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COMMUNICATION

Patterned One-Dimensional Photonic Crystals with Acidic/alkali Vapor Responsibility†

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A series of patterning responsive one-dimensional photonic crystals (1DPCs) were developed by using a photolithography technique to etch the template for acidic/alkali vapor sensing by the naked eye through color change.

Chemical odors and volatile compound detection are a topic of great interest in physics and materials science, owing to concerns about environmental monitoring, industrial quality control and human health care.[1] Ammonia and hydrochloric acid are easily found in many labs and factories, which are harmful to cause diseases. Thus, it is necessary for monitoring these compounds in air.

Fabricating suitable sensing devices with efficient responsibility is the key point in such efforts. Responsive photonic crystals (RPCs), which use stimulus-responsive material as elements can alter their diffraction wavelength or intensities upon exposure to physical[2] or chemical stimuli,[3] have been an express and flexible approach for stimuli sensing.[4] Recent advances in several groups have led to a burst of activities on responsive photonic crystals to detect arrange of odors including water-vapor,[5] CO_2,[6] volatile organic compounds[7] vapor and specific gas mixture.[8] The inherent responsibility of RPCs can be monitored by measuring the shift of stopband position or observed by the remarkable color change. In this case, patterning photonic crystals can be treated as an effective option for their convenient detection signals read-out[9]. Patterning photonic crystals can be fabricated by self-assembly[10], inkjet-printing[11], artificial lithography[12], and so on.[13] Most of these strategies are limited by the structure, stability, high cost, and difficulties associated with template fabrication, together with complex responsive detection means of external stimuli.[14] Therefore, it is highly desirable to carry out an easy fabricate responsive photonic crystals without using intricate fabrication and detection methods.

Currently, a few study points to new strategies to make responsive pattering 1DPCs which show their advantages in fast preparing process[15]. 1DPCs are special kinds of crystal multilayer interference, which consist of alternating layers of high and low-refractive-index materials with planar interfaces between each pair of layers[16]. In particular, most of responsive 1DPCs works are focused on manipulating layer optical thickness,[5a, 17] while conducting polymers focus on tuning the refractive index[18]. Odors can be adsorbed strongly on conducting polymer photonic crystals associated with conducting polymers' doping/de-doping process, leading to effective reflective index change at room temperature[19] while some sensors need complicate facilities to monitor the changes[20]. Making use of the simple ordered titanium dioxide (TiO_2) layer, 1DPCs are easily processed to achieve patterning with the help of state-of-the-art photolithography techniques.[21]

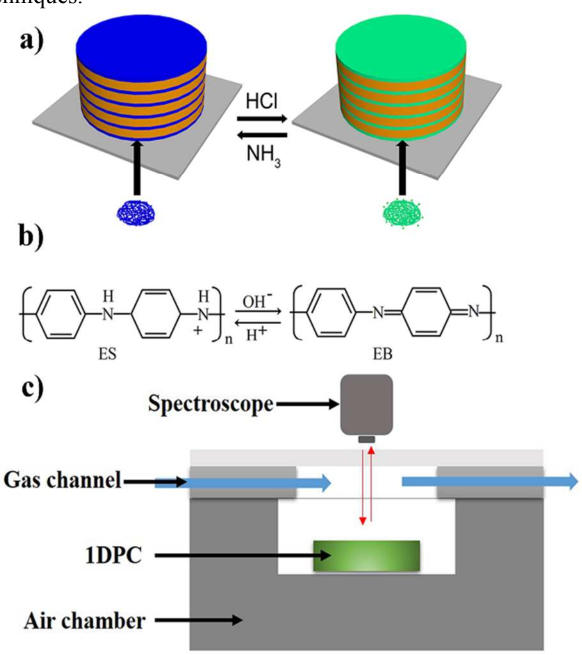

Figure 1. a) Schematic image of organic/inorganic hybrid 1DPCs by alternated spin-coating of TiO_2 and PANI. b) The dedoping/doping transformation from emeraldine salt (ES) to emeraldine base (EB) form of PANI; c) Schematic diagram of gas responsive device and spectra measurement system.

