All-printed magnetically self-healing electrochemical devices

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The present work demonstrates the synthesis and application of permanent magnetic Nd₂Fe₁₄B microparticle (NMP)-loaded graphitic inks for realizing rapidly self-healing inexpensive printed electrochemical devices. The incorporation of NMPs into the printable ink imparts impressive self-healing ability to the printed conducting trace, with rapid (~50 ms) recovery of repeated large (3 mm) damages at the same or different locations without any user intervention or external trigger. The permanent and surrounding-insensitive magnetic properties of the NMPs thus result in long-lasting ability to repair extreme levels of damage, independent of ambient conditions. This remarkable self-healing capability has not been reported for existing man-made self-healing systems and offers distinct advantages over common capsule and intrinsically self-healing systems. The printed system has been characterized by leveraging crystallographic, magnetic hysteresis, microscopic imaging, electrical conductivity, and electrochemical techniques. The real-life applicability of the new self-healing concept is demonstrated for the autonomous repair of all-printed batteries, electrochemical sensors, and wearable textile-based electrical circuits, indicating considerable promise for widespread practical applications and long-lasting printed electronic devices.

INTRODUCTION

Degradation due to mechanical deformation and the concomitant dysfunctioning of man-made systems is a major cause of concern in numerous technological fields (1, 2). Extensive efforts have been devoted to addressing this issue by developing new stretchable and tough materials that can withstand mechanical deformations and thus augment the life span of devices (3, 4). However, stretchable devices fail if the strain exceeds a particular limit. Biological systems have addressed this issue by mastering remarkable self-healing properties (5, 6). Taking a cue from nature, materials scientists have recently focused on developing innovative materials to realize man-made self-healing systems (7, 8). The enhanced lifetime of these self-healing systems is quite attractive, especially in scenarios where replacing a mechanically damaged component is either expensive or cumbersome. Fragility is the “Achilles' heel” of the multibillion dollar field of printed electronics. Development of self-healing inks will thus be germane to printed electronics for their numerous applications in scenarios where mechanical damage of devices is common (9, 10).

Man-made self-healing systems are commonly based on microcapsules (11, 12), vesicles (13), or intrinsic properties (14). Of these, capsule-based systems have been explored recently for realizing self-healing printed devices (12, 15). Although capsule-based systems are attractive, they have several inherent limitations. For example, these systems cannot self-heal multiple damages at the same location because almost all the capsules along the path of the damage become ruptured and in situ refilling of the broken capsules is impossible. These cannot heal macroscopic cracks. Furthermore, the capsules are usually much larger than the conductive particles of the inks and thus compromise their uniform dispersion within the printed film. Therefore, healing takes place only at locations where capsules are present. Increasing the capsule loading is an unavailable route to achieving homogeneous dispersion because the nonconductive nature of the capsules significantly increases the resistivity of the printed films. In addition, the capsules encapsulate an organic solvent, which can gradually evaporate through the minute pore defects in the capsule wall, thus limiting the life span of the healing ability. Finally, an organic solvent-based healing system is unsuitable for various applications, such as wearable/implantable electronics, where the device is in intimate contact with biological tissues.

The present work overcomes all the above challenges by developing magnetically self-healing graphitic ink. The ink has been formulated to include permanent magnetic Nd₂Fe₁₄B microparticles (NMPs) that impart remarkable self-healing ability to the printed films. We refer to the self-healing process as intrinsic-based because the NMPs are uniformly dispersed within the ink, thus allowing the printed system to self-repair irrespective of the location of damage—a property characteristic of intrinsically self-healing systems. The strong magnetic attraction between the NMPs allows the printed films to spontaneously and autonomously recover the mechanical and electrical contacts even when the damage is as wide as 3 mm—a feat that has not been reported to date by any self-healing system (Fig. 1A and movie S1). There have been several demonstrated examples of intrinsically self-healing systems (14, 16–18). However, these are incompatible with printing processes and limited to microscale damages; require an external trigger to initiate the healing process, manual pressing of the broken pieces, and very long self-healing time; and/or must be hydrated. Also, the broken pieces must be joined immediately. Furthermore, almost all the intrinsically self-healing systems rely on special chemistries to initiate the self-recovery process. These chemical interaction-based self-healing processes can be easily inhibited by the ambient conditions. The present magnetic self-healing system addresses the above issues faced by both capsule- and intrinsic-based self-healing systems, because the magnetic nature of the healing process permits the printed devices to instantly self-repair multiple damages at the same or different locations without the requirement of an external trigger. In addition, the conductive nature of the NMPs does not affect the resistivity of the printed trace, and the permanent magnetism of the NMPs imparts remarkably long-lasting self-healing capability for numerous repair events. Compared to many intrinsically self-healing systems, the present self-healing process relies on the physical attraction between NMPs, which is unaffected by a wide range of ambient conditions.

