Electrospun fluorescein/polymer composite nanofibers and their photoluminescent properties*

Zhang Zhi-Hua(张志华)[a)b)], Long Yun-Ze(龙云泽)[a)d)e)†], Yin Hong-Xin(尹红星)[c)], Sun Bin(孙 彬)[a)], Zheng Jie(郑 杰)[a)], Zhang Hong-Di(张红娣)[a)], Ji Xin-Ming(纪新明)[b)], and Gu Chang-Zhi(顾长志)[c)]

[a)] *College of Physics, Qingdao University, Qingdao* 266071, *China*

[b)] *State Key Laboratory of ASIC & System, Department of Microelectronics, Fudan University, Shanghai* 200433, *China*

[c)] *Institute of Physics, Chinese Academy of Sciences, Beijing* 100190, *China*

[d)] *State Key Laboratory Cultivation Base of New Fiber Materials & Modern Textile, Qingdao University, Qingdao* 266071, *China*

[e)] *Key Laboratory of Photonics Materials and Technology in Universities of Shandong (Qingdao University), Qingdao* 266071, *China*

(Received 4 February 2012; revised manuscript received 4 March 2012)

Fluorescein/polyvinyl pyrrolidone (PVP) composite nanofibers with different fluorescein loadings (with weight concentration of 0–5.0%) are fabricated via electrospinning. Morphologies, structures and photoluminescent (PL) properties of these straight, helical or wavelike fibers are characterized by scanning electron microscope (SEM), fluorescence microscope and spectrophotometer. It is found that the maximum emission of the as-spun fluorescein/PVP fibers occurs at 510 nm. The PL intensity of the composite fiber increases with the increase of fluorescein concentration, then fluorescence quenching appears when the concentration reaches 1.67%. The mechanism of fluorescence quenching of fluorescein is discussed. In addition, the composite fibers exhibit much stronger PL intensity than fluorescein/PVP bulk film owing to larger specific surface area, which makes them promising materials for biomedical applications such as probes and sensors.

Keywords: nanofibers, electrospinning, fluorescence, self-quenching

PACS: 78.67.Uh, 81.07.Gf, 81.16.–c **DOI:** 10.1088/1674-1056/21/9/097805

1. Introduction

In the recent years, one-dimensional nanostructures have attracted much attention due to their small size, large specific surface area, and thus unique electrical, magnetic, and optical properties.[1−4] These features make nanofibers have important applications in many fields, such as nano-electronics, filtration, tissue engineering, sensors, protective clothing, and reinforcing components in nanocomposites.[1−7] Electrospinning has been found to be a unique and cost-effective approach to fabricating high long-aspect ratio ultrafine fibers with diameters ranging from several microns down to a few nanometers.[8−12] In a typical electrospinning process, a thin charged jet is formed when the electrostatic force generated by a high operating voltage overcomes the surface tension of the polymer droplet. The jet is accelerated toward the grounded collector and produces fibers in the form of nonwoven mat.[8] Besides fibrous mats with random orientation, partly or even highly aligned nanofibers have also been electrospun via a variety of strategies such as pair electrodes collection, rotating drum collection, auxiliary electric electrospinning, and double spinning.[5,13−16]

Combining with luminescence, luminescent nanofibers fabricated by electrospinning have been extensively reported recently[17−24] due to improved optical properties[17] and their potential applications in light waveguides, gas sensing,[18,19] protein detection,[20] and building blocks of photonic bandgap materials.[21] For example, polyvinyl pyrrolidone (PVP) nanofibers doped with rare-earth elements such as Tb^{3+} show superior emission lines, strong intensities and lengthened lifetime compared with the

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11074138, 11004114, 60906054, and 50825206), the Shandong Provincial Natural Science Foundation for Distinguished Young Scholars, China (Grant No. JQ201103), the Taishan Scholars Program of Shandong Province, China, the National Basic Research Program of China (Grant No. 2012CB722705), and the National High Technology Research and Development Program of China (Grant No. 2011AA100706).

