

College of Engineering



Drexel E-Repository and Archive (iDEA)

<http://idea.library.drexel.edu/>

Drexel University Libraries

www.library.drexel.edu

The following item is made available as a courtesy to scholars by the author(s) and Drexel University Library and may contain materials and content, including computer code and tags, artwork, text, graphics, images, and illustrations (Material) which may be protected by copyright law. Unless otherwise noted, the Material is made available for non profit and educational purposes, such as research, teaching and private study. For these limited purposes, you may reproduce (print, download or make copies) the Material without prior permission. All copies must include any copyright notice originally included with the Material. **You must seek permission from the authors or copyright owners for all uses that are not allowed by fair use and other provisions of the U.S. Copyright Law.** The responsibility for making an independent legal assessment and securing any necessary permission rests with persons desiring to reproduce or use the Material.

Please direct questions to archives@drexel.edu

Sundar Babu · Patrick Ndungu · Jean-Claude Bradley
Maria Pia Rossi · Yury Gogotsi

Guiding water into carbon nanopipes with the aid of bipolar electrochemistry

Received: 23 November 2004 / Accepted: 1 February 2005 / Published online: 10 May 2005
© Springer-Verlag 2005

Abstract The targeted bipolar electrodeposition of polypyrrole was carried out onto the tips of hydrophilic carbon nanopipes. By aligning an external electric field relative to the nanopipes, the deposition of polypyrrole onto selected ends could be achieved without physically contacting the nanopipes. After deposition, carbon nanopipes with both partially open and fully blocked tips were found. Experiments conducted in an environmental scanning electron microscope showed that water enters the nanopipes through the tip with polypyrrole due to the higher hydrophilicity of the polymer compared to the tube walls. As a result, it was possible to guide the entry of water from a specific end of the tube and fill the tube from the selected side. Condensation experiments conducted on nanopipes with polypyrrole on both tips shows the difference in hydrophilicity of the nanopipes compared to the polypyrrole. The ability to selectively control the site of condensation and uptake of fluid by carbon nanotubes or nanopipes is very important for the development of nanotube-based nanofluidic devices.

Keywords Bipolar electrodeposition · Nanofluidics · Nanopipe · Polypyrrole · Water

1 Introduction

Carbon nanotubes (CNTs) can be used as a means to study the behavior of fluids in areas confined to the nanometer scale (Waghe et al. 2002; Werder et al. 2003;

Supple and Quirke 2003; Kalra et al. 2003; Gogotsi et al. 2002; Gogotsi et al. 2001), which renders them ideal for use as nanopipes to transport liquids in nanofluidic devices. Carbon nanotubes can be used in nanofluidic devices to deliver pico (10^{-12}), femto (10^{-15}), and even attoliter (10^{-18}) volumes of liquid to specific locations for applications such as probing cells or delivering drugs and proteins inside cells with minimal intrusion and damage. Therefore, it is important to study the intake of liquids by nanotubes and their transport through the tubes.

Because the diameter of CNTs is smaller than any other fluid delivery conduit available to date, it is possible that the behavior of liquids may differ from that which has been observed at the macroscale and even the microscale. It is probable, for example, that viscosity and capillary forces will play a more significant role in fluid flow through nanochannels than in microchannels. Capillary filling of nanotubes with water depends on the ability of water to spread along or wet the walls of the nanotube, as the surface tension of water does not differ significantly even at the nanoscale (Sobolev et al. 2000). Molecular dynamics simulations and some experimental results suggest that CNTs should be hydrophobic (Werder et al. 2001; Walther et al. 2001; Rossi and Gogotsi 2004). However, recent findings show that CNTs produced by hydrothermal synthesis (Gogotsi et al. 2002) and by chemical vapor deposition (Rossi et al. 2004) are hydrophilic.

It was demonstrated recently that water can enter and flow through open-ended CVD carbon nanotubes at low pressure inside the chamber of an environmental scanning electron microscope (ESEM) (Rossi et al. 2004) and at ambient pressure under optical microscope (Kim et al. 2004). These nanotubes are very straight, and they act like pipes to transport of water from one end to another. By using a cooling stage, to maintain a constant temperature and changing the vapor pressure within the ESEM chamber, it was possible to condense water inside the nanopipes before condensation started on the more hydrophobic steel sample holder.