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There have been some examples of magnetically self-healing systems (19–23). However, these systems rely on iron oxide particles and thus require an external trigger to initiate the self-healing process. In contrast, the present system is based on NMPs that have permanent magnetic properties, and hence, it autonomously initiates the healing process. Furthermore, well-established computer simulations and models to predict a system’s behavior based on the attractive forces between magnetic particles can be exploited to design novel inks with tailor-made self-healing properties (24, 25). The present article demonstrates the synthesis of the magnetically self-healing graphite ink toward realizing all-printed self-healing electrochemical sensors, batteries, and wearable textile-based electrical circuits that can instantly recover repeated macroscopic damages as wide as 3 mm at the same or different locations. The generic self-healing ink formulation technique discussed in this work can be easily applied for developing inks containing other fillers for printing self-healing devices that cater to a wide range of applications and printed electronic devices.

RESULTS
Rationale for ink formulation, printing process, and self-healing property
The aim of the present work was to develop a printable ink that can address the issues inherent to capsule- and intrinsic-based self-healing systems to realize rapidly self-healing low-cost printed electronic devices with special emphasis on electrochemical sensors and batteries. NMPs have several advantages for realizing conductive self-healing systems. For example, NMPs have a strong permanent magnetic field that can span an area much larger than their size. They have high electrical conductivity and therefore can be used to realize conductive devices. Finally, Nd\textsubscript{2}Fe\textsubscript{14}B is inexpensive and widely available. Therefore, NMPs were considered as ink fillers to impart self-healing ability. Although NMPs have high conductivity, they do have poor electrochemical properties, as was noticed during preliminary cyclic voltammetric (CV) experiments. Carbon black (CB) is a widely explored material for fabricating electrochemical systems, such as batteries (26) and sensors (27), owing to its excellent electrochemical properties, high conductivity, large surface area, and low cost. Therefore, CB was considered as the second filler component of the self-healing ink to incorporate favorable electrochemical properties to the printable self-healing ink. Polystyrene-block-polyisoprene-block-polystyrene (SIS) was considered as the ink binder because it offers homogeneous dispersion of both NMPs and CB and firmly binds the fillers to avoid material loss when exposed to liquid media, as demonstrated later in various electrochemical experiments (described below).

The healing ability of the present system relies on the orientation of the net magnetic field of the NMPs dispersed within the printed film. In the absence of an external magnetic field, the magnetic field of an NMP is neutralized by that of neighboring NMPs, leading to printed films with a net zero magnetic field. These films fail to demonstrate self-healing ability. However, when a self-healing circuit is fabricated by aligning the NMPs, the printed film behaves like a bar magnet (left image + scheme). When the trace is severed, the two pieces behave as individual bar magnets, with opposite poles attracting each other (middle image + scheme). The strong magnetic attraction between the two severed pieces forces them to move toward each other to regain the mechanical and electrical connectivity (right image + scheme).
properties because of the absence of an anisotropic magnetic field within the printed film. This issue was addressed by printing the ink in the presence of an external magnetic field (details about printing are discussed in Materials and Methods and illustrated in movie S2). When the ink is printed onto the substrate, the NMPs are initially oriented randomly within the printed trace. However, the NMPs immediately orient themselves along the external magnetic field to produce a net magnetic field along the direction of the trace. The resulting printed film behaves like a permanent magnet, with the two poles at the two ends of the trace (Fig. 1A, top left schematic). When the printed trace is damaged, the two damaged pieces behave as individual permanent magnets (Fig. 1A, top center schematic) that immediately attach to each other via magnetic force and thus self-heal (Fig. 1A, top right schematic). An attractive feature of the permanent magnetic nature of the system is that the printed films demonstrate self-healing ability for a large number of damage-heal cycles under a wide range of ambient conditions. The strength of the magnetic force depends on the amount of NMPs in the ink, and the printed film is expected to have sufficient maximum energy product \((BH)_{\text{max}}\) to impart rapid self-healing of macroscopic damages. \((BH)_{\text{max}}\) is directly proportional to the volume fraction of the nonmagnetic component as described by Eq. 1 (28)

\[
(BH)_{\text{max}} \propto \left(1 - V_{\text{non}}\right) \frac{d}{d_m} B_r(p)
\]

