RSC Advances

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

ARTICLE

Chemical grafting of multi-walled carbon nanotubes on metal phthalocyanines for the preparation of nanocomposites with high dielectric constant and low dielectric loss for energy storage application

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Xuefeng Li[a], Wenhan Xu[a], Yunhe Zhang*[a], Dan Xu[b], Guibin Wang[a], Zhenghua Jiang[a]

Polymer/CNT (carbon nanotube) composites with a high dielectric constant show great potential for energy storage applications. However, these CNT-based composites usually suffer from high dielectric loss and low breakdown strength, and pose difficulties in the tailoring of the dielectric constant. The integration of a CNT cladding insulator filler layer into the polymers provides an effective way to reach a low dielectric loss and a high breakdown strength. But the insulator layer could significantly reduce the dielectric constant, thereby decreasing the energy storage density of composites. Herein, we have designed and fabricated a novel candidate composed of a semiconductor NH_2-CuPc coated multi-walled carbon nanotube (MWCNT-CuPc) through chemical grafting, in which dielectric CuPc layers can act not only as insulation barriers for suppressing leakage current, but also as semi-conductor layers to partially block electron motion. Thus the as-prepared composites exhibit not only a higher dielectric constant but also extremely decreased dielectric loss and excellent dielectric strength. Moreover, the dielectric properties of the composites can be easily tuned by tailoring the loading of MWCNT-CuPc. Our strategy provides a new pathway to achieve polymer/CNT composites with high dielectric performances for energy storage applications.

Introduction

Owing to their unique properties, carbon nanotubes (CNTs) have attracted much attention in the development of polymer composites.[1, 2] Even small quantities of CNTs have led to the enhancement of mechanical[3], thermal[4], electrical[5], and optical[6] properties. Dielectric materials with high energy density and low dielectric loss have attracted ever-increasing attention because of their wide range of applications in the electronics and electrical industries.[7–12] The maximum energy density, a popular parameter for characterizing the storage capacity of dielectric materials, can be written as $U_{max} = 1/2\varepsilon\varepsilon_0 Eb^2$, where E_b is the electric breakdown strength, and ε and ε_0 are the material's dielectric constant and the vacuum dielectric constant, respectively.[13, 14] Therefore, the maximum energy density can be enhanced either by increasing the dielectric constant or increasing the electric breakdown strength of the materials.

Currently, high dielectric constant (high-k) materials based on CNT/polymer composites are of current interest owing their good processing characteristics.[15-24] However, polymer/CNT composites usually suffer high dielectric loss owing to the insulation-conduction transformation generates high dielectric constant, high dielectric loss and low dielectric strength. Therefore, decreasing the dielectric loss and maintaining high dielectric strength is still a challenge in the development high-k CNT/polymer composites for practical applications.

Within polymer/CNT composites, chemical functionalization on CNT surface is necessary to better improve the dispersion of CNTs throughout the polymer and act as insulation barriers for suppressing leakage current and increasing breakdown strength.[25−27] For instance, the poly(styrene-co-butadiene-co-styrene) (SBS)[28], polystyrene (PS)[29] and Mono-Boc-protected 4,4'-diamino diphenylether (Boc-ODA)[30], etc., have been used to modify MWCNT in order to improve the dielectric properties of composites. Researchers have found that forming an insulator coating on the surfaces of the conductors can effectively reduce the dielectric loss of the composite. However, this method results in a drastic decrease in the dielectric constant, thereby decreasing the energy storage density of composites. Additionally, this method also enlarges the percolation threshold, leading to increasingly difficult processing and deterioration in mechanical properties. Therefore, we reported previously that semiconductor polyaniline (PANI) coating MWCNT to prepare sulfonated poly(aryl ether ketone) (SPAEK) /PANI@MWCNT composites results in composites with a high dielectric constant and low dielectric loss.[31] However, poor thermal stability limits the applications of these composites.

---

[a] Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, 2699 Qianjin street, Changchun 130012, China. E-mail: zhangyunhe@jlu.edu.cn
[b] State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry Chinese Academy of Sciences, Changchun 130022, China.

RSC Advances Accepted Manuscript

Since the semiconductivity of metal phthalocyanines has been discovered,[32] these compounds have become some of the most interesting organic semiconductors due to their high chemical, high thermal stability and the variety of possible synthetic modifications. Hitherto, diverse nanostructured Copper Phthalocyanine-Sensitized Multiwall Carbon Nanotube Films have been Preparation. [33,34]As reported, NH_2-CuPc has a very high dielectric constant (>10000) due to the electron delocalization within the big conjugated molecule, which has been used as dielectric filler to prepare composites with high dielectric constant.[35-38]

In our recently study[9], the acidified-MWCNTs (a-MWCNTs) were coated with NH_2-CuPc through π-π stacking interactions to fabricate the a-MWCNTs/NH_2-CuPc/PVDF composites, in which the amount of NH_2-CuPc and the surface coverage of MWCNTs are really hard to balance. With low NH_2-CuPc amount, the surface coverage of a-MWCNTs is insufficient and lead to the tunnel effect between particles，causing current leakage and dielectric loss. Meanwhile excessive NH_2-CuPc and more free NH_2-CuPc will be left within the composites, which will promote electronic transfer and lead to the dielectric loss. To solve this problem, in this paper, chemical grafting has been adopted to balance the amount of NH_2-CuPc and the surface coverage of MWCNTs, thus current leakage and dielectric loss have been effectively reduced. In contrast to our previous method, pristine multi-walled carbon nanotubes (MWCNT) will be oxidized in mixed acid solution and coated with NH_2-CuPc by chemical grafting (Fig. 1). It's found that the as-prepared NH_2-CuPc chemical grafting acidified multi-walled carbon nanotubes (MWCNT-CuPc)/PVDF composites exhibited not only a higher dielectric constant but also extremely decreased dielectric loss and excellent dielectric strength. Moreover, the energy storage capability of the composites was investigated.