†Corresponding author. E-mail: yunze.long@163.com

© 2012 Chinese Physical Society and IOP Publishing Ltd

pure fluorescent material.[17] Similar enhanced fluorescent properties and lifetimes have also been observed in composite nanofibers of polystyrene (or PVP) and rare-earth complexes containing Eu^{3+}.[22,23] Particularly, colourimetric and fluorescent porphyrinated polyimide nanofibrous membrane sensor was electrospun for the detection of ppm level of HCl gas in a sensitive, rapid response-recovery manner.[18]

Fluorescein is a synthetic organic compound widely used as a fluorescent tracer for many applications. Liang *et al.*[24] have prepared fluorescein derivative/ poly (diallyldimethylammonium chloride) fibers by electrospinning and investigated their photoluminescence properties. However, fluorescence quenching of electrospun fluorescein/polymer nanofibers has not been reported yet. In the present work, we investigate the fluorescent naonfibers fabricated by electrospinning, where fluorescein is doped into PVP and ethanol solution. The effect of fluorescein on the morphology of fibers is studied. In addition, fluorescent properties of the fluorescein/PVP composite nanofibers and bulk films are also investigated and discussed.

2. Experimental details

2.1. Materials

PVP (Mw=10000, AR) was supplied by Aldrich Corp., fluorescein ($C_{20}H_{12}O_5$, Mw=332.31, AR) by Shanghai Medical Chemicals Reagent Corp., alcohol (AR) by Tianjin Damao Chemicals Reagent Corp. All the reagents were of analytical grade and used without further purification.

2.2. Preparation of spinning solutions

PVP solution was prepared by dissolving 3.0 g of PVP in 7.0 g of ethanol and stirred thoroughly for 2 h at room temperature. Then a controlled amount of fluorescein (the weight concentrations of fluorescein were 0.17%, 0.67%, 1.67%, 2.67%, 3.67%, and 5.0%, respectively) was added into the PVP solution, and then stirred thoroughly for 2 h. The resulting fluorescein/PVP solutions with different fluorescein loadings were kept at room temperature for 2 h before electrospinning.

2.3. Preparation of composite fibers

Before electrospinning, the precursor solution was injected into a 5-mL plastic syringe with a flattened stainless steel needle (with inner diameter of 0.72 mm and outer diameter of 1.08 mm), which was fixed perpendicularly. The anode of a high-voltage dc power supply (Tianjin Dongwen) was connected to the needle, and the cathode connected to a piece of aluminum foil, the grounded collector. Here, the applied high voltage was 20 kV, and the distance between the needle tip and the collector was 12 cm. All the experiments were carried out at room temperature.

2.4. Characterization

The morphologies of the as-spun fiber mats were characterized by a scanning electron microscope (SEM; JSM-6700F). All samples were coated with an evaporated gold thin film before SEM imaging to ensure a higher conductivity, and the SEM was operated at an accelerating voltage of 20 kV. Fluorescence microscopy images of the resulting fibers were taken by a Leica DM6000B fluorescence microscope. Finally, fluorescence emission spectra were obtained at room temperature by a Hitachi F-4600 spectrophotometer equipped with a 150-W xenon lamp as the excitation source, the scan speed was 240 nm/min and the excitation and emission slits were 2.5 nm.

3. Result and discussion

3.1. Morphologies and structures of electrospun nanofibers

To investigate the best proportion of PVP/ethanol for preparing smooth electrospun fibers, different solutions with PVP weight concentrations of 20%, 25%, and 30%, respectively, are electrospun at a voltage of 20 kV and a collection distance of 12 cm. After investigation of these three samples, 30% PVP solution is chosen for the following studies, since the fibers obtained by this solution have better and smoother morphology.

