SCIENCE CHINA
Technological Sciences

June 2010 Vol.53 No.6: 1489–1494
doi: 10.1007/s11431-010-3142-1

Microstructure of fibrils separated from polyacrylonitrile fibers by ultrasonic etching

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Received December 22, 2009; accepted January 6, 2010

Polyacrylonitrile (PAN) fiber is an important precursor fiber for high performance carbon fiber. The properties of the final carbon fiber depend strongly on the nature of the PAN fibers. The PAN fibrils were separated successfully from fibers by ultrasonic etching and were systematically investigated by field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscopy (HRTEM). It is found that in certain ultrasonic etching conditions (at 75±2ºC for 6 h with a frequency of 40 kHz) the PAN fibers are dissolved in the 95 wt.% aqueous dimethylsulphoxide (DMSO) solution; the fibrils consisting of numerous periodic lamellae with thickness of 30–45 nm and perpendicular to the fiber axis are separated in the 90 wt.% aqueous DMSO solution; and the fibrils with smooth surface exfoliated from the PAN fibers are obtained in the 70–90 wt.% aqueous DMSO solutions. Inner periodical structure of fibrils was observed in HRTEM, which indicates that there are different densities and two phases in fibrils. The PAN fibers are dissolved layer by layer with increasing ultrasonic etching time. The fiber surface experiences ultrasonic cleaning, selective etching, excessive etching and dissolution, and then the sublayer experiences the same process. There are numerous periodic lamellae in fibrils of nascent fibers. This means that the fibrils with lamellae are formed by orientation and crystallization in shearing field of spinning pipe and drawing stress field of coagulation bath.

carbon fibers, PAN fibers, fibrils, microstructure

Citation: Wang Q F, Wang C G, Yu M J, et al. Microstructure of fibrils separated from polyacrylonitrile fibers by ultrasonic etching. Sci China Tech Sci, 2010, 53: 1489–1494, doi: 10.1007/s11431-010-3142-1

1 Introduction

Carbon fibers play an important role in advanced composite materials owing to their excellent properties such as low density, high strength, high modulus, elevated temperatures resistance, corrosion resistance, radioresistance, creep resistance, low thermal expansion, low electric resistance and high-thermal conductivity. Among the various precursors for carbon fibers, polyacrylonitrile (PAN) has wide acceptability due to the high carbon yield, low production cost and low voids of the structure of the final product [1]. So the PAN precursor fibers have excellent potential for commercial exploitation. The manufacture of the PAN-based carbon fibers undergoes precursor fibers formation, oxidative stabilization and carbonization. The properties of the final carbon fibers depend greatly on the precursor. So it is important to understand exactly the microstructures of the PAN fibers.

Much of the earlier work [2–8] about structure of the PAN fibers mainly focused on crystallinity, orientation, surface and cross section of the PAN fibers. However, very few dealt with the fibrils of the PAN fibers. We separate the fibrils from fibers by ultrasonic etching based on the mechanism of ultrasonic breakup and solvent etching. Mechanically weak spots of material structure are broken up by ul-

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trasonication [9] and amorphous regions are selectively etched due to solution speed higher in amorphous region than in crystalline region [10].

In our pilot study [11], the effects of ultrasonic etching treatment on the chemical construction, molecular weight, crystalline morphology, surface morphology and mechanical properties of the PAN fibers were investigated. The result indicated that ultrasonic etching could not influence chemical construction of the PAN fibers. Molecular weight of the undissolved PAN did not change. The crystallinity and crystal grains reduced slightly after ultrasonic etching. The fibrils appeared on the fiber surface under the action of ultrasonic etching. Ultrasonic etching had little effect on linear density of the PAN fibers, but the breaking strength, the breaking extension and initial modulus all decreased. In this paper, the structure of fibrils which were separated from the PAN fibers by ultrasonic etching is examined by field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscopy (HRTEM). The effects of ultrasonic etching conditions on the morphology of fibrils and formation of lamellae in microfibrils are discussed.

2 Experimental

The PAN fiber was prepared by two-step method. Acrylonitrile (AN) and itaconic acid (IA) were copolymerized by aqueous deposited polymerization for the first step. Then spinning solution was prepared by dimethylsulphoxide (DMSO) as solvent for second step. The PAN fiber was manufactured through eight stages in sequence: coagulation, preliminary drawing, washing, drawing in boiling water, collapsing, drawing in vapor, heat setting and drying.