Here, \(V_{\text{non}}\) is the volume fraction of the nonmagnetic components, \(d\) is the density of the magnet, \(d_m\) is the theoretical density of ideal bonded NMPs, and \(B_r(p)\) is the remanence magnetization of the NMPs. As evident from Eq. 1, a higher volume fraction of the NMPs will lead to printed films with a higher healing ability. Therefore, inks containing different ratios of NMPs and CB were first prepared to identify the best composition that offered a strong healing ability and an attractive electrochemical response. Ultimately, a weight ratio of 8:1 (NMPs/CB) was selected because it offered very rapid self-healing and a favorable electrochemical behavior. The self-healed films can be easily lifted against gravity without damaging the film at the healed location because of the strong magnetic attraction between the NMPs (movie S3).

**Microscopic imaging and magnetic property analysis**

The inks were prepared by first pulverizing commercial \(\text{Nd}_2\text{Fe}_{14}\text{B}\) magnets in a high-energy planetary ball milling machine. This process imposes intense mechanical stress on the magnets, which can cause a decrease in crystallinity and lead to decreased magnetic properties (29). Therefore, x-ray diffraction (XRD) studies were performed on the NMPs to analyze their crystallinity (Fig. 2A). The positions of the numerous peaks observed for the sample were well correlated with standard peaks for \(\text{Nd}_2\text{Fe}_{14}\text{B}\), indicating that the pulverizing process has negligible impact on the crystallinity of \(\text{Nd}_2\text{Fe}_{14}\text{B}\). Observing the magnetic hysteresis curve for a material provides a glimpse into its magnetic properties. Therefore, the magnetic hysteresis curve was first recorded for bare NMPs at ambient temperature (Fig. 2B, black plot). The symmetrical hysteresis curve indicates that the intense milling process has minimal effect upon the alloy’s ferromagnetic properties. Thereafter, the magnetic hysteresis curve was also analyzed for a printed self-healing trace (containing NMPs, CB, and SIS) under similar ambient conditions. Figure 2B (red plot) illustrates that the incorporation of the NMPs in the ink does not affect their ferromagnetic nature, indicating that the printed trace behaves as a ferromagnetic composite. It can be easily noted that the remanence for both NMPs and the printed trace is similar, whereas the coercivity for the printed trace is larger than that for the bare NMPs. This can be attributed to the increased resistive nature of the nonmagnetic components (CB and SIS) of the printed trace.

The magnetic alignment of the NMPs within the printed trace to produce a net anisotropic magnetic field is a crucial requirement for the self-healing process to occur. Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Analysis (EDX) technique was exploited to examine the effect of external magnetic field in aligning the NMPs within the printed trace. The alignment of the ink components along the direction of the external magnetic field is visible in the SEM image of aligned traces (Fig. 2C). The alignment is even more noticeable in the EDX image obtained for neodymium (Fig. 2C’). The strong magnetic arrangement of the NMPs also orients the CB particles, as evident from the EDX image captured for carbon (Fig. 2C”). In addition, the EDX study gives insight into the degree of homogeneity for CB and NMPs within the printed trace. During the printing process, the ink is still wet, and thus, the NMPs can possibly separate out because of the external magnetic field and can lead to a printed trace with heterogeneous distribution of NMPs and CB. This nonuniformly distributed trace is undesirable because it leads to self-healing ability only at locations where NMPs are available and also results in poor electrochemical response. The respective EDX data for carbon and neodymium in the aligned printed trace demonstrate that the NMPs do not separate out and that CB and NMPs maintain their uniform dispersion. This could be attributed to the viscous nature of the ink that prohibits physical displacement of the NMPs but permits their rotation to align their respective magnetic fields along that of the external field. In contrast, the SEM-EDX analysis of the nonaligned printed trace (fabricated in the absence of an external magnetic field) reveals a completely different morphology with no alignment of the NMPs (Fig. 2D to D’). Although the NMPs and CB are uniformly distributed within the trace (Fig. 2, D’ and D”), the absence of the NMP alignment is the underlying reason for the printed trace’s inability to demonstrate self-healing properties. Figure 2E depicts the SEM image for a CB ink-based trace (no NMPs) as a control experiment. The image reveals that the trace has a much smoother morphology as compared to the images captured for the aligned and nonaligned printed traces. This indicates that the higher surface roughness of the aligned and nonaligned traces is mainly due to the NMPs. Thereafter, 3D optical imaging was used to study the surface of the aligned and nonaligned printed traces at a much larger scale (Fig. 2, F and G). It can be easily noted that the surface of the aligned printed trace is much smoother than that of its nonaligned counterpart. This can be attributed to the presence of a strong magnet beneath the substrate during the printing of the aligned trace, which causes the NMPs to not only align along the direction of the magnetic field but also to be strongly attracted toward the underlying magnet. This strong downward attraction forces the printed ink into a well-packed printed trace with low surface roughness. In contrast, the absence of the underlying magnet while fabricating the nonaligned printed trace results in higher surface roughness.