It is found that the diameter of the electrospun fiber depends on many processing parameters. Figure 1 shows the SEM images of the pure PVP nanofibers and fluorescein/PVP composite nanofibers (with fluorescein weight concentrations of 0.67%, 1.67%, and 2.67%). We can see that the fibers with diameters ranging from 200 to 800 nm deposited on the collectors are randomly oriented in the form of non-woven fabrics. It was reported that the average fiber diameter is linearly related to the concentration of doping content.[25] In order to investigate the effect of the

doping fluorescein on the average fiber diameter, distribution of the percentage of different fibers diameters is obtained from the corresponding SEM images (Fig. 2). By calculation, the average diameters are 345 nm for the pure PVP nanofibers and 354, 368, and 468 nm for the 0.67%, 1.67%, and 2.67% composite nanofibers, respectively. The results show that the average diameter of fluorescein/PVP composite nanofiber increases. With the fluorescein adding into the PVP/ethanol solution, the viscosity of PVP solution increases, which leads to a larger nanofiber diameter. A similar result has been reported by Liang *et al.*[24]

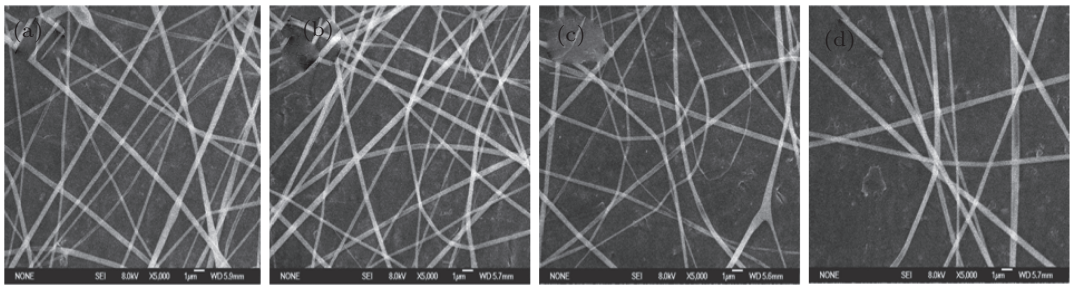


Fig. 1. The SEM images of (a) the pure PVP nanofibers, and (b)–(d) the fluorescein/PVP composite nanofibers with fluorescein weight concentrations of 0.67%, 1.67%, and 2.67%, respectively.

