

# Journal of Materials Chemistry C

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## Remote, fast actuation of programmable multiple shape memory composites by magnetic fields

Received 00th January 20xx,  
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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**Nonwoven fiber composite Nafion/Fe<sub>3</sub>O<sub>4</sub> films can be programmed to adopt over 5 shapes, and several fast transformations in sequence are demonstrated using different intensities of the same stimulus. We use an alternating magnetic field to activate the transformations remotely and investigate the conditions for tunable actuation control. Since the heat is generated inside the shape-changing films, though locally temperatures > 80 or 100 °C are achieved, their surface temperature can be kept below 38-40 °C.**

Discovered in 1980s, shape memory polymers (SMPs) have been engineered to respond to an impressive variety of stimuli, including heat, electricity, magnetism, light, water, microwave, and chemical solvent.[1-4] Their autonomous performance enables development of applications in a variety of industrial and consumer applications, including aerospace, biomedical engineering, sensors and actuators, smart textiles, adaptive optical devices.[5,6] Recently the combination of shape-memory and ionic actuation has been used to program movement.[7,8] They have also been incorporated into programmable SMPs have the ability to be programmed with a specific shape, material stiffness or strain, and then recall to their permanent shapes upon exposure to external stimuli. [9,10] In recent years, increasing numbers of SMP materials have been processed into fiber by electrospinning. [11-13] The resulting structures are nonwoven porous materials with large specific surface area and permeability, bringing potential applications in biomedical technology and tissue engineering.[14-16] There is a need, however, for programmable porous smart materials to perform more than on action, or recall more than one shape, as has

been shown by several investigators.[17] Magnetic field-induced shape change has distinct advantages for effective and fast local heating as well as being a non-contact method allowing remote control. [18] Unlike most light wavelengths, it has full penetration in the human body without attenuation.

Programmable biomedically compatible materials robots and actuator materials promise to bring enhancements to minimally invasive and non-invasive surgery, other medical procedures, and active tissue scaffolds. They are also promising for autonomous sensing-and-response modules in robotics and MEMS devices, responsive filters, and smart fabrics. Current materials need different types of stimuli to perform multiple actions, usually perform single movements, and are driven by stimuli, such as direct heating, which are hard to apply through live human tissues. To actuate SMPs using magnetic fields, some magnetic particles including Fe<sub>3</sub>O<sub>4</sub> and Ni have been added to the polymer matrix. The use of magnetic field heating is advantageous both because it can be applied remotely, and because it has full penetration in the human body without attenuation. For example, Shaobing Zhou and coworkers have found that the addition of Fe<sub>3</sub>O<sub>4</sub> as filler in the polycaprolactone (PCL) matrix induced shape recovery performance, demonstrating the remote actuation. Cytotoxicity tests of the PCL/Fe<sub>3</sub>O<sub>4</sub> composite fibers show these smart nanofibers are suitable for use in the biomedical field. [19] There is a need, however, for programmable porous smart materials to perform.

In this work, we build upon our previous work of electrospun Nafion nanofibers with quintuple shape memory effect, to fabricate composite magnetic Nafion/Fe<sub>3</sub>O<sub>4</sub> nanofibers.[17] The non-woven fibers show excellent porosity, and can be programmed to recall several shapes sequentially. By using different power settings, we can trigger all the transformations in a sequence of < 18 seconds, or achieve a particular desired shape. Since the heating is internal to the shapes, their outside temperature never exceeds 38-40 °C. We show the response speed is fast, on the order of seconds, and perform systematic comparisons between the temperatures

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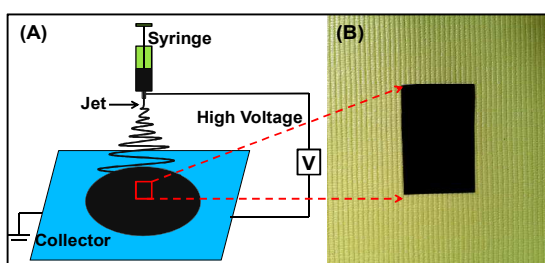
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† Electronic Supplementary Information (ESI) available: Materials and experimental details, Figs. S1, S2, S3, S4, S5 and S6. See DOI: 10.1039/x0xx00000x

needed to trigger the different programmed transitions by direct heating and by magnetic heating.