In this article, an artificial patterning TiO_2/polyaniline (PANI) 1DPCs is fabricated and employed to detect environmental response to NH_3 and HCl vapor (see in Fig. 1a). The color of the as-prepared 1DPCs changes reversibly between green and red when they were placed in HCl and NH_3 atmospheres alternatively, which was derived from the shift of PC's stopband because of the variation of the PANI's refractive index in different acidic and alkali vapor environment, see in Fig. 1b. Compared with other traditional works[22], this method makes a combination of chemistry with materials design and has a better responsibility. The remarkable color change in photolithography pattern makes the naked-eye sensing function a reality, which would be helpful for chemical and biological sensor applications in real-time monitoring of acidic and alkali vapor of optical signal, see in Fig. 1c.

Highly uniform, mechanically stable TiO_2/PANI 1DPCs with alternated layers of TiO_2 and PANI have been realized using the spin-coating method. TiO_2 can form a uniform film easily and has a higher refractive index compared with PANI layer.[23] As the low index layer, we use porous conducting polymer EB form PANI, which allow the stimuli gas to flow through it and do not corrupt the ordered structures, allowing us to demonstrate the platform for developing colorimetric gas sensors. The photonic bandwidth becomes narrower and the intensity of the peak grows with increasing numbers of layers, which are in good agreement with previous theory of the thickness dependence of the optical response of photonic crystal slabs, see in Fig. 2a. The angle dependence results were determined by spectroscopic ellipsometry. When the incident angles are 75 ^{o}, 60 ^{o}, 45 ^{o}, 30 ^{o} and 15 ^{o}, respectively, the corresponding Bragg peaks' positions are 470 nm, 500 nm, 550 nm, 580 nm and 615 nm, see in Fig. S1. The structural colors get a blue shift as the incident angle raises. A change of the period also influences the optical properties of the 1DPCs. By increasing the period only, Bragg peak position will make a red shift, see in Fig. 2b. The Bragg peak can be manipulated in the full visible range from blue to red by choosing proper periods. The obvious photonic stopband and the vivid structure color can be easily obtained in several bilayers. The film is very uniform over a large area, see in Fig. 2b. The cross-sectional SEM image of a stacked film from which we can see that it possesses an ordered multilayer structure in a large area, see in Fig. 2c.

For a stimulus vapor response, PANI/TiO_2 1DPCs were fabricated with their photonic band gaps in the visible spectrum region. When a stimuli gas molecule enters a 1DPC structure, an obvious refractive index change of the conducting polymer can be occurred and the photonic crystals' optical period change at the same. These cooperative, fast structure properties variety leads to a significant gas sensing affinity. The responsive photonic crystals reported the gas sensitive event through a gradual shift of the position of the diffraction peak to long wavelength with an increase of the refractive index. This phenomenon can be explained by the formula, see in Supporting Information Formula. During the process of stimuli gas sensing, the acidic vapor HCl binds to the porous PANI layers of the prepared 1DPCs. The obvious transformation from EB to ES is triggered by a reorganization of the electronic structure, which induces the change of the refractive index, Fig. 1b. As the refractive index of the ES form PANI is larger than that of EB form, the average refractive index increases which present a clear red shift of Bragg diffraction peak at normal incidence. However, in Fig. 3a, we observed a shift maximum of 60 nm which is larger than that caused by the change of refractive index only, see the calculation part in ESI. Thus, the additional shift should be attributed to the increase of the period, which is caused by the porous structure swelling of the PANI layers, see in ESI.

