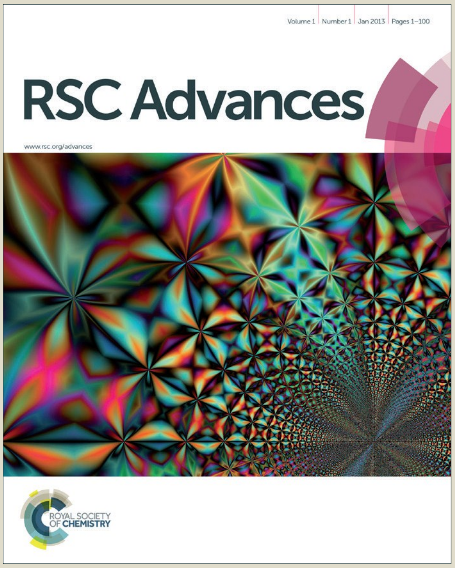
RSC Advances



ROYAL SOCIETY
OF CHEMISTRY

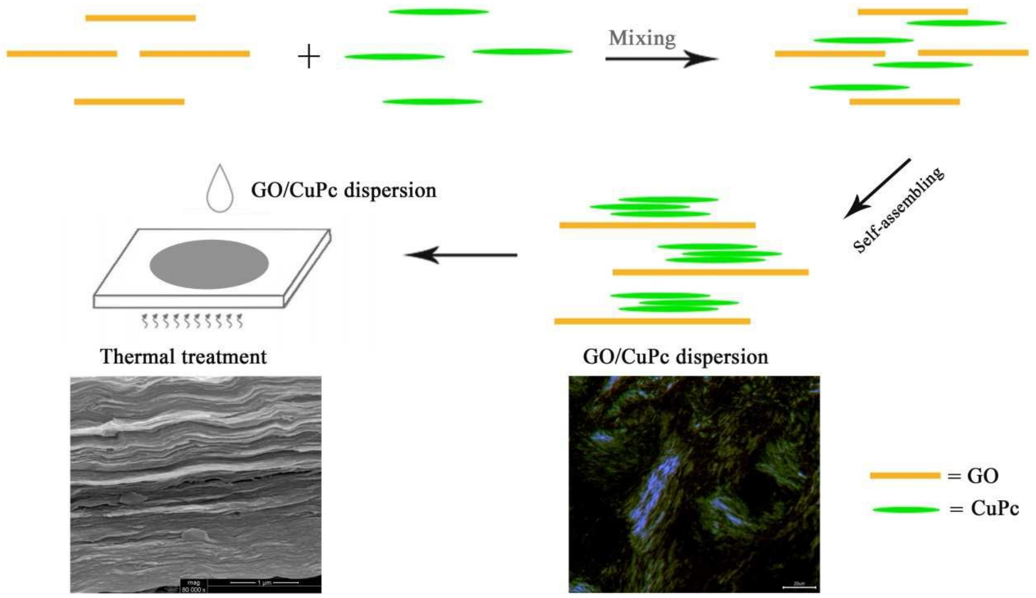
www.rsc.org/advances

Graphical Abstract

Facile fabrication of multilayer films of graphene oxide/copper phthalocyanine with high dielectric properties

Zicheng Wang, Renbo Wei* and Xiaobo Liu*

Novel multilayer films of graphene oxide/copper phthalocyanine (GO/CuPc) were fabricated by self-assembling in the orientational ordered liquid crystalline state and immobilizing of the ordered structure upon casting and drying.



Journal Name

COMMUNICATION

Facile fabrication of multilayer films of graphene oxide/copper phthalocyanine with high dielectric properties

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

Zicheng Wang, Renbo Wei* and Xiaobo Liu*

Abstract: Novel multilayer films of graphene oxide/copper phthalocyanine (GO/CuPc) were fabricated by self-assembling in the orientational ordered liquid crystalline state and immobilizing of the ordered structure upon casting and drying. The formation of the compact and highly ordered structures effectively enhances the dielectric constant of GO/CuPc nanocomposites.

