Carbon materials with quasi-graphene layers: The dielectric, percolation properties and the electronic transport mechanism*

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(Received 12 July 2012; revised manuscript received 5 September 2012)

We investigate the dielectric properties of multi-walled carbon nanotubes (MWCNTs) and graphite filling in SiO_2 with the filling concentration of 2–20 wt.% in the frequency range of 10^2–10^7 Hz. MWCNTs and graphite have general electrical properties and percolation phenomena owing to their quasi-structure made up of graphene layers. Both permittivity ε and conductivity σ exhibit jumps around the percolation threshold. Variations of dielectric properties of the composites are in agreement with the percolation theory. All the percolation phenomena are determined by hopping and migrating electrons, which are attributed to the special electronic transport mechanism of the fillers in the composites. However, the twin-percolation phenomenon exists when the concentration of MWCNTs is between 5–10 wt.% and 15–20 wt.% in the MWCNTs/SiO_2 composites, while in the graphite/SiO_2 composites, there is only one percolation phenomenon in the graphite concentration of 10–15 wt.%. The unique twin-percolation phenomenon of MWCNTs/SiO_2 is described and attributed to the electronic transfer mechanism, especially the network effect of MWCNTs in the composites. The network formation plays an essential role in determining the second percolation threshold of MWCNTs/SiO_2.

Keywords: multi-walled carbon nanotube, quasi-graphene layer, dielectric properties, percolation

PACS: 77.22.Ch, 73.23.–b, 72.80.Tm, 72.20.Ee **DOI:** 10.1088/1674-1056/22/3/037701

1. Introduction

Carbon is one of the most essential and important elements on Earth. Carbon materials which consist of only the carbon element have various multifunctional properties. They can be applied in different fields, such as microwave absorption,[1–5] hydrogen storage,[6,7] supercapacitors,[8,9] batteries,[10,11] and others.[12–17] As a result, carbon materials play an important role in society. Carbon materials are often used as fillers in the preparation of composites.[18–21]

Carbon materials with graphene layers, including carbon nanotubes (CNTs), carbon fibers, and graphite, have significant potential applications. One-dimensional carbon nanomaterials, especially CNTs, have excellent physical and chemical properties due to their unique nanotube structures and the quantum size effect.[22–27] Graphite also has excellent electrical and thermal conductivities due to its lamellar structure. Many researchers have added CNTs and graphite into different matrices to improve their electrical performance.[26–34] Dang *et al*. investigated the dielectric properties and discovered two percolation thresholds in polymer composites.[35–39] The investigation of Kaiser *et al*.[40–43] showed that the electronic migration in multi-walled carbon nanotubes (MWCNTs) mainly includes hopping and migrating of electrons on the outer walls. Weng *et al*.[34] prepared nylon 6/foliated graphite (FG) electrically conducting nanocomposites with a low percolation threshold of less than 0.75 vol.%, the conductivity behavior was modeled and analyzed. They also discussed the percolation phenomenon related to the electricity. However, few researchers have discovered the twin-percolation phenomenon in MWCNT/SiO_2 composites in a wide range of concentrations and discussed the detail of the percolation of composites filled with the quasi-graphene layer carbon material, which is important for electrical applications. In this study, the SiO_2 matrix is filled with a broad range of concentrations of MWCNTs and graphite, respectively. The dielectric properties of MWCNTs/SiO_2 and graphite/SiO_2 composites and the two kinds of percolation phenomena are explored. The corresponding percolation mechanisms are suggested. The special dielectric properties and the percolation phenomenon can help us understand the conductivity mechanism of carbon-based composites with quasi-graphene layers, and can promote the development of high performance function composites.

