Dielectric properties of electrospun titanium compound/polymer composite nanofibres*

Li Meng-Meng(李蒙蒙)[a], Long Yun-Ze(龙云泽)[a]†, Tan Jin-Shan(谭金山)[b], Yin Hong-Xing(尹红星)[a], Sui Wan-Mei(隋万美)[a], and Zhang Zhi-Ming(张志明)[c]

[a] *College of Physics Science, Qingdao University, Qingdao* 266071, *China*
[b] *Laboratory of Fibre Materials and Modern Textile, the Growing Base for State Key Laboratory, Qingdao University, Qingdao* 266071, *China*
[c] *College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao* 266100, *China*

(Received 5 May 2009; revised manuscript received 7 July 2009)

Poly(vinylpyrrolidone)/tetrabutyl titanate (PVP/ $[CH_3(CH_2)_3O]_4Ti$) composite nanofibres are prepared by electrospinning. After calcining parts of composite nanofibres in air at 700 °C, petal-like TiO_2 nanostructures are obtained. The characterizations of composite nanofibres and TiO_2 nanostructures are carried out by a scanning electron microscope, an x-ray diffractometer, and an infrared spectrometer. Electrospun nanofibres are pressed into pellets under different pressures in order to explore their dielectric properties. It is found that the dielectric constants decrease with frequency increasing. The dielectric constant of the composite nanofibre pellet increases whereas its dielectric loss tangent decreases due to the doped titanium ions compared with those of pure PVP nanofibre pellets. In addition, it is observed that the dielectric constant of the composite nanofibre pellet decreases with the increase of the pressure applied in pelletization.

Keywords: composite nanofibres, electrospinning, dielectric properties

PACC: 8120T, 7740, 8116

1. Introduction

Since it was discovered in the 1930s,[1] electrospinning has been known as a simple, versatile and useful method of fabricating ultrafine fibres from polymer solutions with diameters typically ranging from a few micrometers down to 10 nm or less.[2] Due to their special size, electrospun nanofibres manifest a few amazing characteristics such as very large surface-to-volume ratio, flexibility in surface functionalities, and superior mechanical performance in comparison with conventional materials.[3,4] These outstanding properties make the electrospun nanofibres optimal candidates in military, civilian and medicinal applications.[5,6] In a traditional process, a polymer solution is extruded from the orifice of a needle in the presence of a high-voltage electric field, and travels 10–20 cm in air. At the same time, most of the solvent evaporates away. Then, the electrospun nanofibres are collected as a non-woven web on a grounded collector.[7]

By now, a large number of papers have been published about the fabrication and the properties of electrospun TiO_2 nanostructures. For example, Li *et al.*[8] prepared TiO_2 nanofibres in a range from 20 nm to 200 nm via calcining electrospun composite nanofibres in air at 500 °C. Formo *et al.*[9] functionalized electrospun TiO_2 nanofibres with Pt nanoparticles and nanowires, showing excellent catalytic activity for the hydrogenation of azo bonds in methyl red. In addition, hollow TiO_2 containing multilayer nanofibres could be fabricated through the combination of electrospinning with layer-by-layer technique.[10] As is known, dielectric constant and dielectric loss are quite important parameters of nanoscale materials, and dielectric techniques are particularly useful to probe mechanisms of charge transport and charge polarization. Recent studies[11−13] have shown that nanocomposites have interesting dielectric properties and several applications in supercapacitors or high-energy storage systems, electromagnetic interference shielding, microwave absorption, etc. How-

*Project supported by the Program for New Century Excellent Talents in University of China (Grant No. NCET-07-0472) and the National Natural Science Foundation of China (Grant No. 10604038).
†Corresponding author. E-mail: yunze.long@163.com
© 2010 Chinese Physical Society and IOP Publishing Ltd

ever, the dielectric properties of electrospun titanium compound/polymer nanofibres have not been investigated extensively. So in the present paper, we focus our attention on fabricating pure PVP nanofibres and PVP/$[CH_3(CH_2)_3O]_4Ti$ composite nanofibres via electrospinning, and studying their dielectric properties. It is found that the dielectric constant and dielectric loss tangent of the nanofibre pellets are dependent on frequency of applied electric field, doped metallic ions, and the pressure used in pelletization.