Experimental Section

Materials

The MWCNT (purity>95%, diameter 10-20 nm, length about 30 μm, density 2.1 g/cm^3) synthesized by chemical vapor deposition were purchased from Chengdu Organic Chemistry Co., Ltd. (Chinese Academy of Science). The PVDF powder (Kynar 761A) was fabricated by Arkema (Serquigny, France). 1-Methyl-2-Pyrrolidinone （NMP） and N-N-Dimethylacetamide (DMAc) was purchased from Tianjin Tiantai Chemical Co., Ltd. (Tianjin, China). NH_2-CuPc was synthesized according to our previous work.[35]

Preparation of MWCNT-CuPc

A mixture of MWNTs, HNO_3 (30 mL, 60%), and H_2SO_4 (90 mL, 98%) was first sonicated at room temperature for 1 h and then was refluxed for 2 h. After termination of the reaction, it was allowed to cool down to room temperature. This mixture was diluted and washed with water until the aqueous layer reached neutral and then was vacuum-dried at 50° C for 6 h.[39]

The MWCNT-CuPc was synthesized by a classic route.[40] According to Fig. 1, 1.00 g of acidified MWCNT was solved in 70 ml of thionyl chloride ($SOCl_2$), and mixed for 24 h. The carboxyl was converted to acyl chloride in the process, and then thinly chloride was evaporated out and got the back product. The back product was solved in 100 ml of NMP for 30 min with an ultrasonicator. Subsequently, 1.00 g of NH_2-CuPc was solved in this solution for 24 h with mixing. The suspension was filtrated and washed with DMAc until the filtrate was transparent, and then dried at 80 °C in vacuum for 24 h to obtain the MWCNT-CuPc.

Preparation of MWCNT/NH_2-CuPc

In comparison, we prepared a kind of MWCNT/CuPc compound by π–π stacking interactions between MWCNT and NH_2-CuPc. To make for solutions, 0.03 g of NH2-CuPc was dissolved in 30 mL DMAc. Next, 0.07 g of acidified MWCNT was added into the above solution, sonicated for 1 h, and stirred for 12 h to prepare MWCNT/NH_2-CuPc suspensions. Subsequently, the mixtures were filtered and the filtered solids were dried at 80° C in a vacuum for 24 h to obtain a bottle-green product.

Preparation of composites

A certain amount of MWCNT-CuPc was dispersed in 15 ml DMAc under sonication for 1 h. PVDF solution was prepared separately by dissolving 1.5 g of PVDF powder into 15 ml DMAc. Subsequently, the PVDF solution was added into the MWCNT-CuPc suspensions, and the mixtures were stirred for 12 h. Next, each mixture was poured into distilled water and solidified. The agglomeration of the composites was broken into powder and was boiled in water for 30 min. This boiling process was repeated 6 times, and the powder was filtered and dried at 80 °C for 12 h. Four PVDF/MWCNT-CuPc composites were obtained with MWCNT-CuPc content of 5, 7, 10, and 14 wt%, which were named as PVDF/MWCNT-CuPc-5, PVDF/MWCNT-CuPc-7, PVDF/MWCNT-CuPc-10, PVDF/MWCNT-CuPc-14, respectively.

Characterization

Scanning electron microscopy (SEM) images were recorded using a JSM-6700 scanning electron microscope. All samples were prepared by fracturing the composites at liquid nitrogen temperature and then sputter-coated with a homogeneous gold layer to avoid accumulation of charges. Transmission electron microscopy (TEM) images were obtained from a JEOL JEM-2100 instrument operated at an accelerating voltage of 100 kV. A TGA-7 thermogravimetric analyzer was used to analyze the adsorption amount of NH_2-CuPc on a-MWCNT under air atmosphere at a heating rate of 10 °C /min. The surface characteristic of MWCNT will be researched by ESCALAB X-ray photoelectron spectroscopy. For dielectric measurements, electrodes were painted on using silver paste. The nanocomposite films are round shape 1 cm in diameter and about 100μm in thickness. The alternating current (AC) electrical properties of samples were measured by using contacting electrodes with Agilent, 4294A precision impedance analyzer in the frequency range of 10^2~10^6 Hz at room temperature. Dielectric breakdown strength was measured using a dielectric strength tester (GJW-50kV, Changchun Zhineng Co., China) at room temperature. An increasing

RSC Advances Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

voltage was applied to the top 25 mm diameter cylindrical electrode at a rate of 500 V/s until electrical failure.

