$-coated CDNA fibers, which provides a direct evidence of the Cu$^{2+}$ binding on CDNA. The SAED pattern reveals the crystalline structure of the sample (Figure 2d). The inset in Figure 2d shows the typical high-resolution FETEM images and SAED pattern of the Cu$^{2+}$-coated CDNA fibers having 10 and 15 mM, denoted as Cu (10)-CDNA and Cu (15)-CDNA, respectively). (b) High resolution FETEM image of Cu (10)-CDNA. The inset shows an image with a different scan size. (c) High-magnification FETEM image of the Cu$^{2+}$-coated CDNA fiber. (d) SAED pattern revealing the crystalline structure of the sample. (e) ED spectrum and EDS layered electron image (inset) of the Cu$^{2+}$-coated CDNA fiber. (f–j) Corresponding elemental maps of negative ions (O, P, and N) and positive ions (C and Cu) on the Cu$^{2+}$-coated CDNA fibers.

To analyze the distributions of the elements, EDS elemental mapping was performed (Figure 2f–j). In the elemental maps, O, P, N, C, and Cu elements in the Cu$^{2+}$-coated CDNA fibers are presented in yellow, pink, blue, green, and red, respectively, which demonstrate the uniform distributions of the elements throughout the Cu$^{2+}$-coated CDNA fiber.

The characteristic absorption peaks of the pristine CDNA were in the UV region attributed to the electronic transitions between occupied and unoccupied molecular orbitals.$^{20-22}$ Upon the addition of Cu$^{2+}$, the characteristic absorption peak of Cu$^{2+}$ in the Cu$^{2+}$-coated CDNA fibers was observed at around 730 nm. The Cu$^{2+}$ characteristic peak intensity increased and the peak shifted toward larger wavelengths upon the increase in [Cu$^{2+}$], which might be attributed to the d–d electronic transition and surface plasmon resonance generated by Cu$^{2+}$ in the sample.$^{23}$ To understand the interaction between CDNA and Cu$^{2+}$, UV–vis absorption spectra of the Cu$^{2+}$-coated CDNA powders with various [Cu$^{2+}$] were acquired (Figure 3a). The characteristic absorption peaks of the pristine CDNA were in the UV region attributed to the electronic transitions between occupied and unoccupied molecular orbitals.$^{20-22}$ Upon the addition of Cu$^{2+}$, the characteristic absorption peak of Cu$^{2+}$ in the Cu$^{2+}$-coated CDNA fibers was observed at around 730 nm. The Cu$^{2+}$ characteristic peak intensity increased and the peak shifted toward larger wavelengths upon the increase in [Cu$^{2+}$], which might be attributed to the d–d electronic transition and surface plasmon resonance generated by Cu$^{2+}$ in the sample.$^{23}$ To understand the interaction between CDNA and Cu$^{2+}$, UV–vis absorption spectra of the Cu$^{2+}$-coated CDNA powders with various [Cu$^{2+}$] were acquired (Figure 3a). The characteristic absorption peaks of the pristine CDNA were in the UV region attributed to the electronic transitions between occupied and unoccupied molecular orbitals.$^{20-22}$ Upon the addition of Cu$^{2+}$, the characteristic absorption peak of Cu$^{2+}$ in the Cu$^{2+}$-coated CDNA fibers was observed at around 730 nm. The Cu$^{2+}$ characteristic peak intensity increased and the peak shifted toward larger wavelengths upon the increase in [Cu$^{2+}$], which might be attributed to the d–d electronic transition and surface plasmon resonance generated by Cu$^{2+}$ in the sample.$^{23}$ To understand the interaction between CDNA and Cu$^{2+}$, UV–vis absorption spectra of the Cu$^{2+}$-coated CDNA powders with various [Cu$^{2+}$] were acquired (Figure 3a). The characteristic absorption peaks of the pristine CDNA were in the UV region attributed to the electronic transitions between occupied and unoccupied molecular orbitals.$^{20-22}$ Upon the addition of Cu$^{2+}$, the characteristic absorption peak of Cu$^{2+}$ in the Cu$^{2+}$-coated CDNA fibers was observed at around 730 nm. The Cu$^{2+}$ characteristic peak intensity increased and the peak shifted toward larger wavelengths upon the increase in [Cu$^{2+}$], which might be attributed to the d–d electronic transition and surface plasmon resonance generated by Cu$^{2+}$ in the sample.$^{23}$
Figure 3 shows the intensity variation of the Cu$^{2+}$ characteristic peak as a function of [Cu$^{2+}$] in the sample. The Cu$^{2+}$ absorption peak position exhibited a red-shift from 732 to 792 nm with the increase in [Cu$^{2+}$] from 5 to 15 mM. Similarly, with the increase in [Cu$^{2+}$] from 0 to 15 mM, the band edge attributed to the shift in the CDNA from 384 to 539 nm. This implies that the optical band gap of the Cu$^{2+}$-coated CDNA fibers decreased upon the addition of Cu$^{2+}$ by a factor up to ~1.4.

