Polymer Journal (2014) 46, 366–371

www.nature.com/pj

ORIGINAL ARTICLE

Selective accumulation of rare earth metal and heavy metal ions by a DNA-inorganic hybrid material

Masanori Yamada and Kazuhide Abe

A DNA-inorganic hybrid film (DNA film) was prepared by mixing DNA and a silane coupling reagent, bis(trimethoxysilylpropyl) amine. This DNA film can accumulate heavy metal ions in aqueous solution. We have demonstrated the accumulation of rare earth metal and heavy metal ions using DNA-inorganic hybrid-immobilized glass beads (DNA beads), which were prepared by coating the DNA-inorganic hybrid onto glass beads. When these DNA beads were placed in an aqueous solution of metal ions and incubated for 24 h (batch method), the DNA beads selectively accumulated heavy metal and rare earth metal ions. The maximum-accumulated amounts of Cu^{2+}, Cd^{2+}, In^{3+} and La^{3+} were $\sim$1.2, 0.94, 1.6 and 1.3 μmol, respectively, for 1 mg of DNA (3.0 μmol of nucleotide). The molar ratio of DNA to a metal ion was nucleotide:metal ion = 1:0.5. Finally, we demonstrated the accumulation of metal ions by a DNA-bead column (DNA column). As a result, the DNA column effectively accumulated the heavy metal and rare earth metal ions. The DNA column was recycled by washing with an EDTA solution.
Polymer Journal (2014) **46,** 366–371; doi:10.1038/pj.2014.5; published online 19 March 2014

Keywords: DNA; heavy metal; organic–inorganic hybrid material; rare earth metal; silane coupling reagent

INTRODUCTION

Rare earth metal ions, such as indium and yttrium ions, have been used in electronic, magnetic and semiconductive materials. These rare earth ions are essential for electric appliances, catalysts used in synthetic chemistry and fluorescent substances. However, there are limited terrestrial resources and production facilities for these rare earth metal ions.[1,2] These metals are also difficult to purify and expensive.[2] Thus, the production of these rare earth metal ions has resulted in trade friction and economic issues worldwide. Therefore, technologies for accumulating rare earth metal ions from industrial waste and groundwater have become attractive.[3] Bioadsorptions,[4–6] polymer materials[7–9] and inorganic materials[3] have been used in these technologies for metal accumulation.

Double-stranded DNA, one of the most important materials in genetic processes, can be readily purified from salmon milts or shellfish gonads. Double-stranded DNA also performs highly specific functions, such as intercalation, groove binding, complementary interactions between nucleic acid bases and specific interactions with metal ions.[10–14] Therefore, DNA has become a focal point as a novel functional material[15–17] that can be used in electrical,[18] optical,[19] medical[20] and nano-patterning[21] materials and fibers,[22] for example. Recently, we prepared a water-insoluble DNA material by UV irradiation for use as an environmental material, such as for the removal of harmful organic compounds with planar structures, that is, dioxin and polychlorinated biphenyl derivatives[23,24] and to accumulate heavy metal ions.[25] However, these UV-irradiated DNA materials were gels that were produced by cross-linking reactions and did not possess any mechanical strength; therefore, these materials could not be used for a long time under aqueous conditions. The amount of immobilized double-stranded DNA was too low for use under practical and engineering conditions. Therefore, we recently prepared a DNA-inorganic hybrid film (DNA film)[26] and DNA-inorganic hybrid immobilized glass beads (DNA beads)[27] by mixing DNA and a silane coupling reagent, bis(trimethoxysilylpropyl)amine (SiNSi). These hybrid materials exhibit the flexibility of an organic material as well as the strength of an inorganic material. The mechanical strength of a DNA film is twice that of an UV-irradiated DNA film. The DNA in the DNA-inorganic hybrid material also maintains a B-form structure in an aqueous solution. The DNA-inorganic hybrid material can also selectively accumulate harmful compounds with planar structures, such as dioxin and polychlorinated biphenyl derivatives, that can intercalate into the double-stranded DNA.[27] However, there are no reports on using DNA-inorganic hybrid materials to absorb metal ions such as rare earth metal and heavy metal ions. A DNA-inorganic hybrid material that can accumulate rare earth metal and heavy metal ions could be used for environmental applications such as the removal of heavy metal ions from industrial waste or of rare earth metal ions from groundwater.

