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Electrospinning Coating of Nitinol Guidewire with Manganese Ion Chelated Melanin Nanoparticles for Interventional Magnetic Resonance Imaging

Engin Baysoy[1,2], Bora Büyüksaraç[1], İdil Seçkin[1], Berk Kaleli[1], Efe Sönmez[1], Senem Avaz Seven[1], Alpay Özcan[2,3], Gizem Kaleli-Can[4]

[1]Bahçeşehir University,
Department of Biomedical Engineering, 34353, İstanbul, Türkiye
engin.baysoy@bau.edu.tr, bora.buyuksarac@bau.edu.tr, idilseckin@outlook.com.tr, berk.kaleli@bahcesehir.edu.tr, efe.sonmez@bahcesehir.edu.tr, senem.seven@bau.edu.tr
[2]Center for Targeted Therapy Technologies (CT3),
Boğaziçi University, Kandilli Campus, 34685, İstanbul, Türkiye
[3]Boğaziçi University
Department of Electrical and Electronics Engineering, 34342, İstanbul, Türkiye
alpay.ozcan@bogazici.edu.tr
[4]İzmir Demokrasi University,
Department of Biomedical Engineering, İzmir, 35140, Türkiye
gizemkaleli.can@idu.edu.tr

Abstract **-** Unlike X ray-based imaging modalities such as fluoroscopy, C-arm, angiography, and computed tomography which have adverse effects of ionizing radiation on both patient's body and medical staff during the interventional operations, magnetic resonance imaging (MRI) provides X ray free platform, high contrast in soft tissues and physiological data along with anatomical images which improves the accuracy of the diagnosis. Although many promising prototypes were fabricated in the past, the realization of interventional operations with the MRI guidance is still limited due to the lack of both MRI safe and MRI visible invasive medical devices. This study investigated the feasibility of electrospinning coating to enhance the visibility of MRI safe interventional instruments. For this purpose, a nitinol guidewire sample was coated with manganese (Mn^{2+}) chelated melanin nanoparticles (MNPs) using the electrospinning technique. A positive contrast (bright signal) provided by MNPs+Mn^{2+} deposition over nitinol guidewire sample was confirmed in images acquired using 7.0 T animal MRI scanner. Results including contrast to noise ratio values measured by DICOM Viewer and image processing showed that electrospinning presenting a promising coating technique for uniform deposition of metal ion-chelated MNPs over MRI safe invasive medical devices improving their traceability during interventional operations performed with MRI guidance.

Keywords**:** Electrospinning, Natural Melanin Nanoparticles, Magnetic Resonance Imaging, Interventional Magnetic Resonance Imaging.

