

Electromagnetic interference shielding properties of PEDOT/PSS-halloysite nanotube (HNTs) hybrid films

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ABSTRACT: Poly(3,4-ethylenedioxythiophene)/poly(4-styrene sulfonate) (PEDOT/PSS) films hybridized with halloysite nanotubes (HNTs) were for the first time investigated for electromagnetic interference (EMI) shielding. The hybridization of the HNTs induced EMI properties for the pristine PEDOT/PSS films, and the content of the HNTs in the hybrid films significantly influenced the EMI properties of the hybrid films. The highest EMI shielding effectiveness of the hybrid film is -16.3 dB in the measured frequency range from 2 to 13 GHz for the PEDOT/PSS film hybridized with 75% HNTs, using a sample with 4.5 mm thick. The contribution of EMI shielding effectiveness in the hybrid films is mainly due to dielectric loss rather than magnetic loss. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44242.

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INTRODUCTION

In recent years, electromagnetic interference (EMI) and electromagnetic contamination are becoming serious problems with the growing proliferation of mobile communications, wireless networks, and electronic devices and systems because the electronics systems emit electromagnetic waves. When a high-frequency electromagnetic wave enters the human body, it vibrates tissue molecules to give out heat and results in encounter lesions. Biologists have reported that even a short-term exposure to low-density electromagnetic (EM) radiation could result in temporary sterility. Moreover, it could increase the possibility of leukemia and other cancers.^{1–4} Therefore, electromagnetic interference shielding materials are essential in suppressing these electromagnetic aggressions to safer limits. Traditionally, metals have been considered as very important materials for electromagnetic shielding because of their high absorption, good impedance matching, wide bandwidth, and low cost, but they often suffer from disadvantages, such as heavy weight and ease of corrosion, that restrict their widespread use in these materials.^{5–8} A desirable EMI shielding material is expected to be lightweight, environmentally benign, resistant to corrosion, durable in the long term, and versatile in processing. In order to obtain an excellent material for EMI shielding, some main strategies have been investigated for the processing of EM-absorbing polymer-based composites. In one

of these strategies, the shielding materials consist of soft ferromagnetic nanoparticles like FeCo and carbon materials. The soft ferromagnetic nanoparticles are good candidates for this purpose because of their high saturation magnetization, higher Snoek's limit, and high permeability at high frequencies.⁹ However, carbon materials act as a nonmagnetic, highly dielectric material in various morphologies including nanoshells, nanoflakes, nanotubes, and nanofibers along with soft ferromagnetic metallic nanomaterials to enhance the EM wave absorption capability.^{10–13} The main advantage of using hybrid dielectric-magnetic nanoscale materials is increasing the relative complex permeability and permittivity. However, the weight increase and the inhomogeneity of the material resulting from the addition of metallic fillers are two drawbacks. In another strategy, a polymer matrix is filled with inorganic fillers, fibers, or nanoparticles in order to increase the interaction with the EM radiation. In 2002, Kim *et al.*¹⁴ investigated the electrical conductivity of poly(3,4-ethylenedioxythiophene)/poly(4-styrene sulfonate) (PEDOT/PSS) with H₂O and various solvents such as dimethyl sulfoxide, *N,N*-dimethylformamide, and tetrahydrofuran. The two-step synthesis and electromagnetic core-shell Fe₃O₄-PEDOT composites are expected to have a promising application in the microwave-absorbing field: the minimum reflection loss reached approximately 30 dB at the thickness of 4 mm.¹⁵ Superparamagnetic NiFe₂O₄ particles on PEDOT-graphene exhibit excellent microwave absorption properties: the