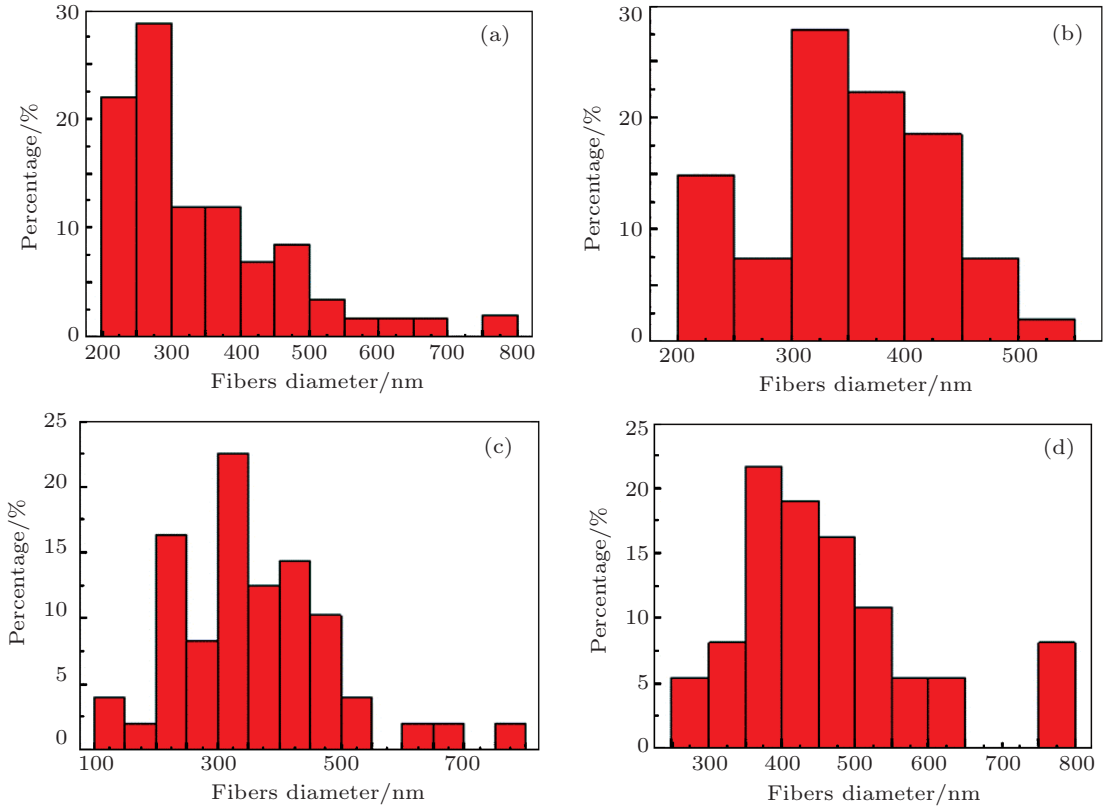


Fig. 2. (colour online) Percentages of fiber diameter provided by (a) the pure PVP nanofibers and (b)–(d) the 0.67%, 1.67%, and 2.67% composite nanofibers, respectively.

Besides straight, uniform fibers (Fig. 1), some helical and wave-like fibers are also observed on the collectors. Figure 3 shows the fluorescence microscope images of the 0.67% fluorescein/PVP nanofibers, which exhibit bright, green, homogeneous fluorescence emission and helical (Fig. 3(a)), wave-like (Fig. 3(b)) structures. Concerning the formation mechanism for the curled fibers observed in these figures, it may be ascribed to Coulomb repulsion forces caused by electrically driven bending instability of the charged jet

and/or mechanical jet buckling when hitting the collector surface.[8,26,27] According to the model developed by Reneker and Yarin,[8] when bending perturbations occurs, the straight electrospinning jet grows rapidly into a coil in response to the repulsive electrical force between the positive charges carried with the jet. Moreover, Han *et al.*[26] also pointed out that the helical or wave-like micro-structures could be formed by buckling that occurred when the moving jet was stopped on the collector during electrospinning. Tang *et al.*[27] prepared curled fibers by electrospinning with tip collector and found that higher operating voltages could increase the proportion of bending fibers and helical structures.

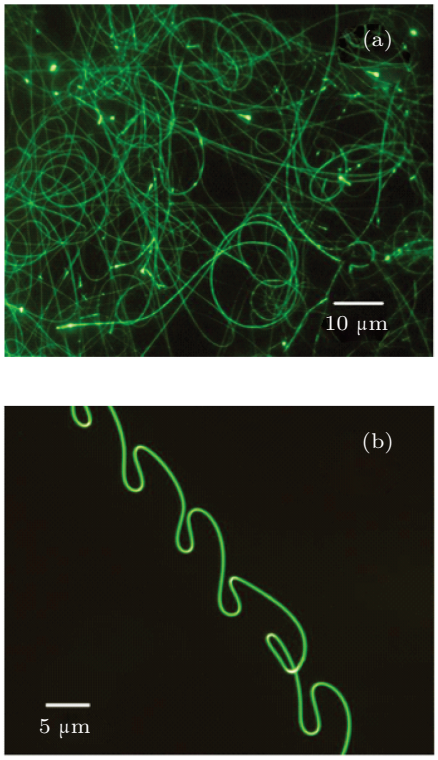


Fig. 3. (colour online) Fluorescence microscope images of the 0.67% fluorescein/PVP composite nanofibers with (a) helical and (b) wave-like structure.