In this study, we demonstrated the accumulation of heavy metal and rare earth metal ions using DNA beads. The DNA beads selectively accumulated heavy metal and rare earth metal ions from

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Received 17 September 2013; revised 14 January 2014; accepted 15 January 2014; published online 19 March 2014

an aqueous solution of metal ions. A DNA-immobilized glass bead column (DNA column) was also used to effectively accumulate heavy metal and rare earth metal ions. The DNA column was recycled by washing with an EDTA solution.

EXPERIMENTAL PROCEDURE

Materials

Double-stranded DNA (sodium salt from a salmon milt, molecular weight $>5\times10^6$) was obtained from Biochem Ltd., Kawagoe, Japan. The silane coupling reagent, SiNSi, was purchased from Tokyo Kasei Industries Ltd., Tokyo, Japan. The molecular structure of SiNSi is shown in Scheme 1. Glass beads were purchased from As One Corp., Osaka, Japan. The diameters of the glass beads ranged from 0.50 to 0.71 mm. Copper(II) chloride, zinc(II) chloride, cadmium(II) chloride, cobalt(II) chloride, calcium chloride, magnesium chloride, yttrium(III) chloride, lanthanum(III) chloride, indium(III) chloride, scandium(III) chloride, xylenol orange, methylthymol blue, 4-(2-pyridylazo)resorcinol and ethylenediamine-*N*, *N*, *N′*, *N′*-tetraacetic acid disodium salt dehydrate (EDTA) were obtained from Wako Pure Chemical Industries Ltd., Osaka, Japan, or Dojindo Co., Kumamoto, Japan. Analytical grade solvents were used in all of the experiments described. Ultra-pure water (Millipore Corporation, Billerica, MA, USA) was used in this study.

Preparation of DNA beads

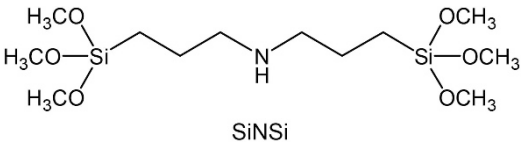
The hydrophilic glass beads were treated using the following procedure:[25] glass beads (500 mg) were heated in 2 ml of 30% H_2O_2 and concentrated sulfuric acid (30:70, v/v) at 90 °C for 30 min.[28] The glass beads were rinsed with distilled water (5 ml × 10 times) and dried overnight at room temperature (RT).

An aqueous double-stranded DNA solution (500 µl, 10 mg ml^{-1}) and a silane coupling reagent SiNSi (1.3 µl) were vigorously mixed in a microtube. The treated glass beads (500 mg) were added to the DNA-SiNSi mixed solution, which was vigorously mixed using a touch mixer for ~30 s and then dried on petri dishes at RT overnight. The glass beads were rinsed with distilled water (10 ml × five times) to remove the water-soluble component. The amount of immobilized DNA was determined using the following procedure:[24] the DNA-immobilized glass beads (100 mg) were hydrolyzed by 1 M hydrochloric acid (5 ml) at 100 °C for 1 h, after which the amount of DNA in the aqueous solution was determined from the absorbance at 260 nm.

The DNA films were treated using the following procedure:[26] the DNA aqueous solution (100 µl, 10 mg/ml) and SiNSi (0.3 µl) were vigorously mixed in a microtube. This solution mixture was applied onto Teflon plates and dried overnight at RT. The DNA films were then stripped from the plates and stored in water.

Accumulation of metal ions by DNA beads

Batch methods were used to demonstrate the accumulation of metal ions by the DNA beads. Copper(II) chloride, zinc(II) chloride, cadmium(II) chloride, calcium chloride, magnesium chloride, yttrium(III) chloride, lanthanum(III) chloride, indium(III) chloride and scandium(III) chloride were dissolved in pure water. The DNA beads (100 mg) were incubated in an aqueous solution of metal ions for 24 h at RT. The DNA beads were then separated from the aqueous solutions. The amount of accumulated metal ions was determined from the absorption spectra of the aqueous solutions in the absence or presence of the DNA beads. The concentration of the aqueous metal ions was estimated from the calibration curve with the metal indicator. The conditions under which the calibration curve was generated are shown in Table 1.



SiNSi

Scheme 1 Chemical structure of SiNSi.

