Regulatable I-V behaviors of graphene nanoplatelets-carbon nanotubes/epoxy resin composite

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Abstract
Graphene nanoplatelets (GNPs) and carbon nanotubes (CNTs) are two kinds of significant carbon fillers of conductive switching composites with excellent nonlinear I-V property for protecting overvoltage damages of electronic equipment. In this research, GNPs-CNTs hybrid were fabricated and mixed with epoxy resin (ER) by the way of solution blending. Due to the better morphological features and conductivity of GNPs-CNTs hybrid than pure GNPs or CNTs, the GNPs-CNTs/ER composite could exhibit regulatable I-V behaviors with diverse weight ratios of graphene oxide (GO) to multiwalled carbon nanotubes (MWCNTs) and filler concentrations. Especially, the samples (A-0.7, C-0.7 and C-0.8) with proper filler concentrations and weight ratios of GO to MWCNTs could not only possess good nonlinear conductive characteristic, but exhibit stable reversibility throughout multiple measurements as well, which indicates the GNPs-CNTs/ER composite is more usable and practicable for actual overvoltage protection than previous carbon composite. Furthermore, the mechanisms of regulatable I-V behavior of GNPs-CNTs/ER composite were discussed.

1. Introduction
With a more complex electromagnetic environment, the protection for overvoltage damages has undoubtedly become more significant for keeping the safety and stability of the devices from surge voltage [1, 2], which is necessary for improving the reliability and safety of electronic devices. Recent years, the materials possessing nonlinear conductive property, which could transform rapidly from an insulator to a conductor once applied voltage get to a certain threshold, have attracted widely interests and been intensely required for preventing electronic devices from the threats and damages in complex electromagnetic environment [3–6].

Polymeric composites consisting of insulating matrix and conductive fillers have displayed great prospect as the materials with nonlinear I-V behavior which could effectively keep the devices from the damage of overvoltage due to their flexibility and tailorable properties [7–11]. Sun et al studied the conductivity switching behavior of ZnO nanoparticle-polyurethane composite under changing applied voltage [12]. Lin et al investigated the nonlinear conductive property of polymer 1-vinylimidazole loading GO as fillers [13]. Recent years, there have been more and more related researches proving that polymeric composites with obvious voltage-induced could be used to meet the challenge of the transit overvoltage [14–19].

GNPs and CNTs are both widely required as effective reinforcing carbon fillers, due to their special microstructures and eminent characteristics. First of all, GNPs possess particularly two-dimensional microstructure and prominent electrical conductivity \(6 \times 10^7 \text{ S m}^{-1} \) [20, 21], which has drawn widely scientific interests as a particularly potential conductive filler. Related studies have indicated graphene flakes with good morphology characteristic could be enhanced the conductivity and dispersity by modification and successfully employed as a filler for efficiently improving the electrical characteristics of resulting polymeric composite [22–26]. Meanwhile, CNTs, namely MWCNTs and single walled (SWCNTs), are also viewed as a
kind of ideal reinforcing filler to fabricate polymeric composites with excellent properties due to their 1D-line microstructure and outstanding electrical, mechanical and chemical properties [27–30]. Moreover, because of the extremely high specific surface area and aspect ratio respectively, GNPs and CNTs are both liable to stack up during the reaction procedures which could seriously harm the excellent characteristics of composites. But there have been some related researches reporting that through proper processing method, GNPs-CNTs hybrids could be fabricated and efficiently keep the GNPs and CNTs from stacking up [31, 32]. Thus, the polymeric composites containing GNPs-CNTs hybrids possessing nonlinear conductive behavior could be a potential replacement to previous inorganic semi-conductive or conductive materials.

