Volume 1 | Number 1 | Jan 2013 | Pages 1–100

ChemComm

Chemical Communications
www.rsc.org/chemcomm

ROYAL SOCIETY OF CHEMISTRY

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. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it 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/chemcomm

Table of Contents

Polyacrylonitrile-derived Polyconjugated Ladder Structures for High Performance All-organic Dielectric Materials

Xiaojian Liao, Yichun Ding, Linlin Chen, Wan Ye, Jian Zhu, Hong Fang and Haoqing Hou*
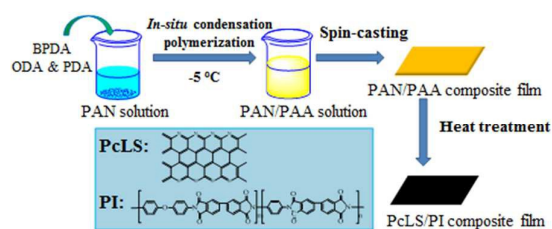
PcLS/PI all-organic dielectric materials containing polyconjugated ladder structures with high dielectric, mechanical and thermal performances are prepared.

Journal Name

COMMUNICATION

Polyacrylonitrile-derived Polyconjugated Ladder Structures for High Performance All-organic Dielectric Materials

Xiaojian Liao, Yichun Ding, Linlin Chen, Wan Ye, Jian Zhu, Hong Fang and Haoqing Hou[*]

A novel all-organic polyconjugated ladder structures/polyimide (PcLS/PI) composite was successfully synthesized, in which the PcLS was derived from polyacrylonitrile (PAN). The PcLS/PI composite not only presents high dielectric performances of high dielectric permittivity, low dielectric loss, high electrical breakdown strength and high energy density, but also has excellent mechanical and thermal properties.

Dielectric materials with high permittivity, low dielectric loss and high energy storage density are highly desired for the advanced electrical applications, especially the modern electronics, such as embedded capacitors, actuators and thin film transistors.[1] The primal high dielectric materials are typically ferroelectric ceramics (such as $BaTiO_3$), however, their applications are largely limited due to the serious drawbacks of high density and brittleness. Thereafter, polymer matrix composites using ferroelectric ceramics or conductive particles as fillers were developed with relatively high dielectric permittivity.[2] However, the mechanical performances are sacrificed to some extent in such composite material, thus the flexibility cannot meet the requirement of modern flexible electronics.[3] Recently, all-organic dielectric materials with high permittivity, low dielectric loss, large breakdown strength and high energy storage density have attracted comprehensive interests thanks to the excellent mechanical flexibility and good processability.[1c, 4]

Typically, to date, the exploration of all-organic high dielectric materials are by incorporating conducting polymers/oligomers into insulation polymer matrix, or synthesizing new polymers containing conjugated functional groups and/or side chains.[1c, 4-5] Polyaniline (PANi) and copper phthalocyanine (CuPc) oligomer are the most particularly used fillers for the preparation of all-organic high dielectric materials till now.[1c, 4-5] However, these two materials are commonly first synthesized as a form of nanoparticles or complex

and then mixed with the insulation polymers. For example, Wang *et al.* prepared PU/CuPc nanocomposites by bonding CuPc oligomer nanoparticles (10-20 nm) with PU. When the content of the CuPc oligomer was 8.78 vol%, it showed the permittivity, breakdown strength and energy density 391, 10 kV/mm and 0.927 J/cm³, respectively.[4a] They also prepared a three phase composite, P(VDF-TrFE–CFE)/PANi/CuPc, which showed the permittivity, breakdown strength of 516 and 28 kV/mm, as well as the elastic modulus of 313 MPa. [4c] However, this mixture(blend) process will result in a multi-phase composite that the fillers might not be dispersed homogeneously, and then the dielectric loss would be high, and also might have a great loss of the electrical breakdown strength. On the other hand, the synthesis of new polymers containing conjugated functional component may also produce high dielectric all-organic polymers. For example, Qiao *et al.* synthesized a polymer containing π-conjugated oligomer side chain (terthiophene),[5f] which showed a permittivity of about 11, electric breakdown strength of 200 kV/mm, and energy density of 1.56 J/cm³. However, not only is the synthesis process complicated and high cost, but also might the resulting conjugated (or partially conjugated) polymers not have good thermal and mechanical properties.