maximum reflection loss is -45.4 dB at 15.6 GHz, and the absorption bandwidths with the reflection loss below -10 dB and -20 dB are 4.6 GHz and 1.7 GHz, respectively, when the thickness of the sample is 2 mm.¹⁶ The enhanced electromagnetic absorption mechanism of the above nanocomposites occurs mainly as follows. First, multi-interfaces in the binary or ternary nanocomposites can serve as polarized centers, which are helpful for excellent microwave absorption properties because of the existing interfacial polarization.¹⁷ Second, impedance matching is a very important characteristic for microwave absorption. Polymers are dielectric loss absorbers, and magnetic nanoparticles are magnetic loss absorbers; an improved impedance matching between the dielectric loss and magnetic loss plays an important role in increasing the microwave-absorption properties. Third, dipole polarizations are presented in the magnetic or nonmagnetic nanoparticles, especially when the size is in the nanoscale; the small particle size will increase the dipole polarizations, which can contribute to the dielectric loss.¹⁸ On the other hand, halloysite nanotubes (HNTs) have also attracted much attention because of their molecule-storage ability and excellent mechanical strength.^{19,20} HNTs consist of one alumina octahedron sheet and one silica tetrahedron sheet in a 1:1 stoichiometric ratio,²¹ both sheets bending as double layers into a hollow nanotubular structure, and have large specific surface area.²² Clay minerals are commonly used as pillars to improve the mechanical properties of polymers.²³

Recently we have for the first time found a new phenomenon where the conductivity of a PEDOT/PSS film is significantly improved by mixing in insulating HNTs.²⁴ Based on experimental evidence, we proposed a plausible mechanism for the phenomenon: (1) the aqueous PEDOT/PSS dispersion is absorbed into the nanochannels (with a diameter of about 30 nm) of the HNTs because of the strong capillary effect; and (2) the PEDOT/PSS colloidal particles with a particle size of several tens of nanometers pack well into the nanochannels into well-ordered structures of PEDOT/PSS films, which show conductivity higher by several orders of magnitude than that of PEDOT/PSS films without the HNTs.²⁴ The PEDOT/PSS–HNT hybrid films with 75.5% HNTs showed the highest conductivity of 0.4 S/cm, and the conductivity was improved by two orders of magnitude after both addition of ethylene glycol or treatment with formic acid. By adding poly(ethylene glycol) we can induce flexibility in the hybrid films. The hybrid films had a porous morphology with a specific surface area of 81 m²/g, promising for applications such as thermoelectric, microwave-absorption, and gas-sensing materials.²⁴ The hybrid films where the nano-sized materials are embedded in a polymer matrix are expected to have outstanding properties of electromagnetic interference shielding.^{25–27} For more deserving causes, HNTs, which are natural clays, are easily obtainable and much cheaper than other nanoparticles like carbon nanotubes (CNTs). It is a question: would the conductive PEDOT/PSS colloidal particles densely packed within the channels of the HNTs, whose aspect ratio could be high, show good EMI properties? To the best of our knowledge there are no previous reports to answer it.

Here we have investigated the EMI shielding properties of the PEDOT/PSS–HNT hybrid films. The highest EMI shielding

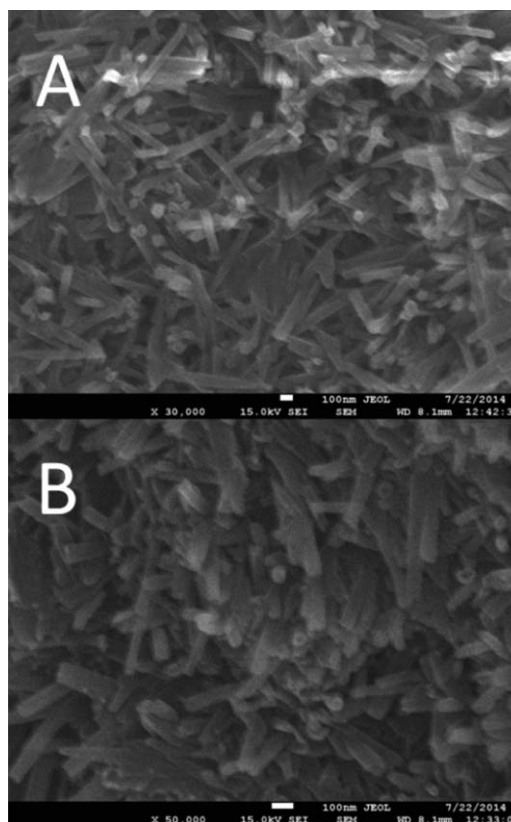


Figure 1. SEM images of the HNTs (A) and a PEDOT/PSS–4% HNTs hybrid film (B). Both scale bars are 100 nm.

effectiveness of the PEDOT/PSS–HNT hybrid film was -16.3 dB in the measured frequency range from 2 to 13 GHz.