The FTIR spectra of the CDNA fibers coated with Cu$^{2+}$ were measured to demonstrate the characteristic peaks of CDNA and Cu$^{2+}$. (Figure 3c). The characteristic absorbance bands of the CDNA fibers in the spectral range of 600–3700 cm$^{-1}$ can be categorized into four regions.24–25 Region 1 (700–1350 cm$^{-1}$) involves the sugar puckering mode, phosphodiester backbone, and deoxyribose. Region 2 (1350–1750 cm$^{-1}$) consisted of bands sensitive to the base pairing and stacking interaction. Region 3 (2850–2950 cm$^{-1}$) included the water stretching modes of CH$_2$ owing to the modification of DNA with cetyltrimethylammonium chloride. Region 4 (3100–3500 cm$^{-1}$) included the water molecular vibrations. It is worth noting that the characteristic FTIR absorbance peak of Cu$^{2+}$ at ~1335 cm$^{-1}$ was observed in the spectra of Cu$^{2+}$-coated CDNA fibers. This peak corresponded to Cu–O–P; its intensity was proportional to Cu$^{2+}$.

To evaluate the influences of CDNA and Cu$^{2+}$ in the Cu$^{2+}$-coated CDNA fibers at specific wavenumbers, we analyzed the FTIR characteristic peaks of deoxyribose in CDNA and Cu$^{2+}$ at 1060 and 1335 cm$^{-1}$, respectively. Figure 3d shows the variations in the peak intensities as a function of [Cu$^{2+}$] at the fixed wavenumbers of 1060 and 1335 cm$^{-1}$, associated with the C–O deoxyribose stretching mode and Cu–O–P, respectively. The absorbance peak intensity at 1060 cm$^{-1}$ gradually decreased with the increase in [Cu$^{2+}$] owing to the reduction in the relative amount of CDNA upon the addition of Cu$^{2+}$. In contrast, the peak intensity of the Cu$^{2+}$-coated CDNA fibers at 1335 cm$^{-1}$ increased with [Cu$^{2+}$] owing to the electrostatic interaction between the phosphate backbone in CDNA and Cu$^{2+}$.

We carried out XPS to analyze the chemical compositions and oxidation states by the photon energy, which was used to probe the chemical binding energies of the samples. The XPS spectra of the Cu$^{2+}$-coated CDNA fibers with 7 and 15 mM of Cu$^{2+}$ are shown in Figure 4. The overview XPS survey spectra showed the elemental characteristic peaks of C, O, N, P, and Cu. They were consistent with the EDS data, which confirmed the existence of the core elements in the Cu$^{2+}$-coated CDNA fibers. The peaks at binding energies of 284.8, 531.8, 406.2, 133.4, and 934.7 eV were attributed to the C 1s, O 1s, N 1s, P 2p, and Cu 2p orbitals, respectively, which confirmed the anchoring of Cu$^{2+}$ on the CDNA fibers.26–29 Figure 4b shows the changes in atomic weight, full width at half-maximum (FWHM) values, and the binding energy shifts of the core elements in the Cu$^{2+}$-coated CDNA fibers with varying [Cu$^{2+}$]. The concentration of C was higher at a lower [Cu$^{2+}$] coated on the CDNA fibers, while the concentrations of O, N, P, and Cu increased with [Cu$^{2+}$] on the CDNA fibers. However, the changes in the FWHM values of the C and N elements were negligible, while significant changes in the FWHM values of the O and P elements were observed. These results suggested the Cu$^{2+}$ coating onto the phosphate backbone in CDNA through self-metallization. The small changes in the binding energies of the core elements between Cu (15)-CDNA and Cu (7)-CDNA (Figure 4d) were attributed to the charge transfer between CDNA and Cu$^{2+}$.

