

Flexible, Magnetic, and Electrically Conductive Graphene/Fe₃O₄ Paper and Its Application for Magnetic-Controlled Switches

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Received: June 18, 2010; Revised Manuscript Received: September 3, 2010

The emerging field of free-standing and flexible paperlike materials based on graphene sheets has become the focus of considerable research in recent years because of the scientific and technological significance of these materials. In particular, multifunctional flexible graphene-based films or papers are in high demand for various applications. Herein, we report the fabrication of magnetic, electrically conducting, and flexible paper composed of graphene and nanoscale Fe₃O₄ particles made using a simple yet versatile solution-processed approach. The conductive, magnetic, and mechanical properties of these free-standing hybrid papers with different loadings of nanoscale Fe₃O₄ particles were investigated. In addition to the excellent electrical conductivity and mechanical strength, the obtained flexible graphene/Fe₃O₄ hybrid papers also show superparamagnetism, which can be tuned easily through modulation of the loading of Fe₃O₄ nanoparticles. Combining all of these outstanding properties, we have fabricated and demonstrated a magnetic-controlled conductive switch using these flexible and multifunctional graphene/Fe₃O₄ hybrid papers.

1. Introduction

Graphene, a one-atom-thick two-dimensional (2D) single layer of sp²-bonded carbon, has garnered much attention in the field of material science in recent years because of its extraordinary electrical,^{1,2} thermal,³ mechanical,^{4,5} and structural properties.^{6,7} These unique and intriguing features make this highly versatile carbon material promising in many potential applications such as nanocomposites,^{8–10} transparent conducting films,^{8,9,11–14} sensors,^{15,16} supercapacitors,¹⁷ nanoelectronics,^{18,19} batteries,²⁰ and so on. Also, its intrinsic low weight and high mechanical and conductive properties make graphene an excellent choice for fabricating various unique and multifunctional structures, such as free-standing flexible paperlike materials with high performance, for a variety of real industry applications.^{21–27} Recent progress has been made toward the fabrication, through vacuum filtration under a directional flow, of graphene oxide (GO), graphene, and graphene-based hybrid papers whose mechanical or electrical performance is superior to that of many other inorganic paperlike materials.^{21–23,27} However, GO itself has many defects in structure, and most of the excellent intrinsic properties of graphene are demolished in GO, so that its direct application is highly limited. Furthermore, whereas GO can be dispersed in the state with entirely dispersed individual graphene sheets for solution processing, after being reduced to restore their intrinsic structure and properties, graphene sheets tend to generate irreversible agglomerates due to strong van der Waals interactions if no other force or accompanying material as a stabilizer is used to prevent such agglomeration.²⁸ Therefore, for high conducting and mechanical performance, as well as other demanded properties, including good solution flexibility, the processing techniques for graphene-based paper and related materials should be carefully selected and designed. To date, several techniques have been developed for the preparation of

stable solutions of single graphene sheets.^{24,26,28–32} Unfortunately, the production of large-area and free-standing graphene-based hybrid paper with high flexibility and multifunctional features is still a challenge. Herein, we present a general method for the fabrication of free-standing graphene/Fe₃O₄ hybrid paper employing a solution process with water-soluble graphene/Fe₃O₄ hybrids. Importantly, the hybrid papers, in addition to having good conductivity and mechanical strength, also exhibit excellent flexibility as well as superparamagnetism. These properties can also be tuned easily by controlling the loadings of the Fe₃O₄ nanoparticles. Furthermore, we also demonstrate that these multifunctional graphene-based papers can be employed as magnetic-controlled switches.

