

NANO EXPRESS

Open Access

Ag nanoparticles/PPV composite nanofibers with high and sensitive opto-electronic response

Jinfeng Chen¹, Peipei Yang¹, Chunjiao Wang², Sumei Zhan¹, Lianji Zhang¹, Zonghao Huang^{1*}, Wenwen Li¹, Cheng Wang^{1,3}, Zijiang Jiang¹, Chen Shao¹

Abstract

The novel Ag nanoparticles/poly(*p*-phenylene vinylene) [PPV] composite nanofibers were prepared by electrospinning. The transmission electron microscope image shows that the average diameter of composite fibers is about 500 nm and Ag nanoparticles are uniformly dispersed in the PPV matrix with an average diameter of about 25 nm. The Fourier transform infrared spectra suggest that there could be a coordination effect to a certain extent between the Ag atom and the π system of PPV, which is significantly favorable for the dissociation of photoexcitons and the charge transfer at the interface between the Ag nanoparticle and the PPV. The Au top electrode device of the single Ag/PPV composite nanofiber exhibits high and sensitive opto-electronic responses. Under light illumination of 5.76 mW/cm² and voltage of 20 V, the photocurrent is over three times larger than the dark current under same voltage, which indicates that this kind of composite fiber is an excellent opto-electronic nanomaterial.

Introduction

Recently, 1D opto-electronic nanomaterials, especially the 1D organic opto-electronic nanomaterials, have received much attention of scientists because of their distinctive geometries, novel opto-electronic properties, and the potential application in nano/micro devices [1-5].

Electrospinning is an efficient technique for the fabrication of 1D polymer-based nanomaterials. Up to now, a lot of polymers and polymer-based composite materials have been fabricated by electrospinning [5-7]. Poly (*p*-phenylene vinylene) [PPV] is a typical conjugated polymer which has good photoluminescent [PL] and electroluminescent properties as well as photovoltaic and nonlinear optical properties [8-10]. Our research group has successfully fabricated the PPV nanofibers and the PPV-based composite nanofibers by electrospinning, such as TiO₂/PPV and CdSe/PPV nanofibers, etc., which showed novel opto-electronic properties [11,12].

Metal nanomaterials exhibit many novel physical and chemical characteristics which arise from their quantum confinement effects and their enormously large specific surface areas. Therefore, metal nanomaterials

are used as a kind of block to build advanced functional materials or to improve the efficiency of devices in many researches. Lee et al. [13] reported that the incorporation of gold nanodots on the indium tin oxide surface can obviously increase the power conversion efficiency of poly(3-hexylthiophene)/[6][6]-phenyl C61-butyric acid methyl ester solar cell. Nah et al. [14] reported that the electrochromic absorption was markedly enhanced in Ag nanoparticles embedded in MEH-PPV composite films. The opto-electronic response of the pristine PPV film device is relative low [10], which makes the investigation of the opto-electronic character of a single PPV nanofiber difficult. We expect that incorporating Ag nano-particles in PPV nanofibers can prepare a novel composite nanofiber with a high opto-electronic response.

In this paper, Ag nanoparticles/PPV composite nanofibers were successfully prepared by electrospinning. Then, the Au top electrode device of a single composite nanofiber was fabricated on a SiO₂ substrate by an 'organic ribbon mask' technique, which showed high and sensitive opto-electronic response.

* Correspondence: huangzh295@nenu.edu.cn

¹Faculty of Chemistry, Northeast Normal University, Changchun, 130024, People's Republic of China

Full list of author information is available at the end of the article

Experimental

Preparation of Ag nanoparticles and Ag/PPV composite nanofibers

Sodium borohydride (NaBH_4) was purchased from Sino-pharm Chemical Reagent Co., Ltd. (Shanghai, China), while ethanol and silver sulfate (Ag_2SO_4) were from Beijing Beihua Fine Chemicals Co., Ltd. (Beijing, China). All reagents were of analytical grade and used without further purification.

The synthesis route of PPV is presented in Figure 1, and the PPV precursor ethanol solution (0.4 wt.%) was prepared according to [15]. Ag nanoparticles were prepared by the reduction of silver ions in Ag_2SO_4 with NaBH_4 .