2. Experiment

2.1. Preparation of precursor solution

A polymer solution was prepared by dissolving 8 g of poly(vinylpyrrolidone) (PVP, $M_W \approx 10000$, its molecular structure is shown in Fig. 1, Shanghai Aibi Chemistry Preparation Co., China) in 30 ml of ethanol (Yantai Sanhe Chemistry Preparation Co., China). The solution was stirred thoroughly for 2 h, and then kept at room temperature for 1 h. Subsequently, the solution was added into the mixture of 2 ml of tetrabutyl titanate ($[CH_3(CH_2)_3O]_4Ti$, Tianjin Regent Chemicals Co., China) and 2 ml of acetic acid (CH_3COOH, Shanghai Aibi Chemistry Preparation Co., China), and then stirred thoroughly for 2 h. Finally, this poly(vinylpyrrolidone)/tetrabutyl titanate (PVP/$[CH_3(CH_2)_3O]_4Ti$) solution was obtained and kept at room temperature for 1 h.

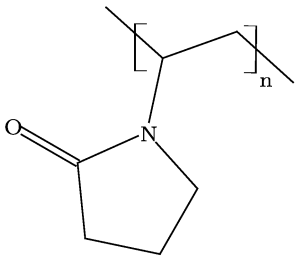


Fig. 1. Molecular structure of poly(vinylpyrrolidone).

2.2. Electrospinning

The electrospinning setup was similar to that shown in Fig. 2. The polymer solution was placed into a 10-ml plastic syringe that was fixed perpendicularly. The polymer solution in the syringe flowed into a stainless steel needle with inner diameter 0.72 mm and outer diameter 1.08 mm under the action of the gravity. The needle was connected to the positive electrode of a high-voltage dc supply (DW-P403-1ACCC, Tianjin Dongwen High Voltage Power Supply Plant, China), and the collector was grounded. A dc voltage of 20.0 kV was applied. The grounded collector, a piece of flat aluminum foil, was placed 15.0 cm below the tip of the needle. Under the action of electric field, the Taylor's cone was formed at the top of the needle. When the force due to the electric field overcame the surface tension force holding the droplet, the polymer solution began to flow to form the charged solution jets moving towards the collector. Before reaching the collecting screen or collector, the solution jets stretched and/or split to form fibres due to "whipping" instability and/or mutual repulsion, and most of the solvent (ethanol) evaporated away.[3] Thus, the nanofibres were collected in the form of the non-woven mat. We calcined parts of composite nanofibres in air at 700 °C with a rate of 5 °C/min for 4 h to obtain TiO_2 nanostructures, which was different from the procedure in Ref. [8].

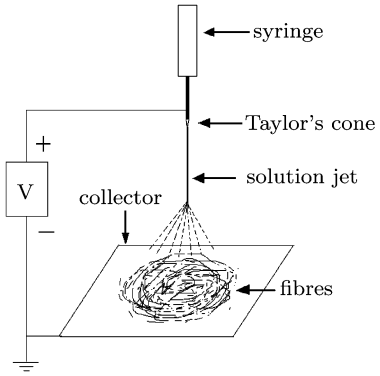


Fig. 2. Schematic diagram of the setup for electrospinning.