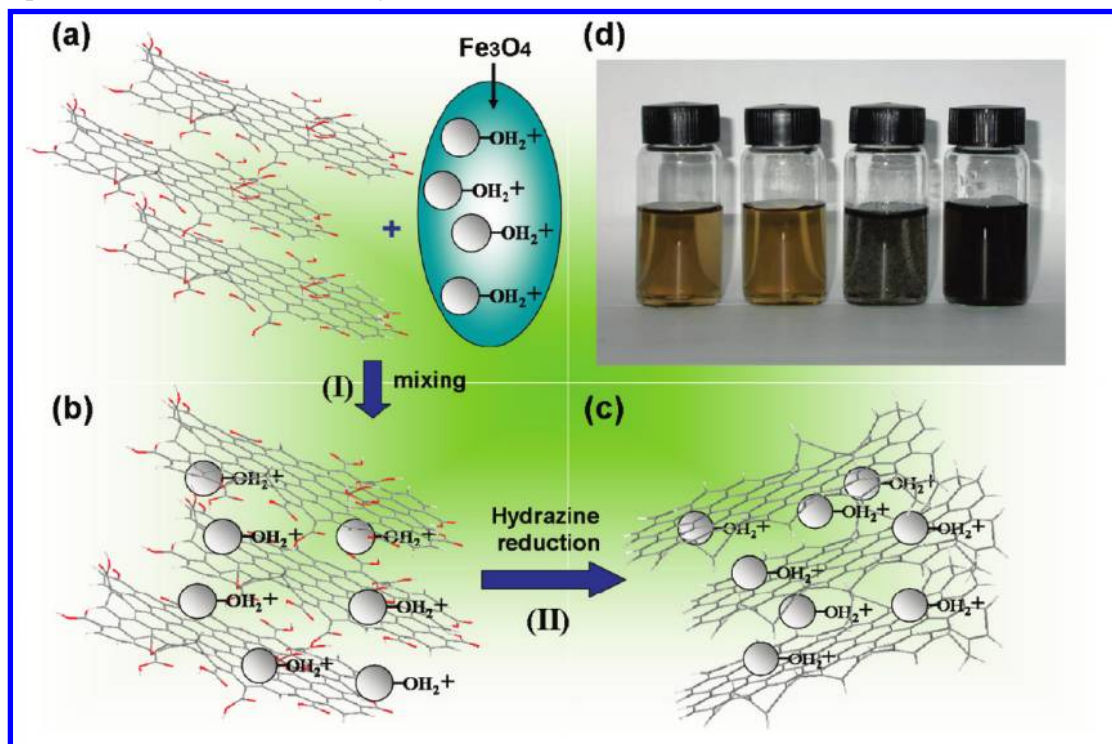
2. Experimental Section

2.1. Raw Materials. Graphite with a particle size of 20 μm was obtained from Qingdao Huarun Graphite Co., Ltd. Hydrazine hydrate (80%) was purchased from Tianjin Ruijint Chemical Co., Ltd. Sulfanilic acid was supplied by the Shanghai Chemical Co., Ltd. Ferric chloride hexahydrate (FeCl₃·6H₂O), ferrous chloride tetrahydrate (FeCl₂·4H₂O), sodium hydroxide, and toluene were purchased from Tianjin No. 3 Chemical Plant. Polyimide (PI) tape, with a thickness of about 50 μm , was purchased from No. 18 Research Institute of China Electronics Technology Group Corporation.

2.2. Preparation of Fe₃O₄ Nanoparticle Solutions. The nano-Fe₃O₄ aqueous solution was prepared following a literature method reported previously.^{33,34} In a typical procedure, a solution of FeCl₂·4H₂O/H₂O (10 mmol, 1.99 g in 25 mL of 1.0 M HCl) was mixed with FeCl₃·6H₂O/H₂O solution (20 mmol, 5.41 g in 25 mL of distilled water) and placed in a 500 mL round-bottom flask. The solution was stirred and purged with N₂. After 30 min, 1.5 M ammonium hydroxide (160 mL) was added dropwise for 1 h under N₂. The mixture was then stirred at room temperature for 24 h under N₂. After that, a black precipitate was obtained by allowing the vessel to stand for 10 min and

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SCHEME 1: Two-Step Preparation of Graphene/Fe₃O₄ Hybrid Papers: (I) Mixing of GO Aqueous Solution with Water-Soluble Fe₃O₄ Nanoparticle Aqueous Solution^{a,b} and (II) Chemical Reduction of the Suspension of Water-Soluble Fe₃O₄ Nanoparticles and GO Sheets with Hydrazine^{c,d}



^a Aqueous GO and water-soluble Fe₃O₄ nanoparticle aqueous solutions. ^b Stable suspension of water-soluble Fe₃O₄ nanoparticles and GO sheets. ^c Stable and homogeneous water-soluble graphene dispersion with Fe₃O₄ nanoparticles. ^d Photographs of water dispersions of (1) water-soluble Fe₃O₄ nanoparticles, (2) water-soluble Fe₃O₄ nanoparticles and GO sheets, (3) reduced graphene without Fe₃O₄ nanoparticles, and (4) reduced graphene with water-soluble Fe₃O₄ nanoparticles, respectively (all samples are 0.1 mg/mL).

removing the supernatant. This black product was placed in the flask again, and after it had been purged with N₂ for 30 min, 2 M HClO₄ (50 mL) was added dropwise into the mixture and stirred for 15 min at room temperature. After centrifugation, the precipitate was redispersed in distilled water, and thorough dialysis was performed until neutrality was reached. The resulting Fe₃O₄ nanoparticle aqueous solution (diluted to 7 mg/mL) was stored in a sealed container.

2.3. Synthesis of Graphene Oxide (GO). GO prepared from natural graphite by the modified Hummer's method^{11,37} was used as the starting material for the fabrication of graphene and graphene/Fe₃O₄ hybrid paper.

2.4. Preparation of Graphene and Graphene-Annealed Papers. Graphene paper was fabricated by vacuum filtration of graphene dispersion according to the literature method.^{23,29} In a typical procedure, 20 mg of GO was first completely exfoliated down to individual graphene oxide sheets in 80 mL of distilled water to form a stable dispersion of graphene oxide solution (0.25 mg/mL). Then, 40 μ L of hydrazine hydrate (80%) and 280 μ L of ammonia solution (25%) were added to this homogeneous solution, and the mixture was stirred vigorously for a few minutes. After that, the dispersion was subjected to reduction by heating to 95 $^{\circ}$ C for 1 h. Pristine graphene paper was obtained by filtration of the above black solution through an Anodisc membrane filter (47-mm diameter, 0.22- μ m pore size; Whatman), followed by air drying and peeling from the filter. To obtain the graphene-annealed paper sample, graphene paper was annealed at 400 $^{\circ}$ C in argon for 1 h.

2.5. Preparation of Graphene/Fe₃O₄ Hybrid Papers. The water-soluble Fe₃O₄ nanoparticles, prepared as described above, were used as an effective stabilizer to prevent the agglomeration

of graphene sheets from GO after reduction in solution. A two-step approach was used, as illustrated in Scheme 1, including a mixing step and a reduction step. Remarkably, only a small amount of Fe₃O₄ nanoparticles (e.g., >2% by weight of the GO used in the hybrid paper) was sufficient to compete with the hydrophobic interaction between graphene sheets and generate a stable homogeneous solution of reduced graphene sheets. In a typical experiment, the required amount of Fe₃O₄ nanoparticles aqueous solution was added to 20 mg of GO dispersion (in 80 mL of distilled water, 0.25 mg/mL) under vigorously stirring or ultrasonication, and then the mixture was reduced with 40 μ L of hydrazine hydrate (80%) at 90 $^{\circ}$ C for 1 h. After that, a homogeneous black dispersion with a small quantity of black precipitate was obtained. The dispersion was centrifuged to remove the precipitate to yield a stable black supernatant. Actually, for contents of Fe₃O₄ nanoparticles larger than 10%, the concentration of the stable and homogeneous dispersion of graphene could reach even more than 2 mg/mL. Graphene/Fe₃O₄ hybrid paper was obtained by filtration of the above black supernatant through an Anodisc membrane filter (47-mm diameter, 0.22- μ m pore size; Whatman), followed by air drying and peeling from the filter. The magnetization of these hybrid papers can be controlled by altering the amount of the water-soluble Fe₃O₄ nanoparticles. In this work, two kinds of graphene/Fe₃O₄ hybrid papers were fabricated for study: Graphene/Fe₃O₄-1, which was composed of about 20 mg of GO and 0.7 mg of water-soluble Fe₃O₄ nanoparticles (about 3.4% Fe₃O₄ content), and graphene/Fe₃O₄-2, which consisted of approximately 20 mg of GO and 1.4 mg of water-soluble Fe₃O₄ nanoparticles (about 6.5% Fe₃O₄ content). The further reduced samples, graphene/Fe₃O₄-1-annealed and graphene/Fe₃O₄-2-annealed, were ob-