The synthesis process of Ag nanoparticles/PPV composite nanofibers is as follows: Firstly Ag_2SO_4 (0.21 g, 0.67 mmol) was dissolved in 100 ml distilled water to get a clear solution, and then NaBH_4 (1.40 g, 0.037 mol) was added into the solution with vigorous stirring under N_2 -saturated atmosphere. After filtering, drying, and triturating, we obtained Ag nanoparticles. Then, 3 mg of Ag nanoparticles was added into 0.4 wt.% PPV precursor ethanol solution (2.63 g) with stirring at room temperature for 24 h to obtain a new solution. Then, the solution was electrospun at room temperature, with positive voltage of 15 kV, humidity of 45%, and tip-to-collector distance of 20 cm. Finally, the electrospun fibers were heated at 180°C for 4 h in a vacuum oven for conversion of the PPV precursor to PPV.

The pristine PPV nanofibers were also prepared in a similar procedure as described above.

Characterization

The small-angle X-ray diffraction [SAXRD] measurements were performed on a small-angle X-ray diffractometer

(PX13-010, Japan). Fourier transform infrared [FTIR] measurements were carried out on a Fourier transform infrared spectrometer (Magana 560, Nicolet Corp., Madison, WI, USA). The photoluminescence excitation [PLE] and PL measurements were made on an Eclipse Fluorescence Spectrophotometer (Varian Corp., Palo Alto, CA, USA). The morphology of nanofibers was observed using a transmission electron microscope [TEM] (FP 5021/20, Czech Republic). A scanning electron microscope [SEM] (ESEM XL-30, FEI Company, Hillsboro, OR, USA) was used to reveal the structure of the Au top electrode device of a single Ag/PPV composite nanofiber. The opto-electronic response of this device was measured with a Keithley 4200 SCS and a Micromanipulator 6150 probe station in a clean and shielded box.

Results and discussion

SAXRD patterns

The SAXRD patterns of Ag nanoparticles, Ag/PPV composite nanofibers, and pure PPV nanofibers are shown in Figure 2, using $\text{CuK}\alpha$ radiation ($\lambda = 0.154060$ nm). The same diffraction peaks at 38.13° , 44.23° , 64.48° , and 77.33° in the SAXRD patterns of Ag particles and Ag/PPV composite fibers can verify the generation of highly crystalline Ag nanoparticles with the face-centered cubic crystal structure (JCPDS card no. 04-0783).

TEM image

The TEM image of an Ag/PPV composite fiber (Figure 3) shows that the fiber diameter was about 500 nm and the average diameter of Ag nanoparticles was about 25 nm. During electrospinning, the Coulomb repulsion among charged Ag nanoparticles should be the main factor making the Ag nanoparticles uniformly dispersed.

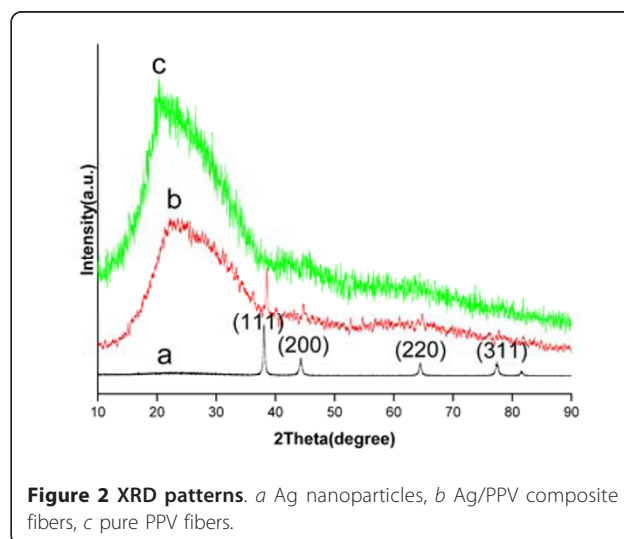
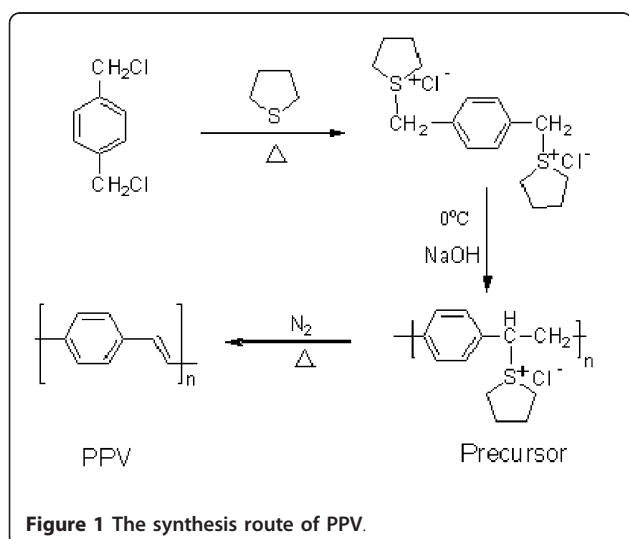


