

Facile synthesis method of poly(3,5-dimethoxyaniline) hollow microsphere through interfacial polymerisation approach using camphorsulfonic acid as the doping agent

Xiaoqin Wang, Jinxin Xu, Zhenzhen Kong, Shanxin Xiong, Zhufeng Li, Jialun Fu, Runlan Zhang, Ming Gong, Bohua Wu, Jia Chu

College of Chemistry and Chemical Engineering, Xi'an University of Science and Technology, Xi'an 710054, People's Republic of China

E-mail: xiongxs689@sohu.com

Published in Micro & Nano Letters; Received on 19th May 2015; Revised on 14th September 2015; Accepted on 15th September 2015

A facile synthesis method of poly(3,5-dimethoxyaniline) (P(3,5-DMA)) hollow microspheres was demonstrated by the interfacial polymerisation of 3,5-dimethoxyaniline (3,5-DMA) using camphorsulfonic acid (CSA) as the doping agent and soft template. The obtained P(3,5-DMA) hollow microspheres possess narrow size distribution and uniform shape. A possible growth mechanism of the hollow microspheres was proposed through studying the change in morphologies of P(3,5-DMA) at different reaction times. It is believed that the slow diffusion speed of monomer from the oil phase to the water phase in the interfacial polymerisation system controls the progress of polymerisation. Moreover, the interaction between amino group of the monomer and the sulfonic acid group of the doping agent micelle guides the formation of the hollow microspheres.

1. Introduction: The conducting polymers with low-dimensional (zero-dimensional, one-dimensional and two-dimensional) nanostructures have been widely utilised in various application areas including chemical senses, catalytic materials and optoelectronic device, owing to their unique nanostructures and novel electric and catalytic performances [1–3]. The application fields of the conducting polymer are strictly related to their morphologies or the dimensions, for example, the one-dimensional conducting polymer can be used as the sensors and energy storages [4, 5], benefiting from its large surface area and high electrochemical activities, and zero-dimensional conducting polymer can be used as the electric ink [6], owing to its high conductivity and nanoparticle structure. Moreover, the conducting polymer possessing hollow microsphere structure can be applied in the controlled drug release, catalyst, dye encapsulation, microwave absorber and so on [7–10]. The conducting polymer hollow microsphere can be prepared by various methods, such as template-assisted chemical polymerisation [11, 12], pulse voltage electrochemical polymerisation [13], emulsion polymerisation [14] and self-assembly methods [15]. Among these methods, the emulsion polymerisation could be the easiest approach and has been adopted by many researchers to prepare conducting polymer microspheres. Ishizu *et al.* [16] synthesised the polypyrrole microsphere using poly(vinyl alcohol) as the emulsifier in various solvent media. Liu and co-workers [14] prepared the polyaniline (PANI) microsphere using the sodium dodecyl benzene sulfonate as the surfactant in an emulsion polymerisation system. Further, a sodium citrate modified Fe_3O_4 nanoparticles was added as a cosurfactant and the magnetic PANI/ Fe_3O_4 hybrid hollow microspheres were synthesised successfully. However, these ordinary emulsion polymerisation routes need relatively large amount of surfactants serving as emulsifiers, which has non-electronic activity and need to be removed after polymerisation. In consideration of the shortcoming of emulsifier, a so-called surfactant-free emulsion polymerisation method was developed. He [17] prepared PANI microspheres using this route, but still a stabiliser ($\text{Cu}_2(\text{OH})_2\text{CO}_3$ particle) was needed in the system.

On the other hand, the interfacial polymerisation has been used widely for preparation of one-dimensional conducting polymer, for example, nanowire or nanotubes in an oil/water interface, which has easy control, large-scale production and low-cost features. Huang [18–20] has prepared successfully the PANI

nanowires using the interfacial polymerisation process. Through adding the surfactant into the interfacial polymerisation system, the structure of PANI can be variable. In Li *et al.*'s work [21], the PANI morphologies can be needle, hollow microsphere or nanowire, according to the various concentration of the surfactant, hexadecyltrimethylammonium bromide. Though the microspheres can be obtained in the interfacial polymerisation, the surfactant is still necessary. So can the conducting polymer microspheres be synthesised without using any surfactant or stabiliser?

