Int. J. Electrochem. Sci., 7 **(2012)** 7762 - 7769

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Electrodeposition of CoPtP/Au Multisegment Nanowires: Synthesis and DNA Functionalization.

T. S. Ramulu[1], *R. Venu* [1], *B. Sinha*[1], *S. S. Yoon*[2] *and C. G. Kim*[1,*]

[1]Department of Materials Science and Engineering, Chungnam National University, Daejeon 305-764, South Korea
[2]Department of Physics, Andong National University, Andong 760-749, South Korea
[*]E-mail: cgkim@cnu.ac.kr

Received: 12 July 2012 / *Accepted:* 11 August 2012 / *Published:* 1 September 2012

We have fabricated CoPtP/Au hard magnetic multisegment nanowires via template assisted electrochemical technique using a polycarbonate membrane with a nominal pore diameter of 50 nm. The synthesized nanowires are average 6 μm in length with Au and CoPtP segments in alternative fashion. The CoPtP/Au exhibits a hard magnetic property with a coercive force of 1.85 kOe, when the applied field is parallel to nanowire's long axis. The magnetization value of CoPtP/Au multisegment nanowires is lower than CoPtP nanowires, which is due to the incorporation of the nonmagnetic Au material in the nanowire vicinity. The surface of the Au segment of multisegmented nanowires was modified with fluorescence loaded ds-DNA through thiol linker. The surface modification of the Au segment was confirmed through a confocal laser microscope and Fourier transform infrared spectroscopy measurement.

Keywords: Biocompatibility, ds-DNA, Electrodeposition, Functionalization, Mutisegmented nanowires

1. INTRODUCTION

Currently, One-dimensional nanostructure materials such as nanowires, nanotubes, multisegment nanowires and core shell nanowires have much interest due to their multiple properties towards the significant application in sensors, medical diagnosis, bioelectronics and bio-devices [1-4]. Among these structures, multisegmented nanowires represent a unique platform towards the important application in multiplexed bioanalysis, biosensors, magnetic cell separation and gene delivery with multiple functionality [5-9]. In particular, much attraction has been drawn to multisegmented nanowires with magnetic and nonmagnetic segments because the magnetic properties such as coercivity, stray field of magnetic segment is useful for the manipulation and detection of

biomolecules by the magnetic method where as the Au segment is applicable for the surface modification with biocompatibility and high surface functionality [10-11]. In previous reports, the syntheses, characterization and growth of multisegmented soft magnetic nanowires like NiFe/Cu, Au/Fe, Co/Pt and Au/Co has been described [12-15]. However, hard magnetic materials have a larger coercivity than soft magnetic materials, which affords nonvolatile memory characteristics in magnetic label or barcode function. Although the synthesis and characterization of the above said multisegmented nanowires are reported earlier, there are no reports on hard magnetic and non magnetic multisegmented nanowires with surface modification by DNA.

The selection of fabrication technique for the synthesis of multisegment nanowires is the most important issue. The ability to control the parameters like length, diameter, grain size, crystallinity etc. is highly dependent on the synthesis technique. The most suitable fabrication technique for the synthesis of multisegment nanowires is a template assisted electrochemical deposition method, in which the nanowires are grown from the pores of the template. This method provides an efficient sequential growth of different segments with a controlled aspect ratio [16].

In this article, we reported the electrochemical synthesis and characterization of multisegment nanowires with immobilization of fluorescent loaded ds-DNA on Au segment of CoPtP/Au barcode nanostructures, which contains both magnetic and nonmagnetic materials in alternative fashion. Our aim of the research work is the simultaneous use of this multi segmented nanowires for multifunctional biological and magnetic applications. In this context, the CoPtP/Au multisegmented nanowires are motivated not only the magnetic properties like high coercivity but also the biocompatibility for the future application in magnetic biosensors.

2. EXPERIMENTAL DETAILS

2.1. Synthesis and extraction of multisegment nanowires

The multisegment nanowires were prepared via sequential electrodeposition (Potentiostatic mode) of CoPtP/Au segments within a polycarbonate membrane (50 nm diameter) by changing the corresponding electrolytes in an electrodeposition cell. The room-temperature electrolyte for the CoPtP contains $CoSO_4 7H_2O$ 60 g/L, H_2PtCl_6 4.1 g/L, NaH_2PO_2 4.5 g/L and H_3BO_3 25 g/L [17] (the above-mentioned chemicals are procured from Sigma-Aldrich) with pH around 4.5 and the electrolyte for the Au contains gold plating solution (SME, Korea).