Figure 2 XRD patterns. a Ag nanoparticles, b Ag/PPV composite fibers, c pure PPV fibers.

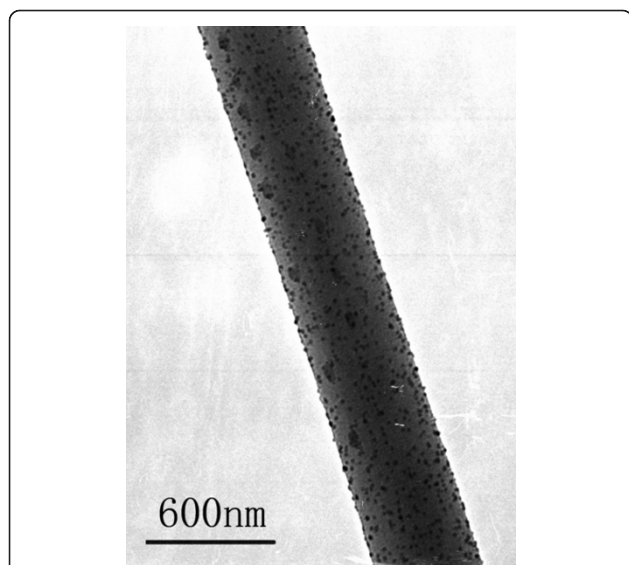


Figure 3 TEM image of an Ag/PPV composite nanofiber.

FTIR spectra

From the FTIR spectra of pristine PPV fibers and composite fibers (Figure 4), we can conclude that both pristine PPV fibers and composite fibers have the three similar characteristic absorption peaks at $1,646\text{ cm}^{-1}$ (C = C bond stretching mode), $1,515\text{ cm}^{-1}$ (C-C ring stretching mode), and 962 cm^{-1} (*trans*-vinylene C-H out-of-plane bending mode), which implies that the conjugation structure of PPV is basically kept in composite fibers. However, the characteristic absorption peak of the pristine PPV fibers at 831 cm^{-1} (*p*-phenylene C-H out-of-plane bending mode) was obviously broadened in the spectrum of composite fibers. This phenomenon could be explained by the coordination effect to a

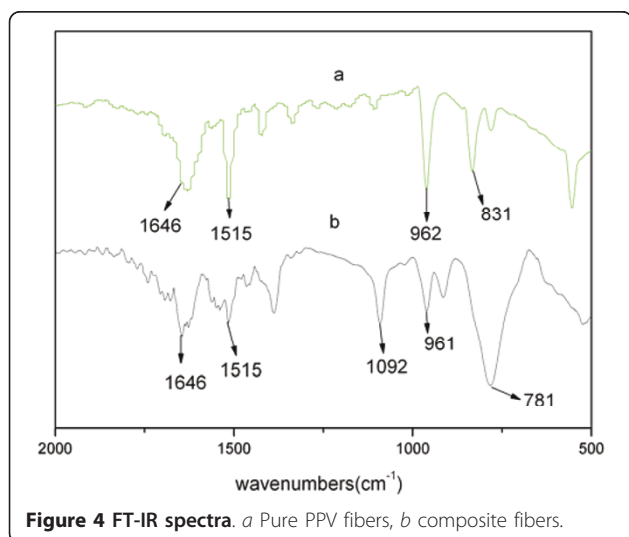


Figure 4 FT-IR spectra. *a* Pure PPV fibers, *b* composite fibers.

certain extent between the 5S orbital of the Ag atom, locating over the conjugation plane of PPV, and the π system of PPV (especially the π system of the benzene ring part). Therefore, the SP^3 hybrid orbital component could be partly introduced into the C-H bond (SP^2 hybrid orbital) of the benzene ring. The occurrence of the coordination effect should be significantly favorable for the charge separation of photoexcitons and the charge transfer at the interface between Ag nanoparticles and PPV so as to obviously improve the optoelectronic response of the composite materials.