1. Introduction

Interventional surgical operations with the guidance of X ray-based imaging modalities with minimal incisions are the primary treatment method for many vascular and cardiac disease that reduce mortality and morbidity rate, infection risk, recovery time, and overall cost of the procedure compared to open surgery. Alternative to X ray-based imaging modalities such as fluoroscopy, C-arm, angiography, and computed tomography that have adverse effects of ionizing radiation on both patient body and medical staff during the procedure, magnetic resonance imaging (MRI) provides X ray free platform, high contrast in soft tissues and physiological data together with anatomical images that improves the accuracy of the diagnosis [1-4]. However, interventional operations with MRI guidance are still challenging due to high magnetic field in the MRI room, heating risk during the radio frequency (RF) transmission at imaging [5-9]. Although implementing diamagnetic, paramagnetic, and ferromagnetic materials at the tip or outer surface of the MRI safe guidewires, catheters, needles is one of the solutions to increase the visibility inside MR images, limited durability, biocompatibility, and contrast to noise ratio (CNR) are the main constraints to overcome for commercial products [11-15]. Over the last decade, natural and synthetic melanin nanoparticles are used in biomedical applications of many researchers with their distinguishable characteristics including high biocompatibility, biodegradability, UV absorption and photocatalytic activity, binding affinity toward various metal ions and biomolecules [16-20]. Sesame, fungi, black tea leaves, chestnut shell, cuttlefish ink can be natural resources of melanin nanoparticles that show high paramagnetic characteristics for MR imaging when they are bound with metal ions [19-24]. To date, cations including iron (Fe^{3+}), manganese (Mn^{2+}), cupper (Cu^{2+}) have been employed to chelate with natural melanin nanoparticles (MNPs) to enhance T1 shortening effect in MR images that result in positive contrast compared to background anatomy [24-26]. One of our recent studies focused on coating of Mn^{2+} chelated MNPs (MNPs-Mn^{2+}) over MRI-compatible guidewires samples made of nitinol, titanium and 316-L stainless steel using a dip coating method and investigating visibility of them under 7T MR scanner [27]. Acquired MR images approved the increased visibility of coated nitinol guidewire samples with MNPs-Mn^{2+} coating by providing a distinctive bright signal compared to uncoated samples. However, the coating quality of nitinol guidewire samples in terms of uniformity was still open to improvement. Therefore, this study focused on improving the deposition of MNPs-Mn^{2+} and enabling more uniform coatings over nitinol guidewire surface by employing electrospinning method. Electrospinning is a cost effective and versatile electro-hydrodynamic-based technique for manufacturing polymeric and non-polymeric fibers within diameters of nanometers and micrometers that can be used in many applications such as biomedical engineering, tissue engineering, electronics and energy [28-30]. Electrospinning applies high voltage to enable nanofibers in varied morphological structures by changing operating parameters like the concentration, conductivity, viscosity, molecular weight of polymer solution, the types of the needle gauge and the collector, the distance between the needle gauge and collector, and the ambient conditions such as temperature and humidity during the procedure [28-30]. This study aimed to improve the traceability of MRI safe nitinol guidewire samples under MRI by coating them with MNPs-Mn^{2+} using modified electrospinning technique.

2. Materials and Methods

2.1. Extraction of MNPs & Chelation with Mn^{2+}

Natural MNPs were extracted from ink sacs of squid (Sepia officinalis) and purified by washing and centrifugation without the use of any chemicals by following the procedures initially described by Eom and his colleagues [31]. The chelation of Mn^{2+} ions with MNPs was provided by a simple mixing technique including a solution of MNPs (1 mg/mL), Mn^{2+} solution (1 mg/mL) in a ratio of 100:1 (v/v). To remove unchelated Mn^{2+} ions, the mixture was centrifuged at 10,000 rpm as described in [27].

2.2. Modified Electrospinning Coating Process

A commercial electrospinning machine (NANOLIZ, NL-ES 02) was enriched with custom-designed sample holder and a controlled rotating system to ensure uniform coating. Remote controlled rotating system incorporates an infrared sensor receiver and transmitter, a DC motor and a L268N DC motor driver allowing precise rotation at predetermined rpm values with remote control capabilities. A 3D CAD application, SolidWorks was used for designing the sample holder that has a modular and Lego-like structure. Coating holder comprises a main box, support box, base system, and elevation plates to facilitate effortless setup and adaptation to diverse experimental configurations including height and distance adjustments as shown in Fig. 1. The solution used for the electrospinning process was prepared using 1 gr of polycaprolactone (PCL), 19 mL of chloroform, 3 mL of methanol, and 100 mg of MNP+Mn^{2+}. The electrospinning process was performed when the distance between the syringe nozzle and nitinol sample was 11cm, the flow rate was 0.2 mL/h, and the applied voltage was 14 kV.

2.3. Visualization of Coated Nitinol Samples with MRI

MR Images of MNPs+Mn^{2+} coated nitinol guidewire samples were acquired using a custom-made phantom (containing saline water) and a 7.0 T animal MRI scanner (MR Solutions, MRS*DRYMAG) by performing a spin echo sequence with TR/TE:400/11 ms, slice thickness:1.0 mm, flip angle: 90^0.