We optimized different parameters such as electrode potential, growth rate, temperature and pH for single segment of CoPtP and Au nanowires in prior to the deposition of multisegmented nanowires. The electrochemical deposition for both CoPtP and Au were performed at a constant potential of -1.0 V with respect to the reference electrode. Nanowires were separated from the polycarbonate membrane by dissolving the template in dichloromethane and washed several times with water and re-suspended in more viscous liquid such as ethylene glycol or 1:1 hexadecane and octadecane for good dispersion [18].

2.2. Functionlization of ds-DNA on Au segment

Immobilization of ds-DNA on the nanowire surface is accompanied through thiol linker. The base sequences used in this study were as follows:

i) Thiolated probe DNA: 5'-SH-$(CH_2)_6$-($CH_2)_3$-TCCGGAGCTGCCCTACGAGGTCAA-3'

ii) Complementary DNA: 5'- Biotin-TTGACCTCGTAGGGCAGCTCCGGA-Cy3-3'

The ds-DNA was synthesized by adding 20 µl of 50 ng/µl SH (thiol) labeled single strand (ss) DNA in 20 mM Tris-HCl buffer (pH 8.0) with 20 µl of 50 ng/µl Cy3 (fluorescent dye) labeled complementary DNA in eppendorff tube. The resulting DNA solution was annealed from 100 ºC to room temperature. The stored nanowires were washed several times with distilled water and dried at 100 ºC in an oven. 100 µg of dried nanowires were taken and dispersed in 200 µl of Tris-HCl buffer for the immobilization of ds-DNA. Then this solution was added to the 40 µl of 50 ng/µl fluorescent ds DNA in eppendorff tube. The resulting solution was kept for overnight at room temperature. After then, the nanowires solution was washed with Trsi-HCl buffer to remove unbounded DNA on the nanowire surfaces. The supernatant of the solution was removed using micropipette by collecting the nanowires at the bottom of the eppendorff tube using a magnet and resuspended in Tris-HCl buffer for further characterization.

2.3. Physiochemical measurements

The synthesis of multisegmented nanowires was carried out using an electrodeposition system (SP-150, BioLogic, France). The structural growth and morphology of metallic nanowires were observed by Field emission scanning electron microscopy (FE-SEM, Nova-230) with an operating voltage of 10 kV. The chemical composition of nanowires was studied by energy dispersive spectroscopy (EDS) coupled with the FE-SEM. The magnetic properties of the as-deposited state of nanowires in the membrane were measured at a room temperature in the applied filed range between 15 kOe and -15 kOe in parallel ($H_{\parallel}$) to the nanowire wire axis by vibrating sample magnetometer (VSM: Lake-Shore 7407) with a sensitivity of 10^{-6} emu. Fluorescent loaded ds-DNA functionalized multisegemnt nanowires were characterized through FT-IR (Brucher Optic GmbH, Germany) spectroscopy and confocal laser microscopy (LSM5 live configuration Variotwo VRGB, Zeiss, USA).

3. RESULTS AND DISCUSSION

3.1. Nanowires synthesis and characterization

Before going to the fabrication of multisegment nanowires, we synthesized the single segment of CoPtP and Au nanowires separately for the estimation and optimization of growth rate with respect to the time. The morphological structure of both CoPtP and CoPtP/Au multisegment nanowires was illustrated by FE-SEM. Fig.1 (a) shows the FE-SEM image of CoPtP nanowires after dissolution of template in dichloromethane. The length of the nanowires is an average of 6 µm in length. The cross-

sectional SEM image of CoPtP nanowires inside the membrane is shown in Fig. 1 (b). It is clear from the inset image that the length of the nanowires is almost equal to the thickness of the membrane.

