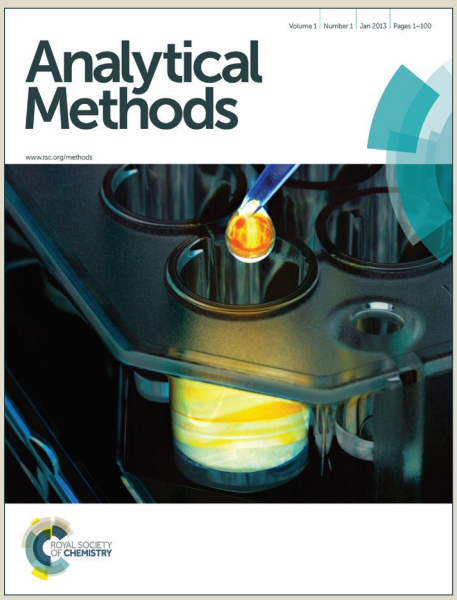
Analytical Methods

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/methods

A new cataluminescence-based gas sensor for simultaneously discriminating benzene and ammonia

Huizhen Fan[1] Zhaokuai Peng[1,2] Hongwei Yang[1,2] Kaowen Zhou[1,2*]

[1] Biochemical Engineering College, Beijing Union University, Beijing 100023, China

[2] Beijing Key Laboratory of Biomass Waste Resource Utilization, Beijing 100023, China

E-mail: zhoukaowen@buu.edu.cn

Abstract

An efficient method based on cross cataluminescence (CTL) on nano-$Bi_4SnV_2O_{13}$ was proposed for simultaneously discriminating benzene and ammonia in air. The experimental conditions meeting the algebraic sum rule of the CTL intensities of benzene and ammonia were sought. They are two analysis wavelengths of 475 nm and 550 nm, the surface temperature of sensing materials of 150 □ and the flow rate of air carrier of 250 mL/min. The limits of detection of this method were 0.12 mg/m^3 for benzene and 0.21 mg/m^3 for ammonia. The linear ranges of CTL intensity versus analyte concentration were 0.2～66.3 mg/m^3 for benzene and 0.4～81.7 mg/m^3 for ammonia. The recoveries of 10 testing standard samples by this method were 97.1%～102.2% for benzene and 97.6%～103.1% for ammonia. Common coexistence matters, such as toluene, ethylbenzene, methylamine, ethylamine, formaldehyde, acetaldehyde, methanol, ethanol, sulfur dioxide and carbon dioxide, did not disturb the determination. The relative deviation (RD) of CTL signals of continuous 120 h detection for gaseous mixture containing benzene and ammonia was less than 2%, which demonstrated the longevity and steady performance of nano-$Bi_4SnV_2O_{13}$ to benzene and ammonia.

Keywords: Benzene, Ammonia, Cross cataluminescence, Gas sensor

1. Introduction

People spend much of their time indoors where they are continuously exposed to low concentrations of a wide variety of air pollutants. Benzene and ammonia are two of the most common indoor air pollutants [1-3]. The main sources of benzene in air are exhaust gas of motor vehicles, the use of paints and glues, the combustion of wood, the fermentation of organic wastes, and smoking of cigarette [4]. Ammonia in indoor air is considered to release mainly due to hydrolysis of urea which may be present in antifreeze additives of concrete buildings in wintertime [5].

Benzene, classified as known human carcinogen by International Agency for Research on Cancer (IARC), can induce oxidative stress which may affect insulin resistance (IR). As a physiological condition comprising an inadequate response to insulin, IR plays a key role in the pathogenic pathways involved in metabolic syndrome, diabetes mellitus (DM), cardiovascular disease, and obesity [6,7]. Ammonia can strongly stimulate the respiratory tract, eye and skin. Prolonged exposure to ammonia, even if low concentration, can cause serious health effects, such as rhinitis, nasopharyngitis, pharyngitis, tracheitis, bronchitis and other inflammation of different types and levels [8].

Various methods were applied to determine benzene [9-14] or ammonia [15-20]. Fast and simple methods were becoming increasingly important [21-27]. There is no report on the simultaneous determination of benzene and ammonia and their cross interference in the literature.