EXPERIMENTAL

Free-standing PEDOT/PSS–HNT hybrid films were prepared by drop-casting the solution on a poly(ethylene terephthalate) (PET) film according to a method we previously reported.²⁴ A PEDOT/PSS dispersion (Clevios PH1000, Germany) was used as an aqueous dispersion of the conductive polymer. Ethylene glycol (EG, from Kanto Chemical Co., Japan) was used as an additive in the PEDOT/PSS dispersion before preparation of the hybrid films, or the prepared hybrid film was immersed in formic acid (FA, from Kanto Chemical Co.) in order to improve the electrical conductivity. The PEDOT/PSS solution, which contained the different weight percentages of the EG and HNTs (denoted $x\%$ EG– $x\%$ HNTs in the obtained hybrid film), was dropped on the PET sheet. The hybrid films on the PET sheet were dried at 50 °C for 15 min and at 120 °C for 15 min. The hybrid films were subsequently removed from the PET substrate. The thicknesses of the hybrid films are in the range of 29 – 76 μ m.

For electromagnetic measurement the samples were prepared as follows. Slices of the hybrid film were mixed with paraffin wax at a weight ratio of $7:3$ and pressed into a ring with an outer diameter of 7 mm, an inner diameter of 3 mm, and different lengths that determine the sample thickness. The relative permittivity and permeability measurements were determined by

Table I. Electrical Conductivity of the PEDOT/PSS Hybrid Films

Sample	Conductivity (S/cm)
HNTs	Insulating
PEDOT/PSS film	0.17
PEDOT/PSS-1% HNTs film	0.20
PEDOT/PSS-2% HNTs film	0.31
PEDOT/PSS-4% HNTs film	0.58
PEDOT/PSS/2% EG-4% HNTs film	19.9
PEDOT/PSS/7% EG-4% HNTs film	47.2
PEDOT/PSS/FA-4% HNTs film	47.5

using a coaxial method with an Agilent E5071C ENA vector network analyzer, USA in the frequency range of 2–13 GHz. Finally, the microwave-absorption properties were evaluated by the transmission line theory.²⁴ The electrical conductivity of the hybrid films was measured by a standard four-probe method with a Resist Meter (Lorester MCP-T610, Japan). The morphology of the PEDOT/PSS–HNT films was observed with a scanning electron microscope (SEM, JEM-2100cx, Japan).

RESULTS AND DISCUSSION

Images of the morphologies of the pristine HNTs and the PEDOT/PSS–HNT hybrid films as observed with an SEM are shown in Figure 1. The SEM image of HNTs [Figure 1(A)] shows a clearly nanotubular structure with diameters in a range of 50–70 nm and lengths in a range of 1–2 μm . The SEM image of the PEDOT/PSS–4% HNTs hybrid film [Figure 1(B)] also shows a mainly nanotubular structure with diameters in a range of 50–70 nm and lengths in a range of 1–2 μm , as we previously reported.²⁴

In the previous work we optimized the hybrid film in terms of conductivity and surface area, changing the content of HNTs in the film.²⁴ We found that the conductivity of the film increased with increasing content of HNTs from zero to 75.5%. It is noteworthy that HNTs are electrically insulating, so it is commonly believed that the conductivity of the hybrid film should decrease with increasing content of the insulating HNTs on a volume-percentage basis when mixing insulating materials into conducting polymer films. It is considered that such an enhancement of conductivity occurs through a novel mechanism where the PEDOT/PSS dispersion fully fills the nanochannels of the HNTs by simple mixing.²⁴ The filled PEDOT/PSS colloidal particles with a particle size of 16–40 nm are well ordered and compactly packed with each other because of the restricted space of the nanochannels with a diameter of about 30 nm.²⁴ The well-ordered and packed domains would show higher conductivity than those of the PEDOT/PSS without the HNTs.²⁴ The conductivity of the optimized hybrid film can be improved by the addition of EG or posttreatment of FA.²⁴ The conductivity of the samples investigated in this work is summarized in Table I. The HNTs were completely insulating²¹ and the other samples were conductive, as shown in Table I. When 4% HNTs are added to the PEDOT/PSS dispersion, the resulting hybrid film showed a conductivity of 0.58 S/cm, but in the case of 1%