In this communication, we developed a composite film (PcLS/PI) containing polyconjugated ladder structures (PcLS) with good dielectric performance. The PcLS was derived from a very common polymer, polyacrylonitrile (PAN). The main feature of this PcLS/PI composite film is its simple fabrication and excellent properties: the composite film was synthesized by *in-situ* condensation polymerization followed with high temperature treatment; and all the polymer/monomers are commercially available. This PcLS/PI composite film possesses excellent dielectric properties (including high dielectric permittivity, low dielectric loss, high electrical breakdown strength and high energy density) and superior mechanical and thermal properties, simultaneously.

Polyacrylonitrile (PAN) is a well-known polymer as its wide application for producing carbon fibers.[6] The preparation of carbon fibers from PAN generally includes three processes namely stabilization, carbonization, and graphitization. Even though PAN

College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang, Jiangxi 330022, People's Republic of China..
† Corresponding author: Tel: (+86)791-88120389; Fax: (+86)791-88120536; E-mail: haoqing@jxnu.edu.cn (H. Hou)

has been widely studied for almost a century since it had been explored as the precursor material for forming carbon fibers, the mechanism of the polymer converting into carbon is still ambiguous and debatable, epically the stabilization mechanism.[7] Thus far, a widely acceptable viewpoint is that: 1) at the initial thermal stabilization (between 200 °C and 300 °C), oxidation, crosslinking and some cyclization occurs through heating in the presence of oxygen; 2) at further higher temperature (between 400 °C and 600 °C), polyconjugated ladder structures (PcLS) will be formed due to the further cyclization and dehydrogenation; and 3) upon continued heating to the temperature higher than 600 °C, the PcLS will convert to graphitic structures with the dehydrogenation and denitrogenation.[6-7] The schematic diagram of the process steps of PAN-carbonization is described in the Electronic Supplementary Information (ESI, Figure S2).

Polyconjugated structures generally contains unsaturated bonds, such as conjugated C=C double bonds, thus it is easy to be polarized due to the existence of "overlapping clouds" of delocalized π-electrons of carbon atoms along the entire chain. Hence, the high polarizability of polyconjugated structures will result in high permittivity and high energy density.[8]
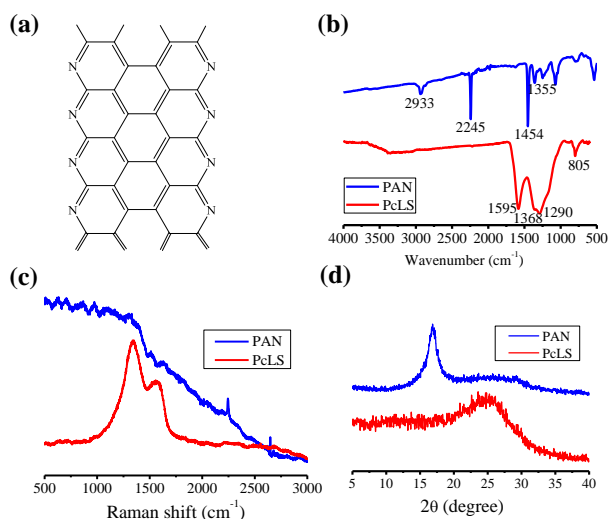

Figure 1 (a) The representational chemical structure of PAN-derived polyconjugated ladder structures (PcLS); (b) FT-IR spectrum of PAN and PcLS; (c) Raman spectrum of PAN and PcLS; (d) XRD patterns of PAN and PcLS.

