Fabrication of Biologically Functionalized, Electrically Conducting, and Aligned Magnetic Nanoparticles

Debasish Sarkar, Madhuri Mandal, Rajasree Das, and Kalyan Mandal

Material Science Department, S N Bose National Centre for Basic Sciences, Salt Lake, Kolkata, West Bengal 700098, India

Fabrication of nanomaterials in precisely 1-D or 2-D fashion is very difficult because the particles are very much active when their dimension is reduced and they tend to aggregate. Self-aggregation of nanoparticles can be avoided by their templating growth. We have biofunctionalized the magnetic nanoparticles (iron), aligned them in a chain-like fashion, made them electrically conducting all by using DNA as template. We coated the particles by gold as gold coating prevents them from oxidization. Average size of the synthesized DNA templated Fe_{core}–Au_{shell} particles are found to be ∼14 nm from transmission electron microscopy (TEM) analysis. Fourier transformed infrared (FTIR) spectroscopic analysis was performed to investigate the bonding between metal ions and the DNA chain. Magnetic measurements of the particles show that the particles are ferromagnetic within 80 $\leq$ T $\leq$ 300 K but saturation magnetization (M_S) and coercivity (H_C) decreases with increasing temperature. These DNA templated, trifunctional Fe_{core}–Au_{shell} particles have great potential of finding applications in magnetically driven, spin-dependent devices as well as in hybrid devices.

I. Introduction

MAGNETIC nanoparticles with some biological functionalization are of immense interest. Therefore, biological molecules, such as proteins and nucleic acids, are used extensively for the organization of nanomaterials. Particularly, the combination of different metallic nanoparticles with DNA and proteins is now being studied extensively for the fabrication of self-assembled hybrid structures, such as DNA-templated nanowires [1]–[4]. Due to the high aspect ratio, self-assembling characteristics, and its unique molecular recognition properties, DNA offers a great potentiality as a building block to create nanowires. With proper engineering, such materials may work as nanorobot, healer, nanomachine, targeted drug delivery agent, etc. That is why manufacturing of various small substances with biological molecules is a very important job. In recent years, many studies have been devoted to develop DNA sensors due to the simplicity, specificity, exceptional sensitivity, and selectivity for the detection of specific genes [5]–[7]. Due to their electrical conductivity it may be useful in biocomputer interconnect and for their magnetic properties they may do many marvelous things in biomedical treatment like treatment of cancer by hyperthermia therapy, magnetic resonance imaging, brain research, etc. But before use, proper engineering with such system and their extensive studies are necessary. Hence, the synthesis and study of nanobiomaterials having the properties of magnetic, electrical conductivity and optical is very important. For these we need to understand how different biomolecules play role with attachment of different tiny magnetic nanoparticles. We have already synthesized DNA attached nickel nanoparticles in our previous work and studied their properties [8]. But as Ni is harmful for biological system we are trying to synthesize some biofriendly materials. In this paper, we have reported the synthesis of gold-coated Fe nanochain by DNA directing method and investigated its conducting, optical, and detailed magnetic properties all together. We have coated the DNA templated Fe nanochain with gold, because after a gold coating Fe becomes very stable as gold is inert to atmospheric oxygen. This kind of material can be monitored by its optical property on the one hand and by magnetic property on the other. Moreover, the electrical property of this material has added some more advantages.

II. Experimental Section

All the reagents used were 99.9% pure and purchased from Sigma-Aldrich. Ultrapure distilled water (UPD water) DNAse, RNAse free was used in all synthesis procedures.

CD and FTIR were pursued by JASCO J-815 CD spectrometer and JASCO 6300 FT/IR spectrometer, respectively. 1-cm quartz cuvette holder was used to measure the CD spectra and KBr of IR quality was used as substrate to take the FTIR spectra. The morphology, phase, surface, and size of the particles were characterized by transmission electron microscopy (JEOL-2010) applying the voltage 200 KV. The magnetic properties were measured by a vibrating sample magnetometer (Lakeshore, model 7144). The sensitivity of magnetization and magnetic field measurements are 10^{-6} emu and 10^{-3} Oe, respectively. I-V measurement was done by four probe electrode method.

A stock DNA solution (1 g/L) was prepared by mixing appropriate amounts of DNA with Tris-EDTA buffer (pH 7.4) and was stirred overnight. The buffer solution helps to prepare a homogeneous DNA solution without any pop off of A and G bases in DNA and was stored in a refrigerator. A stock solution of ferric chloride of 0.1 (M) and a stock solution of 0.05 (M) aqueous gold chloride ($HAuCl_4$) were made. The stock solution of ferric chloride was mixed with stock DNA solution at ratio 2:1 and the mixture was stirred for 30 min using a magnetic stirrer. The resulting solution was then treated with sodium borohydride. The solution color was turned to black, which indicates formation of

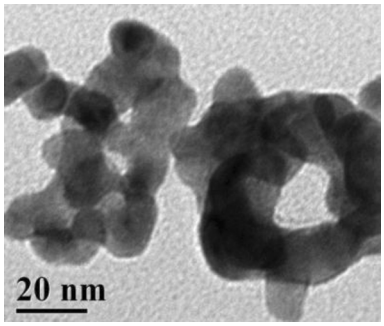

Fig. 1. TEM image of DNA templated core/shell Fe/Au particles.