Introduction

Graphene, a two-dimensional (2D) monolayer of sp^2-bonded carbon arranged in a honeycomb lattice, has received increasing attention due to its outstanding electrical, thermal, mechanical and optical properties.[1-4] However, the strong inter-sheet van der Waals attraction and high cohesive energy of graphene made the nano-sheet inevitably undergo agglomerating and restacking, which greatly hinders its application.[5] Assembly of graphene sheets into functional three-dimensional (3D) micro/nano-architectures is an efficient way to prevent the aggregation of graphene sheets, and maintain the large surface area and exceptional electrical properties at the same time, which offer more practical applications, such as energy storage [6], sensors [7], supercapacitors [8] and catalyst [9]. A variety of techniques including CVD [10, 11], template [12] and aerogel [13, 14] have been developed in assembling various 3D morphologies of graphene in the past few years.

Alternatively, graphene oxide (GO) appears as a very important precursor of graphene, possessing a similar anisotropic nature and comparable mechanical strength with graphene [15], and can be easily reduced into graphene [16-18]. Besides, the presence of versatile oxygen functional groups (hydroxyl, epoxide and carbonyl groups) on the basal planes and edges endow GO with excellent dispersibility in water and polar organic solvents such as N-methyl pyrrolidone (NMP), N,N-dimethylformamide (DMF), Tetrahydrofuran (THF). As a result, the asymmetric GO can form nematic and lamellar liquid crystals (LC) in water and polar organic solvents.[19] Taking advantage of the self-assembly behaviour of liquid crystalline GO opens up a new way to fabricate 3D micro/nano-architectures of these materials.

Copper phthalocyanine (CuPc) and phthalocyanine derivatives have attracted considerable interest owing to their unique structural characteristics of aromatic heterocyclic molecules with high symmetry, planarity and 18 π-electron delocalization system. With the inherent π-π stacking property of phthalocyanine, special architectures (column, microsphere and nanofiber) have been fabricated by self-assembly of CuPc,[20-23] and their potential applications in solar cell, fuel cells, optical-limiting materials, gas sensors and field-effect transistors have been shown.[24-26] For GO, there are two parts on the 2D planar structure: the oxygen-functional groups and the graphitic domain. The graphitic domain is mainly composed of sp^2-bonded carbon. In recent years, 3D micro/nano-architectures made from the local delocalized π-electron system of GO have been developed for supercapacitor electrodes and other applications.[27-29] However, to the best of our knowledge, 3D ordered micro/nano-architectures of graphene oxide/copper phthalocyanine composite through self-assembly under ambient conditions has not been reported so far.

In this communication, we report a facile and effective approach to prepare 3D ordered multilayer films of GO/CuPc. Interdigital dispersion was firstly prepared by self-assembling of CuPc in the ordered liquid crystalline GO template through π-π interactions between the aromatic sheets of GO and phthalocyanine rings of CuPc. After simple casting and drying, free-standing multilayer films could be easily obtained. After reduction of the GO, RGO/CuPc multilayer films would be obtained. The preparation and dielectric properties of the multilayer films of GO/CuPc were studied in detail.

Experimental Section

---

[a] *Research Branch of Advanced Functional Materials, School of Microelectronics and Solid-State Electronics, High Temperature Resistant Polymer and Composites Key Laboratory of Sichuan Province, University of Electronic Science and Technology of China, Chengdu, 610054, P. R. China. E-mail: weirb10@uestc.edu.cn (Renbo Wei), liuxb@uestc.edu.cn (Xiaobo Liu). Tel: +86-28-83207326, Fax: +86-28-83207326.*

[b] *Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x*

Materials Graphene oxide was purchased from XFNANO Materials Tech Co. Ltd. (Nanjing, China). 4,4'-bis(3,4-dicyanophenoxy) biphenyl (BPH) was synthesized according to reference reported previously.[30] Cuprous chloride (CuCl) and N-methyl pyrrolidone (NMP) were supplied by Tianjin BODI chemicals (Tianjin, China). All the other materials were used without any further purification.