Herein, we present a facile synthesis route of conducting polymer hollow microspheres through an interfacial polymerisation method without using any surfactant or stabiliser. The formation process and growth mechanism of hollow microspheres were studied through scanning electron microscopic (SEM) observation.

2. Experimental

2.1. Chemical polymerisation of poly(3,5-dimethoxyaniline) (P(3,5-DMA)): All chemicals are analytical reagents and used as received unless otherwise specified. The P(3,5-DMA) prepared by normal chemical polymerisation method was used as the reference sample. In a typical experiment, the monomer 3,5-dimethoxyaniline (3,5-DMA) was dissolved in a small amount of ethanol, then the 3,5-DMA/ethanol solution was dropped into 0.02 M camphorsulfonic acid (CSA) aqueous solution to form an even monomer/dopant agent mixture solution. The CSA/monomer molar ratio was controlled to 1/2. The oxidant agent ammonium peroxydisulfate (APS) with molar ratio of 1/1 (APS/monomer) was dissolved into 10 ml 0.02 M CSA aqueous solution and dropped into monomer/CSA solution with stirring at room temperature. After 72 h reaction, the product was filtered and washed using ethanol and deionised water for three times, respectively. The final filter cake was dried at 40 °C in a vacuum oven over night, denoted as P(3,5-DMA)-n.

2.2. Interfacial polymerisation of P(3,5-DMA): In a typical experiment, 0.4 mmol 3,5-DMA was dissolved in 10 ml of chloroform as the organic phase. APS of 0.4 mmol was dissolved in 10 ml 0.02 M CSA aqueous solution as the water phase. After the organic phase was added into a reaction vial, the water phase was added carefully on the top of the organic phase without breaking the steady state of the interface. The vial was allowed to

stand vertically for reaction. The reaction time is set as 72 h. Then, the water phase was filtered and washed with ethanol and deionised water for three times, respectively, to remove the unpolymerised monomer and oxidant agent residue. The final product was dried at 40 °C in a vacuum oven over night, denoted as P(3,5-DMA)-i.

2.3. Characterisation: Fourier transform infrared (FTIR) spectra of the materials were obtained on a Perkin Elemer GX spectrometer using KBr method. The field-emission SEM (FE-SEM) images were obtained on a Hitachi S-4800 SEM. For better observation, the surfaces of the samples were sputtered with Au prior to SEM observation.

3. Results and discussion

3.1. Interfacial polymerisation of P(3,5-DMA): As a useful technique for preparation of one-dimensional nanostructure of the conducting polymer, the interfacial polymerisation was widely utilised to prepare nanowire and nanotube of PANI. The formation mechanism of one-dimensional nanostructure is that the separated reactant and product between the oil/water interfaces prevents the PANI aggregation and secondary growth. Unlike the fast growth of PANI, the growth speed of poly(3,5-DMA) is slower, which can be found by the experimental phenomenon. In the interfacial polymerisation system of aniline, the colour at the interface becomes blue in 1 min [19], while for the P(3,5-DMA) system, the colour can only change after 2 h. Owing to the slow polymerisation speed, the monomer cannot form polymer immediately after it diffuse from oil phase to the water phase. The related slower reaction speed of P(3,5-DMA) can be caused by the steric hindrance effect of two $-\text{OCH}_3$ groups at the -3 and -5 position of aniline ring, which affect the attack of radical cation to the -4 position of aniline ring.

Fig. 1a is the typical morphology of P(3,5-DMA)-i synthesised by interfacial polymerisation. The microspheres with diameter of 2–3 μm dominate the whole SEM image. The size distribution of the microspheres is shown in the inset of Fig. 1a. Still some irregular shape can be found between the microspheres, which may be caused by the incomplete growth of microsphere. Besides the individual microsphere structure, several microspheres that grow together and form a complex morphology can also be found. The SEM image with high magnification (Fig. 1b) exhibits that the microsphere is surrounded by the nanoparticles with size of dozens of nanometre due to the random deposition of P(3,5-DMA). Moreover, the hollow structure can be found in an uncompleted growth microsphere as shown in Fig. 1c. Fig. 1d shows the morphologies of the reference sample synthesised by conventional method, which has totally different structure from that of interfacial polymerised P(3,5-DMA)-i. It is typically irregular nanoparticle shape obtained by the chemical polymerisation method with size of dozen of nanometre. An interested fact is that the size and the shape of nanoparticles are similar to the nanoparticles appeared on the surface of P(3,5-DMA)-i microspheres.