In this article, the GNPs-CNTs hybrid is fabricated by blending, coupling and reduction procedures, and GNPs-CNTs/ER composite is obtained by the way of solution blending. Series results of microstructure characterization and I–V property measurements of GNPs-CNTs/ER composite shows the excellent morphology features of GNPs-CNTs hybrids and I–V characteristic with increasing voltage. Compared with traditional conductive composites, GNPs-CNTs/ER composite could exhibit regulatable I–V behavior with diverse weight ratios of GO to MWCNTs and filler concentrations, namely insulator, ohmic behavior, nonlinear I–V behavior and normal resistance, which indicates GNPs-CNTs/ER composite possess wider range and better flexibility of practical application than previous carbon composite. Moreover, due to the excellent microstructure and conductivity of GNPs-CNTs hybrid, the filler concentration of GNPs-CNTs/ER composite of this article is much lower than that of pure GNPs or CNTs composite.

2. Experimental section

2.1. Materials

As precursors of GNPs and CNTs, GO (single layer) and MWCNTs (30–50 nm in external diameter, 10–20 μm in length) are supplied by Tanfeng Tech Company (Suzhou, China). ER (E-51) [33, 34], used as polymer matrix, is bought from Hui-Sheng Material Company (Chuzhou, China). 2-Ethyl-4-methylimidazole (2E4MZ) is supplied by XiYa Reagent Company (Chengdu, China) for curing the E-51. Hydrazine hydrate solution is supplied by Sinopharm Chemical Reagent Company (Tianjin, China) and employed as reducing reagent. Potassium hydroxide (KOH), selected from DaLu Chemical Reagent Company (Tianjin, China), is employed for controlling the pH value of reaction system.

2.2. Preparation of GNPs/ER composites

For enhancing the dispersity, MWCNTs is decanted to the solution of nitric acid and sulfuric acid with 3:1 in volume. After a four-hour stirring at 65 °C, the CNTs/acid mixture is cooled to room temperature and neutralized with prearranged KOH solution. After leached, the filtered powder is dried by vacuum freeze drier for 24 h and gets the purified CNTs.

In order to obtain well-dispersed mixture of GO and purified CNTs, GO powders are first mixed with ethyl alcohol and ultrasonicated for an hour. And then, purified CNTs are dissolved in GO suspension and ultrasonicated for an hour. For modifying the GO and purified CNTs, KH-560 is poured into the suspension and stirred for four hours at 80 °C. After leached, the filtered cake is dried by vacuum freeze drier for 24 h to get KGO–KCNTs powders.

To improve the conductivity of KGO–KCNTs powders and obtain GNPs-CNTs hybrids, KGO–KCNTs and hydrazine hydrate are decanted to ethyl alcohol and ultrasonicated for an hour, while the pH value is kept at 10. After a six-hour stirring at 90 °C, the black suspension is leached and the filtered powder is dried for 24 h for getting GNPs-CNTs hybrid.

The mixture of preheated ER and GNPs–CNTs hybrid are prepared by the way of solution blending method with acetone. The suspension is stirred at 80 °C for h until the acetone is entirely evaporated. And then, a little of 2E4MZ is dropped into the mixture with continuous stirring, the reactive system is decanted to the prepared die. With curing for 24 h at 20 °C and following 4 h at 100 °C, GNPs–CNTs/ER composites are obtained.

2.3. Characterization and measurements

The morphological characterization and microstructural analysis of GNPs-CNTs hybrid and GNPs-CNTs/ER composite are carried out by scanning electron microscope (SEM, GeminiSEM 300, Jena, Germany) and transmission electron microscope (TEM, JEOL JEM-2100, Tokyo, Japan). X-ray diffractions (XRD) of GO, purified CNTs and GNPs–CNTs hybrid are detected with PuXi XD-6 (Beijing, China). For analyzing the oxygen functionalities on the surfaces of GO, reduced graphene oxide (RGO) and GNPs–CNTs hybrid, Fourier transform infrared spectra (FTIR) are performed by GangDong FTIR-650 (Tianjin, China). Raman spectrums of GO, RGO and GNPs–CNTs hybrid are tested with the Raman spectrometer (Horiba Scientific LabRAM HR Evolution, Tokyo, Japan).
3. Results

3.1. Characterization of GNPs-CNTs hybrid and its composite

As the raw materials of GNPs and CNTs, SEM micrographs of GO powders and purified CNTs powders are shown in figure 1. From figure 1(a), most of GO films present excellent morphological microstructure with few defects and extremely big specific surface area. Meanwhile, the purified CNTs shown in figure 1(b) also have even external diameter and big aspect ratio. Therefore, GO and purified CNTs could both satisfy the need of GNPs-CNTs hybrid preparing.