Cataluminescence (CTL) is an emission of electromagnetic radiation produced by catalytic oxidation reactions that yield excited intermediates which can emit rays on falling to the ground state on the surface of catalyst [28]. CTL spectra from different reactions are different, so they can be taken as the basis of analysis. Now, CTL has been considered as a promising energy transduction mechanism for fabricating gas sensor because of its outstanding advantages such as long life, easy miniaturization, fast response, needless luminescent reagent, and etc. In recent years, a series of CTL analytical applications have been attempted to develop for a variety of gaseous molecules by either exclusive sensor or sensor array [29-50].

Utilizing more information in the CTL spectral profile is favorable to monitor multi-component gas. So, we firstly proposed to identify different molecules on single sensitive material [51, 52]. Benzene and formaldehyde, for example, were determined on nano-

$Ti_3Bi_2V_2O_{14}$ by their cross sensitivities at two peak wavelengths where the CTL intensities were higher than other wavelengths [51]. In the same vein, however, the process determining benzene and ammonia on nano-$Bi_4SnV_2O_{13}$ was unusable on account of intolerable error. In-depth study, we found that the algebraic sum rule is applicable to the CTL intensities of benzene and ammonia at partial wavelengths and right temperatures.

In this work, we firstly screened out a desired catalyst with satisfying activity and selectivity for both benzene and ammonia, and then sought the experimental conditions that could meet the algebraic sum rule of the CTL intensities of benzene and ammonia, and finally established a calculable method for determining benzene and ammonia by utilizing their cross sensitivity that used to be thought of intractable defect.

2. Experimental

2.1. Chemical reagents and materials

All reagents used were of analytical grade without further purification. Bismuth acetate, ethyl acetate, stannic chloride, ammonium meta-vanadate, nitric acid and citric acid were purchased from Beijing Chemical Regent Co., LTD. (Beijing, China). Various calibrating gas of benzene, ammonia, toluene, ethyl benzene, methylamine, ethylamine, formaldehyde, acetaldehyde, methanol, ethanol, sulfur dioxide, carbon dioxide and their mixture in nitrogen were purchased from Beijing Ya-nan Gas Co., LTD. (Beijing, China). Distilled water was used throughout the whole experiment.

2.2. Preparation of sensing materials

In order to probe into the efficiencies of different sensing materials in the catalytic oxidation of benzene and ammonia, a great deal of nanosized materials were prepared. The procedure for synthesis of nano-$Bi_4SnV_2O_{13}$ by means of a sol-gel method was as follows: bismuth acetate was dissolved in methanol at room temperature, then 2:1 (v/v) ethyl acetate and distilled water were slowly added into the solution, and Bi sol was formed by continuously stirring the solution more than 10 h. At the same time, stannic chloride and ammonium meta-vanadate were dissolved in 1 mol/L nitric acid solution and then citric acid was added into the solution. This mix solution was added into Bi sol above, and Bi-Sn-V gel was formed after stirring for 4 h at room temperature. The atom ratio of Bi:Sn:V was 4:1:2. This gel was subjected to aging for 12 h at room temperature, drying for 2 h at 105℃, cooling to room temperature, rubbing, and roasting for 3 h at 328℃, successively, to finally get

nano-$Bi_4SnV_2O_{13}$. The TEM photograph in Figure 1 shows that the average granular size was about 20 nm.