S. Babu · P. Ndungu · J.-C. Bradley (✉)
Department of Chemistry, Drexel University, Philadelphia,
PA 19104, USA
E-mail: bradlejc@drexel.edu
Tel.: +1-215-8952647
Fax: +1-215-895-1265

M. P. Rossi · Y. Gogotsi
Department of Materials Science and Engineering and A.J. Drexel
Nanotechnology Institute, Drexel University, Philadelphia,
PA 19104, USA

The studies on the interaction of water with these nanopipes in the ESEM chamber revealed that the contact angle of water with the walls of the nanopipes was below 20° , which shows the hydrophilic nature of the tube walls and demonstrates that these tubes can be used for fabricating nanofluidic devices that involve transport of aqueous fluids. However, it is crucial to be able to control the flow of liquids in a specific direction inside the tubes. The objective of this work was to deposit polypyrrole (PPY) on the ends of carbon nanopipes in order to guide water through them due to the higher hydrophilicity of the polymer in comparison to carbon.

2 Carbon nanotubes

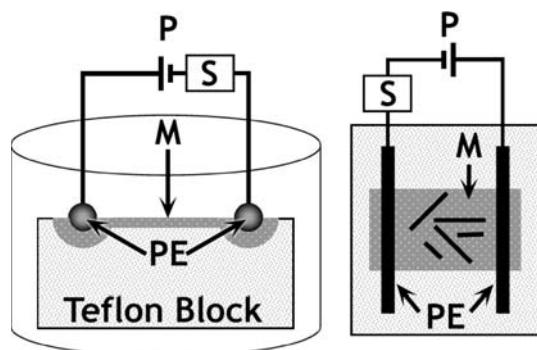
The carbon nanopipes used in these experiments were synthesized by template-assisted chemical vapor deposition of carbon in nanoporous alumina membranes (Miller et al. 2001). Freestanding carbon nanopipes about 250 ± 25 nm in diameter and 5–60 μm in length were obtained by the pyrolysis of ethylene (30% ethylene, 70% helium) at 670°C for 6 h in the pores of an alumina membrane. After the deposition, the membrane was removed by sonicating in 1 M NaOH for 90 min.

3 Bipolar electrodeposition

Polypyrrole has been electrodeposited on CNTs (Gao et al. 2003) for biosensor applications already and its hydrophilic properties (Hwang et al. 2003; Tessier et al. 2000) arise from the presence of the positively charged nitrogen and the dopant material added to increase the conductivity. Though PPY can be deposited by con-

ventional electrodeposition, it is not possible to deposit it specifically on a tip of an isolated CNT without the aid of lithographic procedure. This problem was circumvented with the use of bipolar electrodeposition, as it relies primarily on the difference in conductivity between the materials, in this case the carbon nanopipes, and the electrolyte. In bipolar electrochemistry, an electric field creates a potential difference between the tips of a conductive substrate in line with the electric field. The maximal potential difference can be approximated by the product of the length of the substrate in line with the electric field and the field intensity (Fleischmann et al. 1985). This method does not require an ohmic contact between the material and the feeder electrodes, and the deposition site on the material is addressable. Bipolar electrodeposition has been used effectively for creating ohmic contacts between two isolated millimeter-sized metal particles (Bradley et al. 1999), for deposition of palladium nanoparticles on isolated graphite micro platelets (Bradley et al. 2001), and to grow silver wires from 400 nm diameter silver rings (Bradley et al. 2002).

The experimental design for depositing PPY on the tips of carbon nanopipes is depicted in Fig. 1. A suspension of carbon nanopipes in toluene (1 $\mu\text{g}/\text{ml}$) was filtered through a 200 nm polyester nuclear track-etch membrane obtained from Osmonics, Inc. A portion of the membrane was placed under two platinum wires separated by 5 mm. The electrolyte solution consisted of 0.35 mM sodium salt of *p*-toluene sulfonic acid and 0.70 M pyrrole dissolved in a mixture of 40% acetonitrile and 60% toluene. A pulsed unipolar electric field (pulse parameters: 1 ms on time and 24 ms off time) with an intensity of 10 kV/cm was generated between the two platinum wires for 5 s (total on time value). Pulsing was achieved by placing a high-speed electronic switch in series with the high voltage power supply. The tip of the nanopipe facing the cathode attains a positive charge and vice versa; since polymerization of pyrrole is an anodic reaction, it should be expected on only one tip of the nanopipe. Reversing the field direction after the first deposition resulted in depositing material on the other tip of the nanopipe. A detailed description of the experimental procedure for depositing PPY on one tip of a nanopipe can be found elsewhere (Bradley et al. 2003; Bradley et al. 2004).



