

DOI:10.1002/ejic.201300053

(Pyrenetetrasulfonate/ZnS)_n Ordered Ultrathin Films with ZnAl Layered Double Hydroxide as Precursor and Ethanol-Sensing Properties

Ya-Ping Xiao,^[a] Li-Min Zhang,^[a] Ying Guo,^{*[a]} and Yu-Fei Song^{*[a]}

Keywords: Thin films / Nanostructures / Sensors / Layered compounds / Double hydroxides / Zinc / Aluminum

Well-ordered ultrathin films (UTFs) of {pyrenetetrasulfonate(PyTS)/ZnS}_n were fabricated by alternating assembly of 1,3,6,8-PyTS and exfoliated Zn₂Al layered double hydroxide (LDH) nanosheets through layer-by-layer (LBL) electrostatic deposition, followed by an effective in situ gas/solid sulfurization reaction with H₂S. The assembly process was monitored by UV/Vis spectroscopy, which showed regular stepwise growth of the (PyTS/LDH)_n UTFs with consecutive deposition cycles. It is worth noting that the structure of the well-ordered UTFs is retained after the in situ gas/solid sulf-

urization reaction. Although both (PyTS/LDH)_n UTFs and the sulfurized (PyTS/ZnS)_n UTFs respond to ethanol at a relatively low operating temperature (70 °C), the (PyTS/ZnS)_n UTFs exhibit a much better response, a fact that can be attributed to synergistic interactions between inorganic ZnS and organic pyrene components. Moreover, the well-ordered (PyTS/ZnS)₃₀ UTF exhibits a stronger sensor response to ethanol than to other gases, including NH₃, H₂, CO, C₂H₂, and CH₄.

Introduction

Ethanol sensors are used in industry to detect alcohol leaks and to evaluate wine quality and monitor food safety, amongst other applications.^[1] Sensors for detecting ethanol gas quickly and accurately are much needed. The ethanol sensors currently used are based on metal oxides. However, one significant disadvantage of metal oxide semiconductor gas sensors is that the devices need to be operated at high temperature in order to achieve satisfactory sensitivity and response time, which is dangerous in practical applications.^[2] With more and more strict requirements, the development of new ethanol-sensing systems with low operating temperatures has been a very active research field, in which organic-inorganic hybrid thin-film sensing materials are particularly attractive, since they can be well controlled at a monolayer level as miniaturized devices with low cost and low power consumption.^[3] Furthermore, in contrast to the individual organic and inorganic components, such hybrid thin films could lower the working temperature and improve the long-term stability of the devices.^[4–7]

It is known that both pyrene-containing and ZnS-based materials have remarkable sensing properties as individual components. For instance, ZnS-based materials have been utilized as sensors for UV,^[8] volatile organic compounds,^[9] and ethanol;^[10] pyrene-based derivatives can be used as ion sensors and oxygen sensors, among other applications.^[11,12] Therefore, fabrication of hybrid thin films from a combination of organic pyrene and inorganic ZnS semiconductor could reasonably be expected to produce materials that benefit from synergistic interactions and show great potential in gas-sensing applications.

Layered double hydroxides (LDHs) are a class of anionic intercalated inorganic materials with a general formula of [M²⁺_{1-x}M³⁺_x(OH)₂][Aⁿ⁻_{x/n}mH₂O], in which M²⁺ and M³⁺ are divalent and trivalent metal cations respectively, and Aⁿ⁻ are the intercalated guest anions. LDHs have been widely utilized as catalysts, absorbents, anion exchangers, precursors, and magnets.^[13] In recent years, it has been demonstrated both that LDH ultrathin films (UTFs) can be fabricated by a layer-by-layer (LBL) assembly technique;^[14] and that Zn-containing LDHs can be used as templates for the generation of ZnS nanoparticles implanted in the host layers.^[15,16] In this paper, we describe how organic-inorganic (PyTS/ZnS)_n UTFs have been fabricated by LBL assembly of pyrenetetrasulfonate with the exfoliated Zn₂Al LDH to create (PyTS/LDH)_n UTFs, followed by in situ gas/solid sulfurization. Preliminary studies of gas-sensing behavior indicate that the resulting (PyTS/ZnS)_n UTFs show a highly selective response to ethanol at the relatively low working temperature of 70 °C.

[a] State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China
Fax: +86-10-64431832
E-mail: guoying@mail.buct.edu.cn
songyufei@hotmail.com

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ejic.201300053>.