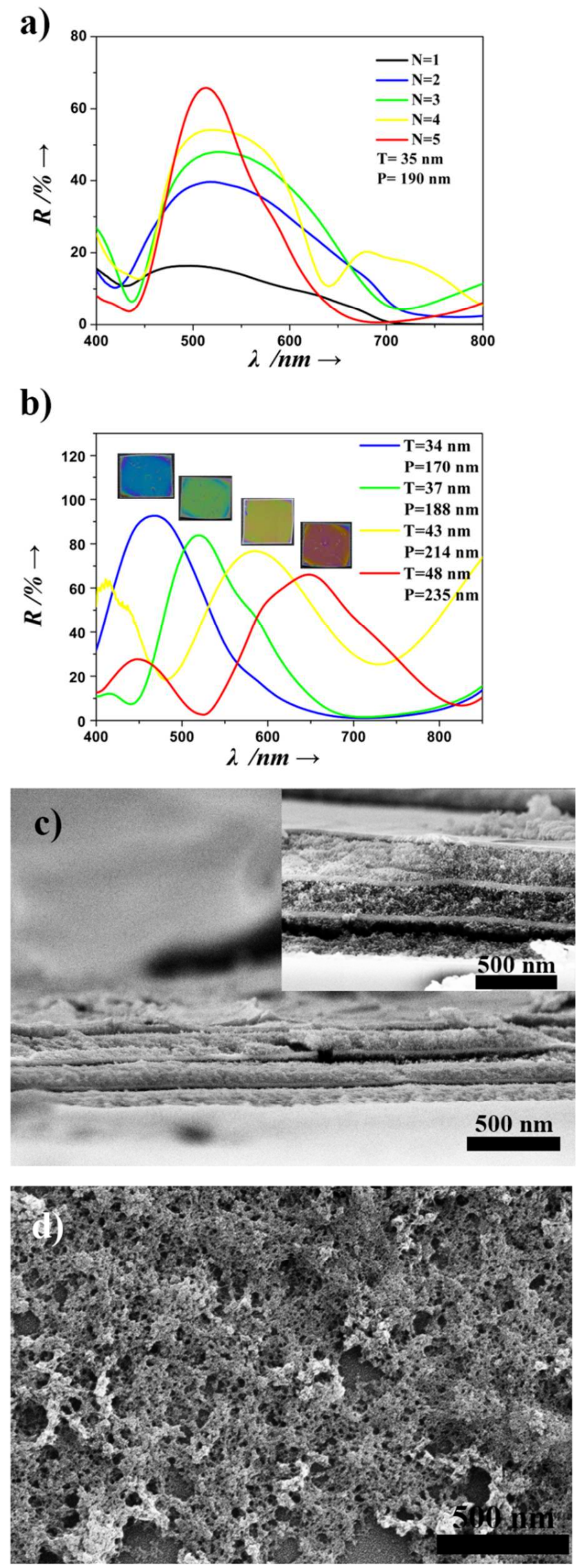

Figure 2. a) Reflection intensity of the 1DPCs with rising number of bilayers; b) Structural color variation and reflection spectrum of the

1DPCs with different layer thickness; c) Cross-section SEM images of a 1DPC film and its enlarged view; d) SEM image of PANI's porous structure.

The porous PANI layers of the prepared 1DPC show excellent gas carrying capacity, the responsive vapor infiltrates into pores of the 1DPCs, see in Fig. 2d. During different sensing environments, TiO_2 layers keep their thicknesses and refractive index invariable. To summarize, the specific response of acidic vapor in the PANI/TiO_2 1DPCs was mainly depends on the increase of average refractive index and the swelling of the porous PANI layers also contribute a little, both of which are reported by layer-by-layer 1DPCs through a red shift of the Bragg diffraction peak.