Figure 2 presents SEM micrographs of GNPs-CNTs hybrids powders with diverse weight ratios of GO to MWCNTs. As shown in figure 2(a), most of GNPs flakes exist as single layer, but some parts of CNTs stack up obviously because of the excessively low weight ratio of GO to MWCNTs, which could influence the morphology of GNPs-CNTs hybrids. On the contrary, as shown in figure 2(b), due to the excessively high weight ratio of GO to MWCNTs, CNTs could not effectively offset the interface energy between adjacent GNPs flakes, which causes some parts of GNPs trend to stack up. Compared with figures 2(a) and 2(b), because of the proper weight ratio of GNPs and CNTs (1:1) and the effective interaction among them, the GNPs-CNTs hybrids shown in figure 2(c) have the best morphological microstructure with almost no obvious stacks and defects of GNPs and CNTs, which can well meet the requirement of this research.

Figure 2(d) presents the EDS measurement of the GNPs-CNTs hybrids powder. As shown the figure, C and O are the two main chemical elements of the hybrids, and the content of C is much more than O, which indicates that most of oxygen-containing groups of GO and purified CNTs have been eliminated by reduction procedure.

Figure 3 presents TEM micrographs of GNPs-CNTs hybrids suspension with diverse weight ratios of GO to MWCNTs. Compared with three figures, the stacks of GNPs or CNTs could be seen in figure 3(a) and 3(b) respectively, and the GNPs-CNTs hybrids shown in figure 3(c) possess the best morphological microstructure and there is almost no defects and stack on the surface because of the proper weight ratio of GNPs and CNTs (1:1) and the effective interaction among them, which is accord with figure 2.

During reducing procedures, the hydrazine hydrate and high temperature remove the oxygen-containing groups on surfaces of GO and purified CNTs, which could transform the sp²-bonded structure to the sp³-bonded structure and effectively improve the conductivity of the GNPs-CNTs hybrids. But this reaction would inevitably bring in more damages and defects on surfaces of GNPs-CNTs hybrid. For analysing the reduction procedure of GNPs-CNTs hybrids, Fourier transform IR (FTIR) spectrums of GO, RGO and GNPs-CNTs hybrid are measured. As presented in figure 4, the corresponding peaks of RGO and GNPs-CNTs hybrids, particularly the O−H stretching vibration at 3440 cm⁻¹, the C=O stretching vibration at 1510 cm⁻¹, the C−O stretching vibration at 1050 cm⁻¹ and the C−O−C stretching vibration at 510 cm⁻¹, are obviously weaker than those of GO. Moreover, above peaks of GNPs-CNTs are slightly stronger than those of RGO, which indicates the residual oxygen-containing groups of GNPs-CNTs hybrid are slightly more than those of RGO after the reductive reaction, because the interaction among GNPs flakes and CNTs prevents some oxygen-containing groups from being removed.

Figure 5 presents the Raman spectrums of GO, RGO and GNPs-CNTs hybrid. According to relate reports [35, 36], the D-band (disordered band) is caused by structural defects, such as sp³ bonds and functional groups. As shown in figure 5, the D-bands of GO, RGO and GNPs-CNTs hybrid locate at 1344.61 cm⁻¹, 1345.06 cm⁻¹ and 1344.17 cm⁻¹ respectively, of which this trend indicates that the intensive interaction among GNPs, CNTs and KH560 of GNPs-CNTs hybrid. Moreover, the I_D/I_G values of GO, RGO and GNPs-CNTs hybrid are respectively 1.017, 1.518 and 1.546, which indicates after a series of reactions the disorder degrees of RGO and GNPs-CNTs hybrids increase because more defects like holes have been brought in and the GNPs and CNTs have been cut into smaller pieces because of the removing of oxygen-containing groups on GO and purified CNTs.

