Magnetic properties of DNA-templated Co/Cu naonoparticle chains*

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According to ultraviolet (UV)-vis absorption spectra recorded in the DNA metallization process, DNA-templated Co/Cu binary nanoparticle chains are fabricated by incubating genome DNA of *paralichthys olivaceus* muscle in $CoCl_2$ and $CuCl_2$ mixture solution for 20 hours and reducing the complex for 2 hours. Transmission electron microscopy observation indicates that Co and Cu nanoparticles with 20 nm in diameter were randomly dispersed on the DNA template. The superconducting quantum interference device (SQUID) measurements display that the magnetic interaction between cobalt particles is greatly decreased by the copper particle. With increasing copper content, the coercivity of the systems enhance from 9 Oe to 100 Oe (1 Oe=79.5775 A/m).

Keywords: DNA-templated, Co/Cu nanoparticle, magnetic interaction

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Nanoparticles with controlled shape, size and composition have been fabricated by a variety of sputtering, lithography techniques and chemical synthesis methods.[1−3] Such particles can be subsequently organized as bottom-up building blocks into unique functional structures and patterns in order to carry out some performance designed for a specific purpose. The process of creating integrated functional architectures, which is driven by interparticle interactions, external forces or/and directed by templates, is named self-assembly.[4] It has been shown that the self-assembly is a powerful nanofabrication technique[5−7] due to the fact that it produces small structure units at scales beyond the spatial limits of other techniques, and precisely manipulates structures on the nanometer scale over large regions. Especially, the templated self-assembly has attracted intense attention nowadays as an efficient method to produce much more complicated, adaptable and evolutionary systems. Deoxyribonucleic acid (DNA) based is a remarkable example.

The DNA is one of the most interesting templates because of two features: (i) it is only 2 nm in diameter and micrometers in length, indicating great mechanical rigidity of short double helices, high physical/chemical stability, and very low conductance; (ii) it can be programmed and manipulated at atomic precision with a large number of biocatalysts, and thus readily shaped for the desired functional nanosystems.[8−11] So far, many DNA-based nanostructures have been developed and applied in nanoelectronics, biosensing, and computation.[12−16] In the typical fabrication process,[17] DNA is first incubated in salt solution and forms chemically active complex by binding cationic species to the phosphate units. Subsequent reduction of the complex results in the formation of nanoparticles along the DNA template. Unitary metal nanoparticles and nanowires of silver,[18] gold,[19] palladium,[20] nickel[21] and platinum[22] have been successfully fabricated on DNA using this method. Currently, researchers are shifting focus to binary systems, whose two kinds of nanoparticles are templated on the same DNA, because such systems are much attractive for application in magnetic storage, magneto-label and biosensor, etc. However, the fabrication of binary systems faces a great challenge due to the difference of chemical activities between the metal ions in the salt solution.

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In this paper, an attempt to fabricate DNA-templated Co/Cu binary nanoparticle systems is reported. Their magnetic properties are measured as well. We choose Co and Cu elements because not only the difference of their chemical activities is not too large, but also they exhibit no intermiscibility in a wide range of concentration.

Genome DNA of *paralichthys olivaceus* muscle (linear and 20000 base-pairs in length) was diluted with a buffer solution of 0.05 M Tris [tris(hydroxymethyl)aminomethame]-HCl, pH 7.6–7.8. The DNA solution (0.2 ml) was stirred vigorously while an aqueous solution of $CoCl_2$ and $CuCl_2$ mixture (4 mM metal ions, 2 ml) was added. The resulting solution was incubated in the dark at room temperature (about 20 °C) for 20 hours. A reduction reagent of dimethylamine borane (DMAB) (0.1 M) was then added. Ratio of DNA solution to DMAB was about 7:1. The reaction continued for 2 hours and was stopped by diluting the solution with deionized water. The whole process of the DNA metallization was monitored by a UV-vis spectrophotometer at wavelength between 200 nm and 900 nm by using 1-cm path-length quartz cuvettes. A salt solution reference was used for baseline calibration. Absorption spectra of the sample containing 50% Co(II) were continuously recorded at a time step of 15 min, as shown in Fig. 1.