3. Results

The effect of the MNPs+Mn^{2+} coating was observed as a conspicuous bright signal at both the shaft and distal tip of the nitinol guidewire in the coronal MR image as shown in Fig. 2. The brighter spots at the tip ease the traceability of the nitinol guidewire compared to the background. The mean contrast to noise ratio (CNR) values of the bright spots and the saline water (used as a control) inside the phantom were measured as 6154 and 1892, respectively using DICOM Viewer. These results indicate that that the deposition of MNPs+Mn^{2+} on the surface of the nitinol guidewire provides significantly higher contrast enhancing the visibility of the MRI safe material within MR image. To further confirm the effect of the MNPs+Mn^{2+} coating along the shaft of the nitinol guidewire within the MR image, a coated section was cropped and rotated 90^0 to highlight the area where the guidewire is visible as shown in Fig. 3. Three regions in this image were then segmented using a region-growing algorithm in MATLAB. Several seed points were selected within these regions, with a maximum distance set to 0.2 mm. The method's accuracy was validated by correctly calculating the wire's diameter, which is 1.00 mm. The coating was labelled as top and bottom based on its position along the wire. The mean and standard deviations of the top and bottom coating thicknesses were calculated as 0.27 ± 0.04 mm and 0.21 ± 0.04 mm, respectively.

4. Conclusion

This study investigated the feasibility of using electrospinning technique to coat MNPs-Mn^{2+} onto the surface of a nitinol guidewire to enhance the visibility in MR images. Results including CNR value measurements via DICOM Viewer and image processing indicated that uniform MNPs-Mn^{2+} deposition was successfully achieved both at the shaft and the tip of the nitinol guidewire, resulting in a distinctive positive contrast shown as bright signal. We believe that optimization of electrospinning parameters such as flow rate, applied voltage, and the distance between the nozzle and samples will further increase the efficiency of the technique in the future. In conclusion, electrospinning presenting a promising coating technique for the uniform deposition of metal ion chelated MNPs onto MRI safe invasive medical devices improving their traceability during interventional operations performed with MRI guidance.

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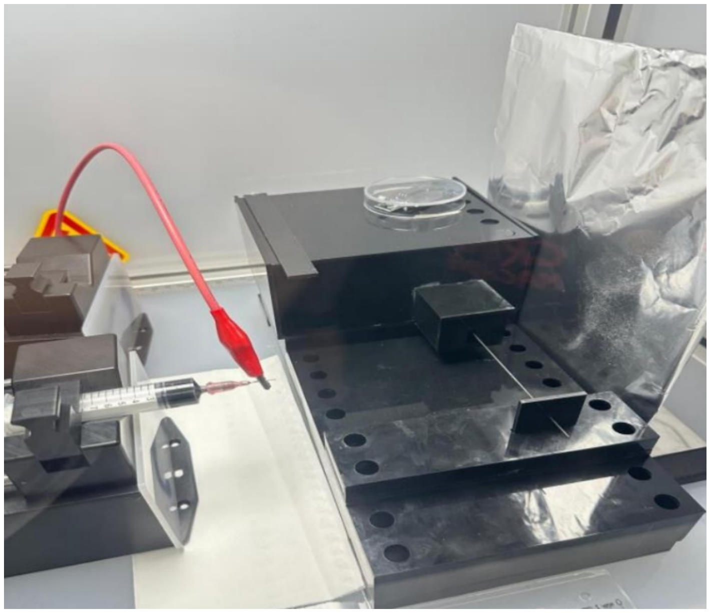

Fig. 1: The View of Electrospinning Coating Process with Nitinol Guidewire Holder Apparatus.