FTIR spectra of P(3,5-DMA)-i and P(3,5-DMA)-n are shown in Fig. 2. It can be seen that though the preparation method and the morphologies are different for these two samples, they present almost same FTIR absorbance curves, except different intensities. As a derivative of PANI, the PANI-like FTIR absorbance band can be found in P(3,5-DMA)-i. The broad band at 3410 cm^{-1} is attributed to the N–H stretching vibration, and the C–H stretching vibrations appear at 2937 and 2840 cm^{-1} , and the C=N and C=C stretching modes for quinoid (Q) and benzoid (B) rings occur at 1610 and 1511 cm^{-1} , respectively. Besides the FTIR band of the conjugated backbone, the FTIR peak of the substituent group of $-\text{OCH}_3$ occurs at 1457 cm^{-1} (asymmetric bending vibration). Moreover, the symmetric and asymmetric stretching vibration bands of $-\text{SO}_3$ can be found at 1044 and 1122 cm^{-1} , respectively [22], which prove the doping state of P(3,5-DMA)-i. The FTIR spectra confirm that the CSA doped P(3,5-DMA)-i can be

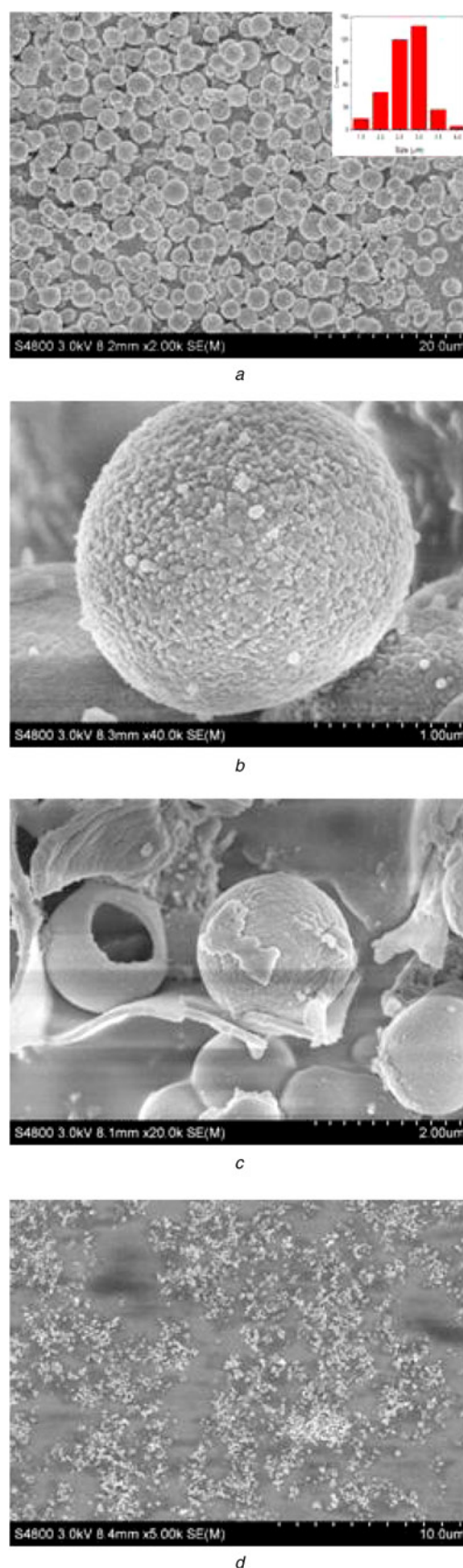


Fig. 1 SEM images of P(3,5-DMA)-i and P(3,5-DMA)-n
a Low magnification image of P(3,5-DMA)-i
b High magnification image of P(3,5-DMA)-i
c Hollow structure of P(3,5-DMA)-i
d SEM image of P(3,5-DMA)-n (d)
Inset in Fig. 1a is the size distribution of microspheres