Results and Discussion

The multilayer assembly processes of the (PyTS/LDH)_n UTFs were monitored by UV/Vis spectroscopy after each deposition cycle (Figure 1). It can be observed that the absorption bands assigned to the π–π* transition of pyrene at 247, 277, and 387 nm^[11] increase linearly with successive deposition cycles, indicating stepwise and regular film growth.

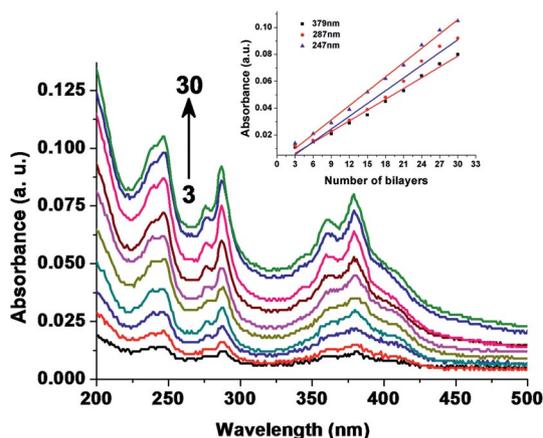


Figure 1. UV/Vis absorption spectra of (PyTS/LDH)_n ($n = 3$ –30) UTFs.

The in situ gas/solid sulfurization of (PyTS/LDH)_n UTFs leads to the formation of the corresponding (PyTS/ZnS)_n UTFs. It can be seen clearly from Figure 2 that the absorption bands of (PyTS/ZnS)_n UTFs are broader than those of (PyTS/LDH)_n UTFs and the absorption intensities are stronger. The apparent increase of the intensities below 300 nm is attributed to the formation of ZnS.^[17] The absorbance at 247, 277, and 387 nm increases linearly with the number of deposition cycles, suggesting that well-ordered thin films have been achieved after the sulfurization process.

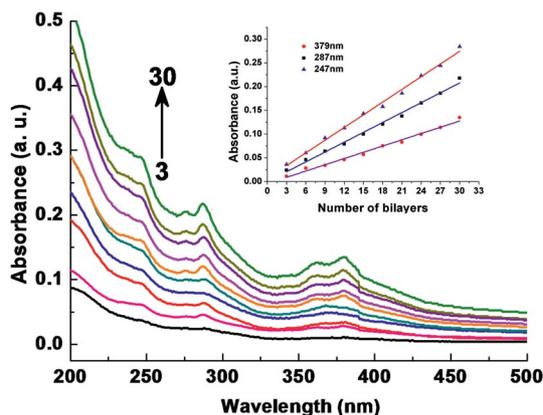


Figure 2. UV/Vis absorption spectra of (PyTS/ZnS)_n ($n = 3$ –30) UTFs.

Deposition cycle $n = 30$ was taken as an example. The gas-sensing behavior of the (PyTS/ZnS)₃₀ UTF for 100 ppm ethanol was investigated at 70 °C (Figure 3). The response to ethanol gas is defined as R_a/R_g , where R_a and R_g are the sensor resistances of the UTFs in air and in the target gas,

respectively. When the reductive ethanol gas is introduced, an electron-releasing process begins. The ethanol gas reacts with the surface oxygen species, leading to an increase in the R_a/R_g value (Figure 3). In contrast, an electron-capturing process starts when the (PyTS/ZnS)₃₀ UTF is exposed to air, and so the R_a/R_g value decreases. The maximum ethanol response for (PyTS/ZnS)₃₀ UTF is 5.0 at the operating temperature of 70 °C. It should be mentioned that the (PyTS/ZnS)₃₀ UTF is easy to handle given the relatively low working temperature applied here compared with those reported in the literature (Table S1).

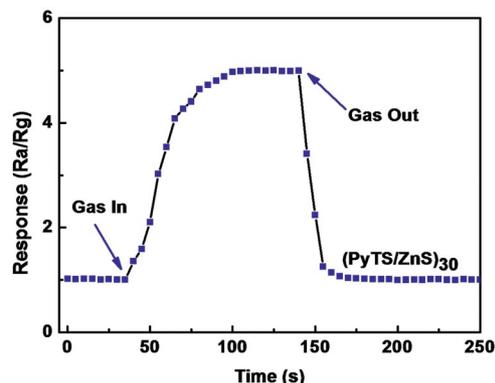


Figure 3. Response of the (PyTS/ZnS)₃₀ UTF to 100 ppm of ethanol at an operating temperature of 70 °C.