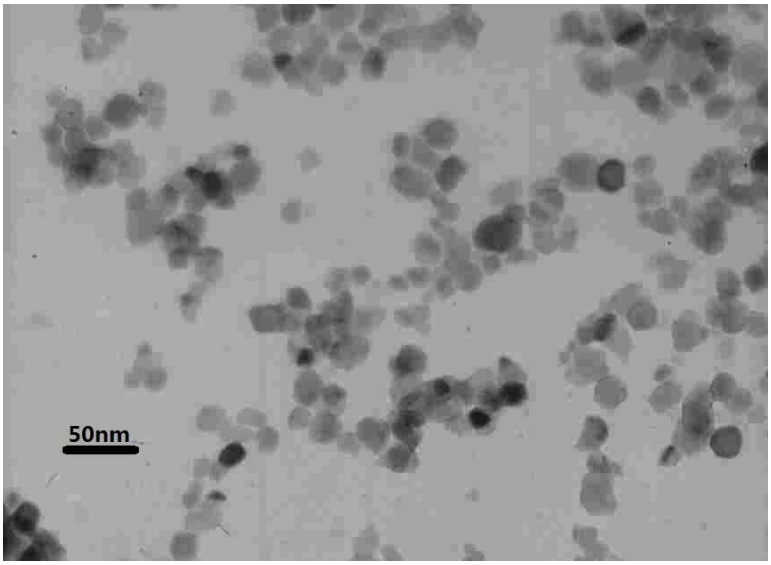


Figure 1 TEM photo of nano- $Bi_4SnV_2O_{13}$

2.3. CTL system

The self-designed dual wavelength CTL system used in this work is shown in Figure 2. The system, an improvement from references [50, 51], mainly includes four parts. They are (1) CTL reactor (a cylindrical ceramic heater of 5 mm in diameter sintered a thickness of 0.08-0.15 mm sensing materials was placed in the middle of a quartz tube of 10mm in diameter possessing gas entrance-exit), (2) temperature controller (the surface temperature of ceramic heater can be adjusted from room temperature to 550□), (3) optical filter (transitable rays can be selected from 400 nm to 745 nm), and (4) weak luminescence analyzer (CTL singles can be processed by photo multiplier, photons counter and computer).

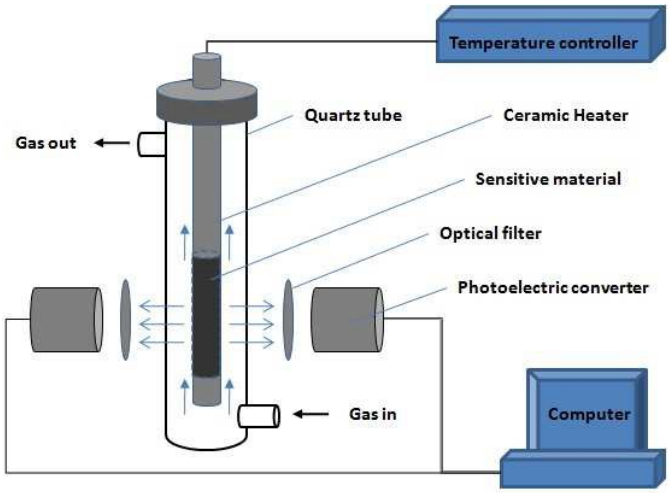


Figure2 Schematic diagram of the dual wavelength CTL system

2.4. Procedures

The gaseous samples are directly introduced through CTL reactor through entrance by air as carrier. Benzene and ammonia in air are selectively oxidized on the surface of sensitive materials at a certain temperature. The luminescence intensities passing through two optical filters are respectively recorded by a BPCL ultra-weak luminescence analyzer (Institute of Biophysics, Chinese Academy of Sciences, Beijing, China). Each CTL signal is a difference value of sample signal and background signal. At the beginning of experiment, every sensitive material is heated at roasting temperature for 30min in pure air to avoid the influence of previous absorbates.

3. Results and discussion

3.1. Selection of sensing materials

CTLs of benzene, toluene, ethyl benzene, ammonia, methylamine, ethylamine, formaldehyde, acetaldehyde, methanol, and ethanol can be observed on the surface of nano-TiO_2, and their spectra are obviously different. Further studies found that composite of two or three oxides frequently showed higher luminescence intensity and better selectivity to benzene and ammonia than single ones. The highest CTL intensity and the best selectivity for benzene and ammonia were obtained on $Bi_4SnV_2O_{13}$ in our experiments. Some results are shown in Table 1.

