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

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Nonwoven fiber composite Nafion/Fe_3O_4 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, microwaves, and chemical solvents.[1–4] Their autonomous performance enables the development of applications in a variety of industrial and consumer applications, including aerospace, biomedical engineering, sensors and actuators, smart textiles, and 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 which have the ability to be programmed with a specific shape, material stiffness or strain, and then recall their permanent shapes upon exposure to external stimuli.[9,10] In recent years, increasing numbers of SMP materials have been processed into fibers 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 one action, or recall more than one shape, as has been shown by several investigators.[17] The 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 such as 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_3O_4 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_3O_4 as a filler into a polycaprolactone (PCL) matrix induced shape recovery performance, demonstrating remote actuation. Cytotoxicity tests of the PCL/Fe_3O_4 composite fibers show that these smart nanofibers are suitable for use in the biomedical field.[19] There is a need, however, for programmable porous smart materials to perform like origami.

In this work, we build upon our previous work of electrospun Nafion nanofibers with a quintuple shape memory effect, to fabricate composite magnetic Nafion/Fe_3O_4 nanofibers.[17] The nonwoven 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 heat is generated inside the shapes, their outside temperature never exceeds 38–40 °C. We show that the response speed is fast, on the order of seconds, and perform systematic comparisons between the temperatures needed to trigger the different

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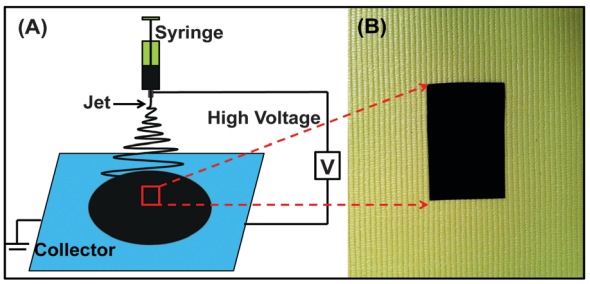

Scheme 1 Schematic illustration of electrospinning (A) and photo of Nafion/Fe_3O_4 nanofibers (B).

programmed transitions by direct heating and by magnetic heating.

1.0 wt% PEO powder was added to 5.0 wt% Nafion solution to form the electrospinning solution, and dissolved after stirring at room temperature for 3 h. Then Fe_3O_4 nanopowder was added to the above solution to prepare the Nafion/Fe_3O_4 composite solutions, named after their respective Fe_3O_4 concentrations as 15% Fe_3O_4, 20% Fe_3O_4, and 25% Fe_3O_4, respectively. A schematic illustration of the electrospinning apparatus is shown in Scheme 1A. The typical electrospinning conditions were: applied voltage 30 kV; distance between the tip and the collector = 15 cm; feed rate = 3 mm min^{-1}; relative humidity = 50%. The inner diameters of the syringe and the 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.

The Fe_3O_4 nanopowders were directly added to the Nafion solutions as functional fillers to obtain composite fibres with both shape-memory and self-heating functionalities. For Fe_3O_4 with a mean diameter of 50 nm, the morphology is shown in Fig. 1A. SEM images demonstrate pure Nafion fibres uniform in diameter of about 350 nm (Fig. 1B) or Nafion/Fe_3O_4 composite nanofibers of about 800 nm (Fig. 1C). The Fe_3O_4 particles are uniformly distributed in the fibres. With the addition of Fe_3O_4, the diameters increase because of the increase in viscosity of the electrospinning solutions. Before characterizing other properties, the electrospun fibres were tested for stability when exposed to

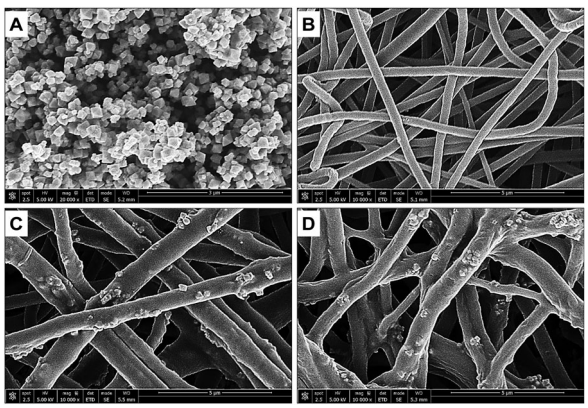

Fig. 1 SEM images of: (A) Fe_3O_4, (B) Nafion fibers, (C) Nafion/Fe_3O_4 composite fibers and (D) recovered Nafion/Fe_3O_4 composite fibres after magnetic field actuation.

different temperatures, their structure remaining stable up to 90 °C with only a slight onset of melting at 110 °C (see Fig. S1, ESI†). 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 fibers 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 internal sources of heat. The magnetic field is applied by a 4-turn coil of a 4 mm tube coiled to 20 mm diameter. AC electric fields of 2 kW and 50–200 kHz were passed through the coil. In addition to power, the concentration of Fe_3O_4 can be used to control the heat generation intensity, as it also increases the saturation magnetization of the composite fibers (Fig. S2, ESI†), and the coupling to the magnetic field. The increase in the amount of Fe_3O_4 induces a slight decrease of the mechanical strength of the composite films (Fig. S3, ESI†), but the addition of Fe_3O_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, ESI†). 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.