2. Experiment

In the present work, the commercial MWCNTs (20–40 nm in diameter and 5–15 μm in length) were fabricated by the catalytic decomposition of CH_4 and purchased from Shenzhen Nanotech Port Co. Ltd. (China). The graphite powder was natural flakes with a diameter of 10 μm. MWCNT/SiO_2 and graphite/SiO_2 composites with different loadings were prepared by the following process. Firstly, the commercial

*Project supported by the National Natural Science Foundation of China (Grant Nos. 50972014, 51072024, and 51132002).
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MWCNTs were purified by dispersion in 30 wt.% nitric acid for 2 h under the ultrasonic condition. The acid-treated MWCNTs were collected by filtration and dried at 70 °C for 12 h in an oven. Then, SiO_2 xerogel nanopowders and MWCNTs (or graphite) were mixed into an ethanol solution to form a uniform mixture slurry under the ultrasonic condition. After the ethanol evaporated completely, the mixture was crushed into powder. Polyvinyl alcohol (2 wt.%) was added into the obtained powder and sieved (150 μm) to obtain the fine powder which was compacted into a sheet (diameter $d = 13$ mm) at the pressure of 20 MPa. The morphologies and the structures of MWCNTs, graphite, and the composites were investigated by scanning electron microscopy (SEM, HITACHI S4800) and high resolution transmission electron microscopy (HRTEM, JEM-2100). For electrical measurements, the silver paste was painted on the surfaces of the sheets as electrodes. The dielectric properties were measured by using an Agilent 4294A impendence analyzer in the 10^2–10^7 Hz frequency range.

3. Results and discussion

3.1. Microstructure analysis

In Fig. 1(a), the SEM image clearly exhibits the aggregation of MWCNTs. MWCNTs are entangled into a complex network. The TEM image in Fig. 1(b) obviously shows the one-dimensional hollow tubular structure of several MWCNTs. The HRTEM image of a single MWCNT is shown in the inset. The observed layer space is about 0.34 nm. Figure 1(c) shows the SEM image of graphite, which demonstrates that graphite presents layered pieces. Figures 2(a) and 2(b) show the XRD patterns of MWCNTs and graphite, respectively. The sharp diffraction peak at 23° observed in Fig. 2(b) indicates the existence of highly crystallographic graphite, while the broad diffraction peak at 23° observed in Fig. 2(a) proves that low-ordered MWCNTs exist in the corresponding composites.

The microstructure features of the composites were further investigated by SEM. The typical morphologies of the two kinds of composites shown in Figs. 3(a) and 4(a) indicate that MWCNTs and graphite exist in the composites. For intensive demonstration, the distributions of elements C, Si, and O in the two kinds of composites are shown in Figs. 3(b)–3(d) and 4(b)–4(d), respectively. In the element distribution map of graphite/SiO_2 composites, several main concentration areas of elements C and Si are labeled by small circles and rectangles, respectively. The result shows that MWCNTs and graphite distribute uniformly. In addition, clusters of MWCNTs link each other to build a network, as shown in Fig. 3(a), while no obvious network of graphite flakes is observed, as shown by the isolated rectangles. The network formation is influenced by the dispersion and the concentration of MWCNTs or graphite. The dielectric properties of the composites are affected by the network and the electronic transfer mechanism, which will be discussed in detail in the following.