Results and Discussions

Preparation and Characterization of MWCNT-CuPc

The XPS spectra of acidified MWCNT and MWCNT-CuPc are shown in Fig. 2. As shown in Fig. 2a, MWCNT-CuPc shows a significant increase in the N 1s and Cu 2p peak intensities compared to MWCNT. This increase can be attributed to the coating of 4NH_2-CuPc. The morphologies of samples before and after coating with 4NH_2-CuPc were determined by TEM. As shown in Fig. 2c, after coating with 4NH_2-CuPc, a flocculent layer was formed on the surface of all the MWCNTs, and a typical TEM image of MWCNT shows that all nanotubes have a smooth surface (Fig. 2d), which indicates that NH_2-CuPc has been grafted on the surface of all MWCNTs.

The thermogravimetric analysis (TGA) measurements of the CuPc, MWCNT/CuPc, and MWCNT-CuPc were carried out to further confirm the successful chemical functionalization of MWCNT by NH_2-CuPc (Fig. 3). The center metal of CuPc is Cu, which will be oxidized to CuO when the temperature reaches 800 °C. The mass percent of residual CuO is about 4.5 wt%, so we calculated the content of the NH_2-CuPc to be about 30 wt% in MWCNT-CuPc. In Fig. 3, the MWCNT/CuPc shows two weight loss temperatures. The first weight loss temperature of MWCNT/CuPc is similar to that of CuPc to explain the decomposition of CuPc, and the second weight loss temperature corresponds to the decomposition of MWCNT. It is noteworthy that the MWCNT-CuPc exhibits a unique decomposition temperature above 540 °C, which indicates NH_2-CuPc of grating to MWCNT no decomposition in 400 °C (the pristine NH_2-CuPc has started decomposition in this temperature as shown Fig. 3). We suggest that this phenomenon is caused by two reasons: the change of structure of conjugated electrons, and the increase of the Van der Waals force. First, the conjugated electron orbits within the NH_2-CuPc molecule overlap with the conjugated system of MWCNT, making it a more stable high π—π conjugated system. Second, based on recent reports, the nature of graphite shows a more stable thermal behavior than neat graphene, which is attributed to the Van der Waals force between layers of graphite.[41] The NH_2-CuPc offers the conjugated and layer structure like scheme 1 shown. Therefore, the layer of NH_2-CuPc is similar to a layer of graphite. The NH_2-CuPc is grafted onto the surface of MWCNT by amide linkage, and its distance is calculated by Angstrom (10^{-10} m). The chemical modification provides a tighter stack than a physical modification. The degree of closeness is decisive for the Van der Waals force, so tremendous Van der Waals forces could greatly change the thermal properties of MWCNT-CuPc. As in Fig. 3, the thermal stability of NH_2-CuPc is enhanced, so it cannot be decomposed at usual temperature. When the MWCNT starts to decompose, the NH_2-CuPc loses its base and starts to decompose as well. Therefore, only one decomposition platform is observed.

Preparation and Micromorphologies of MWCNT-CuPc/PVDF Composites

MWCNT-CuPc/PVDF composite films with different mass fractions (5−14 wt %) of MWCNT-CuPc were prepared by hot-pressing with 10 MPa while holding the temperature at 200 °C for 10 min. The freeze-fractured cross-sections of the composite films with 5 wt% and 14 wt% of MWCNT-CuPc were characterized by SEM to investigate the homogeneity （Fig. 4）. As the mass fraction is 5 wt%, Fig. 4a, all the MWCNTs are embedded in the polymer matrix, and no agglomeration could be found. However, there is partial MWCNT agglomeration with increasing the MWCNT-CuPc content to 14 wt% (Fig. 4b). But particle–matrix de-bonding cannot be found; neither can free NH_2-CuPc in composite be found. The results indicate that the NH_2-CuPc coating can provide strong inter-chain forces with the PVDF matrix, and can improve the interface adhesion between the MWCNT and the matrix. According to the boundary capacitor model, MWCNT-CuPc can construct a large network of microcapacitors with MWCNT cores as the two electrodes and the CuPc coating as the dielectric, thus resulting in composites with a high dielectric constant. Moreover, CuPc coatings not only serve as dielectric layers but also as insulation layers to suppress leakage current by preventing the contact between MWCNTs in the composites, leading to a very low dielectric loss.

Dielectric Properties of the MWCNT-CuPc/PVDF Composites

The dielectric properties of the MWCNT-CuPc/PVDF composite films were studied by dielectric spectroscopy from 100 Hz to 10 MHz at room temperature. At a fixed frequency of 1000 Hz, as shown in Fig. 5, the dielectric constant, dielectric loss tangent, and electric conductivity of the composite samples exhibit a certain dependence on mass fractions. From Fig. 5a, the dielectric constants of the composite samples increase with increasing MWCNT-CuPc content, confirming that the dielectric constant of the composites can be tuned by controlling the content of fillers. On the other hand, although the dielectric loss tangents of the composites increase with increasing the content of MWCNT-CuPc, they still remain low (<0.32) with a high loading of MWCNT-CuPc. This dielectric behavior may be related to the unique coating structure of MWCNT-CuPc. It is noteworthy that the conductivity of the composites exhibits an approximately linear dependence on the filler concentration, suggesting that no clear signature of electrical percolation forms in the composites as shown in Fig. 5b. Such an electrical phenomenon is different from previous CNT/polymer composites and conductive filler composites,[20] [24] indicating that CuPc shells can effectively prevent CNTs from forming the conductive percolation network for the composites even with a high loading of CNTs. This result further confirms that the CuPc coating can effectively reduce the conduction loss by the insulating boundary around the MWCNT.[42]