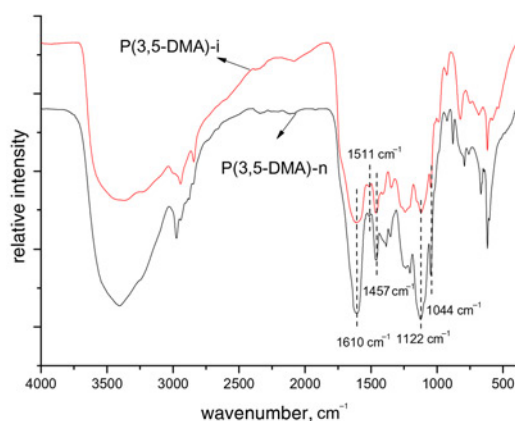


Fig. 2 FTIR spectra of P(3,5-DMA)-i and P(3,5-DMA)-n

synthesized through the interfacial polymerisation and it has similar FTIR absorbance as P(3,5-DMA)-n.

3.2. Growth process of P(3,5-DMA)-i microspheres: In the interfacial polymerisation system, the growth process of P(3,5-DMA)-i includes monomer diffusion, monomer/doping agent interaction, polymerisation of 3,5-DMA and polymer aggregation. So it is totally different from that happening in the conventional polymerisation system. To study the growth process of P(3,5-DMA)-i microspheres, we observe the morphologies of the product at different reaction times using FE-SEM. Fig. 3 exhibits the change in morphologies of P(3,5-DMA)-i from the particle to microsphere. At the initial stage of reaction, no regular shape can

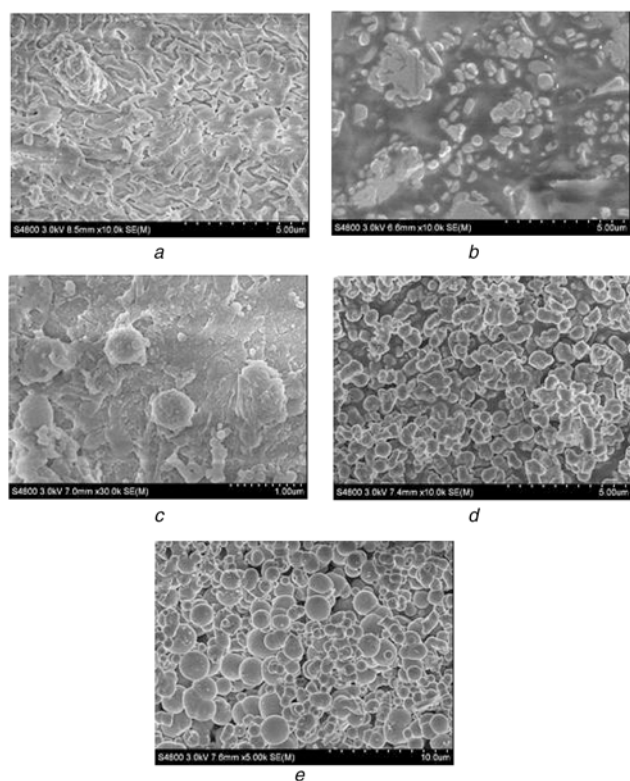


Fig. 3 SEM images of P(3,5-DMA)-i at different reaction times

- a 2 h
- b 3 h
- c 5 h
- d 12 h
- e 24 h

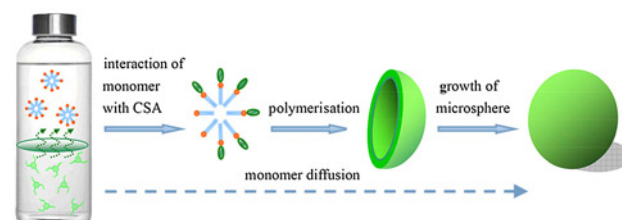


Fig. 4 Polymerisation and growth process of P(3,5-DMA) hollow microsphere

be found (Figs. 3a and b). After 5 h reaction, some individually round-like particle with size of 200–300 nm can be distinguished as shown in Fig. 3c. With the proceeding of reaction, the microsphere shape is formed and the diameter is increased to ~400 nm. After 12 h reaction, most of the P(3,5-DMA)-i exhibit microsphere structures. The diameters of microspheres are in the range from 400 to 600 nm (Fig. 3d). Besides individual microsphere, there are many large aggregations consisting of two to four microspheres. After 24 h reaction (Fig. 3e), the microsphere morphologies dominate the full image. However, the size distribution is very wide. Some of the microsphere has achieved the maximum size of ~3 μm as that of the final product obtained after 72 h reaction. Moreover, the sizes of rest microspheres are ~500 nm. As comparison with the even size distribution of final product, it can be identified that the growth process is still on-going.