CuPc BPH (4.38 g, 10 mmol) and CuCl (0.33 g, 3.33 mmol) were dissolved in 50 ml of NMP and stirred at 200 °C for 2 h, and the reaction mixture was poured into excess of water. The crude product was collected by filtration, washed with water, and dried in vacuum. After refluxing in methanol twice, the product was filtrated and washed with cold methanol for three times. The blue powdery product was obtained by drying in vacuum for 24 h. Yield: 70%. ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 8.15-8.02 (m), 7.85-7.64 (m), 7.47-7.33 (m), 7.30-7.15 (m). IR (KBr, cm^{-1}): 3436 (m), 2230 (m), 1728 (m), 1604 (s), 1489 (s), 1290 (s), 1092 (m). UV-vis (NMP, nm): λ_{max1} = 679, λ_{max2} = 613. GPC: M_n=2317, M_w/M_n=1.41. TGA: 415 °C (5% weight loss). Contents of phthalocyanine ring: 10.7 %. (The ^{1}H NMR, FTIR and UV-Vis spectra are presented in the Supporting Information as **Fig.S1**, **Fig.S2** and **Fig.S3**)

GO/CuPc dispersion Aqueous graphene oxide suspension was prepared by sonication of GO (200 mg in 2 ml H_2O) for 2 h. CuPc (100 mg) and NMP (volume ratio NMP/H_2O = 9:1, resulting concentration of 10 mg GO/ml and 5 mg CuPc/ml) were added with vigorous stirring. After stirring for another 4 h, back-green dispersion of GO/CuPc was obtained. GO and CuPc were allowed to further self-assemble in the dispersion for different time, which was carried out under the dust-free ambient condition at room temperature.

GO/CuPc multilayer films The homogeneous dispersion of GO/CuPc was cast on a clean preheated glass of Indium tin oxide (ITO) plate, and the solvent was evaporated using a sequential mode of temperature program at 80 °C, 100 °C, 120 °C, 140 °C, 160 °C, 180 °C for 2h, respectively, to give the final assembled multilayer films. For comparing, disordered GO/CuPc composite was prepared as follow: homogeneous dispersion of GO/CuPc was prepared under previous protocol, after self-assembling for another 4 days, then the dispersion was dropped into methylbenzene rapidly, disordered GO/CuPc composite was obtained by casting the precipitate on the ITO plate and evaporating the solvent as previous.

Characterization ^{1}H NMR spectrum was recorded on a JEOL JNM-AL spectrometer (300 MHz). Fourier transform infrared (FTIR) measurement was carried out on a Shimadzu 8400S FTIR spectrophotometer by incorporating the samples in the KBr pellets. UV-vis absorption spectra were obtained on a UV2501-PC spectrophotometer. The molecular weights and molecular weight distributions were measured using a gel permeation chromatographic (GPC) instrument equipped with a styragel @ HR column and a refractive index (RI) detector (Waters 2414). TGA analysis was carried out using TA Q50 system under nitrogen atmosphere at a heating rate of 20 °C/min. Polarized optical microscopy (POM) observations were conducted on a Nikon E600POL microscope. Scanning electron microscopic (SEM) measurements were performed on a field emission microscope (JSM 6490LV) with the accelerating voltage of 20 kV. The samples for SEM observations were sputter-coated with Au. X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT 2400 with Cu Kα radiation. Dielectric measurements were carried out by an Agilent 4294A dielectric analyser.