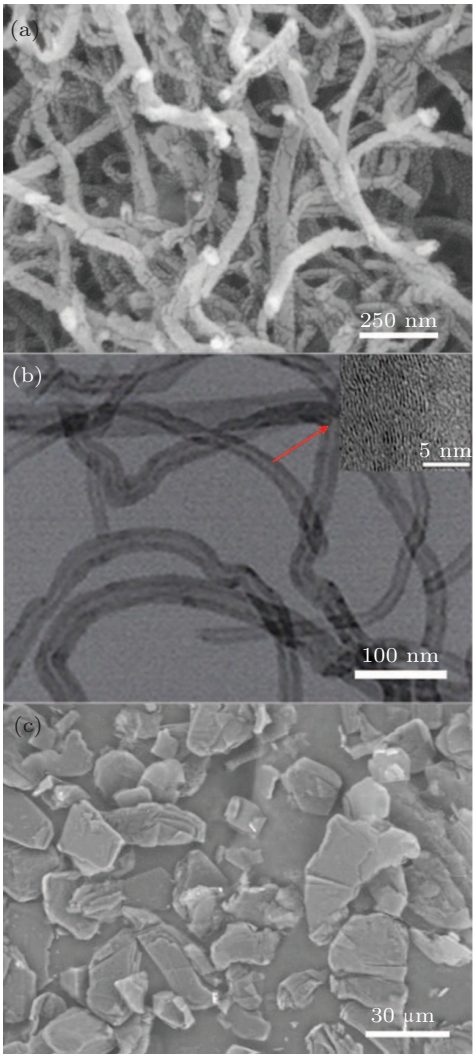


Fig. 1. (a) SEM image of the aggregation of MWCNTs; (b) TEM image of several MWCNTs. The inset shows the HRTEM image of a single MWCNT. (c) SEM image of graphite.

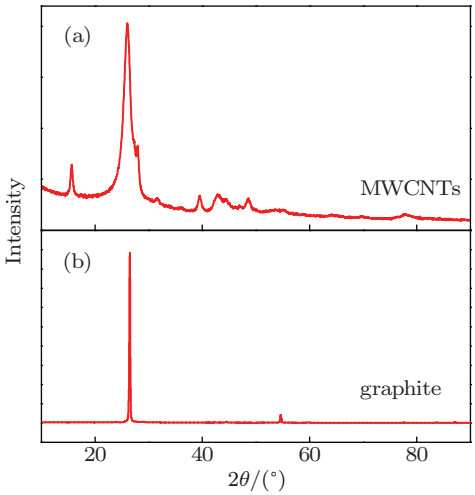


Fig. 2. (color online) XRD patterns of (a) MWCNTs and (b) crystallographic graphite.

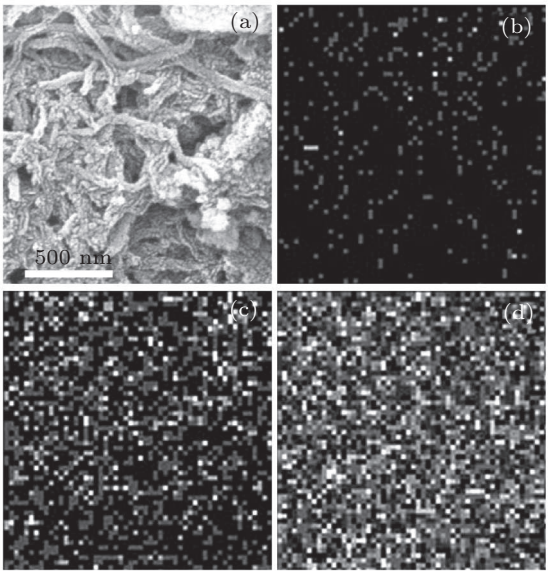


Fig. 3. (a) Analyzed part of the SEM image of the MWCNTs/SiO_2 composites; distributions of elements (b) C, (c) Si, and (d) O in the MWCNTs/SiO_2 composites.

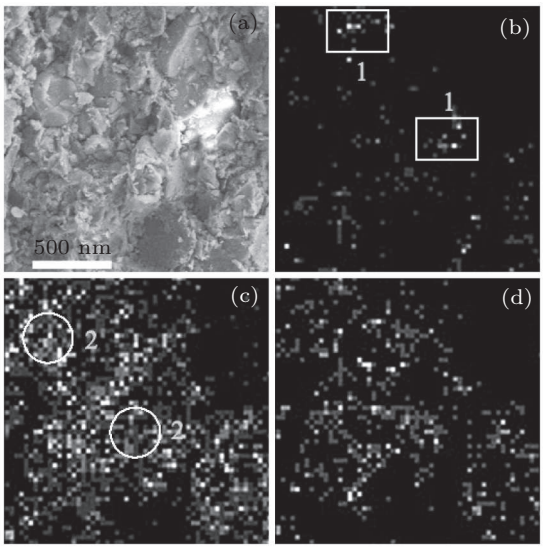


Fig. 4. (a) Analyzed part of the SEM image of the graphite/SiO_2 composites; distributions of elements (b) C, (c) Si, and (d) O in the graphite/SiO_2 composites. Label 1 represents the concentration areas of element C, and label 2 represents the typical areas of element Si.