XRD spectrums of GO, purified CNTs, and GNPs-CNTs hybrid are presented in figure 6. From the XRD spectrum of GO, the characteristic peaks located at 10.6° and 42.8° are corresponded to the (001) and (100) crystal planes respectively, which indicates the abundant oxygen-containing groups and well crystal structure of GO. Meanwhile, based on the XRD spectrum of purified CNTs, peaks located at 26.0° and 42.9°, corresponded to the (002) and (100) crystal planes of well crystalline CNTs. Compared with GO and purified CNTs, the peaks of the XRD spectrum of GNPs-CNTs spectrum mostly locate at 25.8° and 42.6°, indicate GO and purified CNTs have been successfully reduced to GNPs and CNTs.
Figure 7 presents the SEM micrograph of the GNPs-CNTs/ER composites fracture surface. From the figure, it could be seen that GNPs-CNTs hybrid is well dispersed in epoxy, and the surfaces between epoxy and GNPs-CNTs hybrid are unobvious, which indicates the GNPs-CNTs hybrids have good compatibility and dispersity.

3.2. Regulatable I-V behavior of GNPs-CNTs/ER composite

Resistances of GNPs-CNTs hybrids with three different weight ratios of GO to MWCNTs (1:1, 1:2, 2:1) were tested and showed in table 1. From the table 1, it could be seen that with the decreasing weight ratio of GO to MWCNTs, the average resistance of GNPs-CNTs hybrid becomes lower, which could be attributed to the extremely high draw ratio of CNTs and higher probability of conductive paths constructing.

For investigating the I-V behavior of GNPs-CNTs/ER composite, the whole obtained samples are classified into three different groups (A, B, C) according to weight ratios of GO to MWCNTs (1:1, 1:2, 2:1), and the classification and allographs of samples are displayed in table 2.

The I-V behaviors of GNPs-CNTs/ER composites of three groups are shown in figure 8. From figure 8(a), five samples of Group A with different filler concentrations were measured and exhibited regulatable I-V behaviors. Samples A-0.5 and A-0.6 contain relative low filler concentration, which causes too high original resistance to generate no essential transformation of conductivity even under 3000 V applied voltage. In contrast, because of the excessive filler concentration, sample A-0.9 with relative low original resistance directly show linear I-V behavior and ohmic conductivity. Especially, with proper concentration of GNPs-CNTs hybrid, samples A-0.7 and A-0.8 both show linear I-V behavior at relative low voltage (Region 1) and can exhibit distinct nonlinear I-V behavior (Region 2) once applied voltage reaches the switching threshold, which indicates an essential transformation of conductivity happens of the two samples. Moreover, for the further analysis of the I-V behavior, multiple subsequent measurements of the samples A-0.7 and A-0.8 were operated. From figure 8(b), the sample A-0.7 shows stably reversible nonlinear I-V behavior throughout all 20 tests with much...
Figure 2. SEM micrographs (a)–(c) and EDS (d) of GNPs-CNTs hybrids powders with diverse weight ratios of GO to MWCNTs: (a) 1:2, (b) 2:1 and (c) 1:1.
lower switching threshold voltages than that shown in figure 8(a). On the contrary, though the original resistance is also much lower than that of figure 8(a), the sample A-0.8 could only exhibit ohmic behavior with no nonlinear transformation and poor reversibility.

Figure 8(c) shows the measurement results of five Group B samples. Compared with figure 8(a), the samples of Group B could exhibit nonlinear I-V behavior at lower filler concentration (0.4 wt% and 0.5 wt%) and lower applied voltages, because of the lower resistance of fillers than that of Group A. And when the filler concentration exceeds 0.6 wt%, the samples (B-0.6 and B-0.7) could only ohmic characteristic. Subsequent measurements of B-0.6 and B-0.7 were carried out and results are shown in figure 8(d). Compared with A-0.7 with reversible nonlinear I-V behavior, B-0.6 and B-0.7 could both exhibit linear I-V behavior with lower resistance like A-0.8.
Figure 4. FTIR spectrum of GO, RGO and GNPs-CNTs hybrid.