The dependence of the dielectric constant, dielectric loss tangent, and AC conductivity of the composites with different MWCNT-CuPc on frequencies is shown in Fig. 6. As shown in Fig. 6a, the dielectric constant of the PVDF is almost

RSC Advances Accepted Manuscript

Please do not adjust margins

independent of the frequency in the measured range, and the frequency dependence becomes gradually stronger as the content of the MWCNT-CuPc increases. The drop in the dielectric constant at high frequencies may be attributed to the leakage current of the composites. It is noteworthy that the dielectric constant does not rise dramatically in contrast to previous reports[43] by increasing the concentration of MWCNT-CuPc. This phenomenon is mainlydue to the dielectric CuPc layer. Changing the frequency from 10^3 to 10^5 Hz, a low dielectric loss tangent is observed in the all composites, and it is more obvious with a higher loading of MWCNT-CuPc (i.e., 14 wt%) (Fig 6b), which is highly desirable and actively pursued for the applications of dielectric materials in electric energy storage capacitors and actuators.[44]

The conductivity of the composites exhibits strong frequency dependence and increases almost linearly with frequencies (Fig 6c), which is characteristic of the conductor–insulator composites.[37–40] Under an AC field, the conductivity is determined by the highest barrier experienced as the carriers travel for one half-period of the field. At low frequencies, for high MWCNT-CuPc composite content (14 wt%), the carriers undertake random walks and are able to travel through the film along the available conductive network within the long time scale. The AC conductivity equals the DC conductivity at low frequency. As frequency increases, the charge carriers can only scan the limited conductive network in one half period of the AC field, leading to a decrease in the potential barrier that they cover and an increase in the conductivity. Hereafter, the AC conductivity of the composites is higher than the DC conductivity and shows frequency-dependent regions.[45, 46] It is well known that conductivity, dielectric constant, dielectric loss, and electric breakdown strength are four essential indices for dielectric materials, and all four indices are interconnected.[44]As shown in Fig. 5, a change of AC conductivity of the MWCNT-CuPc/PVDF composites slope is clearly visible at 10^5 Hz; meanwhile, a decrease of the dielectric constant and a simultaneous increase of dielectric loss are also visible at the same frequency of measurement.

Energy Storage Capability and Electric Breakdown Strength of MWCNT-CuPc/ PVDF Composites

For an electrically active material used in high-efficiency power capacitors, a high dielectric constant and low dielectric loss are highly desirable characteristics and have been actively pursued. However, the dielectric constant is not the only factor governing the energy storage for a dielectric material, and high breakdown strength is also required for large energy storage. Fig. 7 shows the breakdown strength and maximum energy density of MWCNT-CuPc/PVDF composites with different MWCNT-CuPc. As shown in Fig. 7, the pure PVDF film has high breakdown strength of 299 MV/m. The breakdown strength of the composite films shows a continuous decrease with an increasing MWCNT-CuPc content. This phenomenon can be explained by the high electric conductivity of the MWCNT and the enhancement of electric field near the interface because of the differences of electric properties between fillers and the polymer matrix.[47, 48] Despite a large decrease of breakdown strength, the composites with as high as 10 wt% MWCNT-CuPc still withstand a high electric field (e.g., 130 MV /mm). This is extremely important for energy storage applications.

Theoretically, the maximum energy storage density (U_{max}) of a dielectric material is dependent on the dielectric constant and the strength of the electric field. It can be calculated by the following equation:

$$U_{max} = 1/2\varepsilon\varepsilon_0 E_b^2$$

The higher dielectric constant and breakdown strength will lead to a higher energy storage density. With an increase of the MWCNT-CuPc content, the breakdown strength decreases continuously, while the dielectric constant increases gradually. The combined effect of both the dielectric constant and the breakdown strength results in a maximum value of the energy density at a certain content of MWCNT-CuPc. As shown in Fig. 7, the maximum energy density of the MWCNT-CuPc/PVDF composite films begins to increase, and then decreases. The PVDF/MWCNT-CuPc-7 exhibits a maximum energy density of up to 4.25 J cm^{-3}, which promotes 30% than that of pure PVDF (3.31 J cm^{-3}). It should also be mentioned that the breakdown strength of our composites was measured on relatively thick films (150-200 μm). Considering that the breakdown strength of dielectric materials generally decreases with the increase of the sample thickness, higher energy density of thin composite film can also be expected.[49]

Dielectric materials for pulsed power applications require high-frequency operation conditions. In such a case, large dielectric loss of materials tends to dissipate a fraction of their stored energy in the form of heat. Thus, apart from high energy density, low dielectric loss is another important parameter for dielectric materials in practical applications. The PVDF/MWCNT-CuPc-7 with only 0.039 of dielectric loss tangent is very promising for preparing high energy density polymer composites.