HNTs, 2% HNTs, and no HNTs the conductivities were 0.20, 0.31, and 0.17 S/cm, respectively. The hybrid film with a conductivity of 0.57 S/cm was much improved in conductivity by treatments of 2% EG, 7% EG, and FA to show conductivities of 19.9, 47.2, and 47.5 S/cm, respectively (Table I).

In terms of the features of EM wave absorbers, the PEDOT/PSS–HNT hybrid film can be expected to exhibit outstanding microwave-absorbing properties, due to conductive PEDOT/PSS domains within the nanochannels with high aspect ratios.²⁴ Owing to the absence of magnetic constituents in the nanocomposites, the real part (μ') and the imaginary part (μ'') of the complex permeability are about 1.0 and 0.0, respectively (not shown). In the relative complex permittivity, the real part (ϵ') and the imaginary part (ϵ'') represent the storage and loss capability for EM wave energy, respectively. The frequency dependence of ϵ' and ϵ'' and the dielectric loss tangent ($\tan \delta = \epsilon''/\epsilon'$) for the hybrid film/paraffin composites are shown in Figure 2.

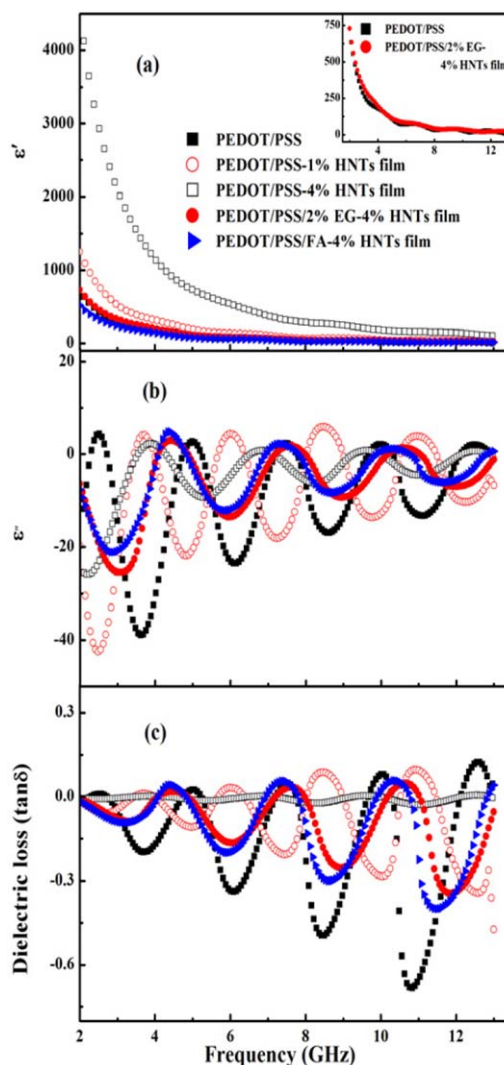


Figure 2. Frequency dependence of ϵ' and ϵ'' and dielectric loss tangent ($\tan \delta = \epsilon''/\epsilon'$) for the hybrid films. Inset in (a): curves at low values of ϵ' for the pristine PEDOT/PSS and the hybrid films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