High-resolution XPS spectra with deconvoluted curves of C 1s, O 1s, N 1s, P 2p, and Cu 2p for the Cu$^{2+}$-coated CDNA...
hybrid fibers are shown in Figure 4e–i, respectively. The deconvolution of the C 1s peak in the XPS spectrum showed two types of carbon bonds, C–C/C–H (at 284.8 eV) and C–O/C–N (at 286 eV). The deconvolution of the O 1s peak showed one type of oxygen bond (C=O/P=O (531.9 eV)) for Cu (7)-CDNA and two types of oxygen bond (C=O/P/C–C/C (531.9 eV) and C=C–P/C–C–C (533.1 eV)) for Cu (15)-CDNA. The N 1s peak after the deconvolution corresponded to three types of nitrogen bonds (C=NH2/C=N–C/N=N–C (399.5 eV), N=C (402.3 eV), and N–H (406.2)). The P 2p peak after the deconvolution corresponded to one type of phosphorus bond (P 2p1/2 (133.5 eV)) for Cu (7)-CDNA and two types of phosphorus bonds (P 2p3/2 (133.2 eV) and P=O (134.1 eV)) for Cu (15)-CDNA. The high-resolution Cu 2p XPS spectra of both Cu (7)-CDNA and Cu (15)-CDNA included peaks around 935.1 and 954.4 eV, which corresponded to Cu 2p1/2 and Cu 2p3/2 respectively. These results confirmed the presence of Cu2+ on CDNA in the Cu2+-coated CDNA fibers. Additionally, for Cu (15)-CDNA, shake-up satellite peaks of Cu 2p at 941.6, 944.9, and 951.6 eV were observed. The satellite peaks at a higher [Cu2+] are well-known characteristics of Cu 2p.

Remarkable changes in the O 1s and P 2p XPS spectrum peaks with [Cu2+] were observed, which revealed the additional deconvoluted peaks of Cu (15)-CDNA compared to Cu (7)-CDNA. The blue shift of the binding energies of O 1s and P 2p for the Cu2+-coated CDNA fibers (compared to the pristine CDNA) indirectly confirmed the formation of O···Cu and Cu–O–P bonds (oxygen-containing molecules prefer to coordinate metal ions). These results suggested that the Cu2+ ions interacted with CDNA as the phosphate backbone in CDNA contained O=P.30

The magnetic characteristics of the Cu2+-coated CDNA hybrid fibers, including the magnetization (M) and susceptibility (χ), were analyzed using VSM (Figures 5 and 6). The M values of the Cu2+-coated CDNA fibers with varied [Cu2+] as a