3.2. Photoluminescence properties of the composite fibers

Figure 4(a) shows the fluorescence spectra of the fluorescein/PVP composite nanofibers with different fluorescein loadings. All the photoluminescent (PL) spectra are obtained under an excitation light of 462 nm. In order to compare the PL intensities, the sizes of the nanofibers tested are much the same and they are calculated by the capacity of the experimental facility to be 0.8 cm in diameter and 1.0 mm in height. It can be seen that the PL intensity of pure PVP nanofibers is zero (curve 1 in Fig. 4(a)), namely, PVP is not a fluorescent material. The PL intensity of composite fibers increases with the increase of fluorescein loading (curves 2–4), and the maximum emission nearly occurs at the same position of 510 nm. The PL relative intensity reaches its maximum when the fluorescein concentration is 1.67% (curve 4), and then the PL intensity decreases with the increase of fluorescein concentration (curves 5–7). Namely, a fluorescence quenching phenomenon appears. Figure 4(b) clearly shows the fluorescein concentration-dependent maximum PL intensity of the composite fibers.

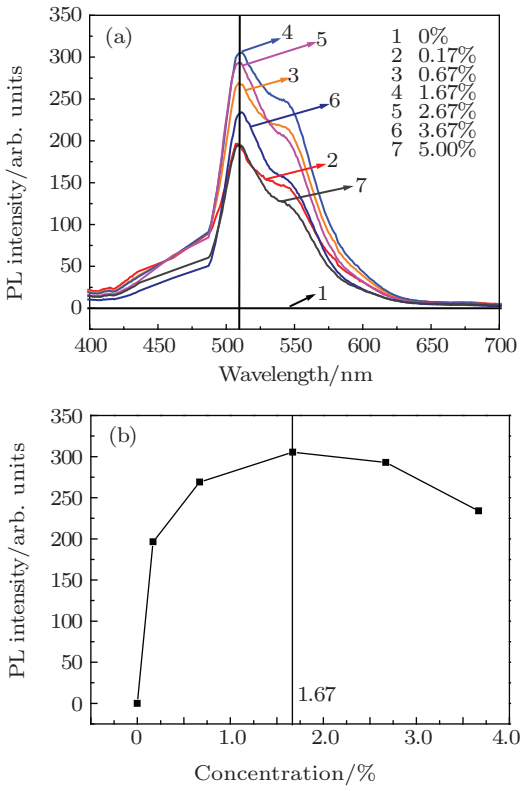


Fig. 4. (colour online) (a) Fluorescence spectra of the pure PVP and fluorescein/PVP composite nanofibers with different fluorescein loadings, (b) variation of the maximum PL intensity with the fluorescein concentration.

Fluorescence quenching has been widely studied as a fundamental phenomenon, owing to the application of fluorescence to biochemical events.[28] In general, the mechanism of fluorescence quenching can be followed either dynamically or statically, and sometimes both.[29] This theory is accepted only when quenchers are added into the solution. However, in the present case, there are no quenchers in the solutions, so fluorescence quenching phenomenon in this work could be ascribed to self-quenching of fluorescein. Firstly, fluorescein has a high potential

for self-quenching because the emission spectrum sufficiently overlaps with the absorption spectrum.[30] Self-quenching of fluorescein has previously been reported and is believed to be a result of two processes: non-fluorescent fluorescein dimer formation and energy transfer from active fluorescein monomers to dark fluorescein dimmers.[31−33] In these reports, self-quenching of fluorescein is believed to be related to fluorescein dimers. Meanwhile, there is another possible way to realize the self-quenching of fluorescein. The fluorescence which is produced by excited state fluorescein molecules is absorbed by ground state fluorescein molecules, which induces the decrease of the PL intensity. In addition, we consider that the collisions among fluorescein molecules make the formation of the fluorescences different. With the increase of fluorescein loading, the inner motion among fluorescein molecules becomes more active and the opportunity of collisions increases. The collisions among fluorescein molecules result in the loss of the energy and the fluorescence self-quenching.