Accumulation of metal ions by DNA column

The following procedure was used to prepare the DNA column. The DNA beads (100 mg) and hydrophilic glass beads (1.4 g) without immobilized DNA were mixed. The mixed glass beads (1.5 g) were packed into a Pasteur pipette (ϕ: 5 mm; Iwaki Glass Co. Ltd., Tokyo, Japan). The mobile phase in the DNA column was ~30 mm long. The flow rate in the DNA column was 1 ml min^{-1}. This DNA column was washed with water (~100 ml) before being used in the experiments.

The accumulation of metal ions by a DNA column was examined using the following procedure. An aqueous solution of the metal ions, Cu^{2+}, Cd^{2+}, Y^{3+} or In^{3+}, was applied to the column of DNA-immobilized glass beads: the eluted solution was then re-applied to the column. In this method, the metal ion concentration was 5 p.p.m. Thus, the metal ion concentration in our experiment was slightly higher than that required by the waste water regulations. The molar concentrations of Cu^{2+}, Cd^{2+}, Y^{3+} and In^{3+} were 0.079, 0.044, 0.056 and 0.044 mM, respectively. This process was repeated 10 times for a total procedural time of 1.5 h. The accumulated amount of metal ions was determined from the absorption spectra of the eluted solution and the starting solution.

The procedure for the re-use of the DNA column with accumulated metal ions was as follows: the DNA column with accumulated metal ions was washed with an EDTA solution (100 mM, 10 ml). The washed DNA column was then rinsed with pure water (10 ml) to remove the EDTA solution. The solution of metal ions was then re-applied to the DNA column. This cycle was repeated five times.

IR measurements of DNA film with accumulated metal ions

A DNA-SiNSi hybrid film (DNA film) was prepared using methods reported in the literature.[26] The DNA film was immersed in 10 ml of aqueous solutions of copper(II) chloride, yttrium(III) chloride or magnesium chloride for 24 h at RT. The DNA film contained 880 µg of DNA. The Cu^{2+}, Y^{3+} and Mg^{2+} concentrations were 1.5, 1.1, 4.1 and 0.044 mM, respectively. The accumulated amount of metal ions was also determined from the calibration curve with the metal indicator. The DNA film with accumulated metal ions was rinsed with ultrapure water (10 ml × five times) to remove the metal ions that did not interact with the DNA film and dried overnight at RT on a Teflon plate. The infrared absorption spectra were measured by KBr methods using a FT-IR 8400 Fourier transform infrared spectrometer (Shimadzu Corp., Kyoto, Japan). The IR spectrum was measured at a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

Accumulation of metal ions by DNA films

Double-stranded DNA films were prepared by mixing DNA and SiNSi.[26] The DNA in these films is known to maintain a B-form structure in aqueous solution and the DNA film can accumulate intercalating reagents such as ethidium bromide.[26] In this study, we

Table 1 Conditions for generating the calibration curve

Metal ion	*pH*	*Buffer solution*[a]	*Indicator*	*Absorption wavelength (nm)*
Cu^{2+}	5.5	A	XO	571
Zn^{2+}	5.5	A	XO	570
Cd^{2+}	7.5	B	PAR	488
Al^{3+}	3.5	A	XO	551[b]
Ca^{2+}	11–12	C	MTB	608
Mg^{2+}	10.8	D	XO	572
Y^{3+}	5.5	A	XO	570
La^{3+}	5.5	A	XO	575
In^{3+}	5.5	A	XO	559
Sc^{3+}	2.6	E	XO	557

Abbreviations: MTB, methylthymol blue; PAR, 4-(2-pyridylazo)resorcinol; XO, xylenol orange
[a]A, 0.1 M CH_3COOH-CH_3COONa; B, 20 mM Tri-HCl; C, 0.1 M KOH; D, 0.1 M NH_3-NH_4Cl; E, 0.1 M $C_6H_4(COOK)(COOH)$-HCl.
[b]This solution was treated at 100 °C for 5 min.

demonstrated that these DNA films can accumulate heavy metal ions, such as copper and cadmium ions. The DNA films were dyed blue by incubation in a $CuCl_2$ solution. Figure 1 is a photograph of the DNA-inorganic hybrid material stained with Cu^{2+}. Generally, Cu^{2+} ions impart a blue color to water; thus, the materials that accumulated Cu^{2+} were dyed blue. In contrast, the DNA films were dyed red (data not shown) by incubation in a $CoCl_2$ solution. These phenomena suggested that the double-stranded DNA in the DNA-inorganic hybrid material could accumulate heavy metal ions such as Cu^{2+} and Co^{2+}. However, the DNA films were flexible and possessed low mechanical strength in aqueous solution; therefore, these DNA films could not be used to accumulate heavy metal ions under practical conditions. Therefore, we prepared DNA beads, that is, the glass beads served as a support for the DNA-hybrid materials to make the accumulation technique more effective.