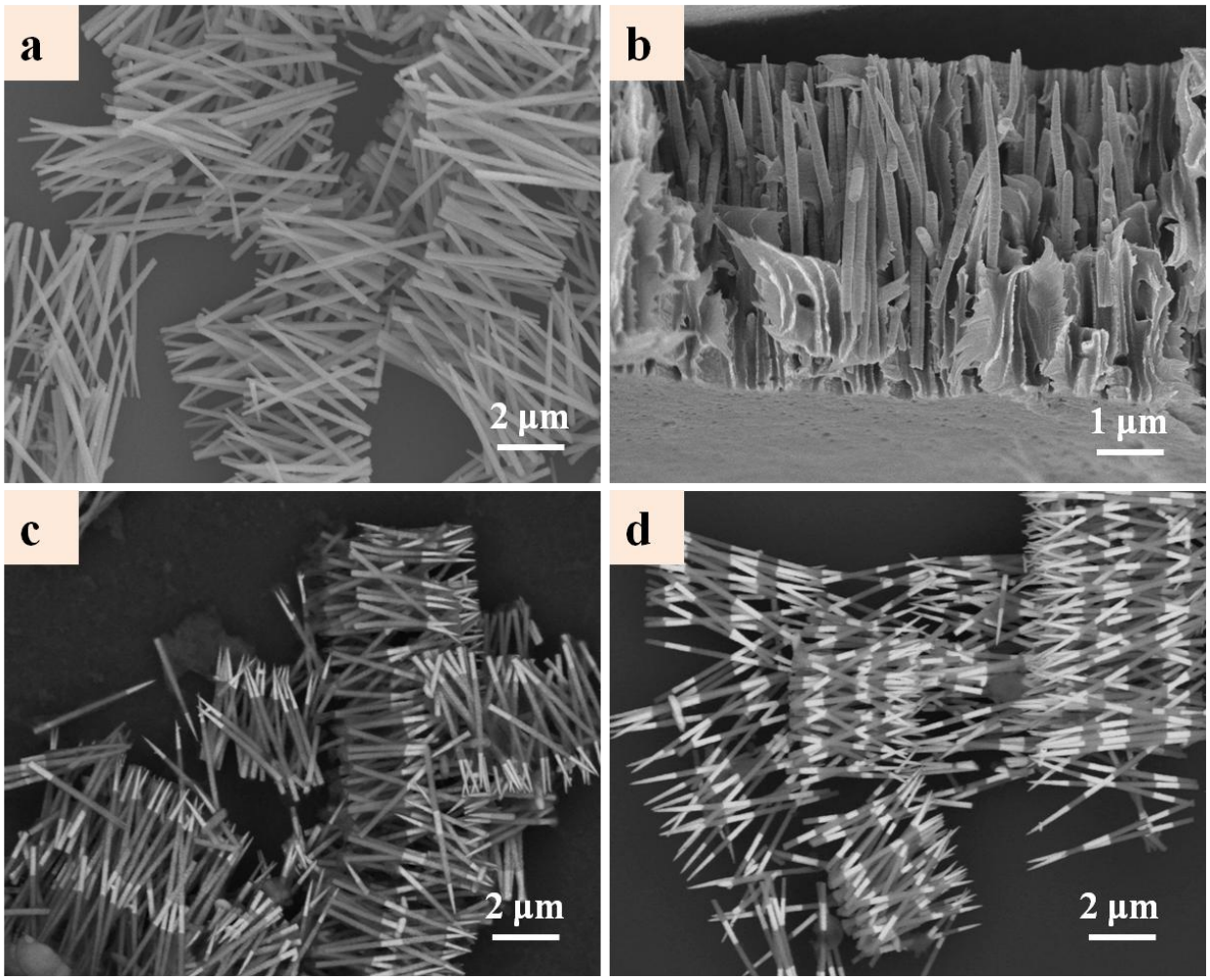

Figure 1. FE-SEM image of CoPtP nanowires (a) after removal of the membrane (b) cross-sectional view of the membrane with nanowires, Backscattering images of CoPtP/Au nanowires (c) four segmented (d) six segmented

Fig.1 (c and d) shows the backscattering SEM images of different number of segmented nanowires. The electron contrast in backscattered SEM images is the difference in atomic weights, which consequences the electron dispersing capability of CoPtP segments being stronger than Au segments, and therefore, the black region corresponds to CoPtP and the white region corresponds to Au. Further confirmation was made by analyzing the elemental composition of each segment through EDS. The Au and CoPtP segments are situated in an alternative fashion in the multisegment nanowires. The length of the CoPtP/Au multisegmented nanowires is nearly same as the CoPtP nanowires.