**Electrical conductivity studies to evaluate self-healing property**

Recording and analyzing the time required to recover a trace’s conductivity upon complete damage offer an attractive route to characterizing the self-healing ability of the present system. Thus, preliminary experiments focused on studying the evolution of resistance of the printed self-healing trace under different conditions of damage. A major advantage
of the present system over the capsule- and intrinsic property–based systems is its ability to autonomously repair multiple macroscopic damages at the same location. The repeated repair ability of the new system was tested by coupling a self-healing printed trace to a digital multimeter, interfaced with a computer, to record its real-time resistance, whereas the trace and the underlying substrate were completely severed multiple times at the same location into two pieces separated by cracks with increasing widths (Fig. 3A and movie S4). The damage width was increased from 1 to 3 mm (1-mm steps). For each damage width, the damage-heal cycle was repeated three times. It is quite evident from Fig. 3A that the trace can easily self-heal repeated damage at the same location even when the crack width is as wide as 3 mm, with almost

Fig. 2. XRD, SEM-EDX, and three-dimensional optical characterization. (A) XRD spectra for NMPs. (B) Magnetic hysteresis curves for NMPs (black plot) and self-healing trace (red plot). SEM (C), EDX (for neodymium) (C’), and EDX (for carbon) (C”) images of an aligned self-healing printed trace. SEM (D), EDX (for neodymium) (D’), and EDX (for carbon) (D”) images of a nonaligned printed trace. (E) SEM image of a printed trace based on a CB ink (no NMPs). Three-dimensional (3D) optical images of (F) aligned and (G) nonaligned printed traces. Scale bars, 200 μm (C to E). Scale bars in μm (F and G). emu, electromagnetic unit; cps, counts per second; kOe, kilo-oersted.
complete recovery of its electrical conductivity. It is important to point out that the actual healing time for the system is significantly shorter than that apparent in Fig. 3A. A major portion of the period where no conductivity is recorded was required to generate the damage of precise width; only a fraction of that time is actually required for the system to self-heal, as observed in movies S1, S3, and S4. The time required to complete the self-healing process was approximately 50 ms (represented by the dotted red line in the inset of Fig. 3A) and was calculated by the time required for the light-emitting diode (LED) to turn on after being damaged, as shown in movie S1.

Practical real-life scenarios of the self-healing printed device may involve simultaneous multiple macroscopic damages at various locations. The ability of the present system to self-heal under this extreme situation was also examined by damaging a printed trace at multiple locations with a width of 1 mm (Fig. 3B). During this study, the trace was first damaged at a location and was allowed to self-heal (Fig. 3B, blue plot). Thereafter, the same trace was subjected to additional damage-heal cycles at locations adjacent to the first damage (Fig. 3B, green, red, and cyan plots). Figure 3B demonstrates the ability of the printed trace to self-heal these multiple macroscopic damages, with almost complete recovery of its conductivity (Fig. 3B, inset). In addition to these experiments, we performed control studies analyzing the self-healing ability of a printed trace containing nonaligned NMPs and a trace printed using CB ink. As expected, the absence of an anisotropic magnetic field along the length of the trace renders the nonaligned printed trace without any self-healing ability (Fig. 3C and movie S5). Similarly, no self-healing ability is observed in the absence of NMPs in the CB ink–based trace (Fig. 3D and movie S6). These control experiments corroborate the importance of not only the incorporation of NMPs but also the need to align them during the printing process to impart autonomous self-healing ability.