The response and recovery speeds are key parameters for the performance of sensing materials. For most low-operating-temperature sensing materials, response and recovery times are relatively long because of the materials' low activation energies at low temperature. In the current work, it is worth noting that the (PyTS/ZnS)₃₀ UTF responds quickly to ethanol gas; the response and recovery times are calculated to be 50 s and 16 s, respectively, which indicate that (PyTS/ZnS)₃₀ UTF is potentially a good candidate for detecting ethanol.

The relationship between the gas-sensing response and the operating temperature was investigated further with (PyTS/LDH)₂₄, (PyTS/LDH)₃₀, (PyTS/ZnS)₂₄, and (PyTS/ZnS)₃₀ UTFs as examples. The ethanol response values for these UTFs were found to grow at first before reaching a maximum value, after which all the ethanol response values start to drop (Figure 4). This phenomenon can be explained by the fact that the ethanol response is related to the chemisorbed oxygen species, and the concentration of chemisorbed oxygen would increase when the operating temperature increases.^[18] Nevertheless, the desorption process of the adsorbed oxygen dominates until the operating temperature reaches a certain point. In other words, the ethanol response has a maximum value at an optimal operating temperature. As shown in Figure 4, the optimal operating temperature for the above UTFs is 70 °C. It should be emphasized that this is a very mild operating temperature.

When the ethanol response values for the above four UTFs are compared, it can be seen that the sulfurized (PyTS/ZnS)_n ($n = 24, 30$) UTFs are more responsive than the corresponding (PyTS/LDH)_n ($n = 24, 30$) UTFs below

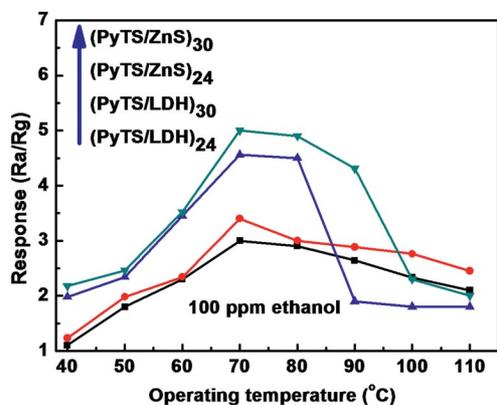


Figure 4. Responses vs operating temperatures of (PyTS/LDH)_n (*n* = 24, 30) UTFs and (PyTS/ZnS)_n (*n* = 24, 30) UTFs exposed to 100 ppm ethanol.

80 °C. This is because, when the UTFs are surrounded by air, oxygen molecules are adsorbed on the film surfaces to form the chemisorbed oxygen species (O²⁻, O₂²⁻, and O⁻) by capturing electrons from the conduction band of the UTFs. In the (PyTS/LDH)₃₀ UTF, the oxygen is mainly adsorbed by the PyTS molecules alone. In contrast, in the (PyTS/ZnS)₃₀ UTF both ZnS and PyTS molecules can adsorb the oxygen; the (PyTS/ZnS)_n UTFs provide ZnS as active sites for adsorbing oxygen species in addition to the PyTS molecules, unlike (PyTS/LDH)_n UTFs. Moreover, ZnS has fertile trapped surface states,^[10,19] which can accelerate the adsorption of oxygen species from the surroundings and the depletion of free electrons from the conduction band in the (PyTS/ZnS)₃₀ UTF, resulting in an improved response to ethanol. Once the reductive ethanol gas is introduced, it reacts with the ionic oxygen species, and then the electrons that had been trapped by the chemisorbed oxygen species are released back to the UTFs, increasing the conductivity of the UTFs and thus elevating the response to ethanol. The surface states of the (PyTS/ZnS)₃₀ UTF therefore play an important role in the contact and subsequent reaction with oxygen species. In addition, the coexistence of ZnS and PyTS may have a synergistic effect in ethanol sensing.

Figure 5 describes the correlation between the ethanol gas concentration and the ethanol responses of four UTFs at 70 °C. As gas concentration increases, the responses of all four UTFs increase remarkably. These UTFs respond even at concentrations as low as 10 ppm. Moreover, with the increase in the number of assembled layers from 24 to 30, ethanol response increases accordingly. The possibility of improving the ethanol response by increasing the number of layers of the UTFs therefore seems very promising.