PE - Platinum electrodes

P - Power supply

M - Nuclepore track etch membrane

S - High speed electronic switch

Fig. 1 Experimental setup for depositing polypyrrole on the tips of carbon nanopipes. (a) Cross-sectional view of the cell, (b) top view of the cell

4 Microscopy

An FEI XL30 ESEM with a Peltier cooling stage and a gaseous secondary electron detector (GSED) were used to investigate water condensation on the carbon nanopipes with and without polypyrrole. These experiments were similar to those performed in the ESEM chamber using single nanotubes (Rossi et al. 2004). In this case; the membrane with PPY-deposited carbon nanopipes was mounted on the stainless steel sample holder and placed on the cooling stage. The ESEM chamber was first evacuated to a low pressure in order to remove any

moisture that remained on the nanopipes. Experiments began when the pressure was increased to about 5 Torr while the temperature was maintained at 4–5°C. The pressure was increased at an approximate rate of 0.1 Torr for every 15 s, while the temperature was kept constant in order to induce condensation of water within the chamber.

5 ESEM analysis

Figure 2a, c show the presence of PPY on only one tip of the nanopipe as a result of the bipolar deposition process and demonstrate our ability to address a specific tip of a

nanopipe. Figure 2b shows a tube with PPY on both tips; this was obtained by reversing the direction of the electric field after the first deposition. The deposits in Fig. 2a, c were obtained after a period of 5 and 10 s, respectively. The tip of the nanopipe in Fig. 2a was partially open, while the tip of the nanopipe in Fig. 2c was fully blocked. Thus, bipolar electrodeposition makes it possible to block the tips of the nanopipes either fully or partially by controlling the deposition time.

The SEM images in Fig. 3 were taken during various stages of filling a carbon nanopipe. The pressure inside the ESEM chamber was maintained at 5.2 Torr (Fig. 3a); the deposited PPY can be seen as a bright, thick line extending from the upper tip of the nanopipe.

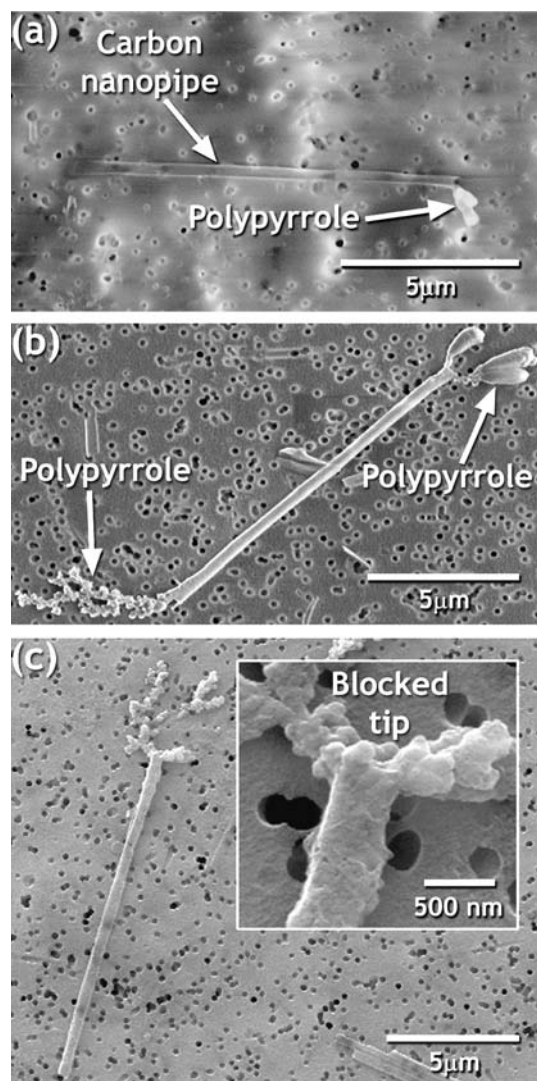


Fig. 2 Environmental scanning electron microscope micrographs of carbon nanopipes with polypyrrole deposited by bipolar electrochemistry. (a) Polypyrrole deposited for 5 s (total on time) on one tip of a carbon nanopipe. (b) Polypyrrole deposited on both tips of a carbon nanopipe by reversing the direction of the electric field after depositing polypyrrole on the first tip. (c) A nanopipe with polypyrrole deposited for 10 s. The end of the nanopipe is fully closed