Accumulation of metal ions by DNA beads

The double-stranded DNA beads were prepared by mixing double-stranded DNA, SiNSi and glass beads.[27] Because the DNA-inorganic hybrid material was hydrolyzed by 1 M HCl, the amount of DNA that was immobilized DNA on the glass beads was quantified by the absorbance at 260 nm. The amount of DNA on the glass beads was 4.9 mg g^{-1}. This immobilized DNA was stable in water, and no DNA release was observed over a long incubation time. A batch method was then used to investigate the accumulation of metal ions by the DNA beads.

The accumulation of metal ions was demonstrated by adding the DNA beads to an aqueous solution of metal ions (batch method). In this experiment, we used 100 mg of DNA beads (0.49 mg DNA; 1.5 μmol nucleotide). The amount of accumulated metal ions was determined from the absorption spectra of the aqueous solutions in the absence and presence of the DNA beads. The accumulated amount of metal ions increased with the incubation time and reached a constant value at 24 h (data not shown). Therefore, the accumulation by the batch method was estimated from the accumulated amount after 24 h incubation. Figure 2a shows the accumulation of Cu^{2+} by the DNA beads. The accumulated amount increased with the initial concentration and reached a constant value of ~0.6 μmol. We defined this constant value as the maximum amount of accumulated metal ions. A similar result was obtained for Cd^{2+} accumulation for which a maximum of ~0.45 μmol of ions was accumulated (see Figure 2b). These results suggested that the DNA beads could accumulate heavy metal ions such as Cu^{2+}, Cd^{2+} and Zn^{2+} (data not shown). We also demonstrated the accumulation of rare earth metal ions, that is, Y^{3+}, La^{3+}, In^{3+} and Sc^{3+}, by the DNA beads. Figures 3a and b show the accumulation of Y^{3+} and La^{3+}, respectively, by the DNA beads. The amount of accumulated ions increased with the initial concentration of the rare earth metal ions and reached a constant value. The amounts of accumulated Y^{3+} and La^{3+} were ~0.6 and 0.65 μmol, respectively. Similar results were obtained for the accumulation of In^{3+} and Sc^{3+} (data not shown). These results suggest that the DNA beads could accumulate both heavy metal and rare earth metal ions. However, the pure glass beads and the hydrophilic glass beads without immobilized DNA did not accumulate metal ions.

Next, we investigated the accumulation of metal ions, such as Mg^{2+} or Ca^{2}, in natural water. Figure 4 shows the accumulation of Mg^{2+} by the DNA beads. The amount of accumulated Mg^{2+} did not correlate with the initial concentration, that is, the DNA beads did not accumulate Mg^{2+}. A similar result was obtained for experiments on Ca^{2+} accumulation (data not shown). Figure 5 shows the maximum amounts of accumulation of various metal ions, such as Cu^{2+}, Zn^{2+}, Cd^{2+}, Ca^{2+}, Mg^{2+}, Y^{3+}, La^{3+}, In^{3+} and Sn^{3+}, by the DNA beads (1 mg DNA; 3.0 μmol nucleotide). Thus, the accumulated amounts for the heavy metal ions of Cu^{2+}, Zn^{2+} and Cd^{2+} were approximately 1.2, 1.4 and 0.94 μmol, respectively. The accumulated amounts for the rare earth metal ions of Y^{3+}, La^{3+}, In^{3+} and Sn^{3+} were approximately 1.2, 1.3, 1.6 and 0.47 μmol, respectively. In contrast, the DNA beads did not accumulate Mg^{2+} and Ca^{2+}. These results indicated that the DNA beads selectively accumulated the heavy metal and rare earth metal ions from the aqueous solution.

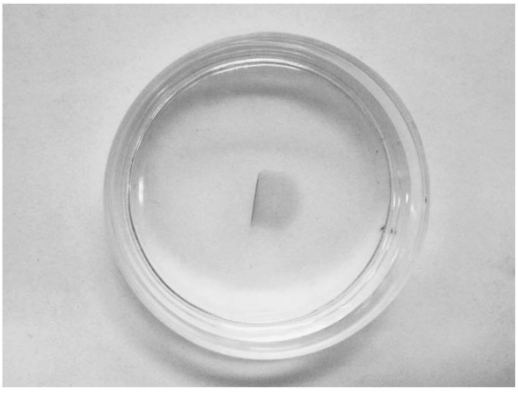


Figure 1 Photograph of DNA film stained with Cu^{2+}. A full color version of this figure is available at *Polymer Journal* online.