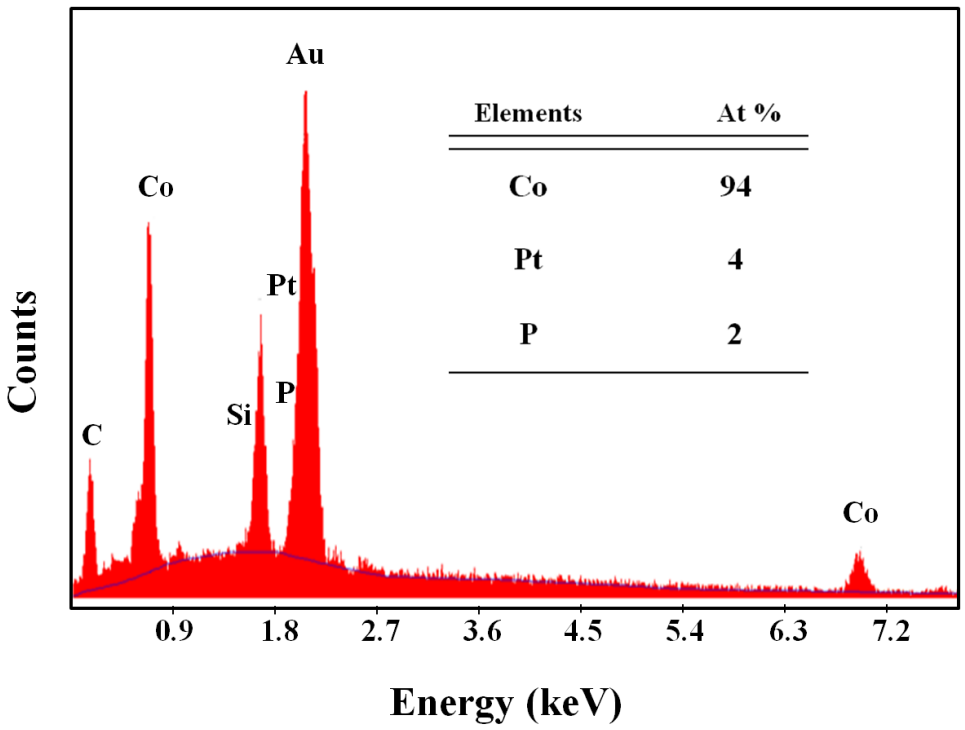

Figure 2. Energy dispersive spectrums of CoPtP/ Au multisegmented nanowires (Inset table shows the elemental composition of CoPtP nanowires)

The nominal elemental composition of multisegment nanowires was investigated by energy EDS associated with the FE-SEM. Fig. 2 shows the EDS spectrum of multisegmented nanowires, which indicates the presence of the Cobalt (Co), Platinum (Pt), Phosphorous (P) and Au elements. There are no other impurity elements present in the nanowires composition, where the physical or chemical properties shown by the nanowires are completely an outcome from Co, Pt, P and Au elements. The individual CoPtP and Au segment was also measured by EDS for the confirmation of purity of Au and CoPtP elements (data not shown here). The nominal elemental atomic percent of CoPtP nanowires were shown as an inset table in Fig. 2.

The magnetic properties of CoPtP/Au multisegment nanowires and the CoPtP single segment nanowires embedded in a polycarbonate membrane were measured at room temperature with applied field parallel ($H_{\parallel}$) to the nanowire's long axis. The measured coercivity (H_c), saturation magnetization (Ms) and remanent magnetization (M_r) of $H_{\parallel}$ to CoPtP nanowires are 1.83 kOe, 35 memu and 28.5 memu, respectively (Fig. 3a). Moreover, the H_c of CoPtP/Au multisegment nanowires (1.85 kOe) is nearly consistent with the CoPtP single segment of nanowires, which indicates the hard magnetic property of the nanowires (Fig. 3b). However, the Ms and M_r values for CoPtP/Au mutisegment nanowires decreases to 3.5 and 2.6 memu, respectively, even though the length of both types of nanowires is almost same. This may be due to the replacement of CoPtP material by nonmagnetic materials Au with the same length of the nanowires.