The PAN fiber was cut into 2–3 mm and processed ultrasonically in the 90 wt % aqueous DMSO solution at 75±2ºC for 6 h with a frequency of 40 kHz in KQ-200KDE ultrasonic cleaner. The solution containing the fibrils was dropped on a grid which was washed rapidly with cool distilled water to prevent recrystallization and dried in air.

After being coated with a thin platinum layer, the microstructure of fibrils was observed by FESEM (JSM-6700F). The fibrils without platinum coating were examined by HRTEM (JEM-2100).

3 Results and discussion

3.1 Morphology of PAN fibrils

Effect of the DMSO concentration on morphology of the PAN fibril was examined. The DMSO concentrations chosen as the study object were 75 wt.%, 80 wt.%, 85 wt.%, 90 wt.% and 95 wt.%, respectively. The PAN fibers were dissolved in 95 wt.% DMSO by ultrasonic etching within 30 min, but existed in other DMSO solution after 6 h. This suggests that 5 wt.% H2O dose not influence dissolving capacity of PAN in DMSO. Du [12] reported that PAN/DMSO/H_2O mixture was homogenous liquid when H_2O concentration was below 6 wt.%. Complex compound of DMSO and H_2O increased with increasing H_2O content, and the PAN and DMSO intermolecular force and dissolving capacity of PAN decreased, thus the PAN fibers were retained in less than 90 wt. % DMSO.

Figure 1(a) shows the surface morphology of the PAN fibers after ultrasonic etching. A mass of fibrils are obvious on the surface of the PAN fiber. It is found that PAN fibrils present two different kinds of morphologies, one with smooth surface and the other with periodic lamellae perpendicular to the fiber axis. Figure 1(b) shows the smooth surface fibrils with diameters of 70–200 nm. These fibrils appear in 70–90 wt.% DMSO. Because the DMSO concentration is low, solution etching effect is not obvious and the fine structure of fibrils is not appeared.

Figure 1(c) shows the microfibrils with periodic lamellae of 100–350 nm in diameter and a few millimeters in length. The thickness of the lamellae perpendicular to the fiber axis are 30–45 nm, and the length of the lamellae is about 100 nm, as shown in the magnified image of Figure 1(d). The lamellae structure appears in 90 wt.% DMSO. It results from loose amorphous region etched and compact crystalline region retained in ultrasonic etching process. It had a similar periodic structure to the drawn PAN which was previously reported [13]. However, there was lack of fine morphological characterization of this structure. The periodic lamellar structure supports the highly orientated acrylic fibers structural model proposed by Warner, et al. [14]. Further looking into Figure 1(d), the exfoliated fibrils with 500–600 nm in diameter were comprised by two microfibrils of 200–350 nm in diameter. The microfibrils combined with each other tightly. The fibrils and the protruding striations along the fiber axis on the surface of the PAN fiber by wet spinning are all at the same dimension. It is proved that nearly parallel grooves and striations in an axial direction are produced from fibril orientation on the PAN fiber surface.

Figure 1(e) shows some irregular fragmentary lamellae with thick outer edge and a few microfibrils among them. Fragmentary lamellae are derived from fibril breakup during ultrasonic etching process. Thus, the microfibrils which comprised numerous lamellae could be regarded as the smallest fibrillar elements in the PAN fiber.

Figure 1(f) is the image of the PAN microspheres which precipitated out from the PAN/DMSO/H_2O solution by ultrasonication in 95% DMSO via natural drying. The irregular microspheroidal precipitation of 300–600 nm in diameter appears. This implies that the lamellae made up of fibril are not formed by reprecipitation.