PL spectra

Figure 5 shows the PL ($\lambda_{\text{ex}} = 350\text{ nm}$) and PLE ($\lambda_{\text{em}} = 550\text{ nm}$) spectra of the pristine PPV nanofibers and the composite nanofibers. The positions of the PPV characteristic peaks (at 515 and 550 nm) did not change, which indicates that the functional structure of PPV in the composite fibers is kept, which is consistent with the FTIR result. However, in the composite fibers' spectrum, the relative enhancement of 515-nm emission peaks, compared with the 550-nm emission peaks, indicates that the addition of Ag nanoparticles decreases the reabsorption among PPV chains.

Opto-electronic characteristics of the single composite fiber device

To measure the opto-electronic property of the composite nanofiber, the novel 'organic ribbon mask' technique of Professor Hu's group [16] was used to construct the Au top electrode device of the single composite fiber shown in Figure 6a,b. The fabrication process of the device is briefly described below: Firstly, a single composite nanofiber was transferred onto the SiO_2 substrate (the white line and the horizontal fiber in Figure 6a,b,

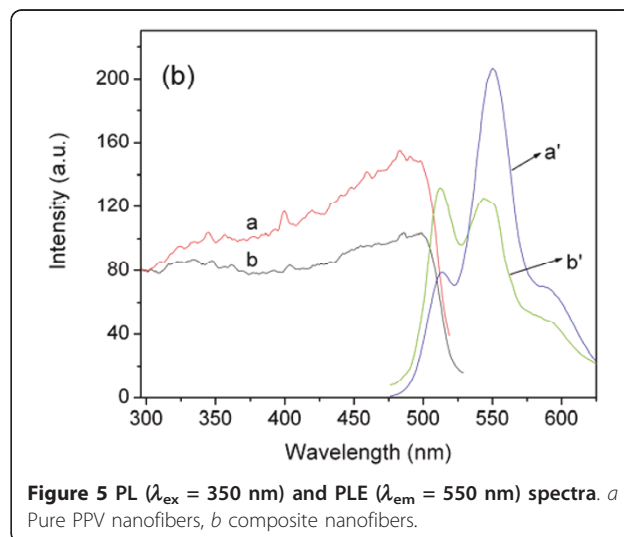


Figure 5 PL ($\lambda_{\text{ex}} = 350\text{ nm}$) and PLE ($\lambda_{\text{em}} = 550\text{ nm}$) spectra. *a* Pure PPV nanofibers, *b* composite nanofibers.

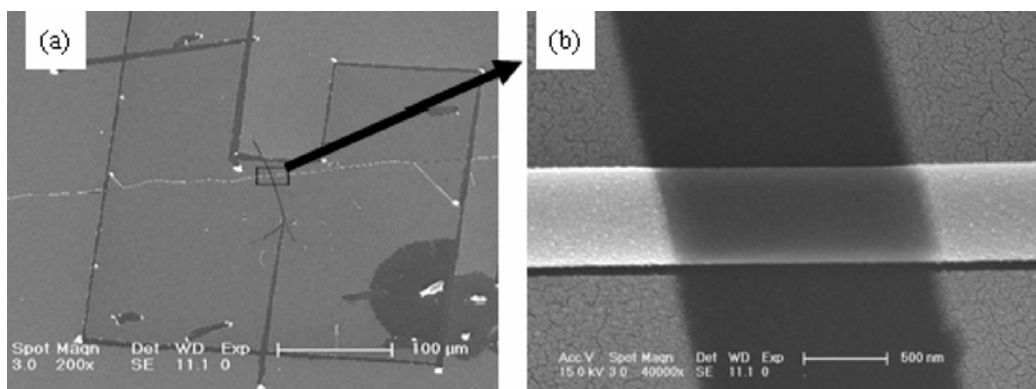


Figure 6 top electrode device of the single composite fiber. **a** SEM image of Au top electrode device (the part closed by polygon indicated by the red arrows). **b** SEM image of the device's channel (insulate gap) and crossed nanofiber.

respectively). Then, an organic ribbon with a diameter of approximately $1.5 \mu\text{m}$ was picked up and crossed over the composite nanofiber. Finally, the gold was vacuum-deposited. After the 'organic ribbon mask' was peeled off, the insulate part acted as the channel of device (see the dark part in Figure 6b). Finally, the insulate lines were drawn on the Au film using a micromanipulator probe to form a polygon (indicated by the arrows in Figure 6a), which was the device outline.