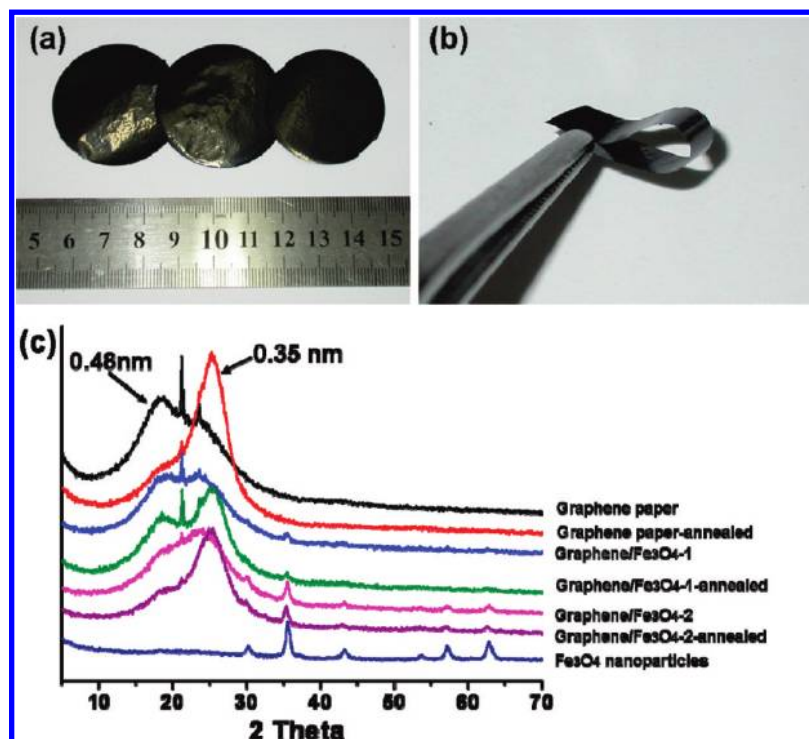


Figure 1. Photographs of (a) the as-prepared graphene/Fe₃O₄-2 paper and (b) a flexible graphene/Fe₃O₄-2-annealed paper. (c) XRD curves of graphene, graphene/Fe₃O₄-1, and graphene/Fe₃O₄-2 papers with and without annealing.

tained by annealing graphene/Fe₃O₄-1 and graphene/Fe₃O₄-2, respectively, at 400 °C in argon for 1 h. The thickness of these hybrid paper and pure graphene paper was in the range of 7–10 μm.

2.6. Characterization. Typical tapping-mode atomic force microscopy (AFM) measurements were performed using a Multimode SPM apparatus from Digital Instruments with a Nanoscope IIIa controller. Samples for AFM images were prepared by depositing the corresponding solutions onto a freshly cleaved mica surface and allowing them to dry in air. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 field-emission scanning electron microscope at an acceleration voltage of 3 kV. Transmission electron microscopy (TEM) was performed using a Philips T20ST electron microscope at an acceleration voltage of 200 kV. X-ray diffraction (XRD) measurements were carried out using a Rigaku D/Max-2500 diffractometer with Cu Kα radiation. Conductivity measurements of these flexible papers were performed using the standard four-point contact method, and the data were collected with a Keithley 2600 instrument. The mechanical properties of these graphene and graphene hybrid papers were measured with a microfiber tensile testing machine (JSF-08, Shanghai Huachen Co., Ltd.) at 20 °C with 50% relative humidity. The extension rate was 0.00844 mm/s.

2.7. Magnetic-Induced Switch Testing. The graphene-based magnetic hybrid papers were exposed to a homemade device's intermittent magnetic field, which is able to generate a magnetic field up to approximate 500 G at a frequency of 0.2 Hz. The response of the samples was recorded by a video camera. The current–potential curve was measured using a constant potential supply and multimeter (Fluke 17B).

3. Results and Discussion

Low-dimensional Fe₃O₄ nanoparticles, whose properties are rather different from those of the bulk magnetite, are particularly promising in widespread applications such as color imaging,

electromagnetic shielding, drug delivery, soft magnetic materials, and so on.^{35,36} Pure Fe₃O₄ nanoparticles are generally insoluble, which severely handicaps their further applications. Previous studies have shown that a surface chemical treatment of Fe₃O₄ nanoparticles in water could result in the formation of a precursor ferrofluid with well-defined magnetic nanoparticles.^{33,34} Therefore, we thought that these water-soluble Fe₃O₄ nanoparticles might act as both a functional and suspension-stabilizing component to impede the agglomeration of graphene sheets during the process of GO reduction and lead to the formation of water-soluble multifunctional graphene materials.

Hence, in this work, we first start by preparing water-soluble Fe₃O₄ nanoparticles (sample 1 in Scheme 1, footnote ^d) and GO as starting materials according to the literature method,^{11,37} as described in the Experimental Section. Then, a stable homogeneous black dispersion of graphene/Fe₃O₄ hybrid (sample 4 in Scheme 1, footnote ^d) can be easily prepared by chemical reduction of a stable suspension of GO in the presence of the as-prepared water-soluble Fe₃O₄ nanoparticles using hydrazine hydrate (Scheme 1; see the Experimental Section for details). It is important to note that, on the other hand, direct reduction of GO aqueous solution using hydrazine hydrate without water-soluble Fe₃O₄ nanoparticles produces irreversible black precipitation as displayed in sample 3 of Scheme 1, footnote ^d. This indicates that the water-soluble Fe₃O₄ nanoparticles are indeed effective in avoiding the irreversible coagulation of graphene sheets in aqueous solution. The existence of individual reduced graphene sheets in the hybrid solution was confirmed by the transmission electron microscopy (TEM) and typical tapping-mode atomic force microscopy (AFM) measurements (see the Supporting Information, Figure S1).