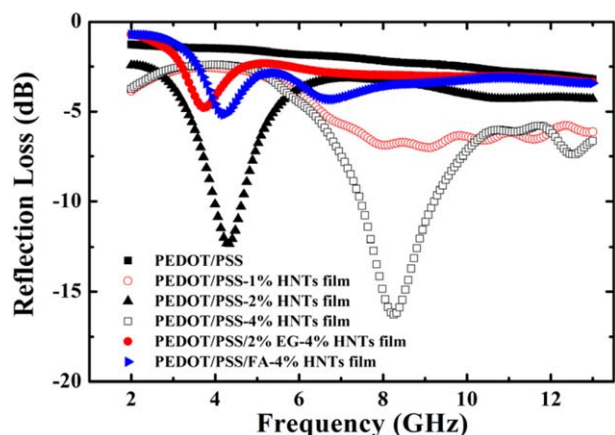


Figure 3. Frequency dependence of the reflection loss (RL) for the hybrid films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As shown in Figure 2(a), the ϵ' for the pristine PEDOT/PSS, which is relatively lower than those composites with added HNTs, declines from 640 to 6.0 with a relatively gentle incline in the range 2–13 GHz. For PEDOT/PSS with 1% HNTs added, ϵ' rapidly declines from 1250 to 14 with the increase in frequency. In contrast with PEDOT/PSS with 1% HNTs added, the trend in the range 2–13 GHz of ϵ' with increasing frequency is similar with different amounts of HNTs added to the PEDOT/PSS matrix. As shown in Figure 2, ϵ' generally rises as the added amount of HNTs increases from 1% to 4%. This result indicates that the added HNTs contribute to the increase in the dielectric permittivity of the hybrid films. It is well known that high dielectric permittivity arises mainly from the conductivity mismatch between the fillers and the matrix in the composites. According to the Maxwell Wagner-Sillars (MWS) principle, the disparity between the conductivities of two adjacent materials results in polarization and charge accumulation at their interfaces.²⁸ Therefore, the dielectric properties of nanocomposites are determined largely by the nature of the filler/matrix interface, the filler surface area, and the inherent conductivity of the fillers. The orientation of the fillers in a certain direction also plays a very important role in obtaining high dielectric constants.²⁸ Therefore it is believed to result from the formation of interfacial polarization sites between PEDOT/PSS and HNTs. The HNTs have a high aspect ratio and active surface atoms,²¹ which induce highly polarized interfaces at PEDOT/PSS/HNT boundaries and support the improvement of dielectric permittivity of the composites. However, for composite samples with the same HNTs loadings (4% HNTs), the ϵ' of the samples, which are modified by adding EG and immersing in FA, are very slow and almost overlap [see inset in Figure 2(a)] with the ones without such treatment. In other words, the higher conductivity for the hybrid films with EG or immersed in FA did not result in a higher dielectric permittivity. In fact, the conductivity is not the only factor in determining the dielectric property. The addition of EG and immersion in FA could deteriorate the conductivity mismatch to result in a decline in dielectric permittivity. The ϵ'' curves are shown in Figure 2(b); ϵ'' reached a lot of peak values in the 2–13 GHz range for all five hybrid film/paraffin

composites of PEDOT/PSS with different contents of HNTs, indicating a resonance behavior that may lead to an intense response in the microwave-absorption performance.^{29,30} The dielectric loss tangent curves [Figure 2(c)] exhibited a behavior similar to the ϵ'' curve.

The EM wave-absorbing performances of the samples were measured according to transmission line theory.² Figure 3 shows the relationship between reflection loss (RL) and frequency for the sample/paraffin composites. The reflection loss of the pristine PEDOT/PSS is from -1.2 to -3.2 decibel (dB) in the 2–13 GHz range. A comparison of the RL curves for the six samples indicates that both the absorbing intensity and the bandwidth in the PEDOT/PSS–HNT hybrid films were improved significantly, compared with those of the pure PEDOT/PSS. For example, the minimum RL reaches -7.0 dB for PEDOT/PSS with 1% HNTs, -12.3 dB for PEDOT/PSS with 2% HNTs, and -16.3 dB for PEDOT/PSS with 4% HNTs. The mentioned phenomenon is easily explained. As discussed above, in the preparation of the PEDOT/PSS–HNT hybrid films, the aqueous PEDOT/PSS dispersion is absorbed into the nanochannels of the HNTs because of the strong capillary effect, and the well-ordered PEDOT/PSS nanosized particles show a conductivity higher by several orders of magnitude than that of PEDOT/PSS particles without HNTs.²⁴ The hybrid films with different amounts of HNTs show higher electrical conductivity than those without HNTs.²⁴ In the hybrid films, there are more free electrons because of the more conductive networks, and they interact with the external electromagnetic field by creating an induction current. The induction current, which dissipates the radiation and converts it into heat, contributes to the great improvement of EMI shielding of the hybrid films with HNTs. Meanwhile, according to the Kubo theory, the energy levels in composite films are not continuous but are split due to the quantum confinement effect. When an energy level is in the range of microwave energy, the electron absorbs a photon and hops from a low energy level to a higher one. The nanosize PEDOT/PSS domain in hybrid films has a large surface area and a high aspect ratio, which create polarized interfaces between PEDOT/PSS in or outside the HNTs and HNTs walls.²⁴ A high density of interfaces between the HNTs and PEDOT/PSS and the boundaries between HNTs are unstable and could be easily excited under an EM wave field,^{31,32} which could act as polarized centers that are prone to space charge polarization by trapping space charges, thus contributing to enhanced microwave absorption. Based on the above discussion, we conclude that the enhanced microwave absorption is mainly due to the geometric effect and the enhanced interfacial effects.