Results and discussion

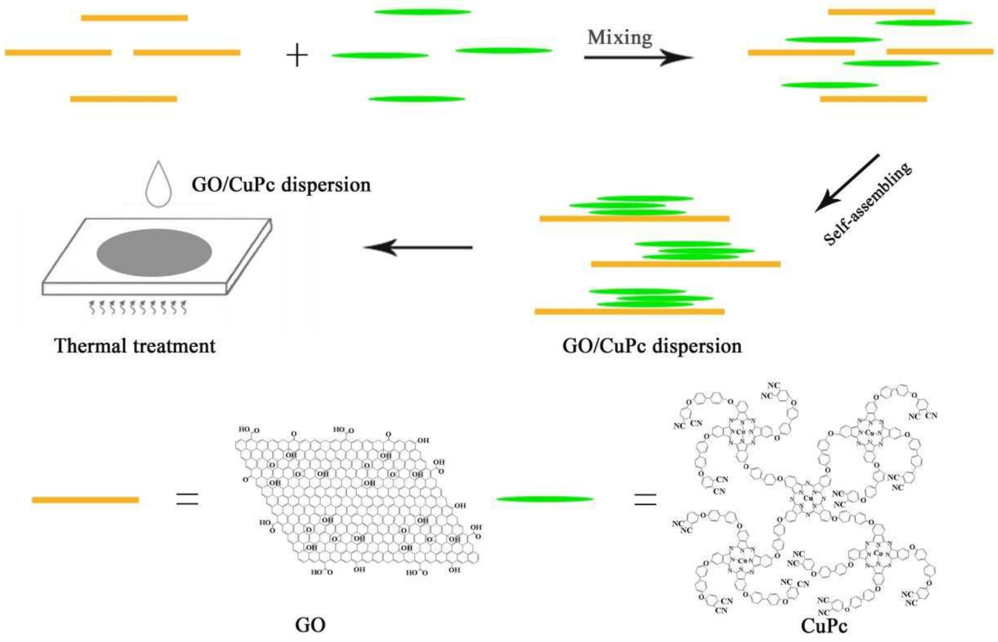


Fig.1 Schematic illustration of the procedure to prepare the GO/CuPc multilayer films.

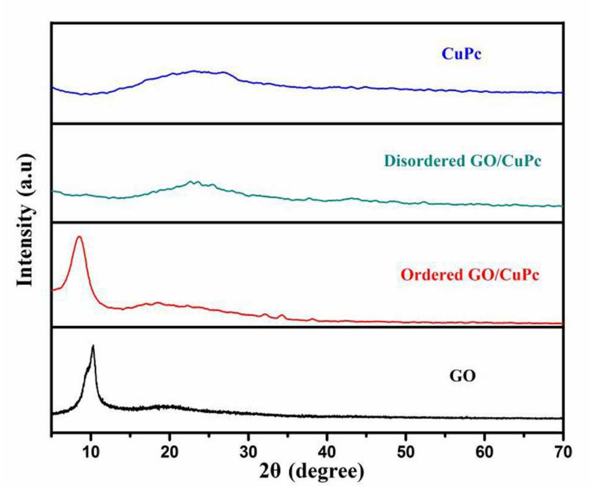


Fig.2 XRD patterns of GO, ordered GO/CuPc multilayer film, disordered GO/CuPc composite and CuPc.

In this study, the GO/CuPc multilayer films were fabricated by a facile approach as shown in the scheme given in **Fig.1**. In a typical preparation process, GO was firstly dispersed in water to form liquid crystals; secondly, CuPc in NMP was added into the GO dispersion, and GO was used as an ordered template for the self-assembly of CuPc; finally, after casting the homogeneous mixture on ITO plate and drying for immobilization of the ordering texture, GO/CuPc multilayer films were obtained.

Fig.2 shows the XRD patterns of the obtained GO/CuPc multilayer films, as well as GO, CuPc and the disordered GO/CuPc composite. The inter-planar spacing of GO is 0.84 nm, indicated by the peak centered at $2\theta = 10.46^{\circ}$. After the introduction of CuPc, the diffraction peak (001) of the multilayer films of GO/CuPc shifts down to a smaller angle, $2\theta = 8.56^{\circ}$, corresponding to a layer-to-layer distance of 1.03 nm.[31] This 0.19 nm expansion of the d-spacing suggests that CuPc was intercalated into the GO sheets, while the ordered stacking structure of GO sheets was not collapsed. This could be further confirmed by adding different amount of CuPc during the fabrication process. The diffraction peak (001) of the obtained multilayer film of GO/CuPc shifts down to a smaller angle when more CuPc is added (**Fig. S4**). As for the disordered GO/CuPc composite, the XRD result is the same as that of CuPc, which shows no obvious stacking peaks of GO on the XRD pattern,[32] indicating the successful of the intercalation of CuPc and the complete exfoliation of GO sheets and rapid precipitation in poor solvent hinders the formation of layer-by-layer 3D ordered structure.