3.2 Fine microstructure of PAN fibrils

Figures 2(a) and 2(b) are the HRTEM images of the fibril

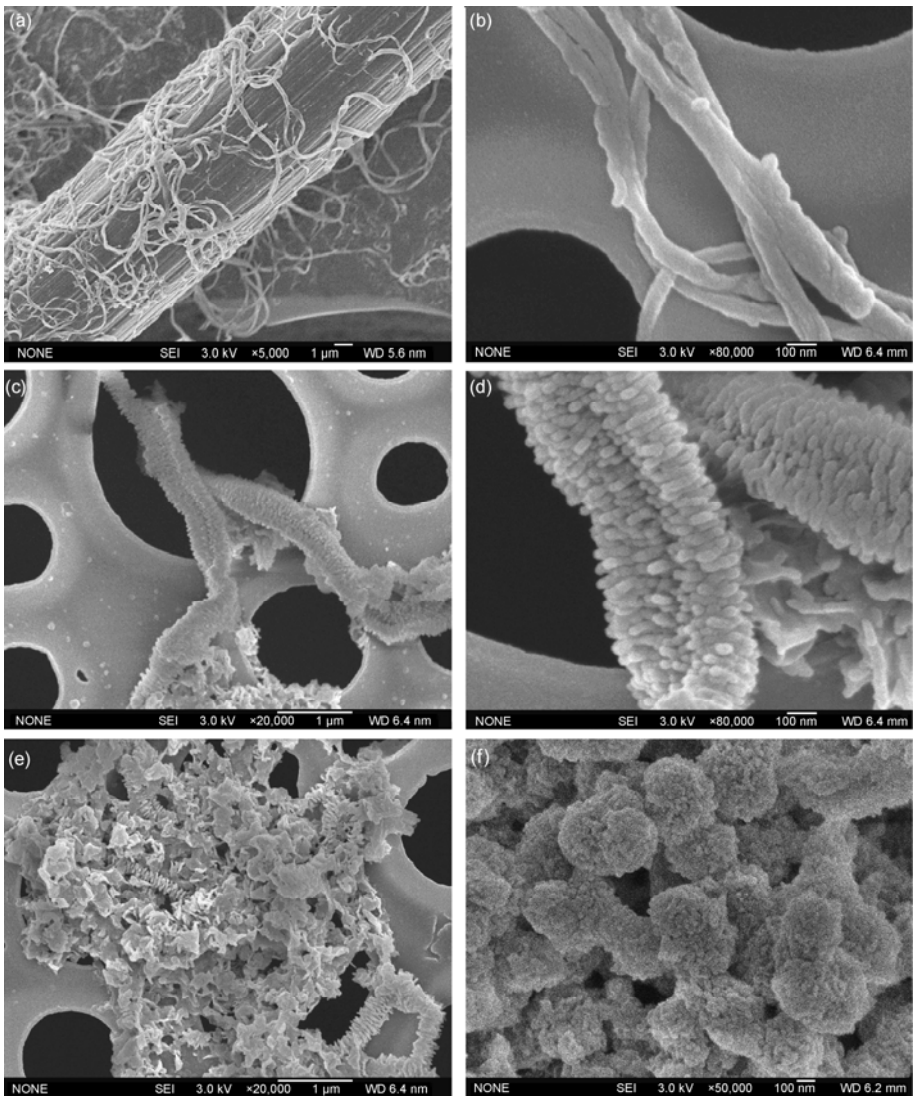

Figure 1 Morphology of PAN fibers ultrasonic etched. (a) Surface morphology of PAN fibers ultrasonic etched; (b) morphology of fibrils with smooth surface; (c) morphology of fibrils with lamellae; (d) high magnification image of fibrils with lamellae; (e) morphology of fragment lamellae and microfibrils; (f) morphology of PAN microspheres.

with smooth surface which is also composed of numerous microfibrils, as shown in Figure 2(a). Alternate dark and bright contrast of lamellar structure with thickness of 10 nm is found in smooth fibrils (arrow), which is enlarged as shown in Figure 2(b). It is found that image contrast is caused by the local density and the local specimen thickness, i.e. mass-thickness contrast. There are periodic density fluctuations in smooth fibrils. It is thought that the region of high density is crystalline phase, and the region of low density is amorphous phase, which supports the two-phase structure of the PAN fiber.

Figure 2(c) is the HRTEM image of the PAN microfibrils with lamellae and some fragmentary lamellae. The morphology of microfibril looks like kebab-shish structure. The kebab-like lamella without shish axis was observed in the PAN microfibrils. Under the present experimental conditions, there is no direct evidence that the PAN microfibril is the kebab-shish structure. The periodic crystal lamella (the kebab structure) perpendicular to the flow direction without the extended chain structure (shish) was also found in i-PP by Somani [15]. The image contrast of microfibril in Figure 2(d) is also caused by periodic density fluctuations.