Free-standing and shiny black graphene/Fe₃O₄ hybrid papers, as depicted in Figure 1a,b, were readily fabricated through vacuum filtering of the homogeneous solutions of water-soluble graphene/Fe₃O₄ hybrid. For comparison, two kinds of graphene/Fe₃O₄ hybrid papers with different loadings of Fe₃O₄, namely,

TABLE 1: Amounts of Fe₃O₄ Nanoparticles Loaded in Our Graphene-Based Hybrid Papers, as Calculated from the Contents of Fe Detected by Atomic Absorption Spectroscopy

sample	amount of Fe ₃ O ₄ (wt %)
graphene/Fe ₃ O ₄ -1 paper	4.11
graphene/Fe ₃ O ₄ -1-annealed paper	5.15
graphene/Fe ₃ O ₄ -2 paper	7.14
graphene/Fe ₃ O ₄ -2-annealed paper	7.54

graphene/Fe₃O₄-1 and graphene/Fe₃O₄-2 hybrid papers, were fabricated for investigation. (See the Experimental Section for details.) The further reduced samples, graphene/Fe₃O₄-1-annealed and graphene/Fe₃O₄-2-annealed, were obtained by annealing graphene/Fe₃O₄-1 and graphene/Fe₃O₄-2 papers, respectively, at 400 °C in argon. The amount of Fe₃O₄ nanoparticles loaded in our hybrid graphene papers, which was relatively low, was calculated from the results of atomic absorption spectroscopy, as reported in Table 1. As a control, the pristine graphene paper from a graphene/NH₃·H₂O solution directly (see the Experimental Section for details) and graphene-annealed paper (400 °C annealed) were also prepared according to the previous literature methods.^{23,29}

As paperlike hybrid materials, the properties of these graphene/Fe₃O₄ hybrid papers are highly associated with their microstructure and the state of the Fe₃O₄ nanoparticles in the hybrid system. Thus, these free-standing hybrid papers were first carefully characterized by X-ray diffraction (XRD) measurements. XRD patterns of graphene, graphene/Fe₃O₄-1, and graphene/Fe₃O₄-2 papers with and without annealing are presented in Figure 1c. The XRD pattern of Fe₃O₄ nanoparticles is used as a reference, and seven peaks at 18.34°, 30.18°, 35.54°, 43.24°, 53.66°, 57.14°, and 62.78°, corresponding to the (111), (220), (311), (400), (422), (511), and (440) planes of the magnetite spinel structure of Fe₃O₄ were observed.³⁵ Compared to the graphene and graphene-annealed papers, only five much weaker peaks (30.18°, 35.54°, 43.24°, 57.14°, and 62.78°) from Fe₃O₄ nanoparticles were observed for the graphene/Fe₃O₄-1 and graphene/Fe₃O₄-2 papers with or without annealing. The disappearance of the other two peaks of Fe₃O₄ nanoparticles is mainly due to the low amount of these magnetic nanoparticles in the hybrid papers and the stronger and broader peaks from graphene at those positions. Moreover, because there are higher contents of Fe₃O₄ nanoparticles in graphene/Fe₃O₄-2 and graphene/Fe₃O₄-2-annealed papers, the intensities of these five peaks are stronger for graphene/Fe₃O₄-2 and graphene/Fe₃O₄-2-annealed papers than for graphene/Fe₃O₄-1 and graphene/Fe₃O₄-1-annealed papers. Furthermore, the XRD patterns of the graphene/Fe₃O₄ hybrid papers also confirm their graphene-based layered structure. The graphene/Fe₃O₄-1-annealed and graphene/Fe₃O₄-2-annealed papers displayed a characteristic 2θ peak for the layered structure of graphene at around 25°, which corresponds to a layer-to-layer distance (*d* spacing) of about 0.35 nm, indicating the well-stacked structure of these hybrid papers.²³ In addition, the characteristic 2θ peaks of graphene/Fe₃O₄-1 and graphene/Fe₃O₄-2 papers without annealing are broader and smaller than those of the corresponding annealed papers, indicating that the *d* spacing is slightly larger (approximately 0.40–0.48 nm) than that after annealing, as expected. Hence, thermal annealing enables the removal of residual oxygen-containing functional groups or other structure defects on the graphene and allows better packing of the two-dimensional graphene sheets. Furthermore, the small loadings of Fe₃O₄ nanoparticles did not affect the graphene sheet packing from the layered structure with macroscopic ordering in the process of vacuum filtration.

The well-stacked structure and the presence of Fe₃O₄ nanoparticles in the hybrid papers were also confirmed by scanning electron microscopy (SEM). As can be seen in Figure 2a, SEM analyses from the top revealed that the surface of graphene-annealed paper was quite smooth. However, it can obviously be seen that plenty of white spots, which are Fe₃O₄ nanoparticles, were uniformly spread around on the surface of the graphene/Fe₃O₄ hybrid papers (Figure 2b,c). Moreover, the fracture edges of graphene/Fe₃O₄-2-annealed papers also displayed a well-packed layered structure through the cross section (Figure 2e), which is similar to the structure of graphene (Figure 2d) or GO paper prepared by the same vacuum-filtration method.^{21,23} In addition, unlike in graphene or GO paper,^{21,23} many Fe₃O₄ nanoparticles appearing as white spots can be observed in the cross section of graphene/Fe₃O₄-2-annealed paper, as illustrated in the high-magnification SEM image in Figure 2f. Nevertheless, the presence of these Fe₃O₄ nanoparticles does not affect the overall well-stacked structure of the hybrid paper on the whole (Figure 2f). This result corresponds to the observed XRD patterns (Figure 1c) described above.