The selectivity of a chemical sensor is an important factor for practical consideration. It can be observed that the (PyTS/ZnS)₃₀ UTF exhibits a strong response to ethanol, but a low response to NH₃, H₂, CO, C₂H₂, and CH₄ at the same concentration of 100 ppm at 70 °C (Figure 6), indicating that the (PyTS/ZnS)₃₀ UTF is a good candidate for highly selective detection of ethanol.

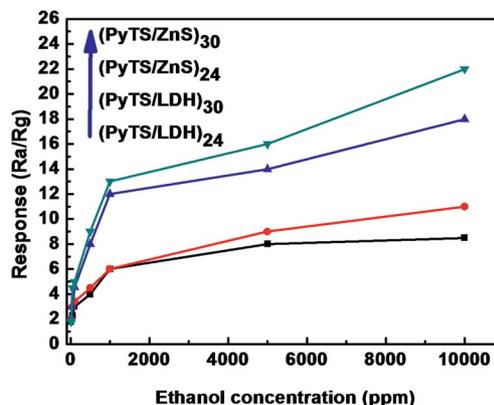


Figure 5. Responses of (PyTS/LDH)_n (*n* = 24, 30) and (PyTS/ZnS)_n (*n* = 24, 30) UTFs to different concentrations of ethanol.

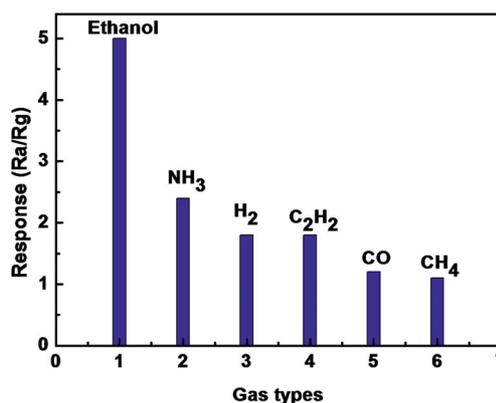


Figure 6. Responses of the (PyTS/ZnS)₃₀ UTF to 100 ppm of different gases at a working temperature of 70 °C.

Conclusions

(PyTS/ZnS)_n UTFs were fabricated through the sulfuration of (PyTS/LDH)_n UTFs, which in turn were prepared by alternating LBL assembly of Zn₂Al LDH and pyrenetetrasulfonate. The resulting (PyTS/ZnS)_n UTFs respond to ethanol gas at the low operating temperature of 70 °C. Moreover, the well-ordered (PyTS/ZnS)₃₀ UTF exhibits a stronger sensor response to ethanol than to other gases including NH₃, H₂, CO, C₂H₂, and CH₄. It can be concluded that the presence of the ZnS improves the ethanol response of the (PyTS/ZnS)_n (*n* = 24, 30) UTFs, which may be attributed to synergistic interactions between inorganic ZnS and organic pyrene components.

Experimental Section

Materials and Methods: Zn₂Al-NO₃ LDH (0.1 g) was shaken in a formamide solution (100 mL) for 24 h to produce a colloidal suspension of exfoliated Zn₂Al-NO₃ LDH nanosheets. The quartz glass substrates were first cleaned in concentrated NH₃/30% H₂O₂ and concentrated H₂SO₄, and then dipped in the colloidal suspension of LDH nanosheets for 10 min and treated with an aqueous solution of 1,3,6,8-pyrenetetrasulfonate (PyTS, 100 mL, 0.025 wt.-%) for another 10 min. The two procedures were repeated alternately for *n* cycles to fabricate (PyTS/LDH)_n UTFs. After each pro-

cedure, the quartz substrates were washed thoroughly with deionized water. The resulting films were dried under nitrogen gas flow at ambient temperature. Afterwards, the (PyTS/LDH)_n UTFs obtained were sealed into a glass vessel, which was evacuated before excess H₂S was injected into the vessel. The sulfurization reaction was allowed to continue for 2 h at room temperature, resulting in the formation of the thin films of (PyTS/ZnS)_n.

Ethanol-Gas-Sensing Measurement: The gas sensing properties were measured using a CGS-1TP intelligent gas-sensing analysis system (Beijing Elite Tech. Co. Ltd., China).

Supporting Information (see footnote on the first page of this article): XRD patterns and FT-IR spectra of Zn₂Al-CO₃ and Zn₂Al-NO₃, ethanol-sensing sensitivity compared with other references.