3.2. Electrical properties of the composites

Figure 5 shows dielectric permittivity ε and conductivity σ of the MWCNT/SiO_2 composites in the 10^2–10^7 Hz frequency range. In Fig. 5(a), ε increases with the increasing concentration of MWCNTs over the whole frequency range. The ε ranges from 4.83 to 115.2 while the concentration ranges from 2 wt.% to 20 wt.% at 202.4 Hz. Particularly, ε has two step-jumps when f_{MWCNT} is in the ranges of 5–10 wt.% and 15–20 wt.%, here f_{MWCNT} is the concentration of MWCNTs. Meanwhile, the ε of the composites displays a rapidly decreasing trend with the increasing frequency when $f_{MWCNT} > f_{C1}$, where f_{C1} is the first percolation threshold. On the contrary, when $f_{MWCNT} < f_{C1}$, ε is almost a constant with the increasing frequency.

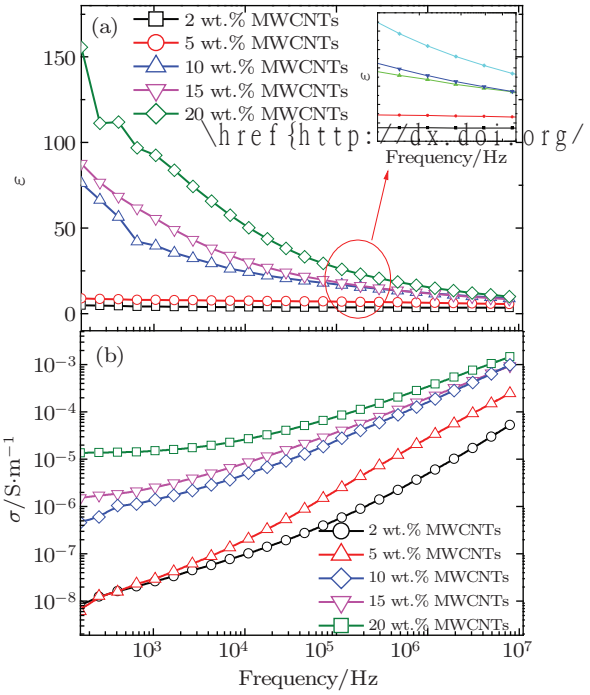


Fig. 5. (color online) (a) Dielectric permittivity and (b) conductivity of the MWCNTs/SiO_2 composites versus frequency of the ac electric field at room temperature.

The interfacial and the orientation polarizations of polar molecules fully cover the MWCNTs and the SiO_2 matrix at a low frequency. With the increasing frequency, the polarizations gradually cannot follow, and the dielectric response decreases correspondingly. As a result, the ε of the composites is maximum at a low frequency. With the increasing frequency, ε will drop or level out. However, when $f_{MWCNT} < f_{C1}$, the network cannot be established effectively. The interfacial polarization mainly caused by the network is small and remains almost a constant in the whole frequency range investigated. Consequently, ε is stable with the changing frequency.

Figure 5(b) shows that the σ of the MWCNTs/SiO_2 composites obviously increases with the increasing frequency and concentration of MWCNTs. The σ ranges from 8.76×10^{-9} S/m to 1.37×10^{-5} S/m while the concentration ranges from 2 wt.% to 20 wt.% at 202.4 Hz. The σ also has two jumps in the MWCNT concentration f_{MWCNT} of 5–10 wt.% and 15–20 wt.%. Meanwhile, the conductivities of the composites with different concentrations all display an increasing trend with the increasing frequency, which agrees with the percolation theory in Ref. [44].