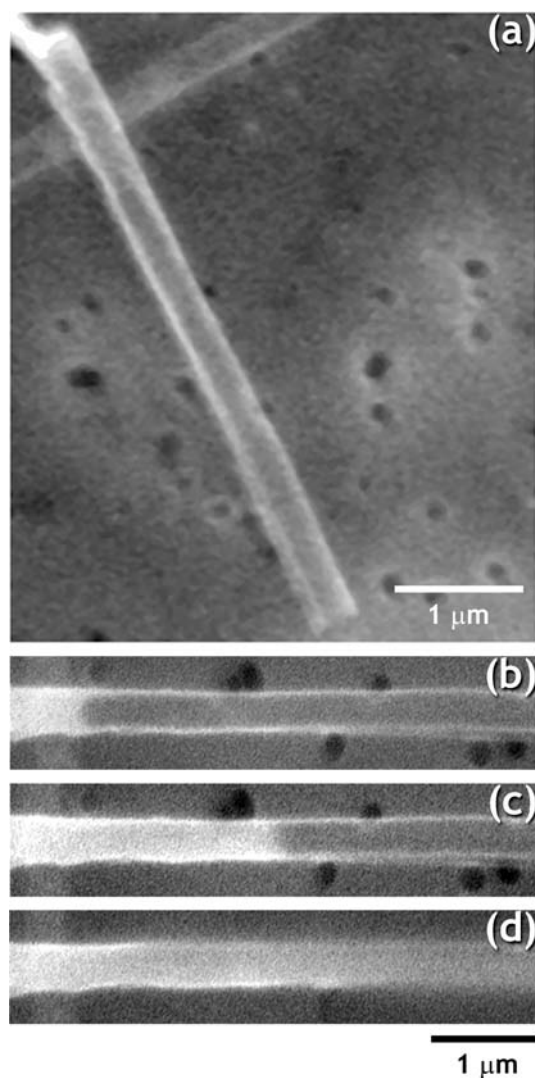
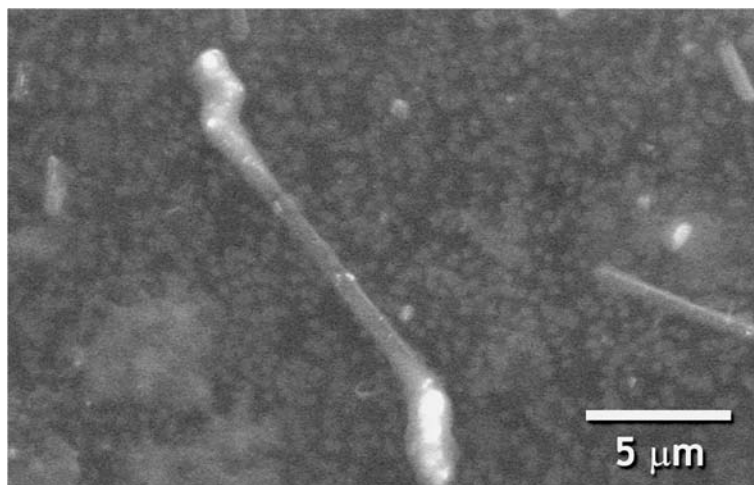


Fig. 3 Environmental scanning electron microscope images demonstrating the changes in water level inside a nanopipe with respect to the increase in humidity inside the chamber. (a) An isolated carbon nanopipe with polypyrrole on one tip when the pressure inside the chamber was 5.2 Torr. (b, c) The water level increased when the pressure inside the chamber was increased to 5.7 and 5.8 Torr, respectively. (d) water filled the nanopipe when the pressure was increased to 5.9 Torr

Fig. 4 Environmental scanning electron microscope images of water condensation on carbon nanopipes with polypyrrole on both tips. Condensation of water occurs preferentially on polypyrrole, which has been deposited at the ends of an isolated carbon nanopipe; at 5.8 Torr, the condensed water is just enough to form a thin layer, entirely covering the deposited polypyrrole



The water condensing outside the nanopipe is expected to flow inside the tube through the small opening left after the deposition of PPY. The nanopipe was empty, as the relative humidity inside the chamber was insufficient for condensation. Condensation of water began when the pressure was increased to 5.7 Torr, and can be observed in Fig. 3b, c by the presence of a meniscus. Increasing the pressure to 5.9 Torr resulted in accumulation of water inside the nanopipe. Excess water covered the substrate surface when the pressure was increased (Fig. 3d).