The I - V characteristics of the device were measured under light illumination from a Xe lamp with different intensities at room temperature in the shielded box. Figure 7 shows that the photocurrent of the composite nanofiber obviously increases with increasing the light intensity from 0 to 5.76 mW/cm^2 . The I - V curves in Figure 7 show the non-ohmic character, which is consistent with the I - V curves of PPV and its composite film devices [17]. Under light illumination of 5.76 mW/cm^2

and voltage of 20 V, the photocurrent is over three times larger than the dark current, which indicates that the composite nanofibers have high and sensitive opto-electronic response. The reason for the improvement (or enhancement) of the opto-electronic response of the composite nanofiber should be attributed to the following factor: there is the coordination effect to a certain extent between the Ag atom and the π system of PPV mentioned in "FTIR spectra."

It is noticed that the two I - V curves under light illumination of 3.04 and 5.76 mW/cm^2 are close to each other before 10 V, e.g., the phenomenon of photoresponse saturation happens, which could be related to the charge accumulation and de-trapping by light effects at the contacts.

Conclusions

The Ag nanoparticles/PPV composite nanofibers with an average diameter of 500 nm were prepared by electrospinning. The TEM image shows that the Ag nanoparticles with an average diameter of 25 nm were dispersed uniformly in the PPV matrix. It was deduced from the FTIR spectra that there was a complexation between the Ag atom and the π system of PPV, which should be significantly favorable for the charge separation of photoexcitons and the charge transport at the interface between the Ag particles and the PPV. The J - V measurement of the device under light illumination with different intensities shows that the Ag nanoparticles/PPV composite nanofibers have high and sensitive opto-electronic response and will have good potential application in the micro/nano organic opto-electronic field.

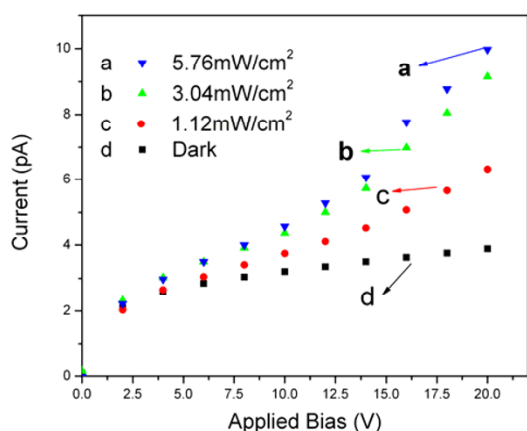


Figure 7 Photocurrent of the composite nanofiber. J - V curves of the single Ag/PPV composite nanofiber under light illumination with different intensities.

Acknowledgements

We thank Prof. Wenping Hu and Dr. Yajie Zhang (Beijing National Laboratory for Molecular Sciences and Key Laboratory of Organic Solids, Institute of Chemistry Chinese Academy of Sciences) for the fabrication of the Au top

electrode device and the measurement of *I-V* curves. The research described herein was supported by the National Natural Science Foundation (grant no. 2077 4017), Natural Science Foundation of Heilongjiang Province of China (grant no. B200606), and Analysis and Testing Foundation of Northeast Normal University.

Author details

¹Faculty of Chemistry, Northeast Normal University, Changchun, 130024, People's Republic of China ²Bilingual Teaching Training Center, Changchun Normal University, Changchun 130032, People's Republic of China ³Faculty of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, People's Republic of China

Authors' contributions

JC and PY carried out the preparation of the fibers and the devices. CW drafted the manuscript. SZ and LZ participated in sequence alignment. ZH contributed to the redaction of the manuscript and in the design of the study. WL and CW and CS participated in the certain measurements. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