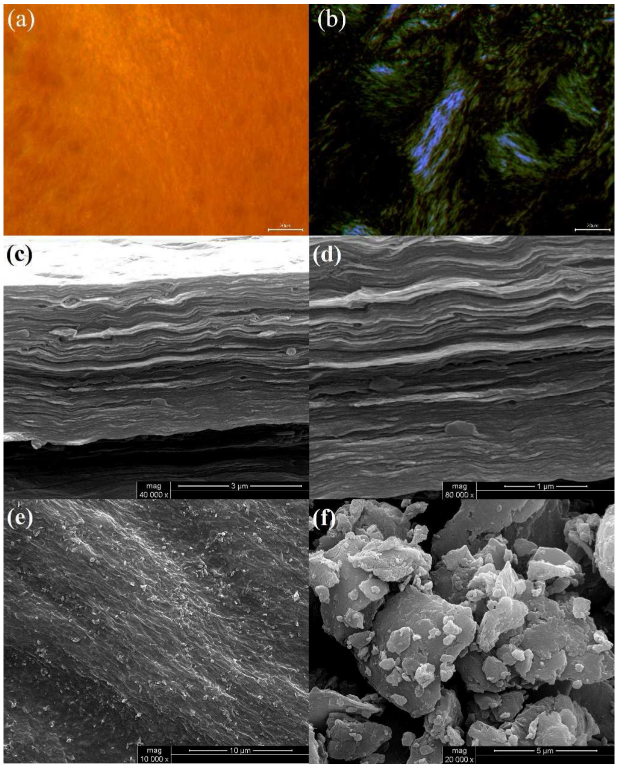


Fig.3 POM images of GO (a) and GO/CuPc dispersions (b) in NMP and H_2O (9:1); SEM images of cross section morphology of GO/CuPc multilayer film (c) and (d); SEM image of surface morphology of GO/CuPc multilayer film (e); SEM image of cross section morphology of disordered GO/CuPc composite (f).

As a large 2D planar structure, extended, delocalized π-electron system, CuPc tends to aggregate at high concentration between adjacent CuPc molecules through the π-π stacking interaction.[33] In this system, no functional groups is available on CuPc for chemical reaction, the intercalation of CuPc into GO sheets should also be accomplished through the π-π stacking interaction between GO and CuPc. Additionally, the formation of lamellar mesophase LC in water and polar organic solvents paves the way to fabricate the highly ordered, 3D functional materials. **Fig.3a** shows the typical POM image of GO sheets dispersed in the mixed solvents of water/NMP (volume ratio $NMP/H_2O = 1:9$), representing typical nematic LCs. After the incorporation of CuPc, the mixture evolves into lamellar LC as shown in **Fig.3b**, obvious orientation and alignment of CuPc is achieved by using GO LC as templates.

In order to further investigate the self-assembling properties of GO and CuPc, UV-vis spectrophotometer was used to monitor the progress. The results show that the absorption of Q-band [34] and shoulder peak [35] on the UV-Vis curve decrease gradually with the increase of time (**Fig.S5**). However, the ratio of the absorption of the shoulder peak and Q-band (I_S/I_Q) increases with the increase of time and concentration of GO (**Fig.S5**, **Fig.S6**, **Table S1** and **Table S2**), indicating more CuPc aggregated. The obvious evolution on UV-vis spectra supports the formation of assembled structures through π-π interaction between CuPc and GO.

After self-assembling in the solvent of NMP and H_2O (volume ratio NMP/H_2O = 9:1) for 4 days at room temperature, the homogeneous dispersion of GO/CuPc was cast on a preheated ITO plate and laxly dried to obtain the multilayer films. **Fig.3c**, **3d** and **3e** show the typical SEM images of the cross section and surface of the obtained GO/CuPc multilayer film. The images show obvious long range tightly stacked 3D ordered layer-by-layer structures. On the contrary, the disordered GO/CuPc composite shows an incompact and randomly aggregated morphology as CuPc is adsorbed on the surface of GO sheets (**Fig.3f**). To further characterize the component of the 3D structures, FTIR and XPS measurement were carried out. Both of FTIR (**Fig. S7**) and XPS (**Fig. S8, Table S3**) proved the existence of CuPc in the 3D structures. Together with the XRD results discussed above, we can conclude that the obtained 3D structure is composited with GO sheets with CuPc intercalated between the layers. These results confirm the π-π stacking interaction between GO and CuPc, and indicate that the layer-by-layer structures could be easily immobilized by casting and drying.