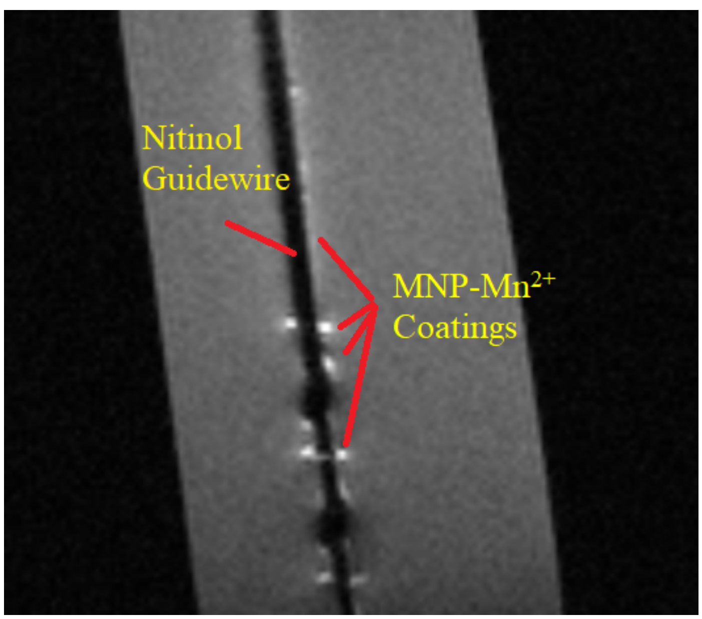

Fig. 2: Coronal image of MNP-Mn^{2+} coated nitinol guidewire was acquired when TR/TE:400/11 ms, slice thickness:1.0 mm, flip angle: 90^0. Positive contrast observed with bright signals indicates the MNP-Mn^{2+} deposition over nitinol guidewire.

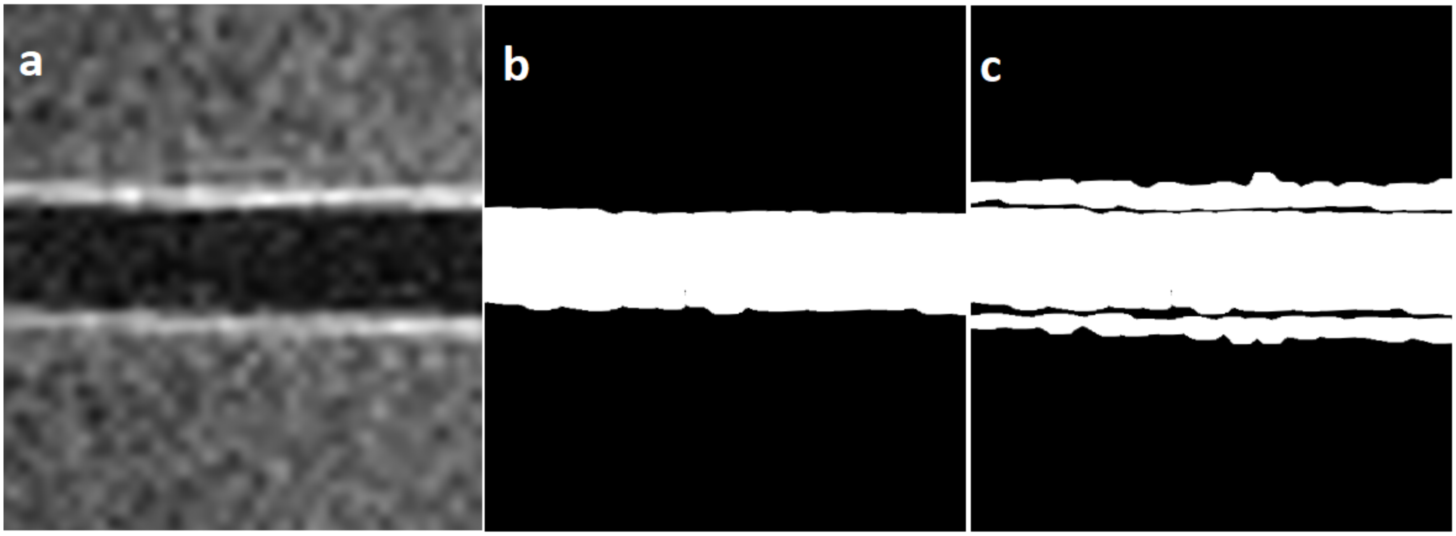

Fig. 3: a) Cropped MR image displaying the wire and coating at the shaft of the nitinol guidewire sample. b) Binary image of the nitinol wire obtained using the region-growing method. c) Binary image of the wire and coating obtained using the region-growing method.

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