In consideration of the separated oil/water phases in the interfacial polymerisation system and the slow growth process, the P(3,5-DMA)-i hollow microsphere formation process was proposed as shown in Fig. 4.

Due to the poor solubility of 3,5-DMA in water, the diffusion process of 3,5-DMA from oil phase to water phase is very slow. However, this diffusion process can be accelerated by CSA through forming water-soluble 3,5-DMA/CSA salts. So the growth process could be that: in the water phase, CSA can form doping agent micelles with the hydrophilic group ($-\text{SO}_3\text{H}$) outside and hydrophobic group inside; the monomer can diffuse into water phase with the help of CSA; due to the interaction between the amino group of monomer and the acid group of CSA, the 3,5-DMA will surround around the CSA micelles; at the same time, the polymerisation process is carried on with the oxidation process by APS. The monomer diffusion and polymerisation are conducted simultaneously. So at the initial stage, the microsphere is not formed. With more monomer diffusing into the water phase, the microsphere is formed. Moreover, as some more monomer diffuses into the water phase, the diameter of microsphere will increase by coating the initial microsphere layer by layer. The diameter of microsphere will stop increase at ~3 μm . With still more monomer added, it will form aggregation on the surface or between the microsphere. If we control the synthesis condition to a suitable reactant ratio and concentration, a narrow size distribution hollow microsphere can be easy obtained.

4. Conclusion: The P(3,5-DMA) hollow microspheres were prepared successfully through the interfacial polymerisation method using CSA as doping agent and soft template. The hollow structure is attributed to the interaction between the monomer and outside $-\text{SO}_3\text{H}$ group of the CSA micelles in the water phase. Though the morphologies of the interfacial polymerised P(3,5-DMA)-i and conventional polymerised P(3,5-DMA)-n are different, they have same molecular structure as proved by FTIR analysis. The growth process study confirms that the interfacial polymerisation process includes monomer diffusion, formation of monomer-CSA micelle, oxidation of monomer and growth of microsphere four steps. The monomer

diffusion is the speed-control step. The diameter of microsphere is increased with continuous supply of monomer diffusion and achieves balance value at $\sim 3\ \mu\text{m}$. This non-surfactant synthesis approach of narrow distribution hollow microsphere has promising application in the fields of controlled drug release, chemical sensor and biosensors.

5. Acknowledgments: The authors thank the National Natural Science Foundation of China (grant no. 51373134, 21406176), the Education Department of Shaanxi Province (2013JK0650) and the Natural Science Foundation of Shaanxi Province (2014JQ2072) for the financial support of this work.