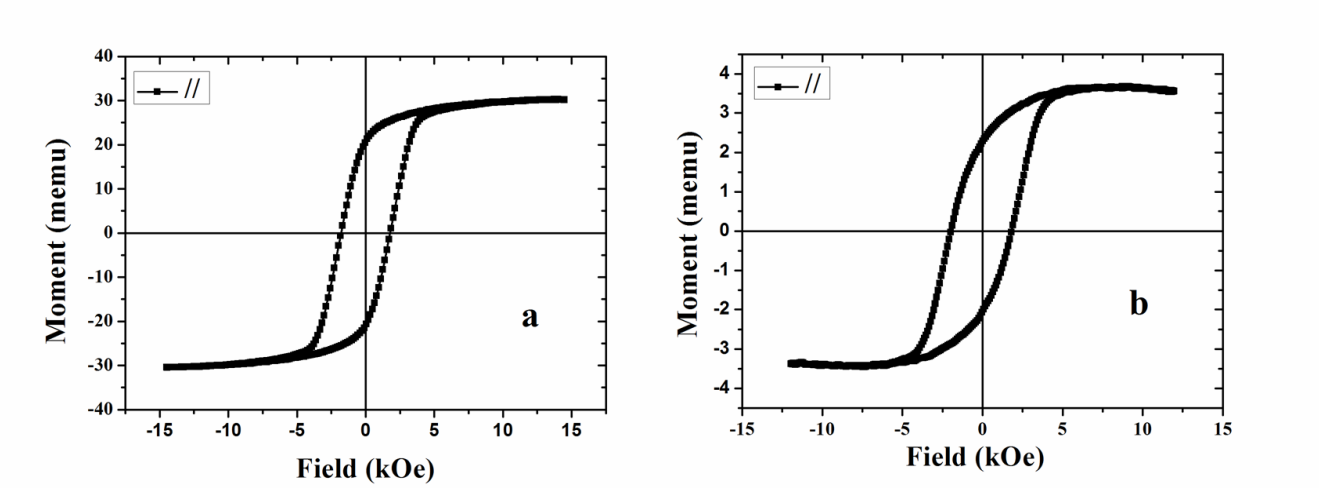

Figure 3. Hysteresis loops measured at room temperature of (a) CoPtP nanowires (b) CoPtP/Au multisegmented nanowires