The presence of PPY appears to have the expected effect on the condensation process, and nucleation of water occurred preferentially on the PPY. The increase in the brightness of PPY at 4.9 Torr suggests the onset of condensation. An image in an ESEM is produced by gas cascade amplification, which relies on the presence of ionizable gases inside the chamber (Thiel et al. 1997), which in this case are the water molecules. When the chamber is saturated with water vapor, the relative abundance of ionizable water molecules closer to or on the substrate will be greater, resulting in an increase in brightness.

The image of a nanopipe with water condensed on PPY attached to both ends of the pipe is shown in Fig. 4. This experiment was designed to observe the behavior of water while it condenses simultaneously on both tips. The condensation of water on PPY deposited on both tips of the nanopipe confirms the difference in wetting of the nanopipes and the PPY. Results from the previous case show that the water level inside the tube depends on the pressure inside the chamber. In this case, water should not flow inside the nanopipes since PPY is expected to block the tips. The nanopipe in Fig. 4 has PPY on both tips fully covered by a thin layer of water. Furthermore, the nanopipe appears to be empty even at 5.8 Torr, confirming that the polypyrrole deposit is blocking the ends. The absence of water along the outer walls of the nanopipe demonstrates the difference in hydrophilicity between the PPY, substrate and the nanopipe. It is important to note that CVD nanopipes

are hydrophilic, with measured contact angles of about 20° or less. The condensation of water only where PPY is deposited despite the presence of another hydrophilic entity confirms the preferential condensation of water on the PPY, which in turn depicts its ability to direct water into the nanopipe from a specific end.

If nanopipes are in physical contact with each other, the aggregate will respond to the electric field as a single conductive object. This may lead to higher induced potentials, depending on the geometry and alignment with respect to the applied field. The effect of the alignment of the nanotubes with respect to the electric field can be seen in the Fig. 4. In addition, proximity between nanopipes can result in field amplification (Keh and Li 1994; Bradley et al. 1999). These factors need to be taken into account when designing applications involving bipolar electrochemistry.

6 Summary and conclusions

In summary, we used a targeted deposition method, to deposit PPY on specific ends of isolated carbon nanopipes. The water uptake point of a particular nanopipe was predetermined by the presence of PPY. The presence of excessive amounts of PPY at the tip allowed blocking of the tip entirely. Furthermore, it was possible to visualize and compare the difference in the hydrophilic nature of carbon nanopipes and PPY, as the condensed water was found to accumulate on the deposited PPY. The water level inside the nanopipe can be controlled dynamically by changing the pressure inside the ESEM chamber. The ability to target a specific location for electrodeposition of conducting polymers on nanotubes can find applications in many fields, ranging from sensors to nanofluidic devices.

Acknowledgements This work was supported by the National Science Foundation under NIRT Grant Number CTS-0235234 and NSF CAREER award CHE-9875855. Purchase of the ESEM was supported by NSF Grant Number BES-0216343.