Acknowledgments

This project was supported by the National Natural Science Foundation of China (NSFC) (grant numbers 21001014, 21076020), Beijing Natural Science Foundation (grant number 2113049), the program for New Century Excellent Talents of the Ministry of Education of China (grant number NCET-09-0201), the Beijing Nova Program (grant number 2009B12), and Fundamental Research Funds for the Central Universities (grant number QN0908, ZZ1227).

- [1] D. R. Kauffman, A. Star, *Angew. Chem.* **2008**, *120*, 6652–6673; *Angew. Chem. Int. Ed.* **2008**, *47*, 6550–6570.
- [2] G. Xie, P. Sun, X. Yan, X. Du, Y. Jiang, *Sens. Actuators B* **2010**, *145*, 373–377.
- [3] N. Chaniotakis, N. Sofikiti, *Anal. Chim. Acta* **2008**, *615*, 1–9.
- [4] H. Tai, Y. Jiang, G. Xie, J. Yu, X. Chen, *Sens. Actuators B* **2007**, *125*, 644–650.
- [5] J. Zhang, S. Wang, M. Xu, Y. Wang, H. Xia, S. Zhang, X. Guo, S. Wu, *J. Phys. Chem. C* **2009**, *113*, 1662–1665.
- [6] K. Hosono, I. Matsubara, N. Murayama, S. Woosuck, N. Izu, *Chem. Mater.* **2005**, *17*, 349–354.
- [7] M. K. Ram, O. Yavuz, V. Lahsangah, M. Aldissi, *Sens. Actuators B* **2005**, *106*, 750–757.
- [8] X. Fang, Y. Bando, M. Liao, T. Zhai, U. K. Gautam, L. Li, Y. Koide, D. Golberg, *Adv. Fun. Mater.* **2010**, *20*, 500–508.
- [9] M. Hasani, A. M. Coto García, J. M. Costa-Fernández, A. Sanz-Medel, *Sens. Actuators B* **2010**, *144*, 198–202.
- [10] L. Xu, H. Song, T. Zhang, H. Fan, L. Fan, Y. Wang, B. Dong, X. Bai, *J. Nanosci. Nanotechnol.* **2011**, *11*, 2121–2125.
- [11] M. Li, P. Xu, J. Yang, H. Ying, K. Haubner, L. Dunsch, S. Yang, *J. Phys. Chem. C* **2011**, *115*, 4584–4593.
- [12] L. Ding, Y. Fang, *Chem. Soc. Rev.* **2010**, *39*, 4258–4273.
- [13] a) D. G. Evans, X. Duan (Eds.), *Structure and Bonding*, vol. 119, *Layered Double Hydroxides* (Series Ed.: D. M. P. Mingos), Springer, Berlin, Heidelberg, **2006**; b) J. H. Choy, S.-Y. Kwak, Y.-J. Jeong, J. S. Park, *Angew. Chem.* **2000**, *112*, 4207–4211; *Angew. Chem. Int. Ed.* **2000**, *39*, 4041–4045; c) Q. Wang, D. O'Hare, *Chem. Rev.* **2012**, *112*, 4124–4155.
- [14] Z. Liu, R. Ma, M. Osada, N. Iyi, Y. Ebina, K. Takada, T. Sasaki, *J. Am. Chem. Soc.* **2006**, *128*, 4872–4880.
- [15] Y. Guo, H. Zhang, Y. Wang, Z. L. Liao, G. D. Li, J. S. Chen, *J. Phys. Chem. B* **2005**, *109*, 21602–21607.
- [16] X. Xu, R. Lu, X. Zhao, S. Xu, X. Lei, F. Zhang, D. G. Evans, *Appl. Catal. B* **2011**, *102*, 147–156.
- [17] X. J. Zheng, Y. Q. Chen, T. Zhang, B. Yang, C. B. Jiang, B. Yuan, Z. Zhu, *Sens. Actuators B* **2010**, *147*, 442–446.
- [18] Z. Chen, M. Cao, C. Hu, *J. Phys. Chem. C* **2011**, *115*, 5522–5529.
- [19] L. Fan, H. Song, H. Zhao, G. Pan, H. Yu, X. Bai, S. Li, Y. Lei, Q. Dai, R. Qin, T. Wang, B. Dong, Z. Zheng, X. Ren, *J. Phys. Chem. B* **2006**, *110*, 12948–12953.

Received: January 16, 2013
Published Online: May 17, 2013