The recovery by magnetic fields is qualitatively different from that by 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 a 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 the max power. DMA mechanical cycle tests were carried out to quantify the triple- and quadruple-shape memory behaviour (Fig. S5, ESI†). The shape fixity and recovery ratios are listed in Table S1 (see ESI†). The shape recovery speed increased with an increase in the output power (Fig. S6, ESI†).

Different output powers can be used to actuate specifically programmed shape transitions for the practical folding of origami and other 3D objects remotely. Fig. 3A shows a 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 by putting it in a

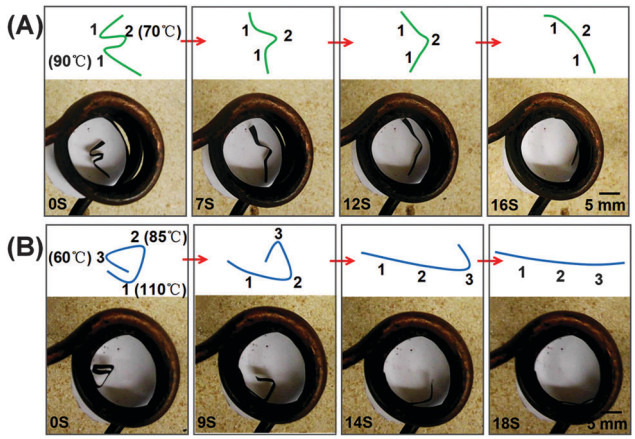

Fig. 2 2D shape recovery performance: (A) visual demonstration triple shape recovery process induced by magnetic fields and (B) quadruple shape recovery performance induced by magnetic fields.

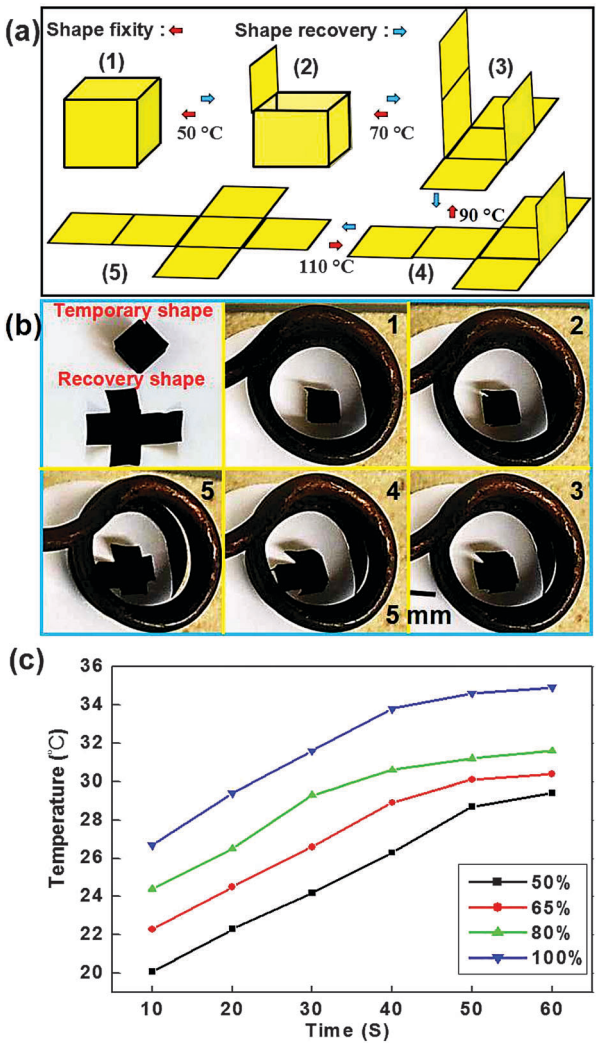

Fig. 3 3D shape recovery performance of: (A) the designed shape recovery process of the box, (B) magnetic field actuated shape recovery, and (C) temperature *vs.* time at different output powers.

magnetic coil with 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 was 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_3O_4 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.

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