Figure 5. Raman spectrums of GO, RGO and GNPs-CNTs hybrid.

Figure 6. XRD spectrums of GO, purified CNTs and GNPs-CNTs hybrid.
As shown in figure 8(e), three samples of Group C (C-0.7, C-0.8 and C-0.9) can exhibit distinct nonlinear I-V behavior and one sample shows ohmic characteristic with the highest switching threshold voltages and resistance of three groups respectively, due to the highest resistance of fillers. Meanwhile, compared with multiple subsequent measurement results of C-0.7, C-0.8 and C-0.9, C-0.7 and C-0.8 can exhibit reversible nonlinear I-V behavior throughout all 20 tests with much lower switching threshold voltages than that shown in figure 8(e) like A-0.7, but C-0.9 can only show linear I-V behavior like A-0.8, B-0.6 and B-0.7.

Furthermore, compared with figure 8(a), Fig 8(c) and figure 8(e), it could be seen that with the decrease of weight ratio of GO to MWCNTs, the original resistance, required filler concentration for nonlinear I-V behavior and switching threshold voltage of composites are lower. And compared with Group B, some special samples of

![Figure 7. SEM micrograph of GNPs-CNTs/ER composite fracture surface.](image)

| Table 1. Resistance of different GNPs-CNTs hybrids. |
|------------------------|------------------------|
| Weight ratio (GO to MWCNTs) | Average Resistance |
| 1:2 | 3.37Ω |
| 2:1 | 11.14Ω |
| 1:1 | 6.83Ω |

| Table 2. Classification of GNPs-CNTs/ER samples. |
|-----------------|-----------------|
| GNPs-CNTs/ER samples | Weight ratio GO to MWCNTs | Filler concentration | Allograph |
| A | 1:1 | 0.5 wt% | A-0.5 |
| | | 0.6 wt% | A-0.6 |
| | | 0.7 wt% | A-0.7 |
| | | 0.8 wt% | A-0.8 |
| | | 0.9 wt% | A-0.9 |
| B | 1:2 | 0.3 wt% | B-0.3 |
| | | 0.4 wt% | B-0.4 |
| | | 0.5 wt% | B-0.5 |
| | | 0.6 wt% | B-0.6 |
| | | 0.7 wt% | B-0.7 |
| C | 2:1 | 0.6 wt% | C-0.6 |
| | | 0.7 wt% | C-0.7 |
| | | 0.8 wt% | C-0.8 |
| | | 0.9 wt% | C-0.9 |
| | | 1.0 wt% | C-1.0 |
Figure 8. I-V behaviors of GNPs-CNTs/ER samples in three groups with different filler concentration of GNPs-CNTs hybrid (a), (c), (e) and multiple measurement results of the samples with nonlinear I-V behavior (b), (d), (f).
Table 3. I-V characteristic coefficients of GNP-CNTs/ER samples.

| Sample Allograph | Region 1 | Reversible Region 1 | Region 2 | Reversible Region 2 |
|------------------|----------|---------------------|----------|---------------------|
| A-0.7            | 1.23     | 1.68                | 57.25    |
| A-0.8            | 1.52     | —                   | —        |
| B-0.4            | 1.26     | —                   | —        |
| B-0.5            | 1.45     | —                   | —        |
| C-0.7            | 1.33     | 1.57                | 95.97    |
| C-0.8            | 1.51     | 1.73                | 38.76    |
| C-0.9            | 1.53     | —                   | —        |

Table 4. Switching threshold voltages of GNP-CNTs/ER samples.

| Sample Allographs | Range (V) | Δ (%) |
|-------------------|-----------|-------|
| A-0.7             | 100.6 ± 16.5 | 16.40 |
| C-0.7             | 264.3 ± 126.2 | 47.75 |
| C-0.8             | 85.6 ± 31.5 | 36.80 |

Group A (A-0.7) and Group C (C-0.7 and C-0.8) can not only exhibit distinct nonlinear I-V behavior, but also possess stable reversibility. So, the resistance and morphology characteristic of GNP-CNTs hybrid are directly related with I-V behaviors of composites.