Table 1 Effect of some nanosized materials on the CTL intensity and selectivity

Nanosized Materials	Relative CTL intensity of different gas molecule(25mg/m^3)						Selected conditions
	Benzene	Ammonia	Toluene	Methylamine	Formaldehyde	Ethanol	
$2Bi_2O_3$-SnO_2-V_2O_5	3313	757	29	19	32	28	475 nm, 150 ºC
Bi_2O_3-$2SnO_2$-V_2O_5	2903	719	120	55	268	363	475 nm, 180 ºC
Bi_2O_3-SnO_2-$2V_2O_5$	2833	635	237	293	154	133	475 nm, 160 ºC
Bi_2O_3-SnO_2-V_2O_5	2782	661	57	281	95	180	475 nm, 153 ºC
Bi_2O_3-SnO_2	1374	848	651	764	878	437	480 nm, 265 ºC
SnO_2-V_2O_5	1191	912	533	617	336	451	420 nm, 312 ºC
SnO_2	614	858	582	522	414	309	515 nm, 408 ºC
$2Bi_2O_3$-SnO_2-V_2O_5	918	2224	15	21	19	17	550 nm, 150 ºC
Bi_2O_3-$2SnO_2$-V_2O_5	765	2172	247	81	71	415	550 nm, 180 ºC
Bi_2O_3-SnO_2-$2V_2O_5$	711	2109	273	715	322	91	550 nm, 160 ºC
Bi_2O_3-SnO_2-V_2O_5	726	1861	56	698	118	216	550 nm, 153 ºC
Bi_2O_3-SnO_2	646	1594	583	617	287	318	565 nm, 265 ºC
SnO_2-V_2O_5	560	1672	327	546	374	302	535 nm, 312 ºC
SnO_2	545	1036	514	439	509	581	605 nm, 408 ºC

3.2. The CTL spectrum

The CTL spectra of benzene and ammonia on various sensing materials were different. Figure 3 showed CTL spectra of 5 mg/m^3 benzene, 5 mg/m^3 ammonia and the mixture

containing 5 mg/m^3 benzene and 5 mg/m^3 ammonia in air with flow rate of 250 ml/min on nanosized $Bi_4SnV_2O_{13}$ at 150□. The CTL intensities were higher at 450 nm for benzene and at 550 nm for ammonia than other wavelength. The measurements of the mixed vapor of benzene and ammonia were almost consistent with the algebraic summation of benzene and ammonia at wavelengths longer than 475 nm, but they did not coincide at wavelengths shorter than 475 nm. This means that different luminescent species emit CTL at the longer and shorter wavelengths, and the observation at wavelengths longer than 475 nm is preferable for the CTL-based sensor because the algebraic sum rule is applicable to the CTL intensities of benzene and ammonia in air. The wavelengths of 475 nm and 550 nm, therefore, were chosen as analysis wavelengths for the determination of benzene and ammonia.

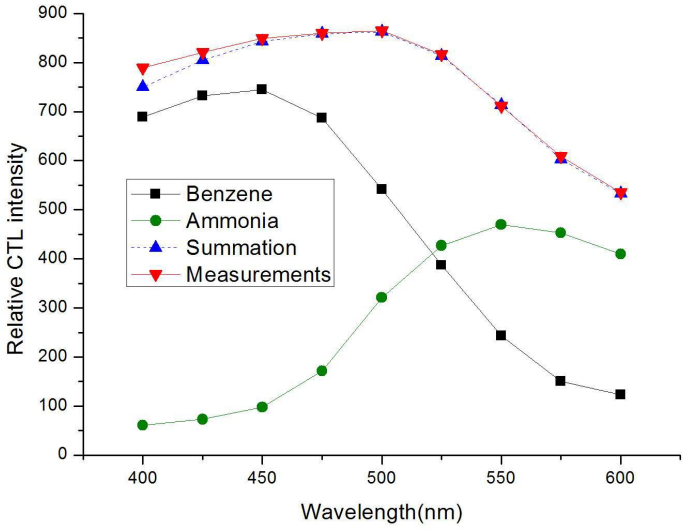


Figure 3 CTL spectra of benzene, ammonia and their mixture on nano- $Bi_4SnV_2O_{13}$

3.3. Interference studies

Besides benzene and ammonia, other pollutants, such as toluene, ethyl benzene, methylamine, ethylamine, formaldehyde, acetaldehyde, methanol, ethanol, sulfur dioxide and carbon dioxide, are often evolved in air. The luminescent signals of 25 mg/m^3 various analyte in air were respectively investigated at 475 nm and 550 nm on nano- $Bi_4SnV_2O_{13}$ at 150℃. The results were shown in Figure 4.