Figure 1a shows the representational chemical structure of the PcLS derived from PAN, where the PAN were first stabilized at 250 °C under air and following processed with an ultimate temperature about 480 °C. We confirmed the chemical structures by using FT-IR spectroscopy, Raman spectroscopy and X-Ray Diffraction (XRD). As shown in Figure 1b, before stabilization (PAN), distinct absorption bands appeared at 2933, 2245, 1454, and 1355 cm^{-1} were assigned to the v_{C-H} in CH_2, $v_{C≡N}$ in C≡N, δ_{C-H} in CH_2, and δ_{C-H} in =CH, respectively.[9] After high temperature treatment at 480 °C, the absorptions at 2933, 2245 and 1454 cm^{-1} were disappeared and new absorption of the asymmetric and symmetric stretching of conjugated C=N and C=C were both appeared near 1595 cm^{-1},[9] and the new absorptions appeared at 1368, 1290 and 805 cm^{-1} were

assigned to the v_{C-H} in =CH, v_{C-N} in C-N and v_{C-H} in aromatic structures.[9b] Hence, the FT-IR spectroscopy indicated that the conjugated C=C and C=N were formed. In Raman spectrum, the carbonaceous materials typically have two characteristic bands at 1340 cm^{-1} and 1580 cm^{-1}, which are known as the "D-band" and "G-band" related to disordered turbostratic structures and ordered graphitic structures, respectively. The appeared "D-band" and "G-band" of PcLS (Figure 1c) indicated that ladder polyconjugated structures were formed under the stabilization and heat treatment of 480 °C. XRD was employed to further investigate the structure changes. As shown in Figure 1d, the pristine PAN showed a strong diffraction peak centered at 2θ angle of 16.8°, represented the X-ray reflection of the (100) crystallographic planes in PAN. After high temperature treatment, the strong diffraction peak at 16.8° disappeared and a weak wide peak around 25° was appeared, indicating that small amount of graphite-like crystallites was formed. This is reasonable that the PcLS is not graphene but graphene-like due to containing a lot of N and H elements, and thus the formed crystallites are graphite-like crystallites.

However, the PAN-derived neat PcLS cannot be used as a dielectric material directly, because the obtained neat PcLS film was brittle. Therefore, we considered to fabricate a composite based on this PcLS. Unlike the traditional method of incorporating fillers into insulation polymer matrix, we developed a homogeneous all-organic film by *in-situ* condensation polymerization rather than using the PcLS as fillers. Polyimide (PI) was employed as the insulation polymer matrix for preparing the homogeneous composite film. As we know, PI is a class of high performance polymer that contains rigid heterocyclic imide rings and aromatic benzene rings in their main backbone, which result in the excellent mechanical and thermal properties, as well as good chemical stability.[10] Typically, PIs are insoluble in common solvents and they are prepared from chemical/thermal imidization of the precursor, polyamic acid (PAA), whereas the PAA is prepared by the condensation polymerization of dianhydride and diamine (Figure S3). Due to the PAN solution was immiscible with PAA solution, we prepared PAN/PAA solution by *in-situ* condensation polymerization for which the dianhydride and diamines were added into the PAN/DMF solution. Experimental details for the preparation of PAN/PAA solution and the following heat treatment are descried in Electronic Supplementary Information (ESI, Figure S1).
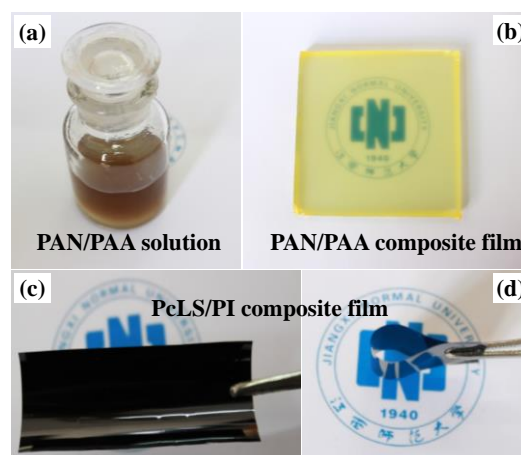

Figure 2 Photographs of the synthesized (a) PAN/PAA solution, (b) spin-casted PAN/PAA composite film, and (c) PcLS/PI composite film;

(d) a photo of the PcLS/PI composite film showing the film being mechanical flexible.