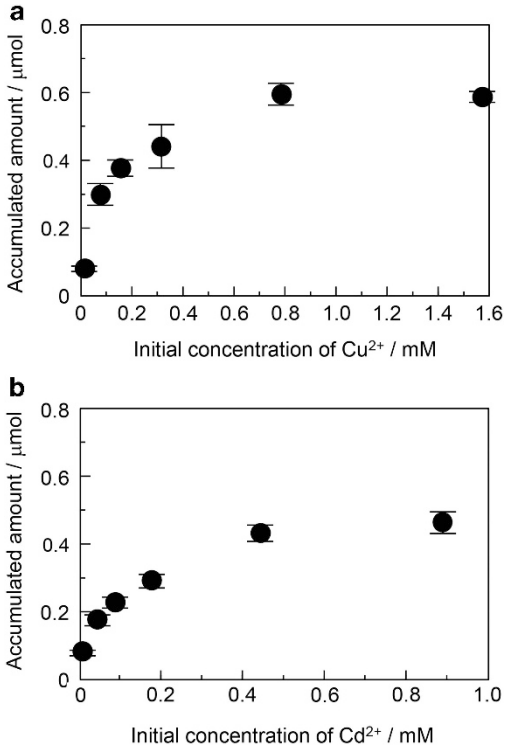


Figure 2 Accumulation of (**a**) Cu^{2+} and (**b**) Cd^{2+} by DNA beads: the DNA beads were placed in an aqueous solution of a metal ion and incubated for 24 h for 1.5 μmol nucleotide; the amount of accumulated metal ions was estimated from the calibration curve; each value in the plot represents the mean of three separate measurements ± s.d.

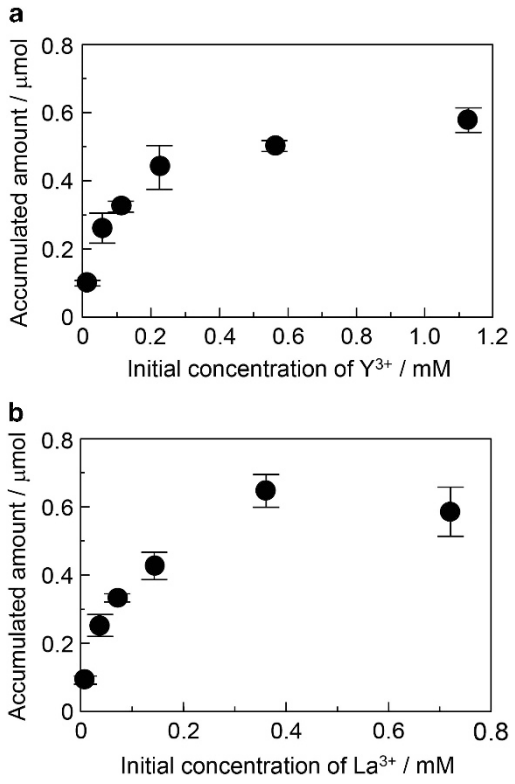


Figure 3 Accumulation of (**a**) Y^{3+} and (**b**) La^{3+} by DNA beads: DNA beads were placed in an aqueous solution of the metal ion and incubated for 24 h for 1.5 μmol nucleotide; the amount of accumulated metal ions was estimated from the calibration curve; each value in the plot represents the mean of three separate measurements ± s.d.

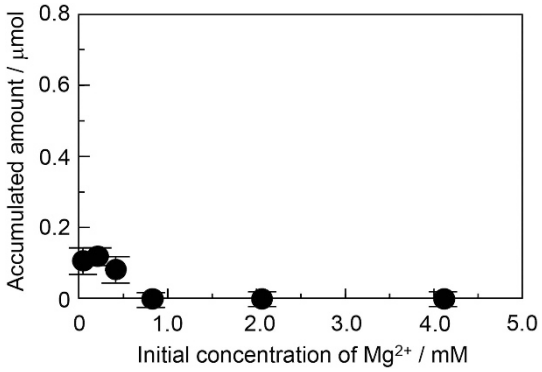


Figure 4 Accumulation of Mg^{2+} by DNA beads: DNA beads were placed in an aqueous solution of Mg^{2+} and incubated for 24 h using 1.5 μmol nucleotide; the amount of accumulated metal ions was estimated from the calibration curve; each value in the plot represents the mean of three separate measurements ± s.d.