It is believed that this well-stacked layered structure plays an important role in the excellent mechanical and conducting performance of paperlike materials.^{21,23} It has been a long-time goal to make free-standing film or paper that shows multifunctional features, including good electrical conductivity, mechanical strength, flexibility, and even tunable magnetism. To date, the primary factors creating significant hurdles for the practical application of inorganic paperlike materials might be their fragileness, low flexibility, or lack of other functionality.²¹ However, our graphene/Fe₃O₄ hybrid papers exhibit all of these desired functionalities.

The electrical conductivity of these graphene-based hybrid papers arises mainly from the reduced graphene sheets. As a consequence of deoxygenation and the restoration of a better aromatic structure through thermal annealing, the electrical conductivities of the graphene and graphene hybrid papers that were annealed at 400 °C in argon were an order of magnitude higher than those of the papers that were not annealed, as shown in Figure 3a. Furthermore, a clear trend for the papers with annealing shows that the electrical conductivity of these papers becomes slightly higher as the content of Fe₃O₄ nanoparticles increases, which might be due to the conductivity of the Fe₃O₄ nanoparticles. In addition, we were surprised to find that good electrical conductivity was not the only superior aspect of the hybrid papers; these graphene-based hybrid papers likewise had increased mechanical strength compared to the pristine graphene papers (see the Supporting Information, Table S1). For example, the tensile strength of the graphene/Fe₃O₄-1-annealed paper reached approximately 32 MPa, which is even higher than those of our pristine graphene paper and other reported graphene-based papers intercalated by organic molecules.^{26,27} In the absence of direct chemical bonding between graphene sheets and Fe₃O₄ nanoparticles, the reasons behind the relatively good mechanical strengths of these hybrid papers must still be elucidated. Moreover, even though intercalated with inorganic Fe₃O₄ nanoparticles, our graphene/Fe₃O₄ hybrid papers (with and without annealing), similarly to graphene and graphene oxide papers,^{21,23} still exhibit outstanding flexibility. As demonstrated in Figure 1b, graphene/Fe₃O₄-2-annealed paper, even though thermally annealed at 400 °C in argon, was still sufficiently flexible to be bent to an angle approaching 180° with tweezers. Of particular significance is that, combined with the excellent flexibility, no visible breakage and no decreasing performance, involving electrical conductivity as well as me-

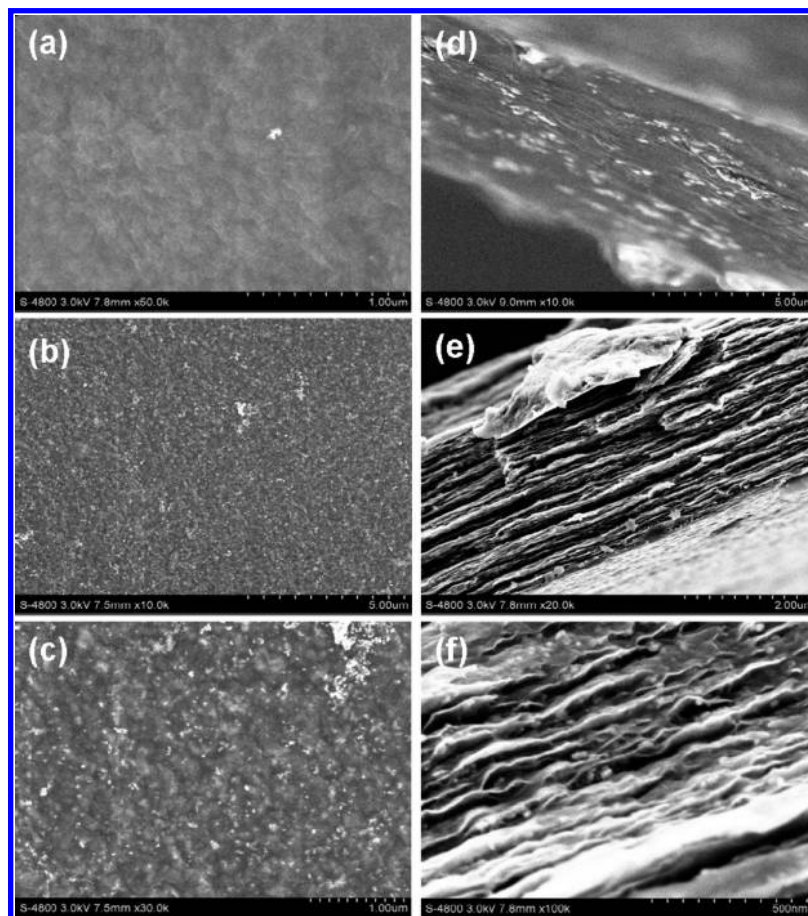


Figure 2. Top-view SEM images of (a) graphene-annealed paper and (b) graphene/Fe₃O₄-2-annealed paper. (c) Enlargement from b. Side-view SEM images of cross sections of (d) graphene-annealed paper and (e) graphene/Fe₃O₄-2-annealed paper. Note the well-packed layered structure. (f) High-resolution side-view SEM image of graphene/Fe₃O₄-2-annealed paper magnified from e. The white spots in images b, c, e, and f are Fe₃O₄ nanoparticles.