Electrochemical studies to evaluate self-healing properties
The main aim of the present work is to develop a self-healing ink for realizing printed electrochemical devices. CV analysis was exploited because it can offer in-depth knowledge about the electrode-electrolyte interface (30) along with useful insights into the effect of an electrode’s composition on its electrochemical properties. In addition, CV allows real-time probing of the electrochemical properties and thus can be used to study time-dependent processes occurring within the electrochemical cell. Printed electrodes with different NMP loadings [0 to 55 weight % (wt %)] were prepared, and their CV plots were recorded. As evident from Fig. 4A, the redox peak potentials for the ferricyanide probe remain nearly unchanged; however, the peak height and the background current increase for electrodes containing NMPs. The increase in peak heights implies that the introduction of NMPs increases the electroactive surface area, whereas the larger capacitive nature of the electrode could be attributed to the increased adsorption of ions onto the electrodes because of the incorporation of NMPs. CV was also used to study the reversibility of electrochemical reactions occurring at the self-healing
electrodes by recording CV plots at different scan rates. Figure 4B reveals that the redox peak positions mildly shift away from each other with increasing scan rate, whereas Fig. 4C shows the linear dependence of the anodic and cathodic peak currents on the square root of the scan rate. These findings imply that the electrochemical reaction occurring at the self-healing electrode is diffusion-controlled and has a quasi-reversible nature, as commonly reported for printed electrodes (31–33). These sets of data indicate that the introduction of NMPs within the graphitic ink has a negligible impact on the nature of the electrochemical reaction occurring at the electrode surface. Therefore, electrochemical impedance spectroscopy (EIS) technique was exploited to identify an equivalent circuit model that represents the self-healing electrode-electrolyte interface (34). Interpretation of the data acquired from this study (Fig. 4D) suggests that the interface can be modeled as a Randles circuit consisting of resistors representing solution resistance (R_s), charge transfer resistance (R_p), Warburg impedance (Z_w) for simulating diffusion-controlled processes, and common phase element (CPE) representing the nonideal capacitive nature of the interface (Fig. 4D, inset).

To study the real-time self-recovery of the electrochemical properties of a printed electrode, we continuously recorded its CV response while the electrode was subjected to multiple healing cycles. The damage width was increased from 1 to 3 mm (1-mm steps). For each damage width, the damage-heal process was repeated three times. Figure 4E depicts the voltammograms recorded for a self-healing printed electrode before (black plot) and after the first healing process for a damage width of 1 mm (red plot) and after it was damaged nine times (three times each for damage widths of 1, 2, and 3 mm) at the same location. It can be observed that the CV response for the electrode shifts mildly for the first and ninth damage-heal cycles (Fig. 4E, red and blue plots, respectively) as compared to its initial undamaged state (Fig. 4E, black plot). These

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**Fig. 4. Electrochemical characterization of self-healing electrodes.** CV plots for printed self-healing traces (A) with varying amounts of NMPs and (B) at different scan rates. (C) Plot showing linear dependence of anodic (black plot) and cathodic (red plot) peak current versus square root of scan rate. (D) Nyquist plot for self-healing printed electrode (inset: schematic showing the electrical circuit simulating the electrode-electrolyte interface). (E) CV plots recorded for a self-healing trace before any damage (black plot), after first damage with a width of 1 mm (red plot), and after nine repeated damages (blue plot) at the same location (three times each for damage widths of 1, 2, and 3 mm). (F) CV plot illustrating real-time recovery of three repeated 3-mm-wide damages. Individual CVs showing the point at which the electrode is damaged and the point where the self-healing is initiated for the (G) first, (H) second, and (I) third consecutive 3-mm-wide damage at the same location (“c_i” to “c_iii” represent the time when the electrode was damaged by 3 mm three times, whereas “h_i” to “h_iii” represent the time when the healing process began after the corresponding damage). (G to I) Green, black, and red colors represent data before cutting, during damage, and after healing, respectively.
mild variations reflect slight resistance changes during the repeated extreme degree of damage the electrode has been subjected to. Figure 4F illustrates the real-time CV recorded for the electrode when it is repeatedly damaged with a crack width of 3 mm three times. The data prove that the electrode recovers its electrochemical properties rapidly even when exposed to repeated severe levels of damage. Figure 4 (G to I) shows a single CV cycle illustrating the self-healing process for each instance of damage. It is quite evident that the self-recovery of the electrochemical response takes place rapidly. Similar to the electrical conductivity studies, as well as in the CV studies, the time required to generate the damage with precise width is much longer than that required by the system to self-heal. Intermediate CV plots illustrating the electrode’s self-healing ability after repeated 1- and 2-mm damages are shown in fig. S1.