Interaction between DNA and metal ions

The DNA beads selectively accumulated the heavy metal and rare earth metal ions. Thus, we discussed the accumulative interaction of metal ions by DNA beads. Table 2 shows the nucleotide: metal ion molar ratio for the DNA beads with accumulated metal ions. These molar ratios were calculated from the maximum amounts of accumulated metal ions. The nucleotide: metal ion molar ratio was approximately 1:0.5 for all of the metal ions. We performed IR

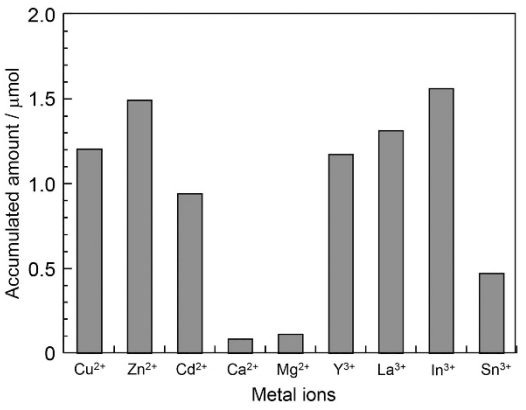


Figure 5 Maximum amounts of various accumulated metal ions, such as Cu^{2+}, Zn^{2+}, Cd^{2+}, Ca^{2+}, Mg^{2+}, Y^{3+}, La^{3+}, In^{3+} and Sn^{3+}, by DNA beads (for 1 mg DNA; 3.0 μmol nucleotide), which were calculated from the curves for the accumulation of metal ions at various ion concentrations, as in Figure 2 or 3.

Table 2 Nucleotide to metal ion molar ratio

Metal ion	*Nucleotide:metal ion*[a]
Zn^{2+}	1:0.49
Cu^{2+}	1:0.40
Cd^{2+}	1:0.31
Y^{3+}	1:0.39
La^{3+}	1:0.43
In^{3+}	1:0.53
Sc^{3+}	1:0.31

[a]Molar ratio was calculated from the maximum-accumulated amount of metal ion.

measurements on the DNA film with accumulated metal ions to elucidate the interaction between the DNA and metal ions.

Figure 6 shows the DNA inorganic hybrid film with accumulated metal ions (DNA film). Plots (a)–(d) in Figure 6 show the IR spectra for the pure DNA film, DNA films with accumulated Cu^{2+} and Y^{3+} and the DNA film incubated in a Mg^{2+} solution, respectively. The amount of accumulated metal ions was estimated from the calibration curve with the metal indicator. The accumulated amounts of Cu^{2+} and Y^{3+} in the DNA films were found to be the same as the maximum-accumulated amounts in the DNA beads. In contrast, there were no indications that the DNA films accumulated Mg^{2+}. The absorption band at 1234 cm^{-1}, which is related to the antisymmetric vibration of the phosphate group,[29–32] was shifted to a lower wavenumber as the Cu^{2+} and Y^{3+} concentrations increased. This shift resulted from the electrostatic interaction between the metal ion and the DNA phosphate group: a similar result has been reported for a DNA-metal ion biomatrix[33] and a DNA-poly(allylamine) composite material.[34,35] The absorption band at 1480–1650 cm^{-1}, which is related to the stretching and bending vibrations of acid bases, also changed when the DNA film accumulated Cu^{2+} and Y^{3+}. These results suggested that Cu^{2+} and Y^{3+} interacted with the phosphate group as well as the nucleic acid bases. Similar interactions, such as the binding of ions to the phosphate group and nucleic acid bases, have been reported.[31,36–38] In contrast, the accumulation of Mg^{2+} did cause any changes in the absorption bands, such as the antisymmetric vibration of the phosphate group and the stretching and bending vibrations of the nucleic acid bases. It is generally known that Mg^{2+} interacts with the DNA phosphate group.[39,40] However, no changes

were observed for the absorption bands associated with Mg^{2+} accumulation of the IR spectra in this study. In our experiments, the interaction between Mg^{2+} and DNA was too weak for the DNA film to accumulate Mg^{2+}; therefore, rinsing the film with water removed Mg^{2+} from the film. That is, Mg^{2+} was not accumulated by the DNA beads. These results suggest that heavy metal ions, such as Cu^{2+}, and rare earth metal ions, such as Y^{3+}, are strongly bound to the phosphate group by an electrostatic interaction. The heavy metal and rare earth metal ions strongly bind to the phosphate group as well as the nucleic acid bases.