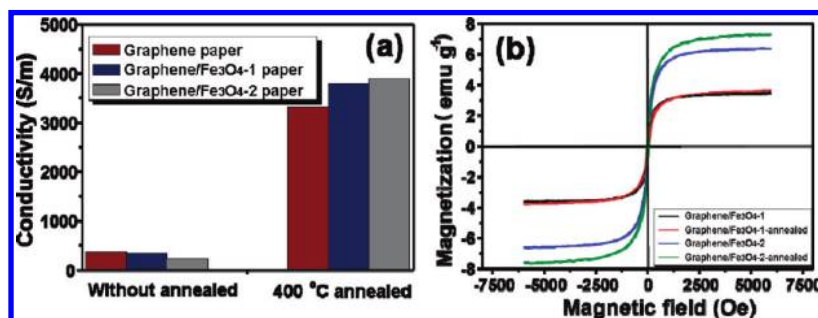


Figure 3. (a) Conductivities of graphene, graphene/Fe₃O₄-1, and graphene/Fe₃O₄-2 papers with and without annealing. All of the annealing was conducted at 400 °C in argon. (b) Hysteresis loops of graphene/Fe₃O₄-1 and graphene/Fe₃O₄-2 papers with and without annealing.

chanical strength, was observed for these graphene-based hybrid papers (with or without annealing) after more than 100 bending cycles (with bending to angles larger than 90°), which is another good indication of the great flexibility of these hybrid papers.

Most importantly, the Fe₃O₄ nanoparticles further endow these hybrid papers with attractive and widely used superparamagnetism. All of the hybrid papers exhibited superparamagnetism, and nearly no coercivity or remnant magnetization was observed.³⁸ Figure 3b shows the magnetization hysteresis loops measured at room temperature in the field range of −6 kOe < *H* < +6 kOe for the four graphene/Fe₃O₄ hybrid papers with and without annealing, where saturation of the magnetization is clearly seen at about *M_s* = 7.29 emu/g after subtraction of the diamagnetic background for the graphene/Fe₃O₄-2-annealed paper with Fe₃O₄ loading of 7.54%. The magnetization for all

hybrid papers was saturated at a low magnetic field of about *H* = 1300 Oe. It has been suggested that Fe₃O₄ nanoparticles would change from ferromagnetic to superparamagnetic when the particle size became smaller than 25 nm,³⁹ which is consistent with our results from SEM and TEM analysis. Clearly, the specific saturation magnetization (*M_s*) of these hybrid papers is primarily dependent on the content of Fe₃O₄ nanoparticles. The *M_s* values for graphene/Fe₃O₄-2 and graphene/Fe₃O₄-2-annealed paper were found to be 6.39 and 7.29 emu/g, respectively, whereas those of graphene/Fe₃O₄-1 and graphene/Fe₃O₄-1-annealed paper were 3.56 and 3.71 emu/g, respectively. The enhancement of *M_s* for the hybrid paper after thermal annealing at 400 °C might be mainly due to the removal of residual oxygen-containing functional groups from the graphene sheets, leading to an increase in the relative contents of Fe₃O₄ nanoparticles in the hybrid papers. As expected, *M_s*

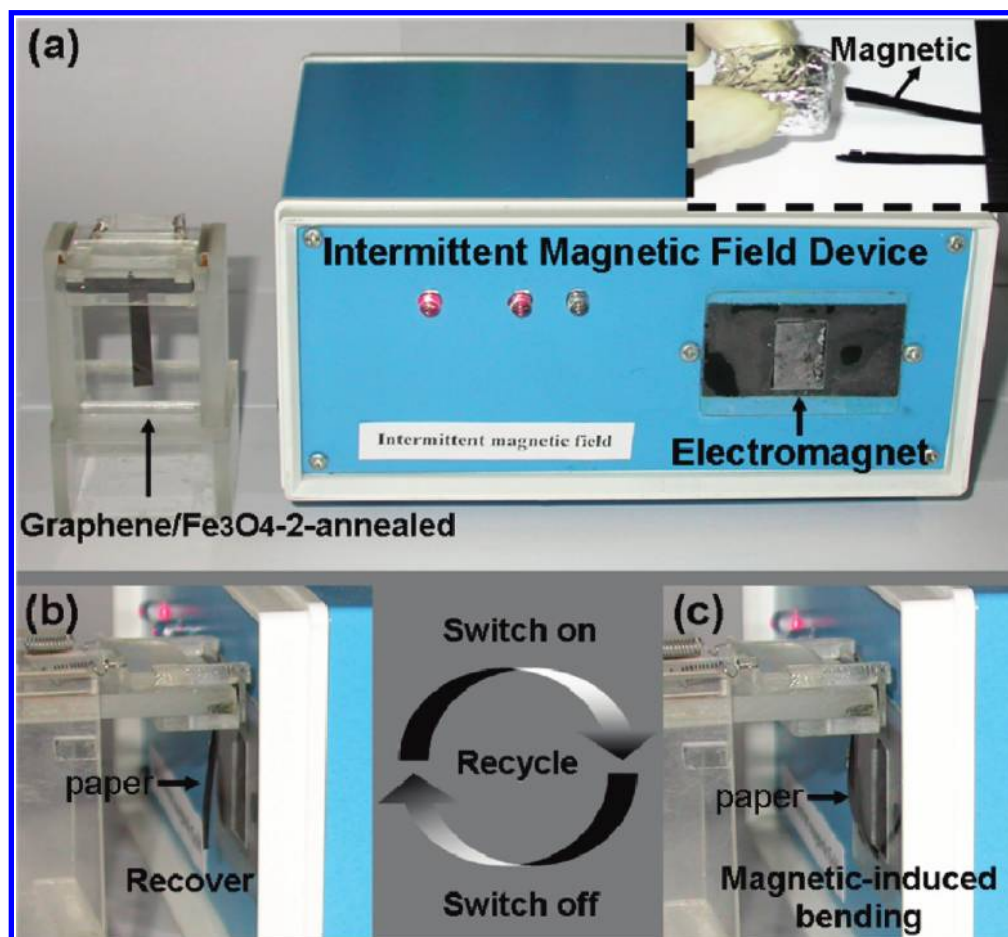


Figure 4. (a) Photograph of an intermittent magnetic field device. The inset at the top right shows that graphene/ Fe_3O_4 hybrid paper responds to a magnet whereas pure graphene paper does not. (b,c) Magnetic-induced switch of graphene/ Fe_3O_4 hybrid paper: (b) magnetic field switches off, (c) magnetic field switches on and induces bending of graphene/ Fe_3O_4 -2-annealed hybrid paper.