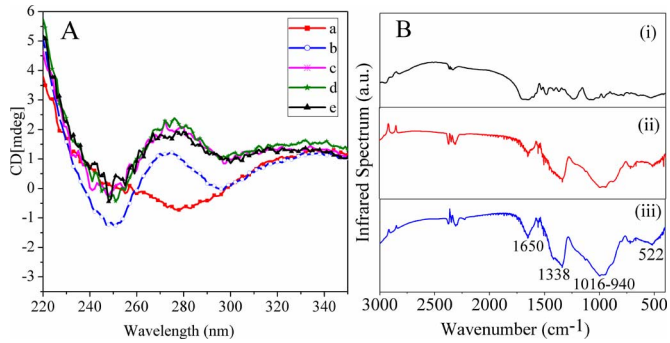

Fig. 2. (A) CD spectra: (a) is for buffer solution, (b) is for DNA in buffer solution, (c) is after addition of ferric chloride to the solution, (d) is after Fe nanoparticles formation on DNA chain, and (e) is after gold coating on Fe nanoparticles attached to DNA chain. (B) FTIR spectra: (i) only DNA, (ii) Fe attached DNA, and (iii) Fe_{core}–Au_{shell} attached on DNA .

iron nanoparticles by the reduction of iron ion to iron metal particles. The 500-μL stock aqueous gold chloride ($HAuCl_4$) solution of 0.05 (M) was added to this dispersion. The formation of gold nanoparticles was evident by appearance of a blackish pink coloration of the solution.

III. Results and Discussion

TEM image after synthesis of gold-coated iron nanoparticles attached on DNA chain is shown in Fig. 1. The image indicates a clear attachment of these metallic nanoparticles on DNA chain. The particle size is of $\sim$14 nm. In our previous work also similar kind of morphological particles were obtained. DNA consists of negatively charged phosphate and amino groups which are good binding agents of positively charged metal ions. Because of these reasons, DNA helps to form such chain-like composite structures.

Circular dichroism (CD) spectra were taken at all the steps of solution preparation and addition of different reagents for particles formation. The secondary structure of DNA can be determined by CD spectroscopy in the UV visible region. CD spectra taken for solutions at different stages of synthesis of material are shown in Fig. 2(A) (a, b, c, d, and e), where (a) is for buffer solution, (b) is for DNA in buffer solution, (c) is after addition of ferric chloride to the solution, (d) is after Fe nanoparticles formation on DNA chain, and (e) is after gold coating on Fe nanoparticles attached to DNA chain. From these spectra it is evident that no denaturization of DNA takes place after attachment of metal nanoparticles onto it as positions of both positive and negative CD spectra remain almost unaltered but a small change in intensity takes place. This indicates a minor change in asymmetric structure with no denaturization of DNA. This structural change takes place due to electrostatic bond formation between DNA and ferric chloride. Hence, DNA without melting or denaturization successfully acts as template to grow the particles in chain-like fashion. To prevent the melting of DNA here the synthesis temperature was maintained at a range between □ °C and 69 °C.

The analysis of FTIR spectra [Fig. 2(B)] taken from only DNA (i), Fe attached DNA (ii), and Fe_{core}–Au_{shell} attached on DNA (iii) authenticates the formation of Fe–Oxygen bond in both cases of spectra (ii) and (iii). In the curve (ii) and (iii), a peak at 522 cm^{-1} is observed which is due to stretching vibration of the bond between iron and the oxygen, present in phosphate backbone of DNA molecule. In curves (ii) and (iii), the major broad peak from 940 to 1016 cm^{-1} is due to overlapping of vibrational mode of PO_3^{-2} and P-OFe bonds of which vibrational mode of PO_3^{-2} appears at lower region (at $\sim$950 cm^{-1}) and P-OFe vibration appears at higher region ($\sim$1016 cm^{-1}). After formation of bonding with Fe and phosphate backbone the peak at $\sim$1016 cm^{-1} becomes intense [9]. The broad peak at $\sim$1750–1600 cm^{-1} is due to the vibration plane of the G-C and A-T base pairs. But after formation of bonding with iron and DNA, the nature of peak changes and it becomes sharper and appears at $\sim$1650 cm^{-1} [10]. This information authenticates interaction of Fe with DNA which directs a growth of chain-like structure of gold-coated iron attached to DNA. The peak at 1338 cm^{-1} is due to stretching mode of vibration of C-N bond present in DNA.

IV. Magnetic Properties

The experimental data of zero field cooled (ZFC) and field cooled (FC) magnetization against temperature at a reference field of 100 Oe is plotted in Fig. 3(a) for DNA templated gold-coated iron samples. In case of ZFC measurement, magnetization of the sample gradually increases within $80 \leq T \leq 400$ K. But in FC condition, magnetization remains almost constant ($\sim$4.6 emu/g) up to 260 K and then it slightly decreases ($\sim$4.4 emu/g) at 400 K. The ZFC magnetization curve does not show any peak within $80 \leq T \leq 400$ K which indicates that the DNA templated Fe/Au nanoparticles remain ferromagnetic within that temperature range.

For a single domain nanoparticle, the ZFC magnetization increases with temperature because the small thermal fluctuation helps the magnetization direction to align along the external field direction. After a certain temperature (T_B) called blocking temperature, anisotropy energy is no longer sufficient to make up large thermal fluctuations and due to randomization of moment directions, magnetization decreases beyond T_B. For FC measurements, the moments were initially oriented along external field direction. With increase of temperature, high thermal fluctuation reduces the component of magnetization along field direction.

A particle is said to have single domain if its dimension is reduced to nanometer range. At a particular temperature and in absence of any magnetic field, the ferromagnetically aligned