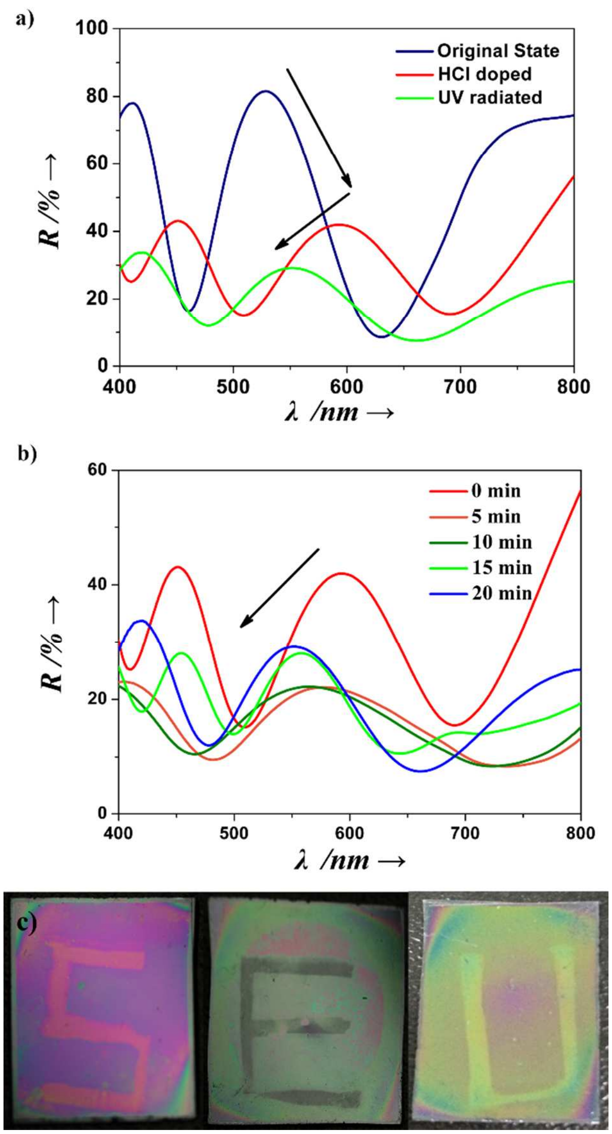

Figure 3. (a) The reflection spectrum of a PANI/TiO_2 1DPCs exposed to HCl and then be irradiated by UV light. (b) The changing reflection spectrum of an HCl doped PANI/TiO_2 1DPCs be irradiated by UV light in 20 min. (c) Digital photographs of the letter pattern displayed after the HCl doping process by UV light irradiated photolithography.

Corresponding "SEU" pattern can be produced with color distinct from the substrate as the 1DPCs is irradiated directly by UV light with a predesigned photo mask, see in Fig. 3c. This colorful 1DPCs exhibited a stopband in the green color region with its stop band position located at 531 nm, see in Fig. 3a. After this 1DPC had been treated with HCl, the stopband was a red shift to the red color region, Fig. 3a. In accordance, the red color 1DPC changed its appearance up to green color after it has been treated with NH_3. Fig. 3b shows 1DPCs covered by a designed hollow pattern mask that was exposed to ultraviolet (UV)-light with wavelengths below 380 nm, for 20 min. After being radiated, 1DPCs shows a pattern image as the yellow-green color area, a demonstration of one time use writing pattern was achieved. An evident shift of the photonic stop band is also observed simultaneously. As the films show "SEU" pattern in the middle area, and the pattern boundary is extremely clear. The photocatalytic process for degradation of PANI with TiO_2 was directly observed using a UV light irradiation. This transformation own to a reorganization of PANI's electronic structure which is different from doping and dedoping process.[19a] The interface interaction between PANI and TiO_2 was caused by UV irradiation. In FT-IR (see Supporting Information Figure S2), it can be clearly seen the main characteristic peaks of PANI. And compared with the main bands of EB form PANI, it shifted to lower wavenumbers after being doped with HCl. However, after irradiation, all bands of the doped ES form PANI showed another shift to lower wavenumbers. The effective refractive index of the pattern area changes as the irradiation process carry on.

To investigate the oscillation of this gas sensing 1DPCs, alkali vapor (NH_3) were introduced to test the 1DPCs after acidic response (Figure 4a). In Fig. 4b, it can be observed that the 1DPCs specifically recognize the alkali vapor NH_3 and display a remarkable response, the color comes back to the original state immediately when exposing the 1DPCs to saturated pressure of concentrated NH_3. Figure 4c plots the reversible conversion of the stopband position of the film when alternately exposed to NH_3 and HCl vapor for five cycles. Figure 4d presents the color difference of the patterning film 'S' over the period of a response cycle, including the initial state, response under acid and alkali atmosphere. Figure S2 shows photographs of the as-prepared 1DPCs without artificial pattern corresponding to different exposure times to HCl and NH_3 vapor. The initial color of the film was green before exposed to the HCl and the color underwent a change from green to nearly red with exposure time in 15 seconds. Its color returned back to green when put it into NH_3 environment. The films of patterning letter 'E' and 'U' were reported in Figure S3. It was clear that the change in peak position was repeatable and reversible, although there was a small fluctuation in the peak position, which is attributable to the reversible transformation between the ES and EB forms of PANI during the dedoping and doping process.