As shown in Figure 2a, a homogeneous PAN/PAA solution without phase separation was obtained by the *in-situ* condensation polymerization, and the PAN/PAA solution presents light brown. Then, by spin-casting, the transparent PAN/PAA composite film was obtained with light yellow colour (Figure 2b). Finally, after the processes of stabilization and high temperature (480 °C) treatment, a mechanical flexible PcLS/PI composite film was obtained, as shown in Figure 2c & 2d. The composite film has black gloss and can be folded. The surface and cross sectional SEM images as well as AFM image (Figure S4) showed that the PcLS/PI composite film was smooth and homogeneous, without any phase separation.
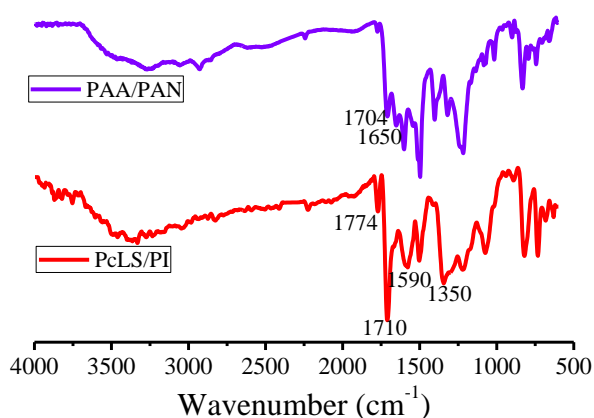

Figure 3 FT-IR spectrum of (a) PAN/PAA composite film, and (b) PcLS/PI composite film with ultimate process temperature of 480 °C.

Figure 3 shows the FT-IR spectrum of PAN/PAA composite film and PcLS/PI composite film with ultimate process temperature of 480 °C. Compared to the FT-IR spectrum of neat PcLS (Figure 1b), the appeared absorptions at 1590 and 1350 cm^{-1} demonstrated the formation of polyconjugated structures. Compared to the FT-IR spectrum of neat PAA and PI films (Figure S5), the absorptions at 1704 cm^{-1} ($v_{C=O}$ in -COOH) and 1650 cm^{-1} ($v_{C=O}$ in -CONH) were disappeared, and the new absorption peaks at 1774 cm^{-1} and strong absorption at 1710 cm^{-1} were appeared, indicating the PAA were completely converted to PI, in which the five-membered aromatic imide cycles were formed.

The ultimate heat treatment temperature for preparing the PcLS/PI composite was first investigated. Because of the starting decomposition temperature of PI was about 500 °C (seen in the TGA curve in Figure S6), the highest processing temperature here we performed was 480 °C. The results showed that when the ultimate treated temperature was low than 400 °C, the prepared composite films did not almost show a significant difference on the dielectric permittivity (Figure S7), indicating that polyconjugated structures were not formed under 400 °C. When further increasing the ultimate treatment temperature to 450 °C and 480 °C, the permittivity was obviously improved and showed increasing trends. This demonstrated that the polyconjugated structures were formed at the temperature higher than 450 °C, and the higher temperature will be benefit for preparing PcLS/PI composites with a higher dielectric permittivity.

Then, different PAN contents in PAN/PAA solution for preparing PcLS/PI composite films were investigated under the ultimate heat temperature of 480 °C. Figure 4 shows the dielectric performance of the PcLS/PI composites with the PAN contents of 15 wt%, 20 wt%, 25wt% and 30 wt%. It can be seen that the dielectric permittivity of PcLS/PI composite films were increased with increasing content of PAN in precursor for preparing PcLS/PI films. At the testing frequency of 100 Hz, the dielectric permittivity of neat PI was 3.14, and it became 5.24 when just added 15 wt% PAN, and it further increased to 7.23, 9.01 and 10.01, when the contents of PAN were 20 wt%, 25 wt%, and 30 wt%, respectively. Within the testing frequency from 100 Hz to 100 kHz, the dielectric permittivity was slightly decreased, which was attributed to the slight decrease of the total polarization as the polarization types (including electronic polarization, atomic polarization, orientation polarization and interfacial polarization) changed within the increasing frequency. For this reason, the dielectric loss was also increased with the frequency. In the other hand, the dielectric loss also increased with increasing the PAN content. Generally, the dielectric loss of the fabricated PcLS/PI film is relative low compared to those of the all-organic dielectric materials prepared by incorporating fillers.[4b, 5a, 5b] For example, the dielectric loss of the PcLS/PI film was just 0.1 (at 100 Hz) with the PAN content of 30 wt% in precursor.
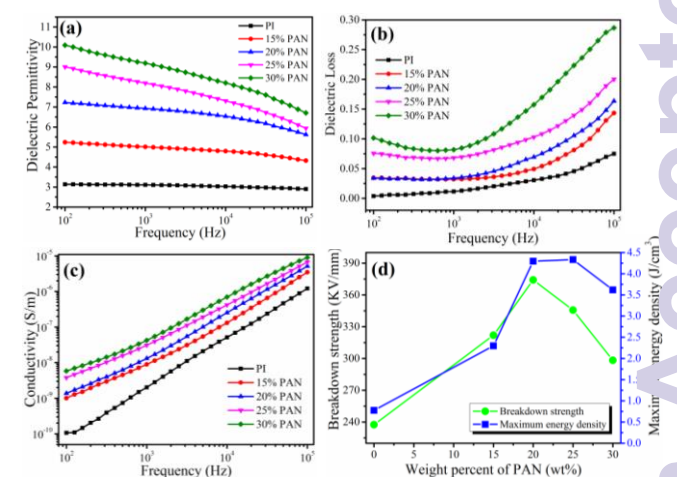