Also, RL values of less than -10 dB were achieved in the range 7.3–9.3 GHz for PEDOT/PSS with 4% HNTs. In fact, a lot of defects, such as pores, lattice distortions, and dangling bonds in the contained HNTs, stacking faults in the HNTs crystallites, and boundaries between HNTs and PEDOT/PSS, could also be easily excited under an EM wave field. As mentioned above, the addition of EG or the immersion in FA could destroy the interaction of microwave radiation with charge multipoles at the interfaces and also contribute to the decline of EMI shielding. And the minimum RLs for the ones with added EG and

immersed in formic acid are respectively -4.8 dB in 3.7 GHz and -5.2 dB in 4.2 GHz, which indicate that the deterioration in EMI shielding results from the addition of EG or the immersion in FA, in contrast with the PEDOT/PSS-4% HNTs hybrid film.

CONCLUSIONS

PEDOT/PSS-HNT hybrid films were for the first time investigated as EMI shielding materials. The hybridization of the HNTs induced EMI properties for the pristine PEDOT/PSS films, and the content of the HNTs in the hybrid films significantly influenced the EMI properties of the hybrid films. The highest EMI shielding effectiveness of the hybrid film is -16.3 dB in the measured frequency range from 2 to 13 GHz for the PEDOT/PSS-4% HNTs hybrid film, using a sample with 4.5 mm thick. The contribution to EMI shielding effectiveness of the hybrid film is mainly due to dielectric loss rather than magnetic loss.