For comparison, ε and σ of the graphite/SiO_2 composites at 10^2–10^7 Hz are shown in Fig. 6. It can be observed from Fig. 6(a) that the ε of the composites increases with the increasing concentration of graphite. The ε ranges from 4.48 to 1.88×10^6 while the concentration ranges from 2 wt.% to

20 wt.% at 202.4 Hz. In particular, ε has a jump when f_g is in the range of 10–15 wt.%, where f_g is the concentration of graphite. Meanwhile, the ε of the composites rapidly decreases with the increasing frequency when $f_g > f_C$, while it is nearly unchanged with the increasing frequency when $f_g < f_C$, where f_C is the percolation threshold.

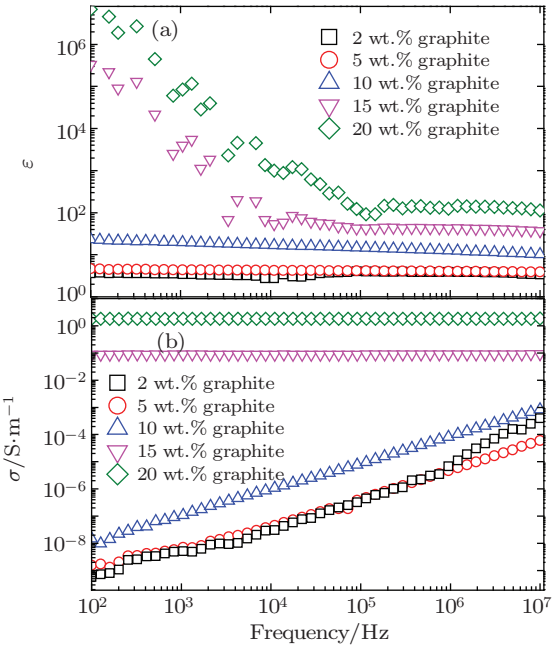


Fig. 6. (color online) (a) Dielectric permittivity and (b) conductivity of the graphite/SiO_2 composites versus frequency of the ac electric field at room temperature.

Figure 6(b) shows that the σ of the graphite/SiO_2 composites increases with the increasing frequency and concentration of graphite. The σ ranges from 2.08×10^{-9} S/m to 1.78 S/m while the concentration ranges from 2 wt.% to 20 wt.% at 202.4 Hz. The σ only has one jump when f_{MWCNT} is in the range of 10–15 wt.%. Meanwhile, the σ of the composites displays an increasing trend with the increasing frequency when $f_g < f_C$, while it is nearly unchanged with the increasing frequency when $f_g > f_C$.

The relationships between the dielectric properties of the two composites and the frequency are similar. Meanwhile, the explanation for the frequency dependence of the dielectric properties of the MWCNT/SiO_2 composites is applied well to the graphite/SiO_2 composites, which mainly attributes to the quasi graphene-layer structures of MWCNTs and graphite.

The percolation phenomenon is reflected through the special variations of dielectric permittivity and conductivity with the concentration of fillers. Figure 7(a) presents the dependence of ε and σ of the MWCNTs/SiO_2 composites on the concentration of MWCNTs at 202.4 Hz at room temperature. The twin-percolation behavior is clearly exhibited at f_{C1} (the first percolation threshold, in the range of 5–10 wt.%) and f_{C2} (the second percolation threshold, in the range of 15–20 wt.%). In Fig. 7(a), when the concentration is close to f_{C1} or f_{C2}, ε has a giant enhancement, from 8.64 to 70.68 and from 81.49 to 115.15, respectively. This phenomenon agrees with the percolation theory.