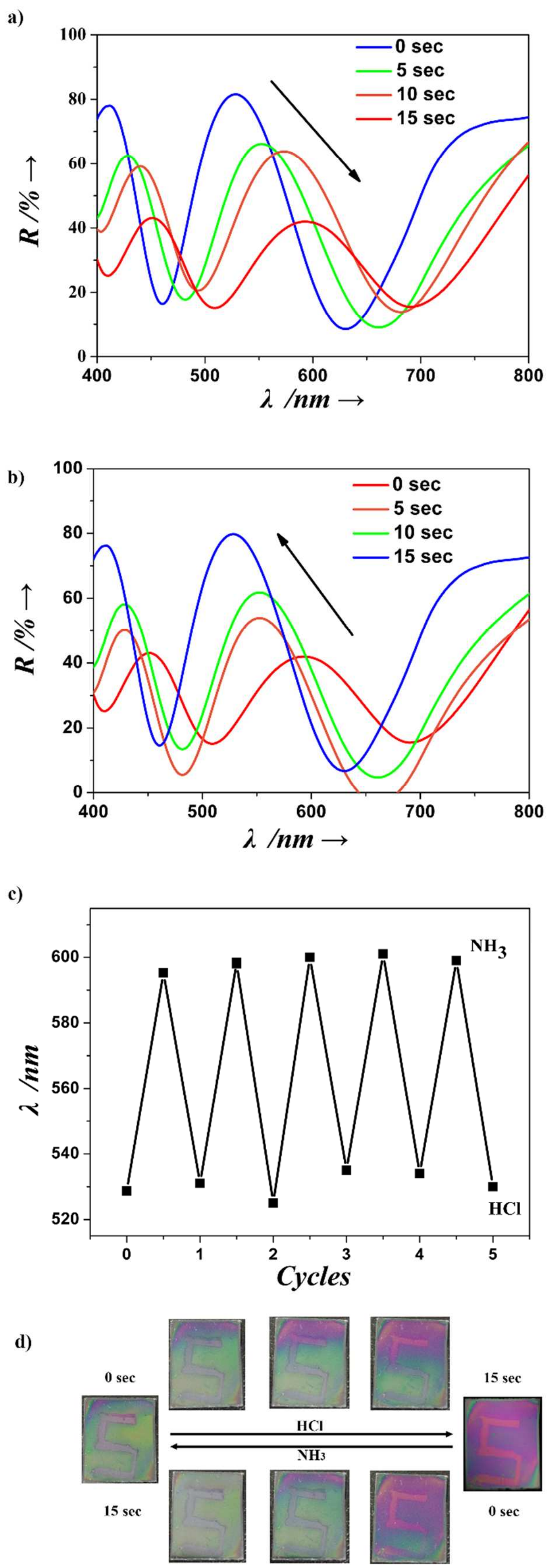

Figure 4. The reflectance spectra of a PANI/TiO_2 1DPCs exposed to HCl (a) and NH_3 (b) vapors, respectively. (c) Reversible changes of the stopband of the PANI/TiO_2 1DPCs with HCl and NH_3 vapors. (d) Photographs of the as-prepared patterned 1DPCs corresponding to different exposure times to HCl and NH_3 vapors.

In conclusion, we have demonstrated a facile method to response acidic/alkali vapor by the naked eye through color change based on patterning responsive 1DPCs. The distinct 'SEU' patterns were etched by photolithography technique by virtue of TiO_2. The responsive process is very fast and the repeatability is perfect. Considering the visible read-out, low-cost fabrication approach and easy packing without the aid of sophisticated instrumentation, our 1DPCs would be promising as economically colorful sensors in chemical and biological fields, and environmental monitoring.

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Notes and references

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† Electronic Supplementary Information (ESI) available: I. Methods and Characterization; II. Bragg's formula of 1DPCs; III. The performance of angle dependence; IV. photograph of 1DPCs without pattern; V. The senor performance with pattern 'E & U'. See DOI: 10.1039/b000000x/