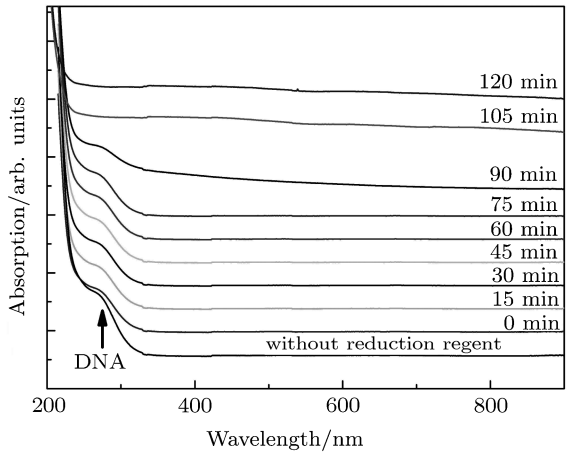


Fig. 1. Absorption spectra of the sample containing 50% Co(II) continuously recorded at a time step of 15 min by a UV-vis spectrophotometer at wavelength between 200 nm and 900 nm using 1-cm path-length quartz cuvettes. A salt solution reference was used for baseline calibration. The peak around 260 nm corresponds to DNA.

It is found that the salt solution indicates an absorption peak at about 260 nm, corresponding to that of DNA, and the spectrum profile almost does not change until 75 min after adding DMAB. With further increase in reaction time, the DNA absorption peak starts to become weak (around 90 min) and disappears rapidly when some black products were observed, indicating that the DNA is completely covered by metal particles. The UV-vis spectra show two characteristic processes of the reduction reaction, i.e., a long nucleation process following by a rapid particle growth process when the nucleus size is over a critical value.

The black products that the reaction continued for 2 hours were cleaned several times with deionized water, and deposited on carbon-coated copper grids for a transmission electron microscopy (TEM, JEM 3000F) observation. The typical bright field TEM image (Fig. 2) shows that DNA strands are covered densely with metal nanoparticles and very few individual particles are found in the background. It infers that a heterogeneous nucleation on DNA is dominated in the reaction process. The growth of metal nanoparticles on DNA results from the strong binding of metal ions and the phosphate backbone. The template locally increases the concentration of metal ions and enhances nucleation.[23,24] It is verified that Co and Cu nanoparticles are about 20 nm in diameter. They are randomly dispersed on the DNA template, attributed to competition in nucleation between Co(II) and Cu(II).

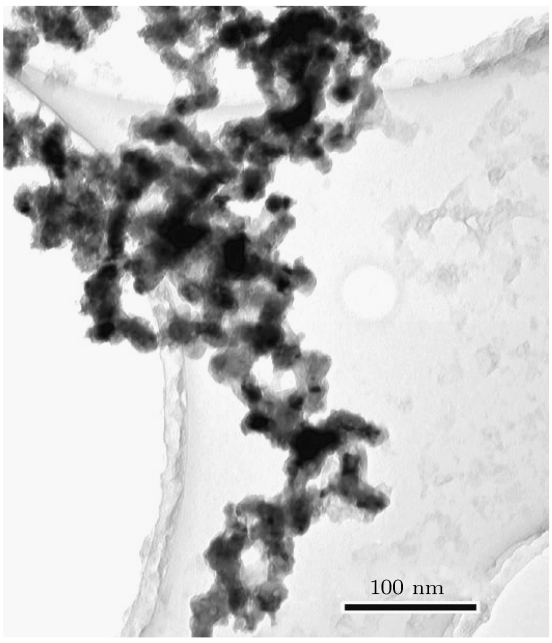


Fig. 2. Typical bright field TEM image of the sample Co(II) 50%.

According to the above procedure, four samples were fabricated by varying the Co(II) concentration in the 4-mM salt mixture solution at 100%, 67%, 50%, and 33% respectively. The reaction time was