The dielectric properties of the GO/CuPc multilayer films were investigated by measuring dielectric constant, dielectric loss and alternating current (AC) conductivity at room temperature using an electric double layer method. A simple parallel-plate capacitor was fabricated by drop-coating GO/CuPc dispersions onto indium-tin-oxide (ITO) glass substrate and subsequent drying, while the top electrode was prepared by evaporation of Au as shown in **Fig.S9**. For comparing, a similar capacitor of the disordered GO/CuPc composite was also prepared. The dielectric constant of the GO/CuPc multilayer film increases obviously compared with that of the disordered GO/CuPc composite in the frequency from 500 Hz to 1 MHz, and reached 164.82 and 31.95 at 1 KHz and 100 KHz, with an increment of 338% and 237%, respectively (**Fig.4a, Fig.S10**). The dielectric losses of both samples are almost the same in the tested frequency range (**Fig.4b, Fig.S11**). The AC conductivity of the GO/CuPc multilayer film is also much higher than that of the disordered GO/CuPc composite in the lower frequency range, and reached 1.54×10^{-5} S/m at 1 KHz (**Fig.4c**).

The obvious changes in dielectric properties and AC conductivity are attributed to the alignment and orientation of the GO/CuPc composites.[36, 37] Although the accumulation of charges at the interfaces of GO and CuPc results in a high dielectric properties [38], the randomly distributed nano-capacitors formed between the flake-like GO and the adsorbed CuPc impeded further enhancement of the dielectric properties and AC conductivity of the disordered GO/CuPc composite. In contrast, parallel connection and series connection of nano-capacitors would be formed in layers and interlayers in the GO/CuPc multilayer film. As a result, more charges would be accumulated, and the dielectric properties and AC conductivity are dramatic improved.

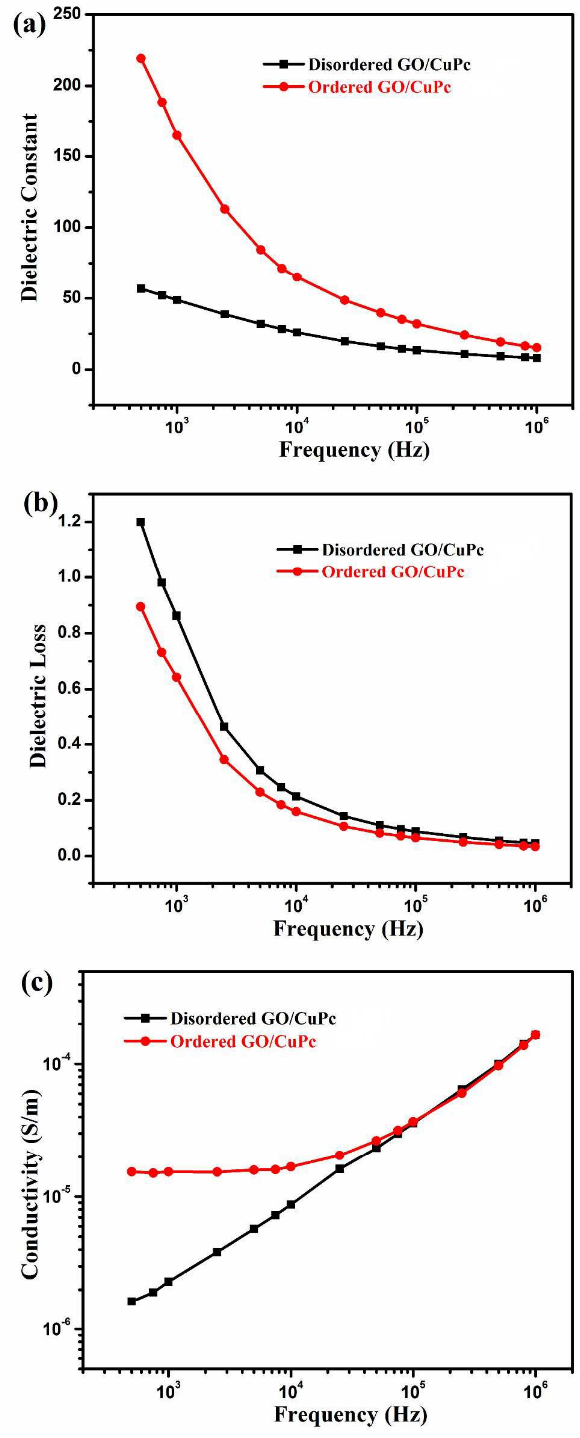


Fig.4 Dielectric constant (a), loss (b) and alternating current conductivity (c) of GO/CuPc multilayer film and disordered GO/CuPc composite measured at room temperature.