Received: 28 April 2010 Accepted: 7 February 2011

Published: 7 February 2011

References

1. Gu FX, Zhang L, Yin XF, Tong LM: **Polymer single-nanowire optical sensors.** *Nano Lett* 2008, **8**:2757.
2. Yu KH, Chen JH: **Enhancing Solar Cell Efficiencies through 1-D Nanostructures.** *Nanoscale Res Lett* 2009, **4**:1.
3. Kjelstrup-Hansen J, Norton JE, da Silva Filho DA, Brédas J-L, Rubahn H-G: **Charge transport in oligo phenylene and phenylene-thiophene nanofibers.** *Org Electron* 2009, **10**:1228.
4. Chang M-Y, Wu C-S, Chen Y-F, Hsieh B-Z, Huang W-Y, Ho K-S, Hsieh T-H, Han Y-K: **Polymer solar cells incorporating one-dimensional polyaniline nanotubes.** *Org Electron* 2008, **9**:1136.
5. Li D, Xia YN: **Fabrication of titania nanofibers by electrospinning.** *Nano Lett* 2003, **3**:555.
6. Li ZY, Huang HM, Wang C: **Electrostatic Forces Induce Poly(vinyl alcohol)-Protected Copper Nanoparticles to Form Copper/Poly(vinyl alcohol) Nanocables via Electrospinning.** *Macromol Rapid Commun* 2006, **27**:152.
7. Xin Y, Huang ZH, Peng L, Wang DJ: **Photoelectric performance of poly(p-phenylene vinylene)/Fe₃O₄ nanofiber array.** *J Appl Phys* 2009, **105**:086106.
8. Burroughes JH, Bradley DDC, Brown AR, Marks RN, Mackay K, Friend RH, Burns PL, Holmes AB: **Light-emitting diodes based on conjugated polymer.** *Nature* 1990, **347**:539.
9. Prasad PN, Williams DJ: **Introduction to Nonlinear Optical Effect in Molecules and Polymers.** New York: Wiley; 1991, 284.
10. Marks RN, Halls JJM, Bradley DDC, Friend RH, Holmes AB: **The photovoltaic response in poly(p-phenylene vinylene) thin-film device.** *J Phys Condens Matter* 1994, **6**:1379.
11. Jiang ZJ, Huang ZH, Yang PP, Chen JF, Xin Y, Xu JW: **High PL-efficiency ZnO nanocrystallites/PPV composite nanofibers.** *Compos Sci Technol* 2008, **68**:3240.
12. Wang C, Yan EY, Huang ZH, Zhao Q, Xin Y: **Fabrication of Highly Photoluminescent TiO₂/PPV Hybrid Nanoparticle-Polymer Fibers by Electrospinning.** *Macromol Rapid Commun* 2007, **28**:205.
13. Lee JH, Park JH, Kim JS, Lee DY, Cho K: **High efficiency polymer solar cells with wet deposited plasmonic gold nanodots.** *Org Electron* 2009, **10**:416.
14. Nah YC, Kim SS, Park JH, Park HJ, Jo J, Kim DY: **Enhanced electrochromic absorption in Ag nanoparticle embedded conjugated polymer composite films.** *Electrochem Commun* 2007, **9**:1542.
15. Halliday DA, Burn PL, Friend RH, Bradley DDC, Holmes AB: **Determination of the average molecular weight of poly(P-phenylenevinylene).** *Synthetic Met* 1993, **55**:902.
16. Jiang L, Gao JH, Wang EJ, Li HX, Wang ZH, Hu WP, Jiang L: **Organic Single-Crystalline Ribbons of a Rigid "H"-type Anthracene Derivative and High-Performance, Short-Channel Field-Effect Transistors of Individual Micro/Nanometer-Sized Ribbons Fabricated by an "Organic Ribbon Mask" Technique.** *Adv Mater* 2008, **20**:2735.

17. Álvaro M, Corma A, Ferrer B, Galletero MS, García H, Peris E: **Increasing the Stability of Electroluminescent Phenylenevinylene Polymers by Encapsulation in Nanoporous Inorganic Materials.** *Chem Mater* 2004, **16**:2142.

doi:10.1186/1556-276X-6-121

Cite this article as: Chen *et al.*: Ag nanoparticles/PPV composite nanofibers with high and sensitive opto-electronic response. *Nanoscale Research Letters* 2011 **6**:121.

Submit your manuscript to a SpringerOpen® journal and benefit from:

- Convenient online submission
- Rigorous peer review
- Immediate publication on acceptance
- Open access: articles freely available online
- High visibility within the field
- Retaining the copyright to your article

Submit your next manuscript at ► springeropen.com