At 475 nm, the luminescent signals from benzene were much larger than from other molecules. The signals from ammonia was between quintile and quarter of benzene's, and from toluene, ethyl benzene, methylamine, ethylamine, formaldehyde, acetaldehyde, methanol,

and ethanol were less than 1% of benzene's. No visible signals were obtained from sulfur dioxide and carbon dioxide. At 550 nm, the luminescent signals from ammonia were much larger than from other molecules. The signals from benzene was about 41% of ammonia's, and from toluene, ethyl benzene, methylamine, ethylamine, formaldehyde, acetaldehyde, methanol, and ethanol were less than 1% of ammonia's. No visible signals were obtained from sulfur dioxide and carbon dioxide. That indicated that nano- $Bi_4SnV_2O_{13}$ had good selectivity for benzene and ammonia.

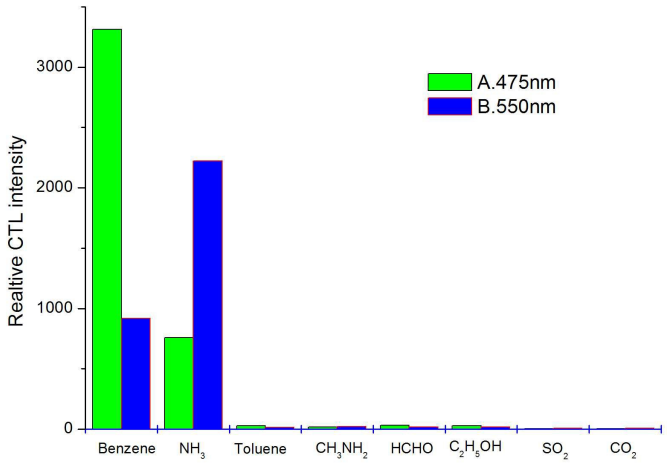


Figure 4 CTL responses of different gases on nano- $Bi_4SnV_2O_{13}$

3.4. Effect of surface temperature of nanosized-materials on the CTL intensity

Figure 5 shows the temperature dependences of the CTL intensity from 5 mg/m^3 benzene, 5 mg/m^3 ammonia and the mixture of 5 mg/m^3 benzene and 5 mg/m^3 ammonia in air at 475 nm under an air flow rate of 250 ml/min.

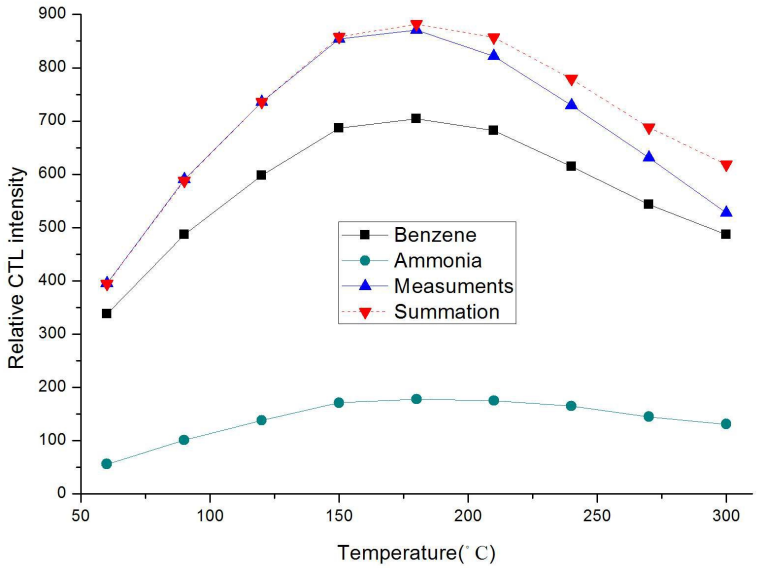


Fig. 5 Temperature dependence of the CTL intensity at 475 nm

As shown in Figure 5, the luminescent signals were much larger at 180 ℃ from benzene and at 150-240 ℃ from ammonia than other temperatures at 475 nm. The measurements of the mixed vapor of benzene and ammonia, however, were not consistent with the algebraic summation of benzene and ammonia at higher temperatures than 150 ℃. This means that the observation at the temperature no higher than 150 ℃ is preferable for the determination at 475 nm because the algebraic sum rule is applicable to the CTL intensities of benzene and ammonia in air at this wavelength.