2.3. Characterization

A scanning electron microscope (SEM; JEOL JSM-6390) operating at 20 kV or 30 kV was used to observe the size and morphology of the electrospun nanofibres. All samples were coated with an evaporated gold thin film before SEM imaging to ensure higher conductivity. The x-ray diffraction (XRD) pattern was recorded by using a Rigaku D/max-2400 diffractometer (Cu K_α radiation, $\lambda = 1.5406$ nm) at a scanning rate of 0.02°/s in 2θ ranging from 5° to 8°, and the infrared (IR) spectra of the electrospun nanofibres were recorded by using a MAGNA-IR 550 spectrometer. Before measuring the dielectric properties, electrospun nanofibres were pressed into pellets by using a pressing machine (YLJ-303/16T, Hefei Kejing Materials Technology Co., China). The applied

pressure was 16.5 MPa for pure PVP nanofibre pellet, 16.5 MPa and 264.2 MPa for PVP/$[CH_3(CH_2)_3O]_4Ti$ composite nanofibre pellets. The dielectric constant and dielectric loss tangent of all pellets were measured by a TH2819 Precision LCR Meter (Changzhou Tonghui Electronic Co., China) at room temperature.

3. Results and discussion

3.1. Electrospun nanofibres and calcined nanostructures

The morphologies of electrospun composite nanofibres and calcined nanostructures were studied by using the scanning electron microscope (SEM). From Fig. 3(a), it can be clearly seen that the electrospun nanofibres are collected as the non-woven web. Figure 3(b) exhibits the size distribution of electrospun composite nanofibres ranging from 200 nm to 1500 nm, and their average diameter is approximate 694 nm. As mentioned in the above section, we calcined parts of composite nanofibres not at 500 °C but at 700 °C, and then we obtained petal-like nanostructures as shown in Figs. 3(c) and 3(d). Their size increases to a microscale value on average possibly due to conglomeration or assembly of TiO_2 nanoparticles during calcination at higher temperatures. Here we note that TiO_2 nanofibres have been obtained by calcining at 500 °C.[8]

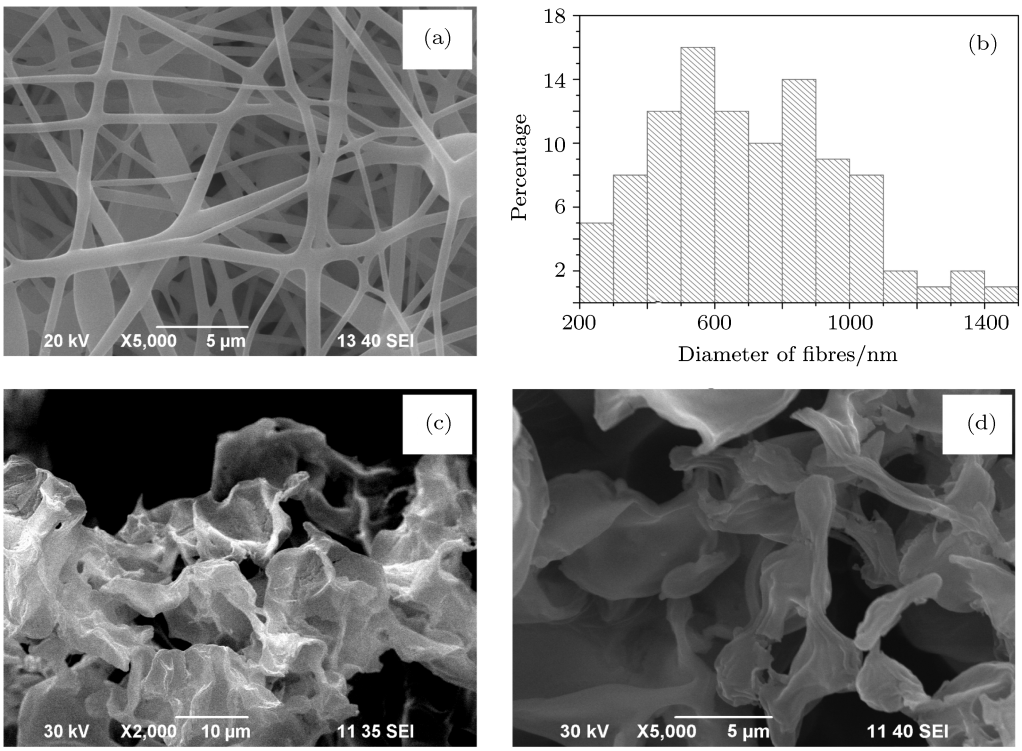


Fig. 3. (a) SEM image of electrospun composite nanofibres. (b) Histogram showing the size distribution of composite nanofibres. The size distribution was obtained from diameter measurements on 100 nanofibres in the SEM images. (c) and (d) SEM images of TiO_2 nanostructures obtained by calcining composite nanofibres at 700 °C for 4 h.