As is well known, nanoscale materials usually show different optical, electrical and magnetic properties from those their bulk counterparts exhibit.[34−36] For example, for conjugated poly [3-(2-methoxyphenyl)-thiophene] (PMP-Th) nanowires (with diameters of 60, 70 and 80 nm, respectively) prepared by hard template synthesis, PL spectra show that the PMP-Th nanowires exhibit an obvious blue-shift and great intensity enhancement compared with the bulk PMP-Th film. [34,35] In order to compare the fluorescent properties of fluorescein/PVP nanofibers and bulk films, we also prepare fluorescein/PVP bulk films. Part of precursor solution, the fluorescein/PVP/ethanol composite solution, is cast onto a glass slide. After drying at room temperature in air for 2 d, a bulk film of thickness about 1.0 mm is obtained. For comparison, the thickness of non-woven nanofiber film is also about 1.0 mm. Figure 5 shows the fluorescence spectra of the 0.67% fluorescein/PVP nanofibers and bulk film. They are also obtained under the excitation at 462 nm. We can see that the PL intensity of the fluorescein/PVP composite fibers has a significant increase compared with that of the bulk film, which may be due to the high surface-to-volume ratio of the electrospun fibers.[37] It demonstrates that nanofibers have some special features for application. Figure 5 also indicates that fluorescence peaks of these two samples are both at 510 nm, and no obvious shift appears.

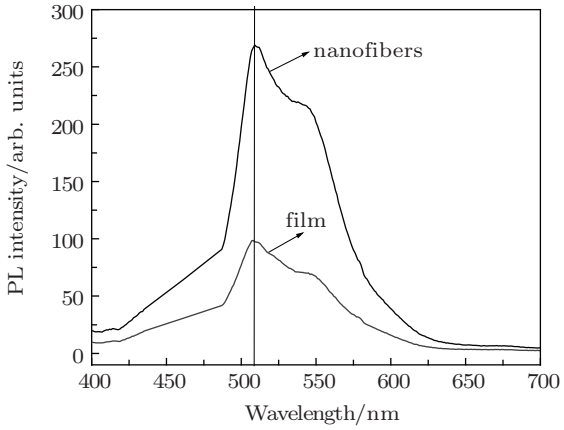


Fig. 5. Fluorescence spectra of the 0.67% fluorescein/PVP film and nanofibers.

4. Conclusion

In the present paper, fluorescein/PVP composite nanofibers with different fluorescein loadings are successfully fabricated by electrospinning. Besides straight, uniform fibers, helical and wave-like fibers are also obtained. The formation mechanism for the curled fibers can be ascribed to electrically driven bending instability and/or mechanical jet bucking. It is found that the maximum emission of the as-spun fluorescent fibers occurs at 510 nm. The PL intensity of the composite fibers increases with fluorescein concentration increasing, and then fluorescence quenching appears when the concentration reaches 1.67%. The mechanism of fluorescence quenching can be ascribed to self-quenching of fluorescein. In addition, the composite fibers exhibit much stronger PL intensity than fluorescein/PVP bulk film, owing to larger specific surface area. These results indicate that fluorescent nanofibers produced by electrospinning are promising materials for biomedical, sensing, and optical applications.

References

[1] Xia Y N, Yang P D, Sun Y G, Wu Y Y, Mayers B, Gates B, Yin Y D, Kim F and Yan H Q 2003 *Adv. Mater.* **15** 353

[2] Huang Y and Lieber C M 2004 *Pure Appl. Chem.* **76** 2051

[3] Yuan H J, Chen Y Q, Yu F, Peng Y H, He X W, Zhao D and Tang D S 2011 *Chin. Phys.* B **20** 036103

[4] Long Y Z, Li M M, Gu C Z, Wan M X, Duvail J L, Liu Z W and Fan Z Y 2011 *Prog. Polym. Sci.* **36** 1415

[5] Huang Z M, Zhang Y Z, Kotaki M and Ramakrishna S 2003 *Compos. Sci. Technol.* **63** 2223