2 hours. All final products were centrifuged and collected for SQUID measurements. In order to obtain the blocking temperature of Co nanoparticle, at which Co nanoparticles transform superparamagnetic state into ferromagnetic state, and then evaluate the mean particle size and interparticle interaction, temperature dependence of magnetic moment of the sample containing 100 % Co(II) was measured in an applied magnetic field of 50 Oe as shown in Fig. 3(a). The curve marked ZFC (for zero-field cooled) was obtained by first cooling the sample in zero field from 300 K to 5 K. The magnetic field was then applied and the magnetization was measured while the temperature was increased. The curve marked FC (for field cooled) was obtained in a similar manner except that the sample was cooled in the measuring field. The ZFC curve gradually increases with increasing temperature, but the FC curve departs from the ZFC curve and almost shows a constant when the temperature decreases from 300 K, reflecting a much higher blocking temperature of cobalt nanoparticle. With increasing temperature, some small particles transform ferromagnetic state (blocked state) into a superparamagnetic state. Magnetic moments of such particles are easily aligned in the applied magnetic field, exhibiting the increase of slow magnetization on the ZFC curve. On the other hand, with decreasing temperature, the aligned magnetic moments of the small particles are frozen during they transform superparamagnetic state into ferromagnetic (blocked) state. This process results the noncoincidence between the FC and ZFC curves. The broad cusp on the ZFC curve demonstrates a strong magnetic interaction between Co nanoparticles and a broad size distribution. Hysteresis loops for all samples observed at 5 K are shown in Fig. 3(b) and the inset. It is found that the loop of the sample containing 100 % Co(II) shows a typical shape of soft magnetic materials, which is easily saturated and has a low coercivity. It is due to the fact that the magnetic anisotropy of Co particle is averaged out by the strong interparticle magnetic interaction. Coercivity H_c of 9 Oe is observed. With increasing copper content, however, the coercivity of the samples enhances from 30 Oe for 67% Co(II), 47 Oe for 50% Co(II) to 100 Oe for 33% Co(II). They are also found to be very difficultly saturated. The main reason inducing such variation in magnetic properties is that the cobalt particles on the template are diluted by those of copper particles, and the inter-particle magnetic interaction is weakened efficiently. It may be revealed from the weak inter-particle interaction in the samples containing Cu particles that there are not any Cu(core)/Co(shell) core–shell heterostructured particles produced in our experiment, which will still indicate a strong interparticle interaction due to the ferromagnetic shell. Core-shell structure of Co(core)/Cu(shell) is also impossible because that Cu(II) is slightly more active than Co(II), and Cu never grows on Co core under our experimental condition. The cobalt particles are single domain. The magnetization process should be a magnetization rotation in a complete diluted system (decoupled system). The loops of the samples of 50% and 33% Co(II) can be then characterized by two magnetization processes: one is linear dependence of M vs. H corresponding to a pure magnetization rotation; another one is rapid change in the magnetization around the coercivity field corresponding to Barkhausen jump reversal of some cobalt particles.

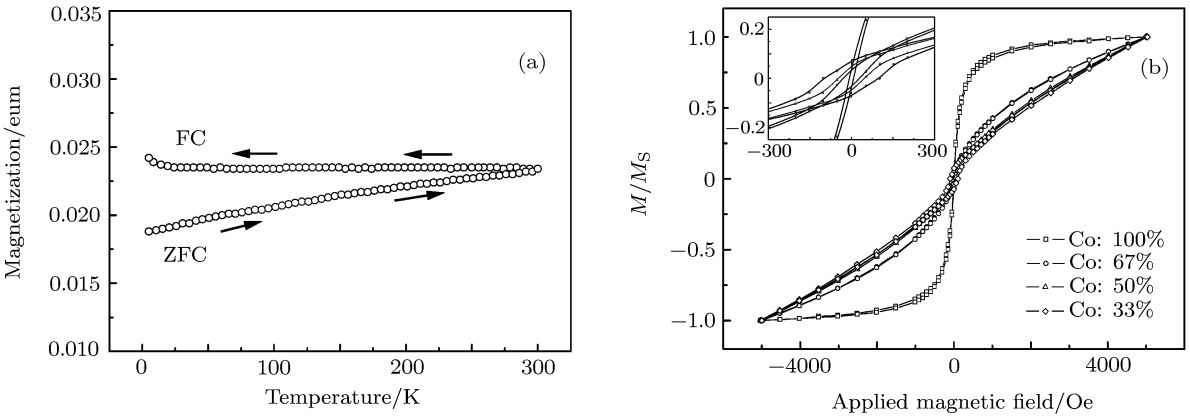


Fig. 3. (a) Field cooling (FC) and zero-field cooling (ZFC) curves of the sample Co(II) 100% measured with a temperature step of 5 K under an applied magnetic field of 50 Oe. (b) Hysteresis loops of the samples 100%, 67%, 50%, 33% Co(II) observed at 5 K. Coercivities of 9, 30, 47 and 100 Oe were observed.

In conclusion, DNA-templated Co/Cu binary nanoparticle chains have been fabricated by incubating the template in $CoCl_2$ and $CuCl_2$ mixture solution for 20 hours and reducing the complex for 2 hours. It has been found that Co and Cu nanoparticles with about 20 nm in diameter densely cover the DNA strands. The ZFC–FC measurement indicates that the systems are ferromagnetic even at room temperature. The magnetic interaction between cobalt particles is greatly decreased by the copper particle.

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