The phases of both composite nanofibres and the resulting nanostructures were determined by XRD (Fig. 4). Curve *a* shows that the pure PVP has a certain degree of crystallinity. The broad peaks can be ascribed to the scattering from PVP chains at interplanar spacing. Curve *b* displays the characteristic pattern of TiO_2, indicating the formation of pure TiO_2 nanostructures after calcination at 700 °C for 4 h, and the main peaks can be indexed to the titanium oxide phase (JCPDS, card no.65-1119). This result also confirms that $[CH_3(CH_2)_3O]_4Ti$ is not electro-sprayed out in the form of droplets (and then as discrete nanoparticles), but trapped in composite nanofibres during electrospinning.[8]

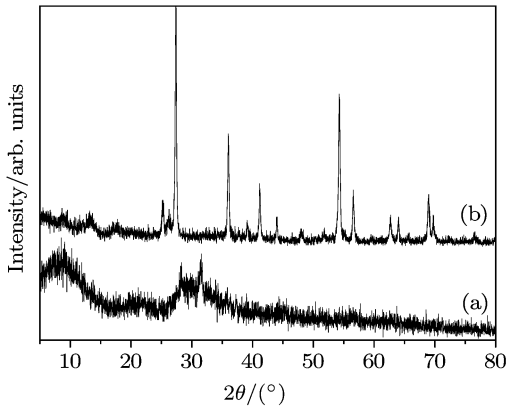


Fig. 4. XRD spectra of electrospun composite nanofibres (a) and resulting pure TiO_2 nanostructures (b).

Figure 5(a) shows the infrared (IR) spectra of composite nanofibres in a region of 700–3900 cm^{-1}. The presence of a heteroatom and a carbonyl group in the pyrrolidone ring sufficiently reduces the symmetry,[14] as shown in Fig. 1. The sharp peak at 1680 cm^{-1} corresponds to the stretching vibration of carboxyl group, which is a typical mode of PVP, while the absorption band around 2940 cm^{-1} can be attributed to the C–H stretching vibrations.[15] In addition, it can be clearly seen that the composite nanofibres contain a trace hydroxyl group due to the electrospun solution. A broad stretching band at about 3440 cm^{-1} appears in the composite nanofibres, which can be assigned to the vibration of the associated hydroxyl groups. It is interesting that the IR spectra of the composite nanofibres are similar to that of the pure PVP nanofibres electrospun from the PVP ethanol solution, and figure 5(b) shows that composite nanofibres contain Ti, suggesting that the titanium complexes are embedded in the PVP matrix.[7]

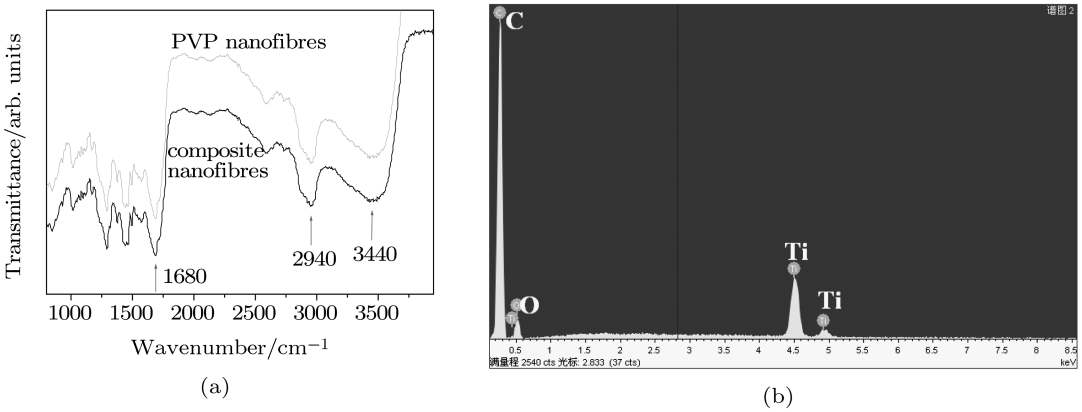


Fig. 5. (a) IR spectra and (b) EDS of the composite nanofibres.