3.3 Effect of ultrasonic time on the morphology of PAN fiber

Figure 3 is the images of the PAN fiber morphologies treated by ultrasonic etching after 2, 4, 6, 8 and 10 h, respectively. Figure 3(a) shows the clean surface of the PAN fiber without impurity after 2 h. Then ultrasonic etching has a cleaning influence on fiber. The fibrils are exfoliated from fiber surface which becomes rough 4 h later in Figure 3(b). The amorphous regions among fibrils are dissolved and etched after 4 h. The lamellae perpendicular to the fiber axis

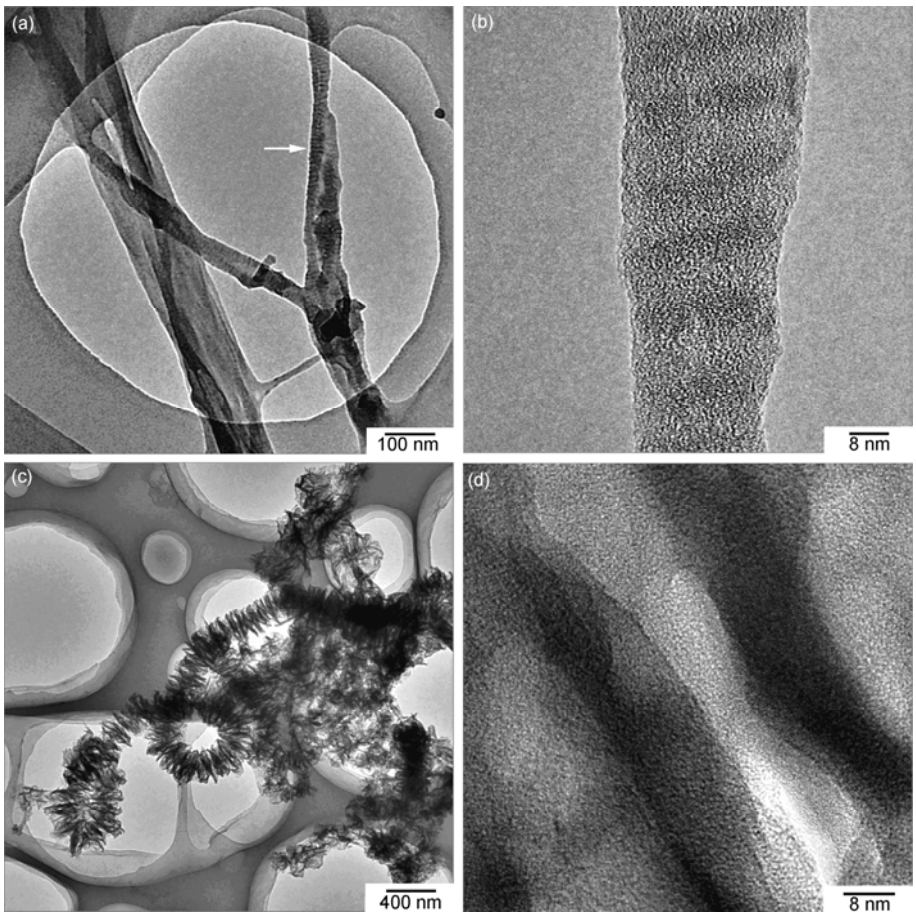

Figure 2 The HRTEM images of microfibrils. (a) The HRTEM image of the smooth surface microfibrils; (b) high magnification image of the smooth surface microfibril; (c) the HRTEM image of the PAN microfibrils with lamellae and fragmentary lamellae; (d) high magnification image of the PAN microfibrils.