Figure 4 Frequency dependent (a) dielectric permittivity, (b) dielectric loss and (c) conductivity of the PcLS/PI composite films; (d) the electrical breakdown strength and maximum energy density of the PcLS/PI composite films.

Figure 4c shows the conductivity of the PcLS/PI composites. The low conductivity and the increasing trend with the increasing frequency indicate that the PcLS/PI composites show insulation nature. The good insulating property will result in high electrical breakdown strength. As shown in Figure 4d, the breakdown strength of neat PI film is 240 kV/mm, and interestingly, the breakdown strength of the PcLS/PI composite film first increases and then decreases with increasing content of PAN in the PAN/PAA solution. When PAN content is 20 wt%, the breakdown strength of the PcLS/PI composite film reaches its highest value 374 kV/mm, then decreases, and becomes 298.3 kV/mm at the PAN content of 30 wt%. This should be explained that the synthesized PcLS/PI composite films were homogeneous and were dense film with seldom defects that

improved the high electric field resistance ability. And at a higher content of PcLS (PAN content in PAN/PAA solution was more than 20 wt%), the breakdown strength was lowered due to a large number of polyconjugated structures within the film. The energy density depends on both the breakdown strength (E_B) and dielectric permittivity (ε_r), for linear dielectrics, $W = 1/2\varepsilon_r\varepsilon_0 E_B^2$. The energy density was summarized in Table. S1. The largest energy density of PcLS/PI composite film was 4.33 J/cm^3, which is about 3 times of the biaxially oriented polypropylenes (BOPP), the benchmark polymer dielectrics of current use in dielectric capacitors.[11]

In addition, for practical application in the modern microelectronics, such as the embedded capacitor on a flexible circuit board, good mechanical and thermal properties are very important. In this wok, PcLS/PI composite films also showed excellent mechanical strength and elasticity modulus (Figure S8), as well as high decomposition temperature (Figure S9). For example, the PcLS/PI composite film derived from PAN/PAA composite film with 30 wt% PAN shows that the tensile strength, elasticity modulus and 5% weight-loss temperature are 115 MPa, 4.3 GPa and 600 **°C**, respectively.

In summary, we developed and investigated a polyconjugated ladder structures (PcLS) derived from polyacrylonitrile (PAN) used for preparing PI-based high dielectric materials. The homogeneous all-organic PcLS/PI composite films were synthesized by in-situ condensation polymerization followed with high temperature treatment. The PcLS/PI composites possessed a good dielectric performance, excellent mechanical and thermal properties, and could be the promising materials for uses in modern microelectronics, such as embedded capacitor, thin film transistors, *etc*.

Notes and references

College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang, Jiangxi 330022, People's Republic of China. Tel: (+86)791-88120389; Fax: (+86)791-88120536; E-mail: haoqing@jxnu.edu.cn (H. Hou)

† Electronic Supplementary Information (ESI) available: [Experimental details, SEM, TGA, FT-IR, dielectric performance of PcLS/PI composites prepared from different heat treatment temperature and typical stress-strain curves]. See DOI: 10.1039/c000000x/

1   (a) Z. Dang, J. Yuan, J. Zha, T. Zhou, S. Li and G. Hu, *Progress in Materials Science*, 2012, **57**, 660; (b) Z. Dang, J. Yuan, S. Yao and R. Liao, *Advanced Materials*, 2013, **25**, 6334; (c) Q. M. Zhang, H. Li, M. Poh, F. Xia, Z. Y. Cheng, H. Xu and C. Huang, *Nature*, 2002, **419**, 284; (d) Y. Yu, C. Liu, Y. Chen, Y. Chiu and W. Chen, *RSC Advances*, 2014, **4**, 62132.