1.0 wt% PEO powder was added in the 5.0 wt% Nafion solution to form the electrospinning solution, and dissolved after stirring at room temperature for 3 h. Then the  $\text{Fe}_3\text{O}_4$  nanopowder was added in the above solution to prepare the Nafion/ $\text{Fe}_3\text{O}_4$  composite solutions, named after their respective  $\text{Fe}_3\text{O}_4$  concentrations 15%  $\text{Fe}_3\text{O}_4$ , 20%  $\text{Fe}_3\text{O}_4$ , and 25%  $\text{Fe}_3\text{O}_4$ , respectively. The schematic illustration of electrospinning apparatus is shown in Scheme 1A. The typical electrospinning condition was: applied voltage 30 kV; distance between tip and collector = 15 cm; feed rate = 3 mm/min; relative humidity = 50%. The inner diameters of syringe and needle are 10 mm and 0.8 mm, respectively. The resulting fibrous membranes were obtained after being annealed at 120 °C for 30 min in air, as shown in Scheme 1B.



Scheme 1 Schematic illustration of electrospinning (A) and photo of Nafion/ $\text{Fe}_3\text{O}_4$  nanofibers (B).

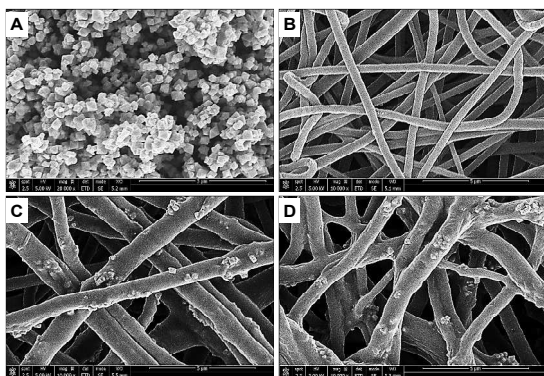


Fig. 1 SEM images: (A)  $\text{Fe}_3\text{O}_4$ , (B) Nafion fibers, (C) Nafion/ $\text{Fe}_3\text{O}_4$  composite fibers and (D) recovered Nafion/ $\text{Fe}_3\text{O}_4$  composite fibres after magnetic field actuation.

The  $\text{Fe}_3\text{O}_4$  nanopowders were directly added to the Nafion solutions as functional fillers to obtain the composite fibres with both shape-memory and self-heating functionalities.  $\text{Fe}_3\text{O}_4$  with the mean diameter of 50 nm, the morphology is shown in Fig 1A. SEM images demonstrate pure Nafion fibres uniform in diameter about 350 nm (Fig 1B) or Nafion/ $\text{Fe}_3\text{O}_4$  composite nanofibers about 800 nm (Fig 1C). The  $\text{Fe}_3\text{O}_4$  particles are uniformly distributed in the fibres. With the addition of  $\text{Fe}_3\text{O}_4$ , the diameters increase because of the increase of viscosity of the electrospinning solutions. Before

characterizing other properties, the electropun fibres were tested for stability to exposure to different temperate, their structure remaining stable up to 90 °C with only a slight onset of melting at 110 °C (see supporting information Fig S1). This morphology is consistent with that of the sample whose shape was recovered after magnetic field heating (Fig. 1D). It is significant to demonstrate that programming and magnetic recovery preserves the porous structure for some applications since sometimes the small diameter of electrospun fibres makes them susceptible to melting at temperatures far below bulk material melting temperatures.