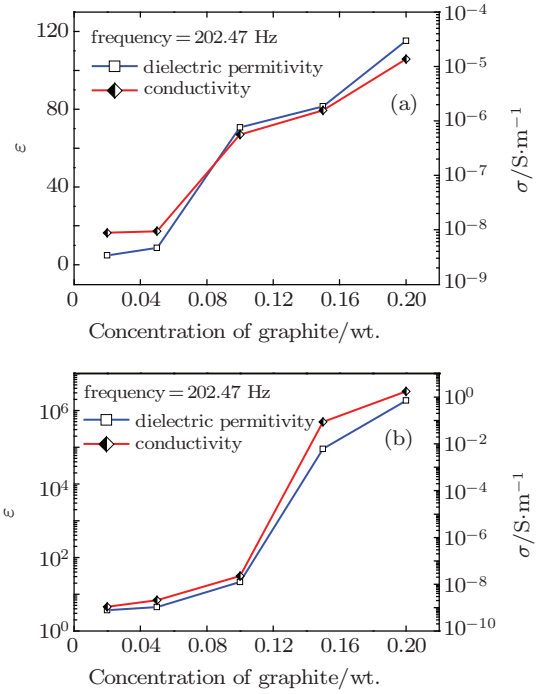


Fig. 7. (color online) (a) Dielectric permittivity and (b) conductivity of the composites versus the filling concentrations of (a) MWCNTs and (b) graphite at room temperature.

At the same time, when f_{MWCNT} changes in the ranges of 5–10 wt.% and 15–20 wt.%, σ increases from 9.37×10^{-9} S/m to 5.59×10^{-7} S/m and from 1.57×10^{-6} S/m to 1.37×10^{-5} S/m, respectively, which also confirms the twin-percolation behavior. According to the percolation theory, σ increases greatly when the filling concentration is close to f_C. The experimental data are of regularity.

For comparison, Fig. 7(b) shows the dependences of ε and σ of the graphite/SiO_2 composites on the concentration of graphite at room temperature. The percolation behavior is only exhibited when f_C is in the range of 10–15 wt.%. When the graphite concentration is close to f_C, ε has a giant enhancement from 21.4 to 90047.6 in the composites.

In Fig. 7(b), when the concentration reaches 10–15 wt.%, σ also increases from 2.22×10^{-8} S/m to 0.0883 S/m. That is to say, when the graphite concentration is close to f_C, the σ of the composites changes greatly, it matches well with the percolation theory.

Comparing the electrical properties of the two composites, we find that the MWCNTs/SiO_2 composites exhibit the twin-percolation phenomenon while the graphite/SiO_2 composites only exhibit the single percolation phenomenon in the investigated range of filling concentration. All the percolation phenomena are determined by hopping and migrating electrons, which are attributed to the special electronic transfer

mechanism of fillers in the composites. A detailed discussion is given below.

3.3. Mechanism of percolation phenomenon

For comprehension, models are suggested to explain the electron transport phenomenon in percolation. Figure 8 is the electronic transport illustration. Due to the special electronic transport structures of one-dimensional MWCNTs, the conductive mechanism of the MWCNTs/SiO_2 composites includes two modes to transport electrons, hopping and migrating, in the relative low filling concentration. Figure 8(a) presents the active hopping of electrons in defects or the top of a single MWCNT. The similar discharge phenomenon appears. Figure 8(b) shows the mode of migrating of electrons on the tube walls.