Conclusions

We have prepared a kind of novel MWCNT-CuPc made up of multi-walled carbon nanotube (MWCNT) and NH_2-CuPc via chemical functionalization. The corresponding MWCNT-CuPc/PVDF composites were prepared, and their dielectric properties and energy storage capabilities were investigated. It is believed that the dielectric CuPc layer around CNTs plays an important role in realizing the high dielectric performances of the composites. Our results show that the composites still withstand a high electric field and exhibit significantly enhanced energy storage capability in comparison with the pure PVDF. For example, with 7% MWCNT-CuPc composite, the breakdown strength is 200 kV mm^{-1}, and the theoretical maximum energy density is 4.25 J cm^{-1}, which is 30% higher than that of the pure PVDF (3.31 J cm^{-1}). More importantly, this composite shows low dielectric loss of only 0.039. All these characteristics suggest that the MWCNT-CuPc/PVDF composites are promising materials for energy storage application. This work also provides a new route for preparing high energy density composites for use in the electronics and electrical industries.

RSC Advances Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

Acknowledgements

We wish to thank the National Science Foundation of China (50803025 and 51173062) for financial support.

References

1 J. E. Mark, *Acc. Chem. Res.*, 2006, **39**, 881.
2 S. Murugesan, T.-J. Park, H. Yang, S. Mousa and R. J. Linhardt, *Langmuir*, 2006, **22**, 3461.
3 R. Sen, B. Zhao, D. Perea, M. E. Itkis, H. Hu, J. Love, E. Bekyarova and R. C. Haddon, *Nano Lett.*, 2004, **4**, 459.
4 M. J. Biercuk, M. C. Llaguno, M. Radosavljevic, J. K. Hyun, A. T. Johnson and J. E. Fischer, *Appl. Phys. Lett.*, 2002, **80**, 2767.
5 S. Liu, B. Lin, X. Yang and Q. Zhang, *J. Phys. Chem. B.*, 2007, **111**, 1182.
6 Y. Yang, X. Wang, L. Liu, X. Xie, Z. Yang, R. K. Y. Li and Y.-W. Mai, *J. Phys. Chem. C*, 2007, **111**, 11231.
7 Q. M. Zhang, H. F. Li, M. Poh, F. Xia, Z. Y. Cheng, H. S. Xu, C. Huang, *Nature*, 2002, **419**, 284.
8 Y. Wang, X. Zhou, Q. Chen, B. J. Chu, Q. M. Zhang, *IEEE Trans. Dielectr. Electr. Insul.*, 2010, **17**, 1036.
9 Y. H. Zhang, D. Xu, W. H. Xu, W. W. Wei, S. W. Guan, *Composites Science and Technology*, 2014, **104**, 89.
10 K.-I. Park, M. Lee, Y. Liu, S. Moon, G.-T. Hwang, G. Zhu, J. E. Kim, S. O. Kim, D. K. Kim, Z. L. Wang, K. J. Lee, *Adv. Mater.*, 2012, **24**, 2999.
11 R. P. Ortiz, A. Facchetti, T. J. Marks, *Chem. Rev.*, 2010, **110**, 205.
12 L. Cao, W. Zhang, X. H. Zhang, L. Yuan, G. Z. Liang, A. J. Gu, *Ind. Eng. Chem. Res.*, 2014, **53**, 2661.
13 B. J. Chu, X. Zhou, K. L. Ren, B. Neese, M. R. Lin, Q.; Wang, F. Bauer, Q. M. Zhang, *Science*, 2006, **313**, 334.
14 J. Azadmanjiri, C. C. Berndt, J. Wang, A. Kapoor, V. K. Srivastavac,C. Wen, *J. Mater. Chem. A*, 2014, **2**, 3695.
15 H. Y. Liu, Y. Shen, Y. Song, C. W. Nan, Y. H. Lin and X. P. Yang, *Adv. Mater.*, 2011, **23**, 5104.
16 C. Wu, X. Huang, L. Xie, X. Wu, J. Yu and P. Jiang, *J. Mater. Chem.*, 2011, **21**, 17729.
17 S. H. Zhang, N. Y. Zhang, C. Huang, K. L. Ren and Q. M. Zhang, *Adv. Mater.*, 2005, **17**, 1897.
18 C. Wu, X. Y. Huang, X. F. Wu, J. H. Yu, L. Y. Xie and P. K. Jiang, *Compos. Sci. Technol.*, 2012, **72**, 521.