The I-V characteristic coefficient $\alpha$ of composites can be obtained based on the equation,

$$\alpha = \frac{\log(I_2) - \log(I_1)}{\log(V_2) - \log(V_1)}$$

where $I_1$ is the test current at $V_1$, and $I_2$ is the test current at $V_2$ respectively [37].

The $\alpha$ values of seven GNP-CNTs/ER samples possessing nonlinear I-V behavior with deverse weight ratios of GO to MWCNTs and filler concentrations after several measurements are exhibited in table 3. For all seven samples, the $\alpha$ values of Region 1 are quite smaller than those of Region 2. That indicates these selected seven GNP-CNTs/ER samples all possess obvious nonlinear conductive characteristic. Moreover, according to the $\alpha$ values of three groups in the Region 2, an increase of filler concentration of composite could lead to a decrease of I-V characteristic coefficient, due to the increase of original resistance of composite. Similarly, with the same filler concentration, higher conductivity of fillers (lower weight ratio of GO to MWCNTs) is also relative to lower I-V characteristic coefficient, such as A-0.7 and C-0.7.

Moreover, the coefficients values of reversible nonlinear I-V behavior of A-0.7, C-0.7 and C-0.8 are also displayed in table 3. From the table, it could be seen that the change rule of coefficients of reversible nonlinear I-V behavior are similar to the first measurement, and the values of Region 1 are slightly higher than those of the first measurement, while the values of Region 2 are obviously lower than those of the first measurement.

Table 4 displays the ranges of switching threshold voltage and standard deviations $\Delta$ of three GNP-CNTs/ER samples with reversible nonlinear I-V behavior. As shown in table 4, the $\Delta$ value of sample A-0.7 is smaller than that of samples C-0.7 and C-0.8, which indicates the high conductivity and better morphology features of fillers could lead to a more stable reversibility of composite. Compared two samples of Group C, the $\Delta$ value of sample C-0.8 is smaller than that of sample C-0.7, which indicates with appropriate increase of filler concentration, the composite could possess more stable reversibility of nonlinear I-V behavior.

3.3. Discussion on the mechanism of the regulatable I-V behavior

According to relevant researches of GNPs composite and CNTs composite, most of them only focus on the methods for improving the conductivity of polymeric composite with GNPs or CNTs fillers and mainly investigate the linear I-V behavior or nonlinear I-V behavior with poor reversibility. But the GNP-CNTs/ER composite obtained of this research are able to exhibit regulatable I-V behaviors with diverse weight ratios of GO to MWCNTs and concentrations of fillers, which indicates this composite possess a wide utilization potentiality. Furthermore, based on the figure 8, table 3 and table 4, the GNP-CNTs/ER composite with proper weight ratios of GO to MWCNTs and concentration of fillers, such as A-0.7, C-0.7 and C-0.8, could display reversible nonlinear I-V behavior, and switching threshold voltages and I-V characteristic coefficients could be changed by adjusting weight ratios of GO to MWCNTs and concentrations of filler. Especially, compared with C-0.7 and
C-0.8, the sample A-0.7 possesses the best reversibility and applicable switching threshold voltage, which is usable and practicable for actual overvoltage protection of electronic device.