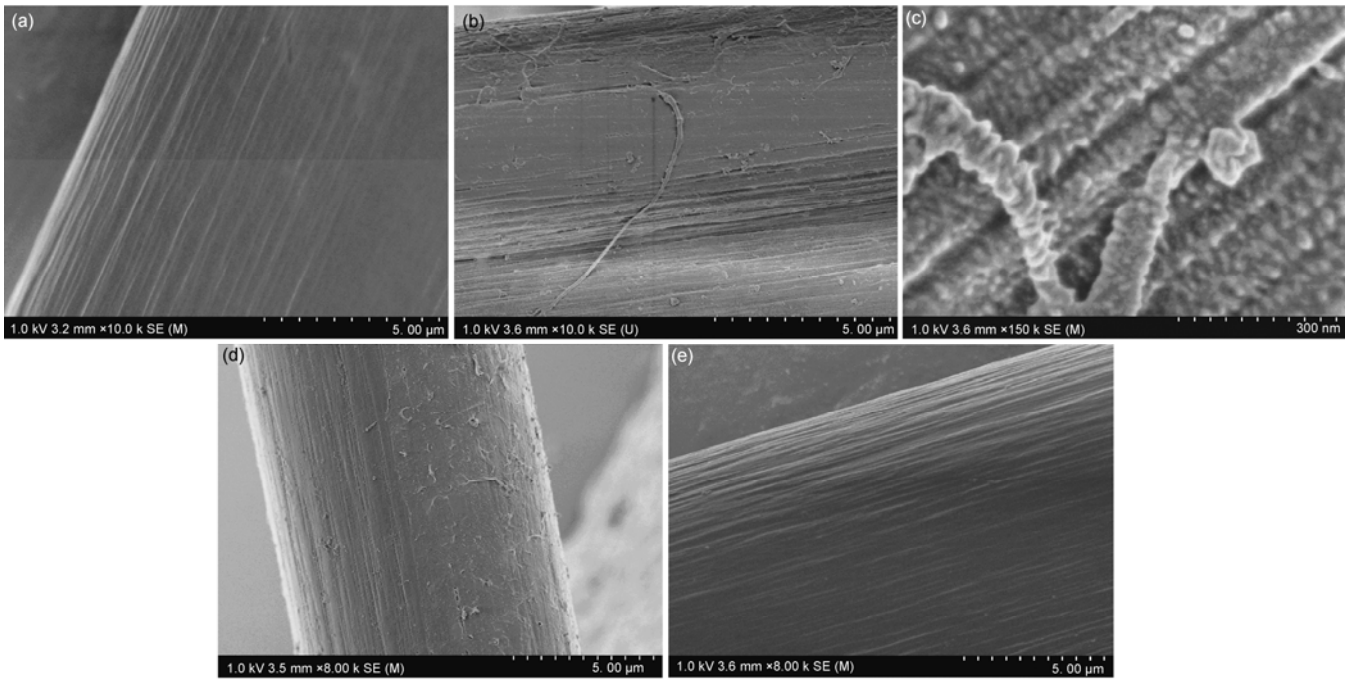

Figure 3 Surface morphology of PAN fibers ultrasonic processed with different time. (a) 2 h; (b) 4 h; (c) 6 h; (d) 8 h; (e) 10 h.

appear after 6 h. Then the amorphous regions between the lamellae in microfibril are etched and the solution etching plays an important part. The fibrils are reduced and dissolved in fiber surface after 8 h, which implies that excessive etching has happened. But the fiber surface is clean again after 10 h, which means that the surface layer has been dissolved completely. It suggests that the PAN fiber is etched and dissolved layer by layer during ultrasonic etching process and each layer goes through ultrasonic cleaning, selective etching, excessive etching and dissolution.

3.4 Formation of lamellae in microfibrils of PAN fiber

Figure 4(a) shows the morphology of fibrils of nascent fiber. There are periodic lamellae in fibrils of nascent fiber. This means that the fibrils with lamellae are formed by orientation and crystallization in shearing field of spinning pipe and drawing stress field of coagulation bath. The schematics in Figure 5 depict the formation of lamellae in spinning initial process. Figure 5(a) schematically illustrates the random distribution of the PAN molecules in spinning solution before spinning. When spinning solution flows in pipe, the PAN molecule chain segments orient along the flow direction in shearing field. When the filaments flow through the spinneret with drawing stress, a bundle of the aligned chain segments of molecules orient further and then primary nuclei are formed, as shown in Figure 5(b). The nuclei are not isolated, and some molecules go through nuclei. Oriented folded chain lamellae grow outward in the perpendicular direction to the microfibril axis in Figure 5(c). Then the lamellae of fibril are formed.