Conclusions

In summary, novel 3D ordered layer-by-layer GO/CuPc multilayer films were fabricated by self-assembling of CuPc in liquid crystalline GO dispersion, and ordering transformation from ordered LC phase into 3D ordered solid materials through simple drying. The results of POM showed that nematic liquid crystal was formed by GO dispersion. After the incorporation of CuPc, the GO/CuPc dispersions exhibited strongly self-assembly behaviour of CuPc by using GO as template and transformed to excellent texture of lamellar liquid crystal. UV-vis spectra indicated that the prolongation of assembling time and the increase of the concentration of GO effectively promote the self-assembly of CuPc and the formation of LC GO/CuPc dispersions. By simple casting and drying, the long range orientation and alignment of GO/CuPc multilayer films can be successfully immobilized, which drastically enhanced the dielectric constant and AC conductivity of GO/CuPc nano-composites. Compared with the disordered GO/CuPc composites, the dielectric constants at 1 KHz and 100 KHz reach 164.82 and 31.95, with an increment of 338% and 237%, respectively. While the AC conductivity of the GO/CuPc multilayer films increases from 2.29×10^{-6} S/m to 1.54×10^{-5} S/m at 1 KHz. In conclusion, this kind of ordered GO/CuPc multilayer film will show great potential in practical application as organic dielectric materials, and will provide a facile way to fabricate functional graphene composites with three-dimensional (3D) micro/nano-architectures.

Acknowledgements

The financial support from National Natural Science Foundation of China (Project No. 51373028, No. 51403029), "863" National Major Program of High Technology (2012AA03A212), South Wisdom Valley Innovative Research Team Program and Ningbo Major (key) Science and Technology Research Plan (2013B06011) are gratefully acknowledged.