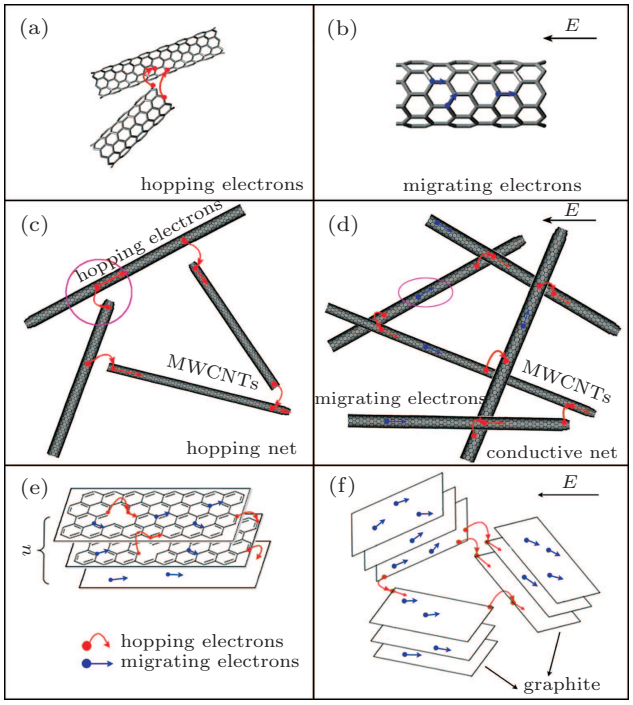


Fig. 8. (color online) (a) Enlarged view of the labeled graph in panel (c); (b) enlarged view of the labeled graph in panel (d); mechanisms of electronic transport of MWCNTs at (c) low filling concentration and (d) high enough filling concentration; (e) an isolated graphite sheet; and (f) several graphite sheets.

On one hand, the conductive network can be formed to provide many migration channels for electrons, which results in the first percolation phenomenon when the filler concentration is high enough to make some fillers contact with each other. Figure 8(d) exhibits that a fine conductive network is formed when the filling concentration of MWCNTs increases beyond the second concentration of percolation. The major way for transport is migrating. On the other hand, hopping electrons are generated between fillers with small distances when the other part of the fillers cannot contact with each other directly owing to the low filling concentration. Electrons can hop from one MWCNT to another nearby MWCNT through the SiO_2 matrix due to the electric field existing between the conductive fillers, which results in the second percolation phenomenon. As shown in Fig. 8(c), the hopping conductive network will be formed when the concentration of MWCNTs increases beyond the first concentration of percolation.

The dependence of electronic transport mode on the filling concentration is the key for the occurrence of the twin-percolation phenomenon. The electrical properties of carbon materials with quasi graphene layers are dominated by the two electronic transport modes, namely, hopping and migrating. However, the conductive mechanism of the graphite/SiO_2 composites mainly depends on the hopping in the investigated range of filling concentration. Graphite is a macroscopic irregular sheet. The volume of graphite is much lower than that of MWCNTs in the composites under the same quality ratio, then graphite is too difficult to form networks in the composites in the investigated range of filling concentration. The main transfer mode for electrons is only hopping, which results in the one-percolation phenomenon. Figure 8(e) shows the electronic transport in an isolated graphite sheet. Figure 8(f) shows the electronic transport among several graphite sheets. The conductive network is scarcely formed in the graphite/SiO_2 composites in the investigated range. The electronic transport mainly depends on the hopping electrons.

4. Conclusion

The MWCNTs/SiO_2 exhibits a twin-percolation phenomenon, and the two percolation thresholds are located in the concentration ranges of 5–10 wt.% and 15–20 wt.% respectively. Meanwhile, the graphite/SiO_2 exhibits only one percolation threshold in the concentration range 10–15 wt.%. The percolation phenomena are determined by the different transfer mechanisms of fillers in the composites. The essence of the twin-percolation behavior is the special electronic transport mode of MWCNTs. In the MWCNTs/SiO_2, hopping electrons lead to the first percolation phenomenon, and the formation of conductive networks results in the second percolation phenomenon. In the graphite/SiO_2, networks are scarcely formed in the investigated range of filling concentration, hopping electrons dominate the one-percolation phenomenon. The special percolation phenomenon of the MWCNTs/SiO_2 and the electrical properties of the two kinds of composites can help us to understand the conductive mechanism of carbon materials with quasi graphene layers loading to inorganic matrices and to promote the development of high performance functional composites.

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