Direct heating limits many practical applications, as the whole environment of the material needs to be heated. A much more efficient strategy and one that can be applied remotely is to use the material itself as the source of heat. Iron oxide particles can be heated by a remote alternating magnetic field and were used as an internal source of heat. The magnetic field is applied by 4-turn coil of a 4 mm tube coiled to 20 mm diameter. AC electric fields of 2 KW, 50-200 kHz were passed through the coil. In addition to power, the concentration of  $\text{Fe}_3\text{O}_4$  can be used to control the heat generation intensity, as it also increases the saturation magnetization of the composite fibers (Fig S2), and the coupling to the magnetic field. The increase of  $\text{Fe}_3\text{O}_4$  induces a slight decrease of mechanical strength of the composite films (Fig S3), but the addition of  $\text{Fe}_3\text{O}_4$  particles has no effect on the shape memory behaviour. For a single shape-change after three consecutive program/recovery cycles induced by heat, the fixity and shape recovery ratios are all above 90% (Fig S4). The sample deformed as an “N” at 90 °C can recover to its original shape when exposed to AC magnetic fields within 16 seconds. Using Nafion’s broad glass transition we were also able to program and recover several shapes in the same sample.

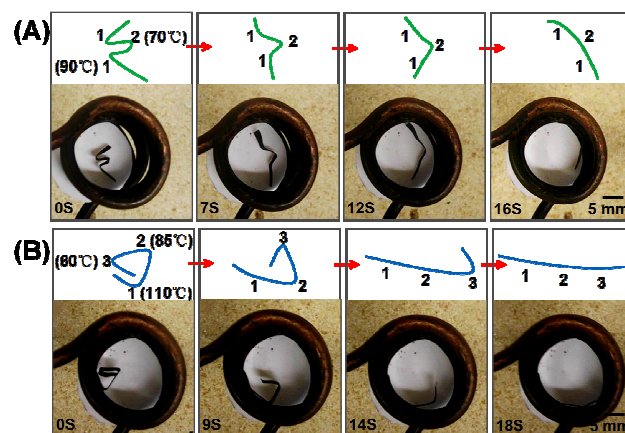


Fig. 2 2D shape recovery performance: (A) Visual demonstration triple shape recovery process induced by magnetic field, (B) quadruple shape recovery performance induced by magnetic field.

The recovery by magnetic fields is qualitatively different from direct heating, where shapes are programmed at specific transition temperatures and traditionally later recovered at the same temperatures.[9] By generating heat internally, the nanoparticles

can activate different parts of the glass transition, corresponding to heating over 110 °C, while heat diffusion maintains the surface temperature of the bulk sample at only 40 °C or less. The samples were cut into strips of 18 mm × 4.5 mm × 0.18 mm. A triple shape memory sample (that can remember two temporary shapes) (Fig 2A) and quadruple-shape memory one (that can remember three temporary shapes)(Fig 2B), programmed between 60 and 110 °C, were recovered sequentially at different magnetic field powers, between 50 and 100 % of max power. DMA mechanical cycle tests were carried out to quantify the triple- and quadruple- shape memory behaviour (Fig S5). The shape fixity and recovery ratios are listed in Tab 1 (see supplementary information). The shape recovery speed increased with increase in the output power (Fig S6).