Notes and references

1. C.X. Guo, M. Wang, T. Chen, X.W. Lou and C.M. Li, *Adv. Energy. Mater.*, 2011, **1**, 736.
2. X. Huang, X. Qi, F. Boey and H. Zhang. *Chem. Soc. Rev.*, 2012, **41**, 666.
3. L. Yan, Y. Zheng, F. Zhao, S. Li, X. Gao, B. Xu, P.S. Weiss and Y. Zhao, *Chem. Soc. Rev.*, 2012, **41**, 97.
4. D. Krishnan, F. Kim, J. Luo, R. Cruz-Silva, L.J. Cote, H.D. Jang and J. Huang, *Nano Today*, 2012, **7**, 137.
5. D. Li, M.B. Muller, S. Gilje, R.B. Kaner and G.G. Wallace, Nat. *Nanotechnol*., 2008, **3**, 101.
6. R. Raccichini, A. Varzi, S. Passerini and B. Scrosati, *Nat. Mater.*, 2015, **14**, 271.
7. W.J. Yuan and G.Q. Shi, *J. Mater. Chem. A.*, 2013, **1**, 10078.
8. C.G. Liu, Z.N. Yu, D. Neff, A. Zhamu and B.Z. Jang, *Nano Lett.*, 2010, **10**, 4863.
9. B.F. Machadoab and P. Serp, *Catal. Sci. Technol.*, 2012, **2**, 54
10. L.L. Jiang and Z.J. Fan, *Nanoscale*, 2014, **6**, 1922.
11. X.H. Cao, Y.M. Shi, W.H. Shi, G. Lu, X. Huang, Q.Y. Yan, Q.C. Zhang and H. Zhang, *Small*, 2011, **7**, 3163.
12. B.G. Choi, M.H. Yang, W.H. Hong, J.W. Choi and Y.S. Huh, *ACS Nano*, 2012, **6**, 4020.
13. S.M. Jung, D.L. Mafra, C.T. Lin, H.Y. Jung and J. Kong, *Nanoscale*, 2015, **7**, 4386.
14. Z.S. Wu, S.B. Yang, Y. Sun, K. Parvez, X.L. Feng and K. Mŭllen, *J. Am. Chem. Soc.* 2012, **134**, 9082.
15. D.A. Dikin, S. Stankovich, E.J. Zimney, R.D. Piner, G.H.B. Dommett, G. Evmenenko, S.T. Nguyen and R.S. Ruoff, *Nature*, 2007, **448**, 457.
16. D.R. Dreyer, S. Park, C.W. Bielawski and R.S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228.
17. R. Rozada, J.I. Paredes, M.J. López, S. Villar-Rodil, I. Cabria, J.A. Alonso, A. Martínez-Alonso and J.M.D. Tascón, *Nanoscale*, 2015, **7**, 2374.
18. H.X. Tang, G.J. Ehlert, Y.R. Lin and H.A. Sodano, *Nano Lett.*, 2012, **12**, 84.
19. Z. Xu and C. Gao, *ACS Nano*, 2011, **5**, 2908.
20. G. Torre, C.G. Claessens and T. Torres, *Chem. Commun.*, 2007, **20**, 2000.
21. R. Zhao, H.L. Tang, H. Guo, Y.J. Lei and X.B. Liu, *J. Mater. Res.*, 2013, **28**, 1609.
22. S.C. Suen, W.T. Whang, F.J. Hou and B.T. Dai, *Org. Electron.*, 2006, **7**, 428.
23. P. Nita, C. Pimentel, F. Luo, B. Milián-Medina, J. Gierschner, C.M. Pina and E. Gnecco, *Nanoscale*, 2014, **6**, 8334.
24. S. Choi, S.H. Hong, S.H. Cho, S. Park, S.M. Park, O. Kim and M. Ree, *Adv. Mater.*, 2008, **20**, 1766.
25. T.W. Lee,Y. Kwon, J.J. Park, L. Pu, T. Hayakawa and M. Kakimoto, *Macromol. Rapid Commun.*, 2007, **28**, 1657.
26. M. Guo, X.Z. Yan and T. Goodson III, *Adv. Mater.*, 2008, **20**, 4167.
27. J.T. Zhang and X.S. Zhao, *J. Phys. Chem. C.*, 2012, **116**, 5420.
28. X.C. Dong, H. Xu, X.W. Wang, Y.X. Huang, M.B. Chan-Park, H. Zhang, L.H. Wang, W. Huang, and P. Chen, *ACS Nano*, 2012, **6**, 3206.
29. W. Ai, Z.Z. Du, J.Q. Liu, F. Zhao, M.D. Yi, L.H. Xie, N.E. Shi, Y.W. Ma, Y. Qian, Q.L. Fan, T. Yu and W. Huang, *RSC Adv.*, 2012, **2**, 12204.
30. T.M. Keller, *J. Polym. Sci. Pol. Chem.*, 1988, **26**, 3199.
31. J.H. Yang, Y.J. Gao, W. Zhang, P. Tang, J. Tan, A.H. Lu and D. Ma, *J. Phys. Chem. C.*, 2013, **117**, 3785.
32. M. Azim-Araghi, S. Haji Mirza Mohamadi and Z. Bisadi, *Acta. Phys. Pol. A.*, 2014, **125**, 87.
33. M. Durmus and T. Nyokong, *Polyhedron.*, 2007, **26**, 2767.
34. A.W. Snow and N.L. Jarvis, *J. Am. Chem. Soc.*, 1984, **106**, 4706.
35. V. Iliev, V. Alexiev and L. Bilyarska, *J. Mol. Catal. A: Chem.*, 1999, **137**, 15.
36. X. Huang, K. Wang, K. Jia and X.B. Liu, *RSC Adv*., 2015, **5**, 51975.
37. S.N. Song, J.W. Zhai, L.N. Gao and X. Yao. *J. Phys. Chem. Solids*, 2009, **70**, 1213.
38. T. Ohta, A. Bostwick, T. Seyller, K. Horn and E. Rotenberg, *Science*, 2006, **313**, 951