19 H. Koerner, G. Price, N. A. Pearce, M. Alexander and R. A. Vaia, *Nat. Mater.*, 2004, **3**, 115.
20 Z. M. Dang, Y. H. Lin, C. W, Nan, *Adv. Mater.*, 2003, **85**, 1625.
21 T. V. Sreekumar, T. Liu, B. G. Min, H. Guo, S. Kumar, R. H. Hauge, R.E. Smalley, *Adv. Mater.*, 2004,**16**, 58.
22 Y. J. Kim, T. S. Shin, H. D. Choi, J. H. Kwon, Y. C. Chung. *Carbon*, 2005, **43**, 23.
23 S. Li, Y. Qin, J. Shi, Z.-X. Guo, Y. Li, D. Zhu, *Chem. Mater.*, 2005, **17**, 130.
24 X. Liu, Y. H. Zhang, M. Zhu, X. Yang, C. R. Rong, G. B. Wang. *Soft Mater.*, 2011, **9**, 94.
25 Y. Chen, Q. X. Zhuang, X. Y. Liu, J. Liu, S. L. Lin, Z. W. Han, *Nanotechnology*, 2013, **24**, 245702.
26 Z. X. Qiang, G. Z. Liang, A. J. Gu, L. Yuan, Ind. Eng. Chem. Res., 2014, **53**, 4726.
27 Q. Li, P. Peng, G. X. Chen, S. Yoon, *J. Mater. Chem. C*. 2014, **2**, 8216.
28 Y. T. Liu, X. M. Xie, X. Y.Ye, *Carbon*, 2011, **49**, 3529.
29 B. Shen, W. Zhai, C. Chen, D. D. Lu, *Appl. Mater. Interfaces.*, 2011, **3**, 3103.
30 Y.Q. Chen, B. Q. Lin, X. Q. Zhang, J. C. Wang, C. W.Lai,Y. Sun, Y.R. Liu, H. Yang, *J. Mater. Chem. A*, 2014, **2**, 14118
31 Y. H. Zhang, P. F. Huo, J. F. Wang, X. Liu, G. B.Wang, *J. Mater. Chem. C*, 2013, **1**, 4035.
32 R. Singh, A. S. Hay, *Macromolecules*, 1992, **25**, 1017.
33 Z. L. Yang, H.Z. Chen, L. Chao, H. Y. Li， M. Wang, *Mat. Sci. Eng. B.*, 2004, **106**, 73.
34 R. A. Hatton, N. P. Blanchard, V. Stolojan, A. J. Miller, S.R. Silva, *Langmuir*, 2007, **23**, 6424.
35 D. F. Ren, W. W. Wei, Z. H. Jiang, Y. H. Zhang, *Polym. Plast. Tech. Engin.* 2012, **51**, 1372
36 Q. T. Wang, W. L. Jiang, S. W. Guan, Y H. Zhang, *J. Inorg. Organomet. Polym.*, 2013, **23**, 743.
37 Y. H Zhang, G. Zhang, D. Xu, J. F. Wang, X. Yang, Z. H. Jiang, *RSC Adv.*, 2014, **4**, 28721
38 X. Yang, Q. T .Wang, Z. H, Jiang, Y. H.Zhang, *Polym. J.*, 2012, **44**, 1042.
39 J. Liu, A. G. Rinzler, H. J. Dai, J. H. Hafner, R. K. Bradley, P. J. RBoul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y. S. Shon, T. R. Lee, D. T. Colbert, R. E. Smalley, *Science*, 1998, **280**, 1253.
40 L. J. Niu, P. P. Li, Y. Chen, J. Wang, J. J. Zhang, B. Zhang, W. J. Blau, *J. Polym. Sci.: Polym. Chem.*, 2011, **49**, 101
41 Y. Hemandez, V. Nicolosi, M. Loty, *Nat. Nanotechnol.*, 2008, **3**, 563.
42 C. Wu, X. Y. Huang, X. F. Wu, L. Y. Xie, K. Yang , P. K. Jiang, *Nanoscale*, 2013, **5**, 3847
43 C. Huang and Q. M. Zhang, *Adv. Funct. Mater.*, 2004, **14**, 501–506.
44 J. W. Shang, Y. H. Zhang, L. Yu, Ax. L. Luan, B. Shen, Z.L Zhang, F. Z. Lv, P. K. Chu, *J. Mater. Chem. A*, 2013, **1**, 884.
45 B. E. Kilbride, J. N. Coleman, J. Fraysse, P. Fournet, M. Cadek, A. Drury, S. Hutzler, S. Roth and W. J. Blau, *J. Appl. Phys.*, 2002, **92**, 4024.
46 H. Xu, S. Zhang, S. M. Anlage, L. Hu, G. Gruner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **77**, 075418.
47 K. Yang, X. Y. Huang, Y. H. Huang, L. Y. Xie and P. K. Jiang, *Chem. Mater.*, 2013, **25**, 2327.
48 Z. M. Dang, J. K. Yuan, J. W. Zha, T. Zhou, S. T. Li and G. H. Hu, *Prog. Mater. Sci.*, 2012, **57**, 660.
49 X. L. Jia, Q. Zhang, M. Q. Zhao, G. H. Xu, J. Q. Huang, W. Z. Qian, Y. F. Lu and F. Wei, *J. Mater. Chem.*, 2012, **22**, 7050.