Compared with fibrils of final fiber, as shown in Figure 4(b), the diameters of fibrils of nascent fiber are nonuniform, about 70–200 nm, and the boundaries of fibrils are ambiguous resulting from low drawing ratio. With increasing drawing ratio, the boundaries of fibrils become clear. Under collapsing at high temperature, lamellae grow rapidly outward and diameter increases. Then the uniform and compact fibrils are obtained.

4 Conclusion

Two fibrils with different morphologies are successfully obtained by ultrasonic etching, one with smooth surface and the other with periodic lamellae. The fibrils with smooth surface are obtained in the 70–90 wt.% DMSO. The fibrils with lamellae are separated in the 90 wt.% DMSO. The lamellae with thickness of 30–45 nm and length of about 100 nm are perpendicular to the fiber axis. The fibers were dissolved in more than 95 wt.% DMSO. Inner periodical structures of fibrils are observed in HRTEM. It indicates that there are different densities and two phases in fibrils. The fiber is etched and dissolved layer by layer during

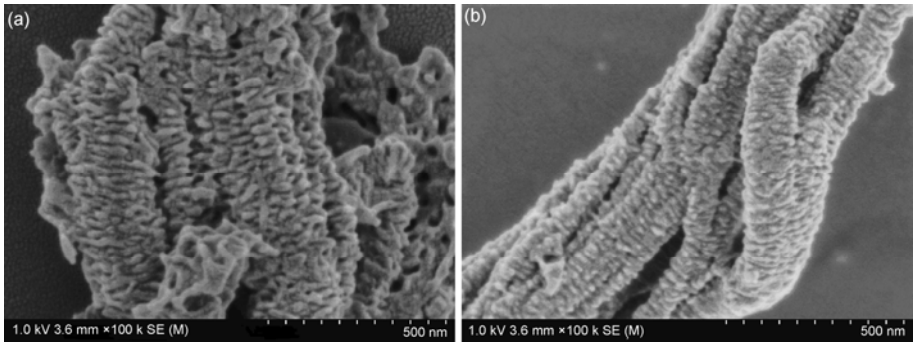

Figure 4 Morphology of fibrils of nascent fiber and final fiber. (a) Fibrils of nascent fiber; (b) fibrils of final fiber.

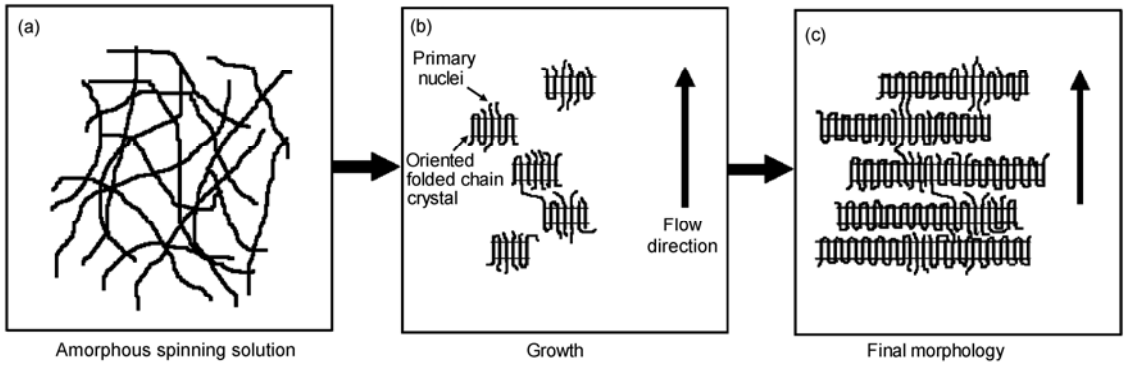

Figure 5 Schematics of formation of lamellar structure in microfibril. (a) Random distribution of PAN molecules; (b) primary nuclei; (c) lamellae

ultrasonic etching process and each layer goes through ultrasonic cleaning, selective etching, excessive etching and dissolution. There are numerous periodic lamellae in fibrils of nascent fibers. This means that the fibrils with lamellae are formed by orientation and crystallization in shearing field of spinning pipe and drawing stress field of coagulation bath.

This work was supported by the National Natural Science Foundation of China (Grant No. 50673052)，the Major State Basic Research Development Program of China (973 Program) (Grant No. 2006CB605314), and the Provincial Natural Science Foundation of Shandong Province (Grant No. Z2008F02).

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