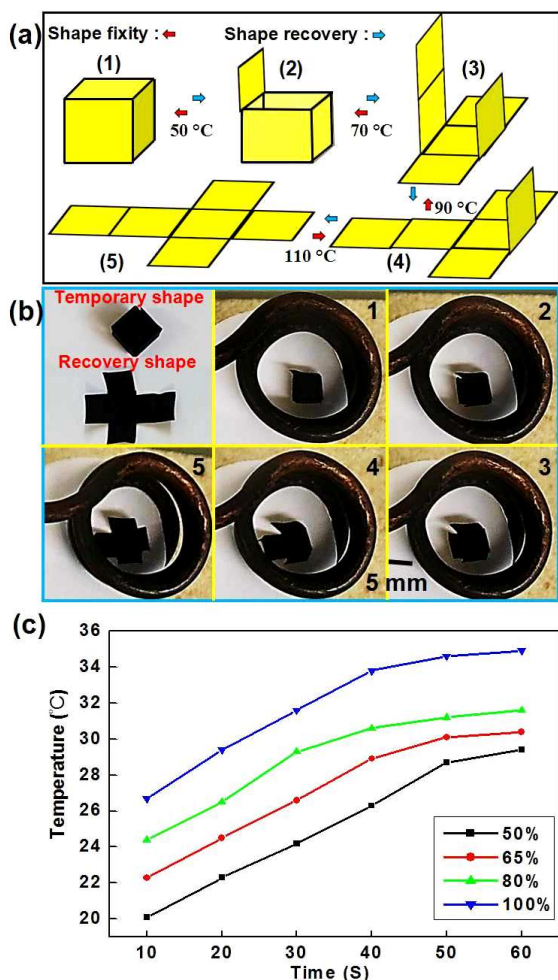


Fig. 3 3D shape recovery performance: (A) the designed shape recovery process of box, (B) magnetic field actuated shape recovery, (C) Temperature vs time at different output powers.

Using different output powers to actuate specific programmed shape transitions can be used for the practical folding of origami and other 3D objects remotely. Fig 3A shows the schematic diagram

of multiple shape programming (at 50 °C, 70 °C, 90 °C and 110 °C) and the subsequent stage-wise recovery process. The composite film was deformed into a box as a complex temporary shape. The unfolding behaviour of the smart box is actuated putting in the magnetic coil by magnetic field heating at different output powers (Fig 3B). The size of the box was 5.5 mm × 5.5 mm × 5.5 mm. The thickness of the film was 0.18 mm. The three dimensional box unfolded back from the temporary shape to a flat sheet step by step. Magnetic field powers of 50%, 65%, 80% and 100% were necessary to activate the folds programmed at 50 °C, 70 °C, 90 °C and 110 °C respectively. During the multi-shape recovery process, the surface temperature of the sample is in the range of 20 to 40 °C (Fig 3C). This result means that the non-direct heating and actuation of multi-shape memory materials can be utilized in implants and elsewhere in biomedical science.

## Conclusions

In summary, we have designed multi- shape programmable actuators that can be controlled remotely by magnetic fields to realize multiple 2D and 3D shape transformations. The samples are fabricated by incorporating Fe<sub>3</sub>O<sub>4</sub> into Nafion nonwoven nanofiber fabrics through electrospinning. The internal triggering of the programmed transformations with a magnetic field is advantageous because magnetic fields have full penetration through the human body without attenuation. Furthermore, the surface temperature of the structures through all the transformations remains at or below body temperature, a sharp departure from direct heating methods. The magnetic field triggered recovery behaviour is fast and controllable and different output powers can be used to recover different shapes. This smart composite material and the method of programming and remote actuation have future potential biomedical applications.

## Acknowledgments

This work is supported by the National Natural Science Foundation of China (Grant No.11225211 and No.11272106). This work is also funded by the European Research Council (ERC) grant EMATTER (#280078). Fenghua Zhang would also like to thank Chinese Scholarship Council (CSC) for funding her research work at the University of Cambridge.

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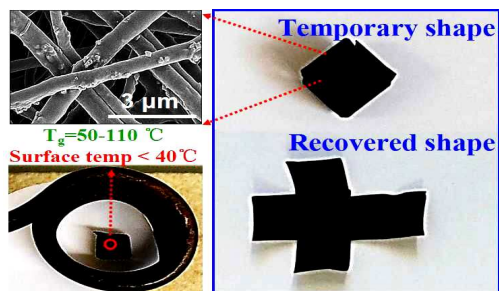
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## Graphical Abstract



Magnetic field actuated shape recovery behavior of 3D box folded by Nafion/ $\text{Fe}_3\text{O}_4$  composite membrane, surface temperature is near body temperature.