**Self-healing batteries, electrochemical sensors, and wearable fabric circuits**

The NMP-based ink was ultimately used to fabricate self-healing batteries, electrochemical sensors, and wearable fabric circuits. Printed batteries are gaining tremendous interest as a viable energy source for a rich variety of applications where mechanical damages are quite common (35). As a proof of principle, a self-healing Zn-Ag2O battery was fabricated and subjected to multiple damage-heal cycles, where the current output was recorded continuously. As shown in Fig. 5A, the battery readily recovers its current output capacity even when it is repeatedly damaged by cracks as wide as 3 mm (Fig. 5B and movie S7). A similar experiment was also conducted for a control system fabricated using CB ink (no NMPs). The data (Fig. 5C) and images (Fig. 5D) along with the corresponding video (movie S8) prove the inability of the control battery system to self-recover its performance. Recently, Sun et al. (36) demonstrated a self-healing battery. However, the reported system mandates that the two severed pieces be manually held together for a considerable amount of time to complete the self-healing process. In contrast, our system does not require user intervention, and it self-heals autonomously and instantaneously within a fraction of a second. Detailed characterization and optimization of the battery system will be a subject of follow-up work.

![Fig. 5. Self-healing batteries and electrochemical sensors.](http://advances.sciencemag.org/)
Similar to printed batteries, electrochemical sensors are being widely used for various applications wherein the sensors can be potentially damaged due to mechanical stress (37–39). As a proof of principle, self-healing electrochemical sensors for detecting H$_2$O$_2$ and Cu were fabricated and tested. These analyses were considered because of their importance in health care (40–42) and environmental (43) applications. Figure 5E shows the amperometric data acquired by the self-healing H$_2$O$_2$ sensor for increasing peroxide concentrations. The electrode was purposely damaged five times at the same location for each H$_2$O$_2$ concentration. Figure 5E reveals that the sensor recovers its properties almost immediately after these repeated damages and that these damages have minimal impact on the sensor’s real-time response and concentration dependence. The Cu sensor was also similarly ruptured during the voltammetric detection process. In Fig. 5F, one can see that these extreme damages have negligible impact on the metal sensor’s performance because the peak position and the linear response of the sensor remain unaffected.

Finally, the NMP-based ink was used to realize a fabric-based self-healing electrical circuit for potential wearable applications. For this demonstration, a self-healing trace was printed on the sleeve of a T-shirt and connected in series with an LED and coin battery via conductive threads. A human subject was requested to wear the T-shirt, and thereafter, the circuit was damaged by cutting the self-healing trace and the underlying fabric. Upon cutting, the circuit was left open and the LED turned off. However, the strong magnetic attraction between the two pieces of the printed trace immediately forced them to move toward each other along with the underlying fabric to regain mechanical and electrical connectivity. The LED gradually turned on as soon as the electrical connectivity was restored between the two pieces. The entire process of damaging and self-restoring of the wearable circuit is shown in movie S9. We also observed that the wearable circuit could rapidly self-heal repeated damages, as illustrated in movie S10. Apart from illustrating the ability of the present system for potential wearable applications, these experiments also demonstrate the competence of the system to self-heal even when the underlying substrate is much heavier than the printed film. This attractive property can be attributed to the strong magnetic nature of the NMPs. A similar experiment with a control system consisting of a trace fabricated using CB ink (no NMPs) was also conducted. As demonstrated in movie S11, the control system fails to recover even when the two pieces are manually forced to stick together. This real-life demonstration of the present self-healing system highlights its potential for realizing self-healing printed devices for diverse practical applications.

**DISCUSSION**

The present work demonstrates the synthesis of magnetically self-healing printable conductive inks for realizing electrical circuits, batteries, and electrochemical sensors that rapidly and autonomously restore their properties after experiencing extreme levels of damage. The underlying self-healing principle relies on the strong attraction between NMPs uniformly dispersed within the ink. Through detailed electrical conductivity, electrochemical, and visual studies, we demonstrate that the printed self-healing devices have the ability to recover their performance almost instantaneously even when repeatedly damaged by microscopic cracks, as wide as 3 mm, at the same or different locations. A self-healing wearable printed LED circuit was also developed by printing a circuit onto a T-shirt. The wearable circuit healed immediately when it was cut along with the underlying fabric. This impressive self-healing ability can be attributed to the strong magnetic properties of the NMPs.