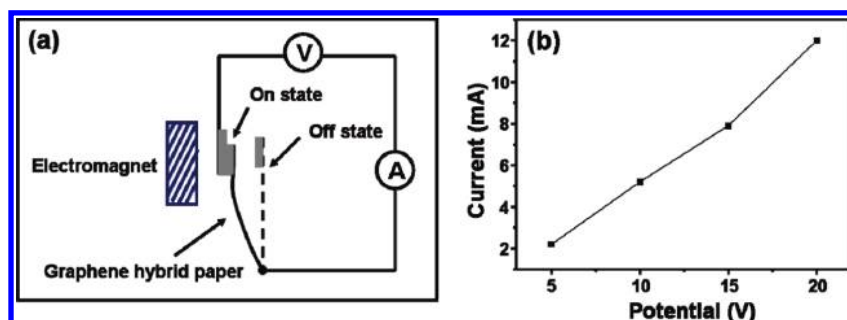


Figure 5. (a) Simple circuit using graphene/ Fe_3O_4 -2-annealed hybrid paper as a magnetic-controlled switch. The contact points for the graphene hybrid paper and the circuit are all coated with silver electrode to reduce the contact resistance. (b) Current–potential curve obtained from the circuit in a when the graphene/ Fe_3O_4 -2-annealed hybrid paper was switched on.

increases corresponding to the loading of Fe_3O_4 nanoparticles. Thus, in addition to maintaining the excellent mechanical and electrical properties of graphene, we further obtained a simple way to add a tunable feature of superparamagnetism to graphene materials and to their flexible papers prepared by a solution process. These combined and tunable properties could then make these graphene/ Fe_3O_4 hybrid papers have great potential in various applications.

Taking into account the fact that our graphene-based hybrid papers exhibit such desired multifunctional properties, they should be useful for various multichannel magnetic-/conducting-related applications. As a demonstration, we present an application that requires overall functionalities including flexibility, mechanical strength, electrical conductivity, and magnetism, as a proof-of-concept. This feasibility is first illustrated by using

a magnet to remotely attract the magnetic hybrid paper as displayed in the top-right inset of Figure 4a. Whereas the pristine graphene paper shows no response to the magnet, the graphene/ Fe_3O_4 hybrid paper is raised by this magnet. Furthermore, an actual homemade intermittent magnetic field device was designed to supply a remote recycling magnetic field to test the magnetic switching performance of these hybrid papers. This automatic setup, which is composed of an electromagnet and a controlling circuit, can offer a repeating intermittent magnetic field up to approximate 500 G at a frequency of 0.2 Hz. As shown in Figure 4b,c, when the magnetic field is turned on, the graphene/ Fe_3O_4 -2-annealed paper is attracted and driven toward the electromagnet, which means the switch is on. Conversely, when the magnetic field is turned off, this hybrid paper instan-

taneously recovers to its original state, which indicates that the switch is off. To depict the concept for practical applications, we further built this magnetic hybrid paper into a simple circuit as a magnetic-controlled switch (Figure 5a) to test its switching reproducibility and electrical performance. When the magnetic field was turned on, the graphene/Fe₃O₄-2-annealed paper made contact with the connecting electrode of the circuit, and current could be detected. Figure 5b presents the current–potential curve for this simple circuit measured when the graphene/Fe₃O₄-2-annealed paper was switched on. It can be seen that the current increased with increasing applied potential and reached about 12 mA when the applied potential was 20 V. Strikingly, because of the excellent flexibility and relatively good mechanical strength of this graphene-based hybrid paper, this on–off process was highly reproducible, and no cracks or downgraded electric performance for the hybrid paper was observed after even more than 1 000 000 cycles (at a frequency of 0.2 Hz, with a testing time more than 1390 h) for a bending angle of about 30°. Even though the electrical conductivity of the graphene-based hybrid papers is lower than that of a traditional mechanical switch or relay based on iron film, the unique features, such as light weight, flexibility, and easy processing, of these graphene-based hybrid papers still make them extraordinarily competitive in applications of considerable frontier technologies including sensitive switches, microrobotics, electronic circuitry, and even memory devices where both electrical conductive and magnetic-controlled channels are needed simultaneously.

4. Conclusions

In summary, free-standing graphene/Fe₃O₄ hybrid papers have been successfully fabricated using a simple water solution process. It has been demonstrated that these multifunctional hybrid papers not only exhibit good flexibility, electrical conductivity, and mechanical strength, but also are provided with superparamagnetism. These features can be easily modulated by controlling the loading of Fe₃O₄ nanoparticles in the hybrid system. We have also presented the experimental results for magnetic-controlled switching performance, which indicate that these graphene-based hybrid papers might be suitable for multichannel-related applications. Consequently, combined with the low cost of graphene material (the raw material of which is graphite), relative simplicity of the manufacturing procedure (solution process), and the good properties of the graphene-based paper, it is reasonable to anticipate that these graphene/Fe₃O₄ hybrid papers could find potential applications in fields such as magnetic controlling devices, data storage, magnetic detection, electromagnetism shielding materials, electrochemical devices, batteries, and so on.

Acknowledgment. The authors gratefully acknowledge the financial support from the NSFC (#50933003, 50902073, 50903044, 20774047), MOST (#2009AA032304), and NSF of Tianjin City (#08JCZDJ25300).