3.2. Functionalization of ds-DNA on nanowire surfaces

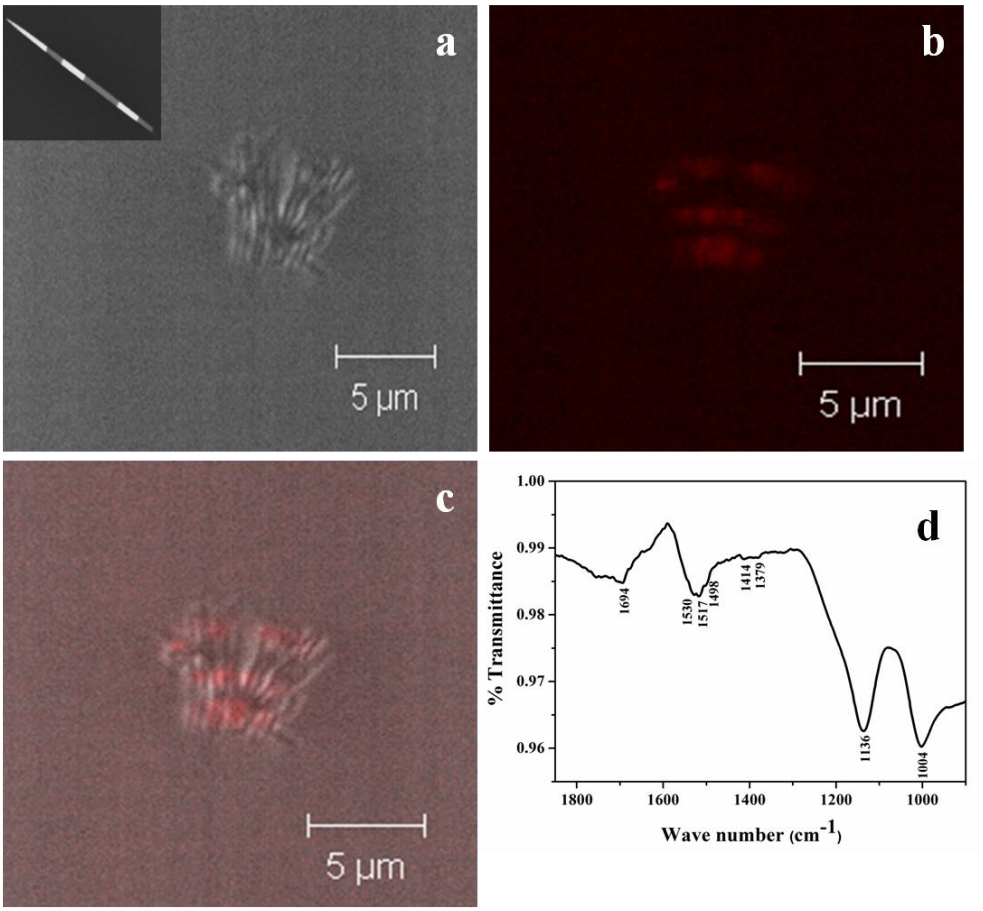

Figure 4. Confocal laser microscopy images of fluorescence ds-DNA loaded CoPtP/Au multisegment nanowires (a) Optical image (inset shows BS-SEM image of single nanowire) (b) Fluorescence image (c) overlapped image of optical and fluorescence image (d) FT-IR spectra of ds-DNA functionalized multisegmented nanowires.

Multisegment nanowires allot multiple ligands to adsorb on a different segment with multiple surface linkers. Especially, a carboxylic acid group has an affinity for metal oxide surfaces whereas thiols are a well known binding group for gold surfaces [19]. Here, we used thiolated fluorescent loaded ds-DNA for the surface functionalization of Au segment. The direct evidence of functionalization of ds-DNA on Au surface was confirmed by confocal laser microscopy. Fig. 4 (a) shows the optical image of a cluster of CoPtP/Au multisegmented nanowires. Fig.4 (b) represents the fluorescence images of the multisegment nanowires.

The fluorescence image shows that the fluorescence intensity is in alternative fashion as like the inset of Fig. 4 (a) (Inset shows the backscattering SEM image of single nanowire), which represents the Au and CoPtP segments in alternative. From the fluorescence image, it is clearly visible that the difference in intensity between Au and CoPtP segments, indicating the fluorescence comes from the Au segment as the thiolated ds-DNA is more specific to Au surface. Fig. 4 (c) represents the overlapped image of Fig. 3 (a & b), where both fluorescence and optical properties of nanowires is reflected.

The FT-IR spectrum of DNA functionalized multisegment nanowires is shown in Fig.4 (d). The broad absorption peaks observed at1004 and 1136 cm^{-1} were assigned to the stretching vibrations of P-O or C-O and C-O-P respectively. The peaks belonging to the phosphate backbone at ~ 1086 and ~1225 cm^{-1} are overlapped in the C-O-P stretching peak [20]. The peaks obtained at 1498, 1414 and 1379 cm^{-1} were arisen due to presence of base sugar moieties present in the DNA [21]. The two peaks observed at 1517 and 1530 cm^{-1} reflect the vibrations of C=C or C=N. FT-IR spectra of DNA loaded nanowires also showed the peak at 1694 cm^{-1} represents C=O groups in the guanine base present in the DNA. The overall observation confirms the DNA is successfully immobilized on the Au surface of the multisegment nanowires.

4. CONCLUSIONS

In summary, we have synthesized magnetic and nonmagnetic multisegment nanowires through electrochemical deposition technique, which indicates the hard magnetic property with high coercivity. We characterized the nanowires through different characterization techniques such as SEM, EDS and VSM. The length of the multisegmented nanowires is found to be around 6μm with CoPtP and Au in alternative fashion. We have functionalized the Au segment of the multisegment nanowires with fluorescent labeled ds-DNA and confirmed through confocal laser microscopy. The possible applications of this multisegment nanowires will be future multiplexing bioanalysis for simultaneous detection multiple analytes through magnetic methods.

ACKNOWLEDGMENT

This research was supported by World Class University (WCU) program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (R32-20026).

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