6 References

- [1] Yoon H., Jang J.: 'Conducting-polymer nanomaterials for high-performance sensor applications: issues and challenges', *Adv. Funct. Mater.*, 2009, **19**, pp. 1567–1576
- [2] Ghosh S., Kouam N.A., Ramos L., *ET AL.*: 'Conducting polymer nanostructures for photocatalysis under visible light', *Nat. Mater.*, 2015, **14**, doi: 10.1038/nmat4220, pp. 505–511
- [3] Jang S.-Y., Seshadri V., Khil M.-S., *ET AL.*: 'Welded electrochromic conductive polymer nanofibers by electrostatic spinning', *Adv. Mater.*, 2005, **17**, pp. 2177–2180
- [4] Kannan B., Williams D.E., Laslau C., *ET AL.*: 'A highly sensitive, label-free gene sensor based on a single conducting polymer nanowire', *Biosens. Bioelectron.*, 2012, **35**, pp. 258–264
- [5] Aradilla D., Bidan G., Gentile P., *ET AL.*: 'Novel hybrid micro-supercapacitor based on conducting polymer coated silicon nanowires for electrochemical energy storage', *RSC Adv.*, 2014, **4**, pp. 26462–26467
- [6] Lee J., Varadan V.K.: 'Preparation and characterization of nanocomposites with carbon nanotubes and core-shell type polyaniline for the conductive colloidal ink', *Proc. of SPIE, Int. Society Optical Engineering, Nanosensors and Biosensors Information Technology Sensory Systems*, 2012, vol. 8344, doi: 10.1117/12.915274
- [7] Fujii S., Hamasaki H., Abe H., *ET AL.*: 'One-step synthesis of magnetic iron-conducting polymer-palladium ternary nanocomposite microspheres with applications as a recyclable catalyst', *J. Mater. Chem. A*, 2013, **1**, pp. 4427–4430
- [8] Beesabathuni S.N., Stockham J.G., Kim J.H., *ET AL.*: 'Fabrication of conducting polyaniline microspheres using droplet microfluidics', *RSC Adv.*, 2013, **3**, pp. 24423–24429
- [9] Ni X., Hu X., Zhou S., *ET AL.*: 'Synthesis and microwave absorbing properties of poly(3,4-ethylenedioxythiophene) (PEDOT) microspheres', *Polym. Adv. Technol.*, 2011, **22**, pp. 532–537
- [10] Xia Y., Gates B., Yin Y., *ET AL.*: 'Monodispersed colloidal spheres: old materials with new applications', *Adv. Mater.*, 2000, **12**, pp. 693–713
- [11] Yang Y., Chu Y., Yang F., *ET AL.*: 'Uniform hollow conductive polymer microspheres synthesized with the sulfonated polystyrene template', *Mater. Chem. Phys.*, 2005, **92**, pp. 164–171
- [12] Liu J., Hu X., Wang X., *ET AL.*: 'Facile synthesis of hollow microspheres of polyaniline using poly(sodium 4-styrenesulfonate) as dopant', *Polym. Int.*, 2014, **63**, pp. 722–726
- [13] Atohe M., Ishikawa K., Asami R., *ET AL.*: 'Size-controlled synthesis of conducting-polymer microspheres by pulsed sonoelectrochemical polymerization', *Angew. Chem. Int. Ed.*, 2009, **48**, pp. 6069–6072
- [14] Zhang L., Liu P., Wang T.: 'Preparation of superparamagnetic polyaniline hybrid hollow microspheres in oil/water emulsion with magnetic nanoparticles as cosurfactant', *Chem. Eng. J.*, 2011, **171**, pp. 711–716
- [15] Li Y., Li Z., Zheng F.: 'Polyaniline hollow microspheres synthesized via self-assembly method in a polymer acid aqueous solution', *Mater. Lett.*, 2015, **148**, pp. 34–36
- [16] Ishizu K., Tanaka H., Saito R., *ET AL.*: 'Microsphere synthesis of polypyrrole by oxidation polymerization', *Polymer*, 1996, **37**, pp. 863–867
- [17] He Y.: 'Preparation of polyaniline microspheres with nanostructured surfaces by a solids-stabilized emulsion', *Mater. Lett.*, 2005, **59**, pp. 2133–2136
- [18] Huang J., Virji S., Weiller B.H., *ET AL.*: 'Nanostructured polyaniline sensors', *Chem. Eur. J.*, 2004, **10**, pp. 1314–1319
- [19] Huang J., Kaner R.B.: 'Nanofiber formation in the chemical polymerization of aniline: a mechanistic study', *Angew. Chem. Int. Ed.*, 2004, **43**, pp. 5817–5821
- [20] Huang J., Kaner R.B.: 'A general chemical route to polyaniline nanofibers', *J. Am. Chem. Soc.*, 2004, **126**, pp. 851–855
- [21] Li J., Jia Q., Zhu J., *ET AL.*: 'Interfacial polymerization of morphologically modified polyaniline: from hollow microspheres to nanowires', *Polym. Int.*, 2008, **57**, pp. 337–341
- [22] Neelgund G.M., Hrehorova E., Joyce M., *ET AL.*: 'Synthesis and characterization of polyaniline derivative and silver nanoparticle composites', *Polym. Int.*, 2008, **57**, pp. 1083–1089