[6] Agarwal S, Wendorff J H and Greiner A 2008 *Polymer* **49** 5603

[7] Greiner A and Wendorff J H 2008 *Adv. Polym. Sci.* **219** 107
[8] Reneker D H and Yarin A L 2008 *Polymer* **49** 2387
[9] Zheng J, Long Y Z, Sun B, Zhang Z H, Shao F, Zhang H D, Zhang Z M and Huang J Y 2012 *Chin. Phys.* B **21** 048102
[10] Xiang J, Song F Z, Shen X Q and Chu Y Q 2010 *Acta Phys. Sin.* **59** 4794 (in Chinese)
[11] Xiang J, Shen X Q, Song F Z and Liu M Q 2009 *Chin. Phys.* B **18** 4960
[12] Li M M, Long Y Z, Tan J S, Yin H X, Sui W M and Zhang Z M 2010 *Chin. Phys.* B **19** 028102
[13] Li D, Wang Y L and Xia Y N 2003 *Nano. Lett.* **3** 1167
[14] Wu Y Q, Carnell L A and Clark R L 2007 *Polymer* **48** 5653
[15] Tan J S, Long Y Z and Li M M 2008 *Chin. Phys. Lett.* **25** 3067
[16] Li M M, Long Y Z, Yang D Y, Sun J S, Yin H X, Zhao Z L, Kong W H, Jiang X Y and Fan Z Y 2011 *J. Mater. Chem.* **21** 13159
[17] Liu W and Wang C 2007 *Polish. J. Chem.* **81** 79
[18] Lv Y Y, Wu J and Xu Z K 2010 *Sens. Actuators B Chem.* **148** 233
[19] Mosinger J, Lang K, Plíštil L, Jesenská S, Hostomský J, Zelinger Z and Kubát P 2010 *Langmuir* **26** 10050
[20] Davis B W, Niamnont N, Hare C D, Sukwattanasinitt M and Cheng Q 2010 *ACS Appl. Mater. Interf.* **2** 1798
[21] Dersch R, Steinhart M, Boudriot U, Greiner A and Wendorff J H 2005 *Polym. Adv. Technol.* **16** 276
[22] Yin H X, Long Y Z, Yu F, Zhao S J and She X L 2011 *Mater. Sci. Forum* **688** 74
[23] Zhang H, Song H, Yu H Q, Bai X, Li S, Pan G, Dai Q, Wang T, Li W, Lu S, Ren X and Zhao H 2007 *J. Phys. Chem.* C **111** 6524
[24] Liang X F, Li Y X, Peng W, Bai J, Zhang C Q and Yang Q B 2008 *Eur. Polym. J.* **44** 3156
[25] Li M M, Long Y Z, Yin H X and Zhang Z M 2011 *Chin. Phys.* B **20** 048101
[26] Han T, Reneker D H and Yarin A L 2007 *Polymer* **48** 6064
[27] Tang C C, Chen J C, Long Y Z, Yin H X, Sun B and Zhang H D 2011 *Chin. Phys. Lett.* **28** 056801
[28] Lakowicz J R 1986 *Principles of Fluorescence Spectroscopy* (New York: Plenum Press)
[29] Arık M, Çelebi N and Onganer Y 2005 *J. Photochem. Photobiol.* A **170** 105
[30] Egawa Y, Hayashida R, Seki T and Anzai J 2008 *Talanta* **76** 736
[31] Agranovich V M and Galanin M D 1982 *Electronic Excitation Energy Transfer in Condensed Matter* (New York: North-Holland Publishing)
[32] Chen R F and Knutson J R 1988 *Anal. Biochem.* **172** 61
[33] Sims P J and Wiedmer T 1984 *Biochem.* **23** 3260
[34] Liu X L, Xu F Q, Li Z M and Zhang W H 2008 *Polymer* **49** 2197
[35] Liu X L, Xu F Q, Li Z M, Zhu J F and Zhang W H 2008 *Opt. Mater.* **30** 1861
[36] Massuyeau F, Duvail J L, Athalin H, Lorcy J M, Lefrant S, Wéry J and Faulques E 2009 *Nanotechnology* **20** 155701
[37] Sui X M, Shao C L and Liu Y C 2005 *Appl. Phys. Lett.* **87** 113