1 Y. Chen, A. Ebenstein, M. Greenstone and H. Li, *Proc. Natl. Acad. Sci.*, 2013, DOI:10.1073/pnas.1300018110.
2 Y. Zhao, X. Zhao and Z. Gu, *Adv. Funct. Mater.* 2010, **20**, 2970;
3 C. Chen, Y. Zhu, H. Bao, J. Shen, H. Jiang, L. Peng, X. Yang, C. Li and G. Chen, *Chem. Commun.*, 2011, **47**, 5530.
4 J. Ge and Y. Yin, *Angew Chem. Int. Edit.*, 2011, **50**, 1492.
5 Z. Wang, J. Zhang, J. Xie, C. Li, Y. Li, S. Liang, Z. Tian, T. Wang, H. Zhang, H. Li, W. Xu and B. Yang, *Adv. Funct. Mater.*, 2010, **20**, 3784; E. Tian, J. Wang, Y. Zheng, Y. Song, L. Jiang and D. Zhu, *J. Mater. Chem.,* 2008, **18**, 1116.
6 W. Hong, Y. Chen, X. Feng, Y. Yan, X. Hu, B. Zhao, F. Zhang, D. Zhang, Z. Xu and Y. Lai, *Chem. Commun.*, 2013, **49**, 8229.
7 Z. Xie, K. Cao, Y. Zhao, L. Bai, H. Gu, H. Xu and Z.-Z. Gu, *Adv. Mater.*, 2013, DOI:10.1002/adma.201304775; A. M. Ruminski, M. M. Moore and M. J. Sailor, *Adv. Funct. Mater.*, 2008, **18**, 3418.
8 J. R. Askim, M. Mahmoudi and K. S. Suslick, *Chem. Soc.Rev.*, 2013, **42**, 8649.
9 A. Stein, B. E. Wilson and S. G. Rudisill, *Chem. Soc.Rev.*, 2013, **42**, 2763.
10 Y. Zhao, Z. Xie, H. Gu, C. Zhu and Z. Gu, *Chem. Soc.Rev,* 2012, **41**, 3297;
11 L. Wang, J. Wang, Y. Huang, M. Liu, M. Kuang, Y. Li, L. Jiang and Y. Song, *J. Mater. Chem.* 2012, **22**, 21405.
12 J. Zhang and B. Yang, *Adv. Funct. Mater.*, 2010, **20**, 3411.
13 B. Ye, F. Rong, H. Gu, Z. Xie, Y. Cheng, Y. Zhao and Z. Gu, *Chem. Commun.*, 2013, **49**, 5331.
14 H. Li, J. Wang, Z. Pan, L. Cui, L. Xu, R. Wang, Y. Song and L. Jiang, *J. Mater. Chem.*, 2011, **21**, 1730; K. Liu, H. Yi, A. A. Kosterev, W. Chen, L. Dong, L. Wang, T. Tan, W. Zhang, F. K. Tittel and X. Gao, *Rev. Sci. Instrum.*, 2010, **81**, 103103; Y. Huang, F. Li, M. Qin, L. Jiang and Y. Song, *Angew Chem. Int. Edit.*, 2013, **52**, 7296.

15 Z. Wang, J. Zhang, J. Xie, Y. Yin, Z. Wang, H. Shen, Y. Li, J. Li, S. Liang, L. Cui, L. Zhang, H. Zhang and B. Yang, *ACS Appl. Mater. Interfaces,* 2012, **4**, 1397.

16 S. Colodrero, M. Ocana and H. Miguez, *Langmuir*, 2008, **24**, 4430; L. D. Bonifacio, B. V. Lotsch, D. P. Puzzo, F. Scotognella and G. A. Ozin, *Adv. Mater.*, 2009, **21**, 1641;

17 M. C. Chiappelli and R. C. Hayward, *Adv. Mater.*, 2012, **24**, 6100;E. Redel, C. Huai, M. Renner, G. von Freymann and G. A. Ozin, *Small*, 2011, **7**, 3465.

18 C. Liu, G. Gao, Y. Zhang, L. Wang, J. Wang and Y. Song, *Macromol. Rapid Commun.*, 2012, **33**, 380.

19 C. O. Baker, B. Shedd, P. C. Innis, P. G. Whitten, G. M. Spinks, G. G. Wallace and R. B. Kaner, *Adv. Mater.*, 2008, **20**, 155; H. Tai, Y. Jiang, G. Xie, J. Yu, X. Chen and Z. Ying, *Sens. Actuators, B,* 2008, **129**, 319.

20 M. Gerard, A. Chaubey and B. D. Malhotra, *Biosens. Bioelectron.*, 2002, **17**, 345; M. K. Ram, Ö. Yavuz, V. Lahsangah and M. Aldissi, *Sens. Actuators, B*, 2005, **106**, 750.

21 J. Ge, J. Goebl, L. He, Z. Lu and Y. Yin, *Adv. Mater.*, 2009, **21**, 4259.

22 R. Ganesan and A. Gedanken, *Nanotechnology*, 2008, **19**, 435709; H. Zhang, R. Zong, J. Zhao and Y. Zhu, *Environ. Sci. Technol.*, 2008, **42**, 3803.

23 A. G. MacDiarmid, *Angew Chem. Int. Edit.*, 2001, **40**, 2581.