3.2. Dielectric properties of electrospun nanofibres

Dielectric constant and dielectric loss are quite important parameters of the composite materials. The complex permittivity is $\varepsilon^* = \varepsilon' - \mathrm{i}\,\varepsilon''$, where ε' and ε'' represent the real and the imaginary parts respectively, and the dielectric loss tangent is $\tan\delta = \varepsilon''/\varepsilon'$. The dielectric properties of electrospun nanofibres have not been investigated intensively yet. In the present study, the dielectric properties have been explored at room temperature, and several interesting behaviours have been observed.

3.2.1. Effect of frequency

From Fig. 6, it is seen that all samples show the frequency-dependent phenomena at frequencies ranging from 10 kHz to 200 kHz, which indicates that the dielectric constant values for both the pure PVP nanofibre pellet and the composite nanofibre pellets decrease to some extent with frequency increasing. This behaviour may be attributed to interfacial polarization[16] and dipole relaxation.[17] Due to the chain segmental motions in the amorphous region and the dipolar relaxation in the crystalline region,[18] the dielectric loss tangent peaks appear around 5 kHz, 100 kHz and 100 kHz for the pure PVP nanofibre pellet and the composite nanofibre pellets at pressures of 16.5 MPa and 264.2 MPa, respectively as shown in Fig. 7.

3.2.2. Effect of titanium ions

Compared with the pure PVP nanofibre pellet, composite nanofibre pellets with doped metallic ions are rather different in dielectric property. Figure 6 exhibits that the dielectric constant values of composite nanofibre pellets are larger than those of the pure PVP nanofibre pellets. For instance, the dielectric constant of composite nanofibre pellet at a pressure of 16.5 MPa is enhanced approximately up to 50, about 3.5 times larger than that of the pure PVP nanofibre pellet.

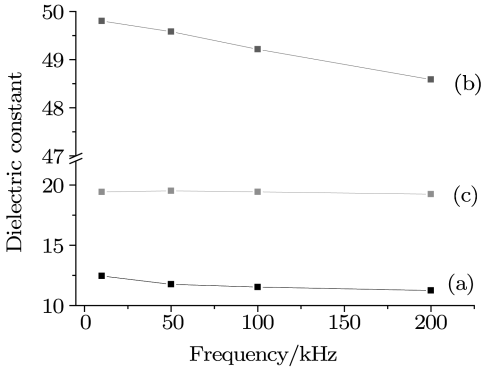


Fig. 6. Dielectric constants of the pure PVP nanofibre pellet at a pressure of 16.5 MPa (a), and the composite nanofibre pellets at pressures of 16.5 MPa (b) and 264.2 MPa (c).

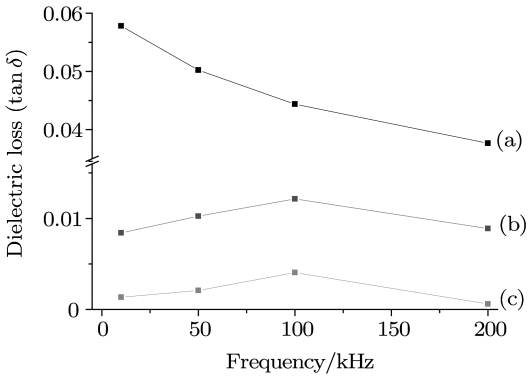


Fig. 7. Dielectric losses of the pure PVP nanofibre pellet at a pressure of 16.5 MPa (a) and the composite nanofibre pellets at pressures of 16.5 MPa (b) and 264.2 MPa (c).