The present NMP-based self-healing system has several distinct advantages over capsule- and intrinsic property–based self-healing systems, such as long-lasting self-healing nature, ability to instantly (~50 ms) heal multiple macroscopic damages without an external trigger or user intervention, and insensitivity toward ambient conditions. This remarkable self-healing of repeated extreme degree of damage has not been reported yet for existing man-made self-healing systems. The impressive healing ability of the NMPs can be further improved by enhancing their magnetic properties via techniques widely reported in the literature (44, 45). An attractive feature of the permanent magnetic system is its ability to undergo a large number of healing cycles under a wide range of ambient conditions. By incorporating various fillers within the NMP-based system, one can formulate a rich variety of magnetically self-healing inks for a wide range of applications. In addition, the magnetic interaction between the NMPs can be modeled via well-established computer simulations to develop new self-healing inks with tailor-made self-healing properties for a variety of applications and broad range of industries. The present work thus has great promise for developing long-lasting printed electronic devices that can rapidly self-heal macroscopic damages and recover their properties. These devices are expected to play a crucial role in different practical settings where mechanical damage–related device failure is common.

**MATERIALS AND METHODS**

**Chemicals and reagents**

Potassium ferricyanide, potassium hydroxide (KOH), lithium hydroxide (LiOH), hydrogen peroxide solution (30 wt % in H$_2$O stabilized), polyacrylic acid, and polystyrene-block-polypisoprene-block-polystyrene (SIS; styrene 14 wt %) were purchased from Sigma-Aldrich. Xylene was purchased from Macron Fine Chemicals, whereas TIMCAL Graphite & Carbon Super P® Conductive Carbon Black (CB) was obtained from MTI Corporation. Anhydrous sodium carbonate, Zn, and Ag$_2$O powder were purchased from Fisher Scientific. Copper standard solution for AAS (TraceCERT grade) was obtained from Fluka.

**Nd$_3$Fe$_{14}$B magnet grinding process**

A typical milling process first involved manually breaking commercially available Nd$_3$Fe$_{14}$B magnets into small pieces (~1 mm in size). Subsequently, the Nd$_3$Fe$_{14}$B magnetic powder was further ground into finer microparticles (~5 μm in size) in a high-energy planetary ball milling machine (Planetary Mill PULVERISETTE 5 classic line, Fritsch). An 80-ml tempered steel milling bowl and 20 milling balls with diameters of 10 mm were used in the milling process. The milling speed was set at 220 rpm for 3 min and repeated 17 times to obtain NMPs of the desired size.

**Ink synthesis**

A typical synthesis of the magnetically self-healing ink consisted of first manually grinding conductive CB powder (150 mg) with NMPs (1173.33 mg). Thereafter, the CB-NMP composite powder was mixed in the SIS polymer suspension (810 mg) using a vortex mixer for a couple of minutes. The SIS suspension was previously prepared by dispersing the SIS polymer (2000 mg) in xylene (8 ml) for 60 min under continuous stirring. Ultimately, the CB and NMPs were thoroughly mixed within the SIS suspension to obtain the self-healing ink, using a mechanical mixer (SpeedMixer, FlackTek Inc.) five times at 2300 rpm for 1 min.
Fabrication of magnetically self-healing printed electrodes

The fabrication process involved screen printing of the self-healing conductive ink using an MPM SPM semiautomatic screen printer (Speedline Technologies) on a 50-μm-thick flexible polyester substrate (MELINEX 453, which was provided by Tekra Inc.). The stencils were designed in AutoCAD (Autodesk) and outsourced for fabrication on stainless steel through-hole 30.48 cm × 30.48 cm framed stencils with a thickness of 500 μm (Metal Etch Services). A typical fabrication process consisted of first thoroughly cleaning the polyester substrate with acetone to remove contaminants. Then, a ~75-μm-thick polyurethane layer (RheoFlex 20, Smooth-On) was screen-printed on top of the substrate and cured at 65°C for 20 min in a convection oven. The polyurethane layer was included to enhance the adhesion of the self-healing ink to the polyester substrate.