References

- Bradley J, Ma Z, Christoffer S, Crawford J, Ernazarova K, Stephens SG (1999) The construction of circuitry using spatially coupled bipolar electrochemistry. *ACS Symp Ser* 735:429–439
- Bradley JC, Dengra S, Gonzalez GA, Marshall G, Molina FV (1999) Ion transport and deposit growth in spatially coupled bipolar electrochemistry. *J Electroanal Chem* 478:128–139
- Bradley J, Babu S, Mittal A, Ndungu P, Carroll B, Samuel B (2001) Pulsed bipolar electrodeposition of palladium onto graphite powder. *J Electrochem Soc* 148:C647–C651
- Bradley J, Babu S, Carroll B, Mittal A (2002) A study of spatially coupled bipolar electrochemistry on the sub-micrometer scale: colloidal particles on surfaces and cylinders in nuclear-track etched membranes. *J Electroanal Chem* 522:75–85
- Bradley J, Ndungu P, Babu S, Tromp J, Hackett N (2003) Bipolar electrodeposition of polypyrrole onto carbon nanotubes 1. Chemistry Preprint Server, Miscellaneous 1–4, CPS: chemistry/0308001
- Bradley J-C, Babu S, Ndungu P (2004) Site selective electrodeposition of metals and conductive polymer nano-structures on isolated carbon nanotubes using electric fields. *Mat Res Soc Symp Proc* 818: 361–369
- Fleischmann M, Ghoroghchian J, Pons S (1985) Electrochemical behavior of dispersions of spherical ultramicroelectrodes. 1. Theoretical considerations. *J Phys Chem* 89:5530–5536
- Gao M, Dai L, Wallace GG (2003) Biosensors based on aligned carbon nanotubes coated with inherently conducting polymers. *Electroanalysis* 15:1089–1094
- Gogotsi Y, Libera JA, Guvenc-Yazicioglu A, Megaridis CM (2001) In situ multiphase fluid experiments in hydrothermal carbon nanotubes. *Appl Phys Lett* 79:1021–1023
- Gogotsi Y, Naguib N, Libera JA (2002) In situ chemical experiments in carbon nanotubes. *Chem Phys Lett* 365:354–360
- Hwang HR, Roh JG, Lee DD, Lim JO, Huh JS (2003) Sensing behavior of the polypyrrole and polyaniline sensor for several volatile organic compounds. *Met Mater Int* 9:287–291
- Kalra A, Garde S, Hummer G (2003) Osmotic water transport through carbon nanotube membranes. *Proc Natl Acad Sci USA* 100:10175–10180
- Keh HJ, Li WJ (1994) Interactions among bipolar spheres in an electrolytic cell. *J Electrochem Soc* 141:3103–3114
- Kim BM, Sinha S, Bau HH (2004) Optical microscope study of liquid transport in carbon nanotubes. *Nano Lett* 4:2203–2208
- Miller SA, Young VY, Martin CR (2001) Electroosmotic flow in template-prepared carbon nanotube membranes. *J Am Chem Soc* 123:12335–12342
- Rossi M, Gogotsi Y (2004) Environmental SEM studies of nano-fiber-liquid interactions. *Microsc Anal (The Americas Edition)* 18:9
- Rossi MP, Ye H, Gogotsi Y, Babu S, Ndungu P, Bradley J (2004) Environmental scanning electron microscopy study of water in carbon nanotubes. *Nano Lett* 4:989–993
- Sobolev VD, Churaev NV, Velarde MG, Zorin ZM (2000) Surface Tension and Dynamic Contact Angle of Water in Thin Quartz Capillaries. *J Colloid Interface Sci* 222:51–54
- Supple S, Quirke N (2003) Rapid imbibition of fluids in carbon nanotubes. *Phys Rev Lett* 90:214501/1–214501/4
- Tessier D, Dao LH, Zhang Z, King MW, Guidoin R (2000) Polymerization and surface analysis of electrically-conductive polypyrrole on surface-activated polyester fabrics for biomedical applications. *J Biomat Sci Polym E* 11:87–99
- Thiel BL, Bache IC, Fletcher AL, Meredith P, Donald AM (1997) An improved model for gaseous amplification in the environmental SEM. *J Microsc Oxford* 187:143–157
- Waghe A, Rasaiah JC, Hummer G (2002) Filling and emptying kinetics of carbon nanotubes in water. *J Chem Phys* 117:10789–10795
- Walther JH, Jaffe R, Halicioglu T, Koumoutsakos P (2001) Carbon nanotubes in water: structural characteristics and energetics. *J Phys Chem B* 105:9980–9987
- Werder T, Walther JH, Jaffe RL, Halicioglu T, Noca F, Koumoutsakos P (2001) Molecular dynamics simulation of contact angles of water droplets in carbon nanotubes. *Nano Lett* 1:697–702
- Werder T, Walther JH, Jaffe RL, Halicioglu T, Koumoutsakos P (2003) On the water-carbon interaction for use in molecular dynamics simulations of graphite and carbon nanotubes. *J Phys Chem B* 107:1345–1352