RSC Advances Accepted Manuscript

Please do not adjust margins

Journal Name

ARTICLE

RSC Advances Accepted Manuscript

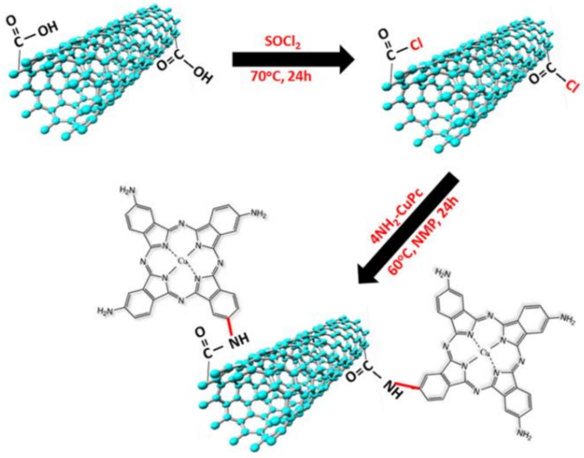

Fig. 1 Schematic of the reaction scheme to form MWCNT-CuPc

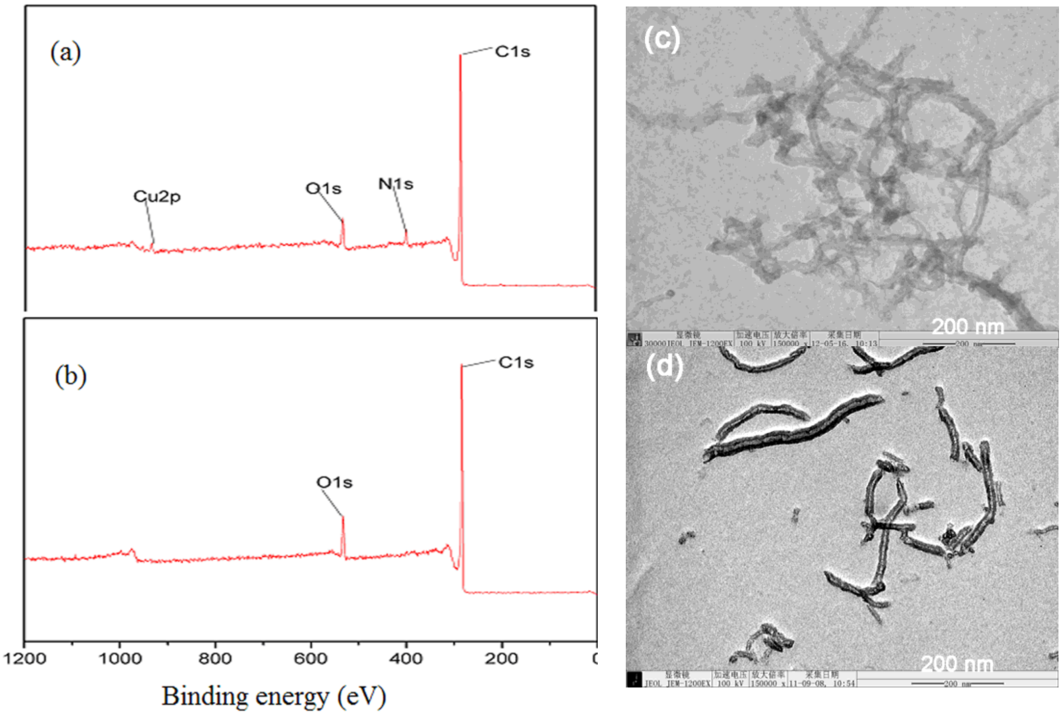

Fig. 2 XPS general spectra of (a) MWCNTs-CuPc, (b) a-MWCNTs, typical TEM image of (c) MWCNTs-CuPc and (d) a-MWCNTs at 200 nm

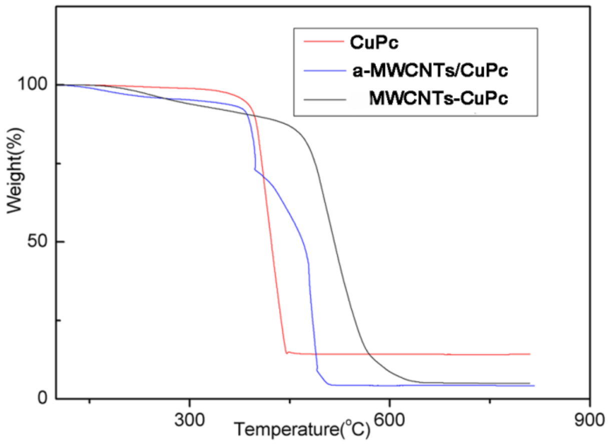

Fig. 3 TGA curves of CuPc, a-MWCNTs/CuPc by π–π stacking interactions, MWCNTs-CuPc by chemical grafting.