Figure 6 shows the temperature dependences of the CTL intensity from 5 mg/m^3 benzene, 5 mg/m^3 ammonia and the mixture of 5 mg/m^3 benzene and 5 mg/m^3 ammonia in air at 550 nm under an air flow rate of 250 ml/min.

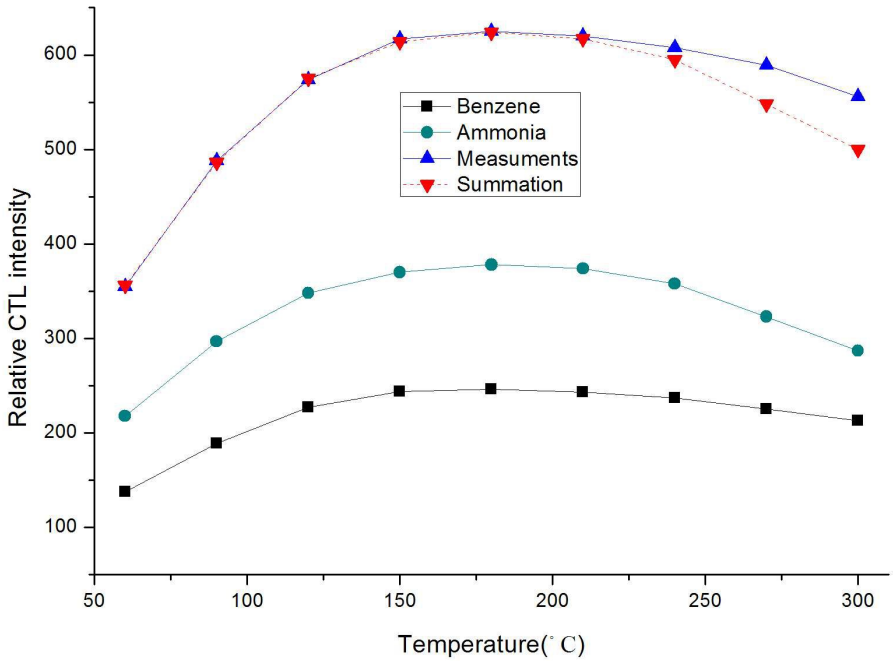


Figure 6 Temperature dependence of the CTL intensity at 550 nm

As shown in Fig. 6, the luminescent signals were much larger at 150-210 ℃ from benzene and at 150-240 ℃ from ammonia than other temperatures at 550 nm, and the measurements of the mixed vapor of benzen and ammonia were almost consistent with the algebraic summation of benzene and ammonia at temperatures no higher than 210 ℃. This means that the observation at 550 nm under the temperature no higher than 210 ℃ is preferable for the determination because the algebraic sum rule is also applicable to the CTL intensities of benzene and ammonia in air at this wavelength.

From the above, the algebraic sum rule is applicable to the CTL intensities of benzene and ammonia in air when the surface temperature of nanosized-materials no higher than 150℃ at both 475 nm and 550 nm. The temperature of 150℃, therefore, was chosen in following experiments. 150℃ can be thought of as a very low temperature in catalytic oxidation reaction and has a great advantage in transducer fabrication.

3.5. Effect of flow rate of carrier gas

Figure 7 shows the dependences of the CTL intensity from 1mg/m^3 benzene at 475 nm and from 1 mg/m^3 ammonia at 550 nm on flow rate of carrier gas at 150□. The CTL intensity from benzene increased with an increase in the flow rate below 150 ml/min, and it was strong and steady above this flow rate. The CTL intensity from ammonia steadied above 240 ml/min. They showed that the catalytic oxidation processes which produces the luminescent

intermediates are under a diffusion controlled condition at low flow rates and are under a reaction controlled condition at high flow rates for both benzene and ammonia [50]. The flow rate of 250 ml/min was chosen for the detection because strong and steady CTL signals could be obtained from both benzene and ammonia.