Supporting Information Available: AFM and TEM characterizations of water-soluble nano-Fe₃O₄ particles and graphene/Fe₃O₄ aqueous solution. The tensile stresses of the pristine graphene and hybrid paper with and without annealing. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Magnetic, Electrical Conductive and Flexible Graphene/Fe₃O₄ Paper and Its Application for Magnetic- Controlled Switch

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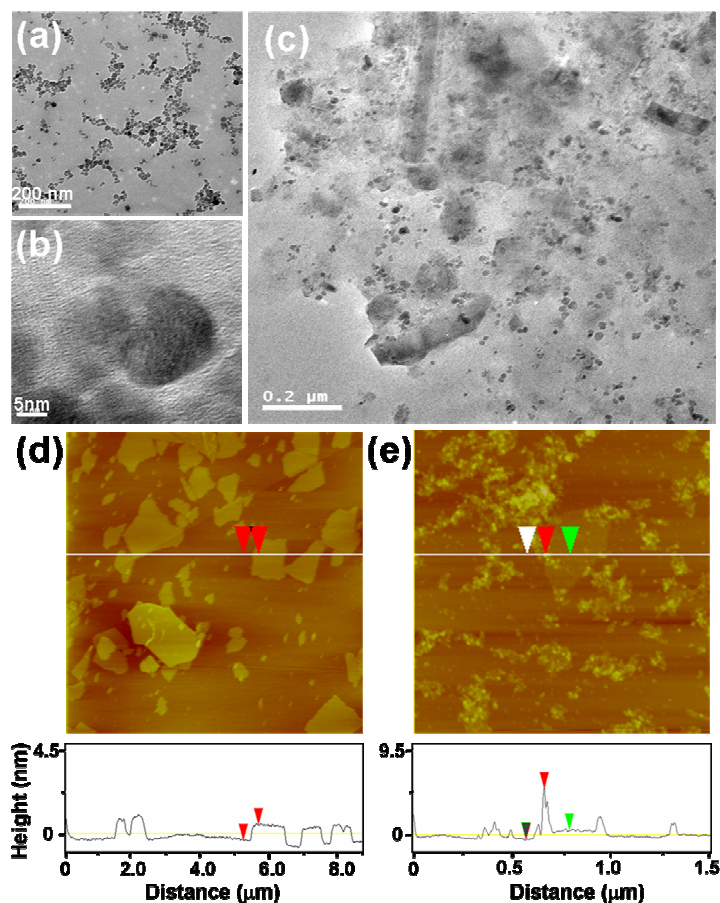


Figure S1. Morphological characterization of water-soluble nano-Fe₃O₄ particles and graphene/Fe₃O₄ aqueous solution. (a) TEM and (b) HRTEM images of water-soluble nano-Fe₃O₄ particles (0.2 mg/ml). (c) TEM image of graphene sheets coated with uniform dispersion of nano-Fe₃O₄ particles (from the solution of sample graphene/Fe₃O₄-1). (d) Typical tapping-mode AFM image of GO sheets deposited on mica substrate from an aqueous dispersion (0.2 mg/ml); the height difference between the red arrows is ~ 1 nm, indicating the typical height of an individual GO sheet. (e) AFM image of reduced Graphene/Fe₃O₄ aqueous solution (from the solution of sample graphene/Fe₃O₄-1), the height difference revealed that nano-Fe₃O₄ particles depositing on individual graphene sheets.

Whether the graphene sheets remain individual dispersed or not after reduction in the presence of precursor ferrofluid is the core factor to affect the quality of the hybrid papers. Transmission electron microscopy (TEM) and typical tapping-mode atomic force microscopy (AFM) measurements are important tools to study the morphological properties of water-soluble nano-Fe₃O₄ particles and graphene/Fe₃O₄ hybrid. Figure 1(a) shows a TEM image of water-soluble nano-Fe₃O₄ particles from

their aqueous solution (0.2 mg/ml). It can be seen that the nano-Fe₃O₄ particles are able to readily disperse in water, which renders them can act as efficient stabilizers to guarantee the exfoliation of graphene sheets. The size of the water-soluble nano-Fe₃O₄ nanoparticles is around 10 nm as displayed by the high-resolution TEM (HRTEM) image in Figure 1(b). Interestingly, though without the aid of chemical covalent bonding and π - π interaction, these water-soluble nano-Fe₃O₄ particles, which appear as dark spots in Figure 1(c), still well spread out in the graphene/Fe₃O₄ hybrid. The morphology and dispersion quality of the graphene/Fe₃O₄ hybrid are also further characterized by AFM. Figure 1(d) and 1(e) display the AFM images and the cross section analyses of pristine GO sheets and reduced graphene/Fe₃O₄ sheets deposited onto mica substrates from corresponding aqueous dispersion, respectively. Analysis of a large number of AFM images revealed most GO sheets had heights of about 0.8 - 1 nm, which is characteristic of a fully exfoliated graphene sheet^[8,37,38].¹⁻³ Noticeable, as depicted in Figure 1(e), a mass of round surface protuberances with 5–10 nm height, coincident with the TEM results, are found on the surface of the graphene for graphene/Fe₃O₄-1 hybrid and some aggregated nano-Fe₃O₄ nanoparticles are also observed. The height of the graphene from the graphene/Fe₃O₄-1 hybrid is about 0.8 nm, which suggests the existing of water-soluble nano-Fe₃O₄ particles indeed prevents the aggregation of the reduced individual graphene sheets.⁴⁻⁶ Furthermore, instead of depositing on graphene sheets, a small quantity of these magnetic particles dissociate from the hybrid, indicating that the requirements of water-soluble nano-Fe₃O₄ particles as effective stabilizers could be farther decreased. It is important that the possible of altering the content of magnetic nano-Fe₃O₄ particles provides a facile and feasible approach to adjust the performance of the graphene/Fe₃O₄ hybrid, such as conductive, magnetic and switching properties, as stated below.

Table S1. The tensile stress of the pristine graphene and hybrid paper with and without annealing.

Samples	Tensile Stress (MPa)
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Graphene paper	8.22
Graphene-annealed paper	9.08
Graphene/Fe ₃ O ₄ -1 paper	9.82
Graphene/Fe ₃ O ₄ -1-annealed paper	32.05
Graphene/Fe ₃ O ₄ -2 paper	23.4
Graphene/Fe ₃ O ₄ -2-annealed paper	16.77

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