The next step involved the printing of the magnetically self-healing ink. Before printing the self-healing ink, a commercial bar magnet with poles directed parallel to the stencil was placed underneath the substrate. After printing the self-healing ink, the substrate was left unmoved for 15 min to allow the NMPs to orient along the direction of the external magnetic field produced by the magnet placed under the substrate. Finally, the printed electrodes were lifted from the magnet and cured at 60°C for 10 min in a convection oven. A transparent insulator was ultimately printed onto the self-healing electrodes to define the active electrode area and contact pads.

Fabrication of magnetically self-healing printed Zn-Ag2O batteries

Initially, Ag2O and Zn inks were formulated by manually mixing the respective powders (263 mg) in a SIS binder (500 mg). The fabrication of magnetically self-healing printed Zn-Ag2O batteries first involved printing two current collectors using the magnetically self-healing ink. Then, Zn and Ag2O inks were separately printed over each of the current collector electrodes to transform them into the anode and cathode of the printed self-healing battery. The Ag2O and Zn electrodes were later covered by a gel electrolyte containing 10% polyacrylic acid dispersed in a solution of 6 M KOH containing 1 M LiOH.

Electrochemical, SEM-EDX, and XRD studies

CV studies were performed at room temperature using a CH Instruments electrochemical analyzer (model 1232A). The printed electrode was used as a working electrode, whereas commercial Ag/AgCl and platinum wire electrodes were used as reference and counter electrodes, respectively. Ferrocyanide [10 mM in 0.1 M phosphate buffer (pH 7.0)] was used as the electrolyte. A scan rate of 0.1 V/s was used for all experiments unless mentioned. EIS data were recorded, similar to CV studies, using a Gamry Instruments potentiostat in a frequency range of 50 mHz to 0.3 MHz and at a constant dc voltage of 0.2 V. SEM experiments were performed by an FEI/Phillips XL30 ESEM instrument. EDX mapping analysis was performed using an Oxford EDX detector attached to the SEM instrument and operated using the INCA software. The images were captured at ×200 magnification. XRD data were recorded using a Rigaku Rotaflex diffractometer using Cu Kα radiation (λ = 0.15418 nm) with an acceleration voltage of 40 kV and tube current of 100 mA. The samples were scanned at a scan rate of 0.5%/s in the range of 2θ = 20 to 80.

Electrochemical detection of H2O2 and Cu at self-healing electrodes

The amperometric detection of H2O2 was performed at −0.15 V in 0.1 M phosphate buffer (pH 7). The magnetic self-healing ability of the electrochemical devices was analyzed while recording the amperometric responses for 0, 5, 10, 15, and 20 mM H2O2. The self-healing electrode was damaged five times by a crack width of 1 mm for each peroxide addition. The self-healing electrode was used for the detection of Cu (0, 5, 10, 15, 20, and 25 ppm) by anodic stripping voltammetry [square-wave voltammetry (SWV)]. The deposition of Cu was performed by applying a constant potential of −0.7 V for 60 s. Subsequently SWV plots were recorded by a potential scan from −0.5 to 0.4 V (amplitude, 25 mV; frequency, 2 Hz; increment E, 4 mV). The electrode was damaged twice during the stripping process for each addition. The electrode was electrochemically cleaned by applying a constant potential of 0.3 V for 120 s before each deposition process.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/2/11/e1601465/DC1

Fig. S1. Real-time CV studies for characterizing the self-healing process.

movie S1. A magnetically self-healing printed LED circuit immediately recovering repeated macroscopic damages.

movie S2. Printing process and magnetic orientation of the NMPs dispersed within the printed film required for realizing magnetically self-healing films.

movie S3. Lifting of the self-healed printed trace against gravity to demonstrate the strength of the self-healing process.

movie S4. Self-healing of a printed trace after repeated macroscopic damages.

movie S5. Inability of a printed trace, comprising nonaligned NMPs fabricated in the absence of external magnetic field, to self-heal incurred damage.

movie S6. Inability of a CB ink (no NMPs)-based printed trace to self-heal incurred damage.

movie S7. Self-healing printed Zn-Ag2O battery recovering immediately after experiencing repeated macroscopic damages.

movie S8. Inability of a printed Zn-Ag2O battery, fabricated using CB ink (no NMPs), to recover macroscopic damages.

movie S9. Damage and autonomous recovery demonstrated by a self-healing wearable LED circuit.

movie S10. Self-healing of a wearable LED circuit under repeated damage.

movie S11. Inability of a wearable LED circuit fabricated using CB ink (no NMPs) to recover electrical connectivity after being damaged.

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