Figure 7 shows that the dielectric loss tangent of composite nanofibre pellet is much smaller than that of the pure PVP nanofibre pellet. All these results are reasonable and can be explained. The embedded titanium ions in the composite nanofibre pellets induce charge carriers in the pellets, namely, they increase the polarization ability of the pellets, and thus the dielectric constant. In addition, as reported by Yin *et al.*[19,20] a low dielectric loss can be attributed to fast ionic or atomic polarization. For the present case, greater and faster polarization caused by doped metallic ions may result in smaller dielectric loss tangent for the composite nanofibre pellets in contrast with the case of the pure PVP nanofibre pellet.

3.2.3. Effect of pressure

As described in the above section, the electrospun nanofibres were pressed into pellets in order to measure their dielectric properties. Under the action of the pressure, some of nanofibres were forced to stick together as shown in Fig. 8. When the pressure used in pelletization increases, more and more nanoscale fibres will be conglutinated gradually. Therefore, compared with the pellet at a pressure of 264.2 MPa, composite nanofibre pellet at a pressure of 16.5 MPa contains more nanoscale fibres which result in a large surface-to-volume ratio and high density of interfacial atoms. Thus, more interfacial polarizations occur, thereby increasing the dielectric constant.[21] So it is expectable that the dielectric constant of composite nanofibre pellet at a pressure of 16.5 MPa is larger than that of pellet at a pressure of 264.2 MPa as shown in Fig. 6. In addition, more multiple scatterings may appear due to larger surface-to-volume ratio, resulting in larger dielectric relaxation when the applied electric field changes.[21] As a result, the dielectric loss tangent of composite nanofibre pellet at a pressure of 16.5 MPa is much larger than that of pellet at a pressure of 264.2 MPa (Fig. 7).

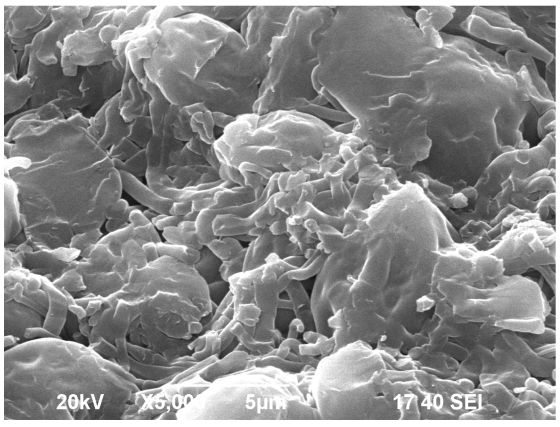


Fig. 8. SEM image of cross section of the compressed pellet.

4. Conclusion

The pure PVP nanofibres and PVP/$[CH_3(CH_2)_3O]_4Ti$ composite nanofibres are prepared via electrospinning. TiO_2 nanostructures are obtained by calcin-

ing the composite nanofibres at 700 °C for 4 h. Both XRD and IR spectra indicate that $[CH_3(CH_2)_3O]_4Ti$ is trapped in composite nanofibres. After being pressed by a pressing machine, some nanoscale fibres in the pellets are forced to stick together, and their size increases with the increase of pressure. The dielectric properties of the pure PVP nanofibre pellet and composite nanofibre pellets are studied and several interesting behaviours are observed: (i) with the increase of frequency, the dielectric constant values decrease; (ii) because of doped metallic ions, the dielectric constant of the composite nanofibre pellets increases while their dielectric loss tangent decreases compared with those of the pure PVP nanofibre pellet; (iii) in comparison with the pellet at a pressure of 264.2 MPa, both dielectric constant and dielectric loss tangent are enhanced for the composite nanofibre pellet at a pressure of 16.5 MPa. These results indicate that the dielectric properties of the composite fibres are dependent on the frequency of the applied electric field, the doped metallic ions and the pressure applied in pelletization.