2   (a) W. Xu, Y. Ding, S. Jiang, L. Chen, X. Liao and H. Hou, *Materials Letters*, 2014, **135**, 158; (b) Z. Dang, L. Wang, Y. Yin, Q. Zhang and Q. Lei, *Advanced Materials*, 2007, **19**, 852; (c) Y. Ding, Q. Wu, D. Zhao, W. Ye, M. Hanif and H. Hou, *European Polymer Journal*, 2013, **49**, 2567.

3   W. Xu, Y. Ding, S. Jiang, J. Zhu, W. Ye, Y. Shen and H. Hou, *European Polymer Journal*, 2014, **59**, 129; (b) W. Xu, Y. Ding, S. Jiang, W. Ye, X. Liao and H. Hou, *Polymer Composites*, 2014, n/a.

4   (a) J. Wang, C. Wu, R. Liu and S. Li, *Polymers for Advanced Technologies*, 2014, **25**, 657; (b) C. Huang and Q. M. Zhang, *Advanced Materials*, 2005, **17**, 1153; (c) J. Wang, C. Wu, R. Liu and S. Li, *Polym. Bull.*, 2013, **70**, 1327.

5   (a) C. Huang and Q. Zhang, *Advanced Functional Materials*, 2004, **14**, 501; (b) J. Yang, X. Yang, Z. Pu, L. Chen and X. Liu, *Materials Letters*, 2013, **93**, 199; (c) L. Dunn, W. Ford, N. Hilal, P. Vijayakumar and H. Pohl, *Journal of Polymer Science: Polymer Physics Edition*, 1984, **22**, 2243; (d) X. Qian, S. Lu, X. Li, H. Gu, L. Chien and Q. Zhang, *Advanced Functional Materials*, 2013, **23**, 2894; (e) X. Zhao, M. Wang, J. Ji, T. Wang, F. Yang and J. Du, *Polymer Engineering & Science*, 2014, **54**, 812; (f) Y. Qiao, M. Islam, K. Han, E. Leonhardt, J. Zhang, Q. Wang, H. Ploehn and C. Tang, *Advanced Functional Materials*, 2013, **23**, 5638.

6   S. Nataraj, K. Yang and T. Aminabhavi, *Progress in Polymer Science*, 2012, **37**, 487.

7   (a) M. Rahaman, A. Ismail and A. Mustafa, *Polymer Degradation and Stability*, 2007, **92**, 1421; (b) Z. Bashir, *Carbon*, 1991, **29**, 1081; (c) O. Bahl and L. Manocha, *Carbon*, 1974, **12**, 417.

8   L. Zhu, *The Journal of Physical Chemistry Letters*, 2014, **5**, 3677.

9   (a) M. Ji, C. Wang, Y. Bai, M. Yu and Y. Wang, *Polym. Bull.*, 2007, **59**, 527; (b) Z. Zhou, K. Liu, C. Lai, L. Zhang, J. Li, H. Hou, D. H. Reneker and H. Fong, *Polymer*, 2010, **51**, 2360.

10 (a) D. Liaw, K. Wang, Y. Huang, K. Lee, J. Lai and C. Ha, *Progress in Polymer Science*, 2012, **37**, 907; (b) M. Ding, *Progress in Polymer Science*, 2007, **32**, 623; (c) C. Huang, S. Chen, D. H. Reneker, C. Lai and H. Hou, *Advanced Materials*, 2006, **18**, 668; (d) S. Chen, P. Hu, A. Greiner, C. Cheng, H. Cheng, F. Chen and H. Hou, *Nanotechnology*, 2008, **19**, 015604.

11 M. Rabuffi and G. Picci, *Plasma Science, IEEE Transactions on*, 2002, **30**, 1939.