Accumulation of metal ions by DNA column

The observation that DNA beads accumulated heavy metal and rare earth metal ions from aqueous solutions in the batch method motivated us to fabricate a DNA column that could more effectively accumulate heavy metal and rare earth metal ions. For this column, the metal ion concentration was 5 p.p.m. A solution of metal ions (10 ml) was applied to the DNA column, and the eluted solution was then re-applied to the column. The total duration of this method was 1.5 h.

Figure 7 shows the accumulation of Cu^{2+}, Cd^{2+}, Y^{3+} and In^{3+} using the DNA column and batch methods. The accumulated amounts of Cu^{2+}, Cd^{2+}, Y^{3+} and In^{3+} were 0.26, 0.20, 0.22 and 0.25 μmol, respectively (see the solid bars in Figure 7). The same amount of ions was accumulated using the column and the batch method (see the unfilled bars in Figure 7). The total accumulation times for the column and batch methods were 1.5 and 24 h, respectively. These results suggested that the DNA column method was more effective than the batch method in accumulating metal ions. However, the DNA column also did not accumulate Mg^{2+}, as was found for the batch method (data not shown).

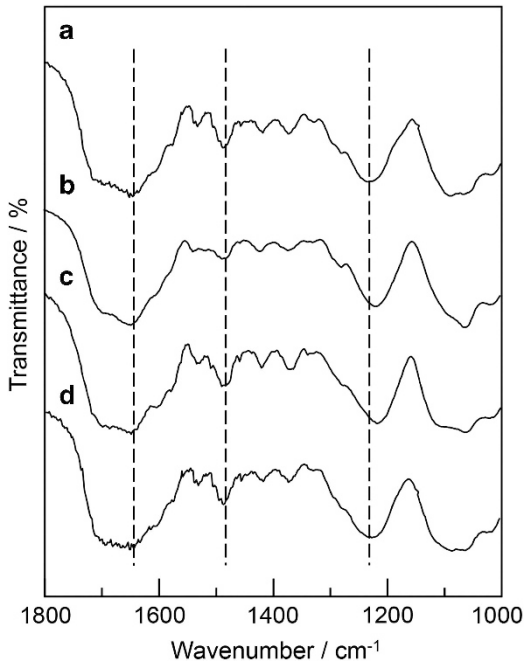


Figure 6 IR spectra of (**a**) a pure DNA film, (**b**) a DNA film with accumulated Cu^{2+}, (**c**) a DNA film with accumulated Y^{3+} and (**d**) a DNA film incubated in a Mg^{2+} solution, respectively; the amount of accumulated metal ions was estimated from the calibration curve; the IR spectrum was measured at a resolution of 4 cm^{-1}; triplicate experiments yielded similar results.

DNA column reuse

Finally, we demonstrated the reuse of the DNA column. We used a well-known chelating reagent, EDTA, to perform this experiment. The EDTA solution was to the column that had accumulated metal ions, and the chelating effect caused the DNA beads to release metal ions into the EDTA solution. The solution of metal ions was then

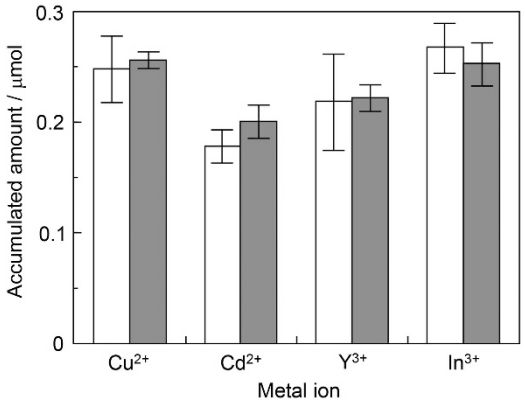


Figure 7 Amounts of Cu^{2+}, Cd^{2+}, Y^{3+} and In^{3+} accumulated by the DNA column (solid bars) and batch methods (unfilled bars) using 1.5 μmol nucleotide; the Cu^{2+}, Cd^{2+}, Y^{3+} and In^{3+} concentrations were 0.079, 0.044, 0.056 and 0.044 mM, respectively; the total duration of the column and batch experiments were 1.5 and 24 h, respectively; each value in the plot represents the mean of three separate measurements ± s.d.