Figure 4. Overview XP spectra, high-resolution XP spectra, and results of the compositional and fitting analyses of the Cu2+-coated CDNA hybrid fibers. (a) Overview XP spectra of the Cu2+-coated CDNA fibers as a function of the binding energy. (b–d) Variations in atomic weight, full width at half-maximum (FWHM) values, and binding energy shifts of the core elements in the Cu2+-coated CDNA fibers with varying [Cu2+]. (e–i) High-resolution XP spectra with fitting curves of C 1s, O 1s, N 1s, P 2p, and Cu 2p in the Cu2+-coated CDNA fibers. The gray lines in (e–h) represent the core elements in the pristine CDNA.
function of applied magnetic field \((H)\) in the range of \(-20\) to \(+20\) kOe were recorded at 300 K (Figure 5a). The pristine CDNA fibers exhibited the inherent diamagnetic characteristic reflected in the ratio of \(M\) and \(H\) (i.e., \(\chi = M/H\)) in the \(M-H\) curve (which shows a negative slope \((-\chi)\)). In contrast, the CDNA fibers with Cu\(^{2+}\) exhibited an increased \(M\) corresponding to a ferromagnetic behavior with smaller coercive field \((H_c)\) and remanent magnetization \((M_r)\). The Cu\(^{2+}\)-coated CDNA fibers showed a positive slope \((\chi)\) due to the ferromagnetic interaction between the paramagnetic Cu\(^{2+}\) ions and the diamagnetic CDNA fibers.
fibers exhibited the saturation magnetization ($M_s$) up to 10 mM of Cu$^{2+}$, owing to the spin alignment of Cu$^{2+}$ in CDNA at a relatively high applied $H$. Above 10 mM of Cu$^{2+}$, the Cu$^{2+}$-coated CDNA fibers did not exhibit $M_s$ even at a higher applied $H$ owing to the excess Cu$^{2+}$ at a given [CDNA], which led to noncollinear spin alignment and canted spins of Cu$^{2+}$. The inset in Figure 5a shows the average $\chi$ of the Cu$^{2+}$-coated CDNA fibers as a function of [Cu$^{2+}$], which revealed the negative and positive $\chi$ values of the pristine CDNA and Cu$^{2+}$-coated CDNA fibers, respectively. Figure 5b,c shows the $M$ vs $H$ curves of the pristine CDNA and Cu$^{2+}$-coated CDNA fibers, respectively, with 15 mM of Cu$^{2+}$ (Cu (15)-CDNA) measured at three different temperatures ($T$) of 5, 100, and 300 K. The pristine CDNA fibers at 100 and 5 K exhibited diamagnetic and ferromagnetic behaviors, respectively, whereas Cu (15)-CDNA at 100 and 5 K exhibited a strong ferromagnetism. $M$ of Cu (15)-CDNA (pristine CDNA) was increased from 0.02 to 1.5 emu/g (from $\sim$0.01 to 0.04 emu/g) at a fixed applied $H$ of 20 kOe upon the decrease in $T$ from 300 to 5 K. At 5 K, the spins were easily aligned by the external applied $H$, leading to a higher $M$ than that at the high $T$. Figure 5d–f shows the $\chi$ values of the Cu$^{2+}$-coated CDNA fibers with various [Cu$^{2+}$] as a function of applied $H$ at 300 K and changes in $\chi$ of the CDNA fibers without and with 15 mM Cu$^{2+}$ measured at 5, 100, and 300 K. $\chi$ gradually decreased with the increase in the applied $H$ and increased with the decrease in $T$. The change in $\chi$ between the pristine CDNA and Cu$^{2+}$-coated CDNA fibers was significant owing to the presence of Cu$^{2+}$, which strongly influenced $M$ of the sample through the applied $H$. The values of $\chi$ (negative) for the diamagnetic behavior of the pristine CDNA and for either para- or ferromagnetic behavior of the Cu$^{2+}$-coated CDNA fibers) provided valuable information on the magnetic characteristics of the samples. Owing to the ferromagnetic characteristic and feasibility for mass production, the Cu$^{2+}$-coated CDNA fibers could be used in memory devices and flexible magnets.

In addition, we studied the $T$-dependent magnetic characteristics ($M$, $\chi$, and $\chi'$) of the Cu$^{2+}$-coated CDNA fibers at a constant applied $H$ of 1000 Oe and used them to estimate the Curie temperature ($T_c$) (Figure 6). The $M$ values of the Cu$^{2+}$-coated CDNA fibers with [Cu$^{2+}$] of 0, 5, 10, and 15 mM measured in the $T$ range of 2–300 K are shown in Figure 6a. For the CDNA fibers with Cu$^{2+}$, we observed a significant increase in $M$ particularly at a low $T$ ($\leq 30$ K). We observed nonzero $M$ of the Cu$^{2+}$-coated CDNA fibers up to 300 K, which suggested that no magnetic transition occurred in the measured $T$ range. This implies that $T_c$ of the Cu$^{2+}$-coated CDNA fibers was above 300 K. For practical application, ferromagnetic materials having $T_c$ higher than 300 K (e.g., Cu$^{2+}$-coated CDNA fibers) are useful to prevent thermal damage.

Figure 6b–d shows the $\chi$ vs $T$ and $\chi'$ vs $T$ curves of the Cu$^{2+}$-coated CDNA fibers with various [Cu$^{2+}$]. Although the $M$ vs $H$ curve of the pristine CDNA fibers reveals a negative $\chi$, which indicates a diamagnetic behavior of the sample (Figure 5a), the nonzero $M$ with a positive $\chi$ for the pristine CDNA fibers suggested a weak ferromagnetism at a low applied $H$ of 1000 Oe (inset in Figure 6a). The [Cu$^{2+}$]-dependent $\chi$ of the Cu$^{2+}$-coated CDNA fibers exhibited a gradual increase with [Cu$^{2+}$] in CDNA. The values of $\chi'$ were used to differentiate the magnetic structure. For the paramagnetic structure, the slope ($\Delta \chi'/\Delta T$) was roughly constant in the entire $T$ range, while for the ferromagnetic structure, the slope was significant at a low $T$. Consequently, the Cu$^{2+}$-coated CDNA fibers were ferromagnetic as a large slope change was observed at a low $T$ compared to that at a high $T$.