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REFERENCES

- Ortlek, H. G.; Saracoglu, O. G.; Saritas, O.; Bilgin, S. *Fibers Polym.* **2012**, *13*, 63.
- Celozzi, S.; Araneo, R.; Lova, G. *Electromagnetic Shielding*; John Wiley & Sons: Hoboken, NJ, **2008**.
- Yang, Y. L.; Gupta, M. C.; Dudley, K. L.; Lawrence, R. W. *Nano Lett.* **2005**, *5*, 2131.
- Gupta, T. K.; Singh, B. P.; Mathur, R. B.; Dhakate, S. R. *Nanoscale* **2014**, *6*, 842.
- Liu, J. R.; Itoh, M.; Machida, K. I. *Appl. Phys. Lett.* **2003**, *83*, 4017.
- Zhang, X. F.; Dong, X. L.; Huang, H.; Liu, Y. Y.; Wang, W. N.; Zhu, X. G.; Lv, B.; Lei, J. P.; Lee, C. G. *Appl. Phys. Lett.* **2006**, *89*, 053115.
- Liu, X. G.; Geng, D. Y.; Meng, H.; Shang, P. J.; Zhang, Z. D. *Appl. Phys. Lett.* **2008**, *92*, 173117.
- Wen, F. S.; Zhang, F.; Liu, Z. Y. *J. Phys. Chem. C* **2011**, *115*, 14025.
- Liu, X.; Or, S. W.; Ho, S. L.; Cheung, C. C.; Leung, C. M.; Han, Z.; Geng, D.; Zhang, Z. *J. Alloys Compd.* **2011**, *509*, 9071.
- Liu, Q.; Cao, B.; Feng, C.; Zhang, W.; Zhu, S.; Zhang, D. *Compos. Sci. Technol.* **2012**, *72*, 1632.
- Che, R. C.; Peng, L. M.; Duan, X. F.; Chen, Q.; Liang, X. L. *Adv. Mater.* **2004**, *16*, 401.
- Jiang, J.; Li, D.; Geng, D.; An, J.; He, J.; Liu, W.; Zhang, Z. *Nanoscale* **2014**, *6*, 3967.
- Zhang, H.; Xie, A.-J.; Wang, C. P.; Wang, H. S.; Shen, Y. H.; Tian, X. Y. *RSC Adv.* **2014**, *4*, 14441.
- Kim, J. Y.; Jung, J. H.; Lee, D. E.; Joo, J. *Synth. Met.* **2002**, *126*, 311.
- Zhou, W. C.; Hu, X. J.; Bai, X. X.; Zhou, S. Y.; Sun, C. H.; Yan, J.; Chen, P. *ACS Appl. Mater. Interfaces* **2011**, *3*, 3839.
- Liu, P. B.; Huang, Y.; Zhang, X. *Compos. Sci. Technol.* **2014**, *95*, 107.
- Zhou, R. F.; Feng, H. T.; Chen, J. T.; Yan, D.; Feng, J. J.; Li, H. J.; Geng, B. S.; Cheng, S.; Xu, X. Y.; Yan, P. X. *J. Phys. Chem. C* **2008**, *112*, 11767.
- Liu, P. B.; Huang, Y.; Zhang, X. *Powder Technol.* **2015**, *276*, 112.
- Agarwal, M.; Lvov, Y.; Varahramyan, K. *Nanotechnology* **2006**, *17*, 5319.
- Zhai, R.; Zhang, B.; Wan, Y.; Li, C.; Wang, J.; Liu, J. *Chem. Eng. J.* **2013**, *214*, 304.
- Yuan, P.; Southon, P. D.; Liu, Z.; Green, M. E. R.; Hook, J. M.; Antill, S. J.; Kepert, C. J. *J. Phys. Chem. C* **2008**, *112*, 15742.
- Dmitry, G.; Shchukin, G. B.; Sukhorukov, R. R.; Price, Yuri, M. L. *Small* **2005**, *1*, 510.
- Oya, A.; Kurokawa, Y.; Yasuda, H. *J. Mater. Sci.* **2000**, *35*, 1045.
- Yan, H.; Zhang, P.; Li, J.; Zhao, X.-L.; Zhang, K.; Zhang, B. *Sci. Rep.* **2015**, *5*, 18641.
- Wang, Z.; Wei, G. D.; Zhao, G.-L. *Appl. Phys. Lett.* **2013**, *103*, 183109.
- Chen, M. T.; Zhang, L.; Duan, S. S.; Jing, S. L.; Jiang, H.; Luo, M. F.; Li, C. Z. *Nanoscale* **2014**, *6*, 3796.
- Yousefi, N.; Sun, X. Y.; Lin, X. Y.; Shen, X.; Jia, J. J.; Zhang, B.; Tang, B. Z.; Chan, M.; Kim, J.-K. *Adv. Mater.* **2014**, *26*, 5480.
- Dang, Z.-M.; Yuan, J.-K.; Zha, J.-W.; Zhou, T.; Li, S.-T.; Hu, G.-H. *Prog. Mater. Sci.* **2012**, *57*, 660.
- Chen, Y.; Liu, X. Y.; Mao, X. Y.; Zhuang, Q. X.; Xie, Z.; Han, Z. W. *Nanoscale* **2014**, *6*, 6440.
- Miles, P. A.; Westphal, W. B.; Von Hippel, A. *Rev. Mod. Phys.* **1957**, *29*, 279.
- Watts, P. C. P.; Hsu, W. K.; Barnes, A.; Chambers, B. *Adv. Mater.* **2003**, *15*, 600.
- Meng, B.; Klein, B.; Booske, J.; Cooper, R. *Phys. Rev. B* **1996**, *53*, 12777.