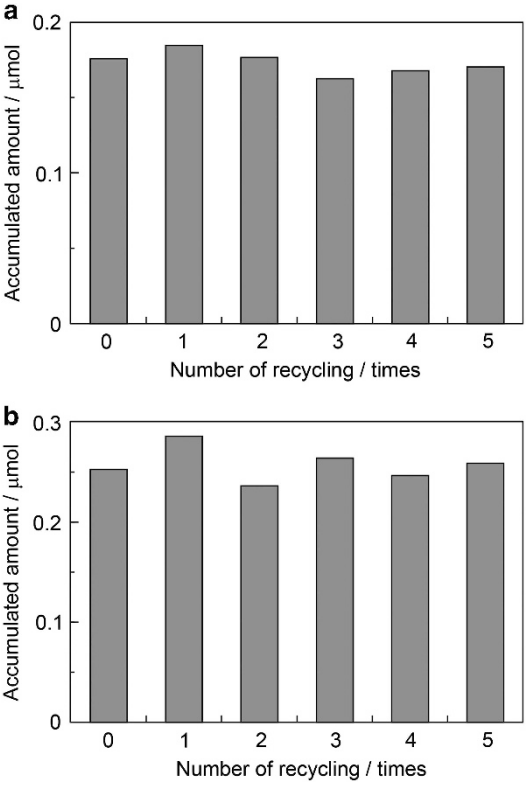


Figure 8 Reuse of DNA column with accumulated (**a**) Cd^{2+} and (**b**) In^{3+} for 1.5 μmol nucleotide; the used DNA column was recycled by washing with 10 ml of 100 mM EDTA solution and water; the concentrations of the Cd^{2+} and In^{3+} were 0.044 and 0.044 mM, respectively.

re-applied to the DNA column. This cycle was repeated five times. Figure 8a shows the accumulated amount of Cd^{2+} versus the number of recycles. The used DNA column was recycled by washing with 10 ml of a 100 mM EDTA solution and water. Before recycling, the DNA column had accumulated ~0.18 μmol of Cd^{2+}. The DNA column was recycled five times by applying the EDTA solution the accumulated amount of Cd^{2+} was maintained at ~0.18 μmol and did not appear to decrease. This result showed that the DNA column that had accumulated heavy metal ions could be recycled by washing with an EDTA solution. Similar results were obtained for the reuse of a DNA column that had accumulated rare earth metal ions, that is, In^{3+}. Figure 8b shows the accumulated amount of In^{3+} versus the number of recycles. Although the DNA column was recycled five times, the accumulated amount of In^{3+} was maintained at ~0.25 μmol and did not appear to decrease. Similar results were obtained for the reuse of DNA columns that had accumulated Cu^{2+} and Y^{3+}. These results showed that the DNA column could be recycled by washing with an EDTA solution. The accumulated metal ions could be recovered by adding an EDTA solution to the DNA column. Although the DNA column could be recycled by washing with 10 ml of a 10 mM EDTA solution, the amount of accumulated metal ions decreased with each recycle. The amounts of accumulated metal ions that were obtained from recycling the DNA column with 30 ml of a 100 mM EDTA solution were similar to the those obtained using the batch methods. Therefore, all of the accumulated metal ions were released from the DNA columns under the experimental conditions investigated, for example, using 10 ml of 100 mM EDTA.

CONCLUSION

DNA beads were prepared by coating a DNA-inorganic hybrid material onto glass beads. The DNA beads selectively accumulated heavy metal and rare earth metal ions from an aqueous solution of metal ions. The DNA and the metal ions interacted at a molar ratio of nucleotide:metal ion = 1:0.5. The metal ions interacted with the DNA phosphate group as well as the nucleic acid base. The DNA column was able to accumulate metal ions more effectively than the DNA beads. The DNA column was recycled by washing with an aqueous EDTA solution. The DNA beads and DNA column could be used for environmental applications, such as the removal of heavy metal ions from drinking water, as well as for engineering applications such as the accumulation of rare earth metal ions from industrial waste or groundwater.

ACKNOWLEDGEMENTS

This work was supported by the Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan (No. 25410195) and a matching fund subsidy for private universities from MEXT.

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