References

[1] Formhals A 1934 *U. S. Patent* No1975504

[2] Li D and Xia Y N 2004 *Adv. Mater.* **16** 1151

[3] Tan J S, Long Y Z and Li M M 2008 *Chin. Phys. Lett.* **25** 3067
Zhao J G, Zhang Z X, Ma Z W, Duan H G, Guo X S and Xie E Q 2008 *Chin. Phys. Lett.* **25** 3787

[4] Huang Z M, Zhang Y Z, Kotaki M and Ramakrishna S 2003 *Compos. Sci. Technol.* **63** 2223
Long Y Z, Yin Z H, Li M M, Gu C Z, Duvail J L, Jin A Z and Wan M X 2009 *Chin. Phys.* B **18** 2514
Long Y Z, Yin Z H, Hui W, Chen Z J and Wan M X 2009 *Chin. Phys.* B **18** 2707

[5] Hajra M G, Mehta K and Chase G G 2003 *Sep. Purif. Technol.* **30** 79

[6] Gensheimer M, Becker M, Brandis-Heep A, Wendorff J H, Thauer R K and Greiner A 2007 *Adv. Mater.* **19** 2480

[7] Zhang H, Song H W, Yu H Q, Bai X, Li S W, Pan G H, Dai Q L, Wang T, Li W L, Lu S Z, Ren X G and Zhao H F 2007 *J. Phys. Chem.* C **111** 6524

[8] Li D and Xia Y N 2003 *Nano Lett.* **3** 555

[9] Formo E, Lee E, Campbell D and Xia Y 2008 *Nano Lett.* **8** 668

[10] Zhang T Z, Ge L Q, Wang X and Gu Z Z 2008 *Polymer* **49** 2898

[11] Wang D W, Zhang D Q, Yuan J, Zhao Q L, Liu H M, Wang Z Y and Cao M S 2009 *Chin. Phys.* B **18** 2596
Zhou Y, Kang Y Q, Fang X Y, Yuan J, Shi X L, Song W L and Cao M S 2008 *Chin. Phys. Lett.* **25** 1902

[12] Long Y Z, Li M M, Sui W M, Kong Q S and Zhang L 2009 *Chin. Phys.* B **18** 1221
Sang Z F and Li Z Y 2005 *Chin. Phys.* **14** 1657

[13] Xu F, Bai Y, Ai F and Qiao L J 2008 *Chin. Phys.* B **17** 4652
Wang X J, Gong Z Q, Zhu J and Chen X B 2009 *Chin. Phys.* B **18** 803

[14] Borodko Y, Habas S E, Koebel M, Yang P D, Frei H and Somorjai G A 2006 *J. Phys. Chem.* B **110** 23052

[15] Zhang H, Song H W, Dong B, Han L L, Pan G H, Bai X, Fan L B, Lu S Z, Zhao H F and Wang F 2008 *J. Phys. Chem.* C **112** 9155

[16] Selvan R K, Krishnan V, Augustin C O, Bertagnolli H, Kim C S and Gedanken A 2008 *Chem. Mater.* **20** 429

[17] Ye Q, Song Y M, Wang G X, Chen K, Fu D W, Chan P W H, Zhu J S, Huang S D and Xiong R G 2006 *J. Am. Chem. Soc.* **128** 6554

[18] Wang J W, Shen Q D, Bao H M and Yang C Z 2005 *Macromolecules* **38** 2247

[19] Yin J B and Zhao X P 2004 *Chem. Mater.* **16** 321
Mu C H, Liu P, He Y, Zhang D, Meng L and Bian X B 2008 *Acta Phys. Sin.* **57** 2432 (in Chinese)

[20] Zhao X P and Yin J B 2002 *Chem. Mater.* **14** 2258
Zhao M L, Yi X J, Wang C L, Wang J F and Zhang J L 2006 *Chin. Phys.* **15** 1611

[21] Liu J G, Wang T G, Du H, Gong J, Sun C and Wen L S 2006 *Metallic Functional Materials* **13** 24 (in Chinese)
Yin G L, Li J Y and Li S T 2009 *Acta Phys. Sin.* **58** 4219 (in Chinese)