As a relative complex conductive characteristic of inhomogeneous materials, several theories have been put forward for analyzing the mechanism of nonlinear I-V behavior, such as field-enhancing tunneling, filamentary conduction, electronic hopping and fuller-matrix charge transfer \[38-44\]. After the blending with GNPs and CNTs, some available conductive paths and potential conductive paths are set up by GNPs-CNTs hybrid among ER matrix because of the high specific surface area of GNPs and CNTs, which effectively improves the original conductivity of the composite. Then, two typical units, namely GNPs-CNTs-GNPs-CNTs and GNPs-CNTs-ER-GNPs-CNTs are established in composite. Compared with GNPs-CNTs-GNPs-CNTs units, GNPs-CNTs-ER-GNPs-CNTs units not only improve the original conductivity of the composite, but also set up equipotential barrier models between contiguous fillers. Figure 9 illustrates the equipotential barrier model in GNPs-CNTs-ER-GNPs-CNTs unit, of which \(E_a + E_b\) is the equipotential barrier energy and \(V\) is the applied voltage between contiguous GNPs-CNTs hybrids. Because the filler concentration does not reach the percolation threshold, there are few available conductive paths and the free electrons of GNPs-CNTs hybrid could not transfer through the equipotential barrier, which make GNPs-CNTs/ER composite keep insulating under the normal condition. With the increase of applied voltage, the higher original energy of free electrons leads to a higher possibility for the occurrence of tunneling effect and electronic hopping. So when applied voltage reaches the switching threshold, free electrons transfer through the equipotential barrier of thin enough ER layers and GNPs-CNTs/ER composite exhibit the nonlinear I-V behavior.

Figure 10(a) displays the microstructural model of GNPs-CNTs/ER composite. Because the filler concentration does not reach the percolation threshold, GNPs-CNTs-GNPs-CNTs units widely exist in composite, and these indirect connections provide high resistance of composite at low applied voltage. With the increase of applied voltage, the stronger joule heating gradually reduces the resistance of the thin enough epoxy layers between contiguous GNPs-CNTs hybrids, and these insulating epoxy layers suddenly transform to conductor once the applied voltage reach the switching threshold, which leads to the very high switching voltage at the first occurrence of nonlinear I-V behavior.
The schematic illustration of conductive paths in composite is shown in figure 10(b). Filler concentration, resistance of fillers and morphological characteristic are all influence the conductive characteristic of GNPs-CNTs/ER composite, which essentially influence the constructing of conductive paths. Apparently, too low concentration of fillers would make the distance between contiguous GNPs-CNTs hybrids too long to build effective conductive paths, which causes the sample possess high resistance even under 3000 V applied voltage. In contrast, too high filler concentration would build too many direct connections of GNPs-CNTs hybrids, which leads to the sample originally become a conductor. When the filler is at a proper concentration, indirect connections of the sample with appropriate distance between contiguous GNPs-CNTs hybrids could provide sufficient potential conductive paths, which cause the nonlinear I-V behavior under switching threshold voltage. Moreover, with appropriate weight ratio of GO to MWCNTs and filler concentration, the GNPs-CNTs hybrids, such as Group A and B, not only possess sufficient conductivity, good dispersion in matrix and excellent morphological characteristic, especially high enough specific surface area, but also keep an appropriate distance with contiguous fillers, which make the samples (A-0.7, B-0.7 and C-0.8) still keep insulating at the beginning of following measurements and show nonlinear behavior at relative high applied voltage. In addition, because of the joule heating of ER layers at the first measurement, the resistance and equipotential barrier of insulating layers of potential conductive paths obviously decrease. Thus, the conductive paths of composites become more easily to be built and the switching threshold voltage of following measurements are distinctly lower than that of the initial one.
4. Conclusions

The regulatable I-V behaviors of GNPs-CNTs/ER composite are investigated in this article. According to the results of characterizations and I-V measurements, different weight ratio of GO to MWCNTs not only influences the morphological and conductive characteristic of GNPs-CNTs hybrid, but also could highly affect the I-V behavior of GNPs-CNTs/ER composite with different filler concentrations, namely insulator, ohmic behavior, nonlinear I-V behavior and normal resistance, which indicates GNPs-CNTs/ER composite possess wider range and better flexibility of practical application than previous carbon composite. Especially, with appropriate filler concentrations and weight ratios of GO to MWCNTs, the samples (A-0.7, C-0.7 and C-0.8) could exhibit reversible nonlinear I-V behavior throughout repetitive measurements. Meanwhile, compared with two other samples, A-0.7 possesses relative high I-V characteristic coefficients and the least standard deviation of switching threshold voltage, which indicates A-0.7 have the most stable reversible nonlinear I-V behavior and the best usable and practicable for actual overvoltage protection of electronic device.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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