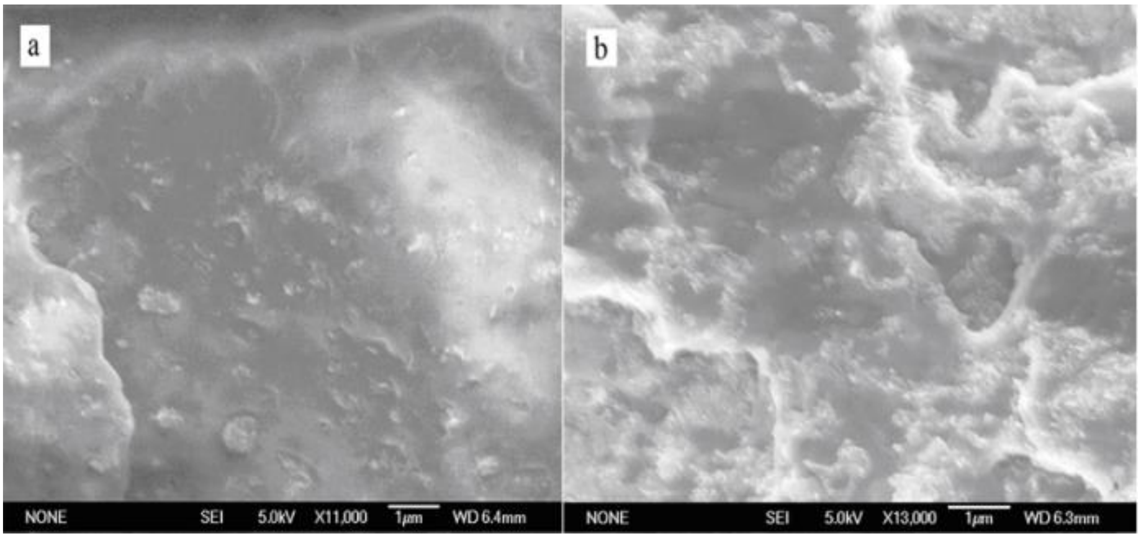

Fig. 4 SEM images of PVDF/MWCNT-CuPc-5 (a), PVDF/MWCNT-CuPc-14 (b) at 1μm.

RSC Advances Accepted Manuscript

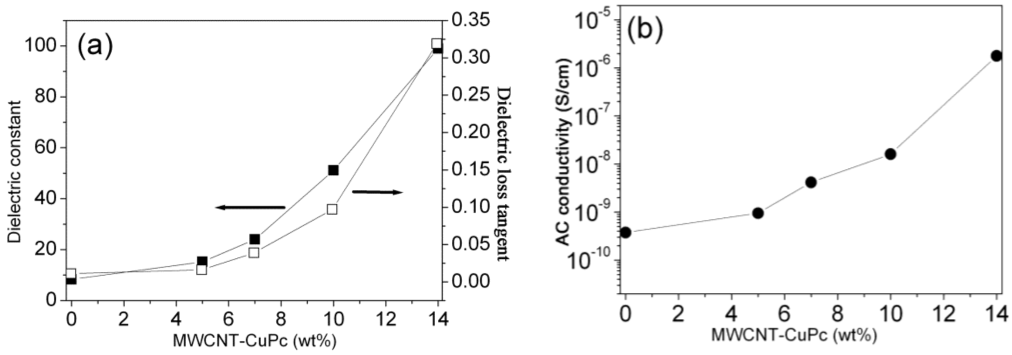

Fig. 5 Variation of dielectric constant and dielectric loss tangent (a) and electrical conductivity (b) of the MWCNTs-CuPc/PVDF composite films as a function of the mass fraction of MWCNTs-CuPc at 10^3 Hz.

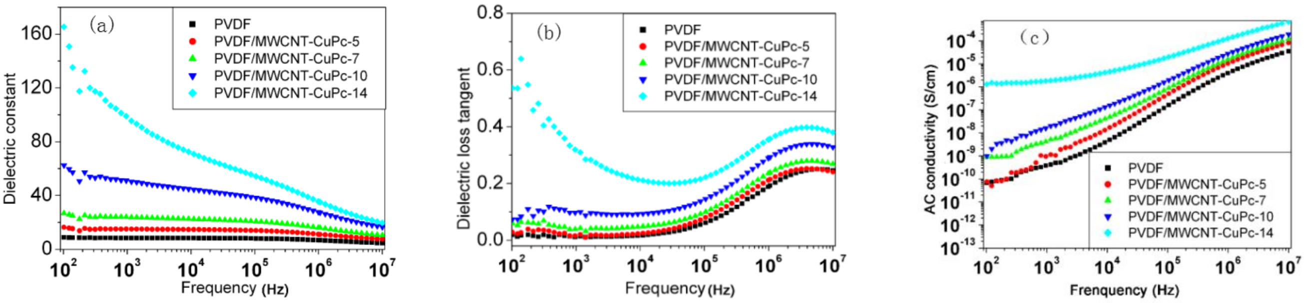

Fig. 6 Frequency-dependent dielectric constant (a), dielectric loss tangent (b), and electrical conductivity (c) of the composites as a function of the MWCNTs-CuPc loading

RSC Advances Accepted Manuscript

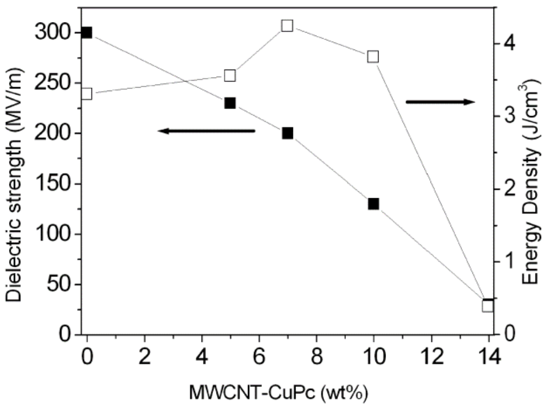

Fig. 7 Breakdown strength and the calculated maximum energy storage density of the composite

RSC Advances Accepted Manuscript