The thermal stabilities of the pristine CDNA and Cu (15)-CDNA fibers were analyzed by a TGA through the weight loss and DTG and DTA through heat flow. The $T$-dependent weights ($W$), derivative weights ($-\Delta W/\Delta T$), and heat flows of the fibers at a heating rate of 10 $^\circ$C/min in the range of 30–600 $^\circ$C under nitrogen atmosphere are shown in Figure 7. The weights slowly decreased with the increase in $T$ up to 220 $^\circ$C; weight losses ($-\Delta W$) of 11% for the pristine CDNA and 19% for the Cu (15)-CDNA fibers were observed at 220 $^\circ$C. These weight losses were attributed to the volatilization of water molecules from the DNA. In the $T$ range of 220–325 $^\circ$C, the weights of the pristine CDNA and Cu (15)-CDNA fibers rapidly decreased to 35 and 38%, respectively (at 325 $^\circ$C) owing to the degradation of the DNA backbone. Finally, the weights reached 24% for the pristine CDNA and 28% for the Cu (15)-CDNA fibers at the relatively high $T$ of 600 $^\circ$C owing to the decomposition of molecules. Owing to the Cu$^{2+}$ coating around CDNA, a smaller weight loss than that of the pristine CDNA was observed at a high $T$. Figure 7b shows the DTG curves obtained using the slope ($-\Delta W/\Delta T$) in the TG curve during the heating of the samples. Significant peaks are observed around 265 $^\circ$C for both pristine CDNA and Cu (15)-CDNA fibers. This indicated that the weight was severely influenced up to a certain critical $T$ (i.e., 265 $^\circ$C).
The flow of the samples as a function of T (DTA curve) exhibited local minima and local maxima related to the endothermic (absorbed heat) and exothermic (released heat) reactions (Figure 7c), respectively. We observed endothermic peaks at 207, 260, and 308 °C and exothermic peaks at 225 and 290 °C for the pristine CDNA fibers. Similarly, the Cu (15)-CDNA fibers exhibited endothermic peaks at 95, 193, and 278 °C and exothermic peaks at 181 and 215 °C. Considerable endothermic and exothermic peaks of the Cu (15)-CDNA fibers were observed owing to the interaction between Cu2+ and CDNA fibers, which helps prevent thermal damage up to a certain T; hence, the thermal stability is increased with the Cu2+ coating.

4. CONCLUSIONS

Ferromagnetic Cu2+-coated CDNA hybrid fibers were synthesized by ion-exchange and self-metallization processes. The fibers exhibited a polycrystalline triclinic crystal structure of copper phosphate, uniform distribution of elements, surface plasmon resonance effect in the visible region, preferential interaction of Cu2+ with DNA, O−Cu and Cu−O−P bonds confirmed by the blue shifts of O 1s and P 2p, ferromagnetism even at room temperature, and thermally stable characteristics. The core–shell structure of the Cu2+-coated CDNA fibers with enhanced structural, optical, magnetic, and thermal properties is feasible for use in various applications such as flexible magnets, memory storage, electromagnetic shielding, and optoelectronics in the future.

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Notes
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ABBREVIATIONS
DNA, deoxyribonucleic acid; CDNA, cetyltrimethylammonium chloride modified DNA; XRD, X-ray diffraction; FETEM, field emission transmission electron microscope; EDS, energy-dispersive X-ray spectroscopy; UV, ultraviolet; FTIR, Fourier transform infrared; XPS, X-ray photoelectron spectroscopy; VSM, vibrating-sample magnetometry; Cu(NO3)2, copper nitrate; Cu-CDNA, Cu2+-coated CDNA; SAED, selected-area electron diffraction; H, magnetic field; M, magnetization; T, temperature; TGA, thermogravimetric analysis; DTA, derivative thermogravimetry; DTA, differential thermal analysis; JCPSD, Joint Committee on Powder Diffraction Standards; FWHM, full width at half-maximum; χ, susceptibility; Hc, coercive field; Ms, saturation magnetization; Tc, Curie temperature; W, weight

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