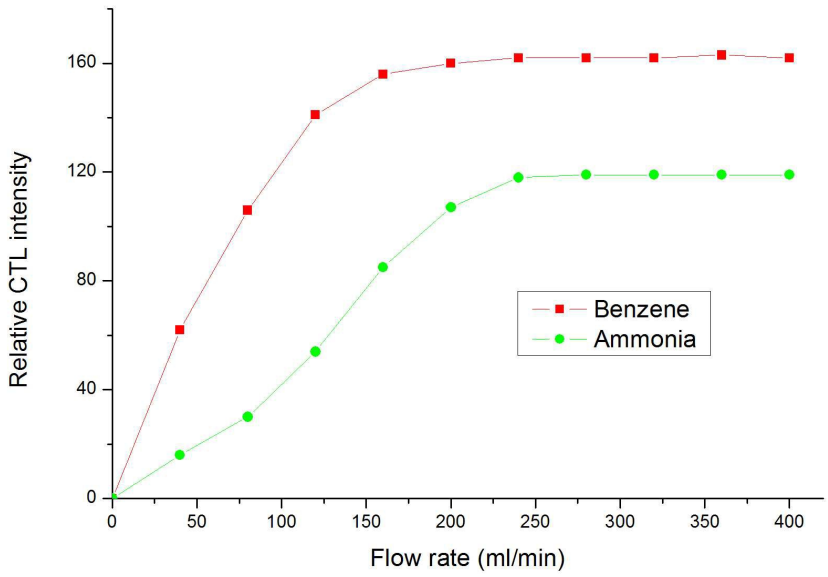


Figure 7 Effect of flow rate on CTL intensity

3.6. Lifetime test

To investigate the lifetime of the sensing materials $Bi_4SnV_2O_{13}$, an experiment was carried out by continually introducing the mixed gas containing 10 mg/m^3 benzene and 10 mg/m^3 ammonia with a flow rate of 250 ml/min to the surface of composite oxides at 150°C, and the CTL intensities were detected once every hour at 475 nm and 550 nm. The results showed that the relative deviation (RD) of CTL intensities was less than 3% for continuous 150 h detection. Further experiments showed that the RD of the CTL intensities was within 4% for daily use above 6 months. This result attested the long lifetime of $Bi_3SnV_2O_{13}$ for monitoring benzene and ammonia.

3.7. Performance of the gas sensor

The CTL intensities from standard gases of various concentrations of benzene and ammonia were respectively determined at 475 nm and 550 nm under the selected experimental conditions described above. Experiments found that both benzene and ammonia have good linear relations at two wavelengths. The regression equations, linear ranges and correlation coefficients are shown in Table 2. The TCL intensities of 12 repetitive tests from 1 mg/m^3 benzene at 475nm and 1 mg/m^3 ammonia at 550nm were respectively determined, and the detection limits (3σ) calculated following prescribed method from IUPAC were 0.12 mg/m^3 for benzene at 475 nm and 0.21 mg/m^3 for ammonia at 550 nm.

Table 2 The regression equation of benzene and ammonia

The total CTL intensity from a gaseous mixture containing benzene and ammonia at a certain wavelength was a superposition of respective CTL intensities from benzene and ammonia at this wavelength. The accurate concentrations of benzene and ammonia in air could be calculated by substituting the total CTL intensities at 475 nm and 550 nm into the equations as follows.

Analyte	Wavelength(nm)	Regression equation	Linear range (mg/m^3)	Correlation coefficient
Benzene	475	$I^{475}_{Benzene} = 131.3C_{Benzene} + 30.5$	0.20—87.5	0.9991
Benzene	550	$I^{550}_{Benzene} = 33.7C_{Benzene} + 75.1$	0.18—66.3	0.9989
Ammonia	475	$I^{475}_{Ammonia} = 29.3C_{Ammonia} + 24.8$	0.25—81.7	0.9985
Ammonia	550	$I^{550}_{Ammonia} = 87.7C_{Ammonia} + 31.3$	0.30—101.4	0.9990

$$I^{475} = I^{475}_{\text{Benzene}} + I^{475}_{Ammonia} = 131.3C_{Benzene} + 29.3C_{Ammonia} + 55.3$$

$$I^{550} = I^{550}_{Benzene} + I^{550}_{Ammonia} = 33.7C_{Benzene} + 87.7C_{Ammonia} + 106.4$$

The linear ranges of CTL intensity versus analyte concentration were 0.2～66.3 mg/m^3 for benzene and 0.3～81.7 mg/m^3 for ammonia on the basis of Table 2.

4. Applications

In order to examine the reliability of the developed method, ten artificial air samples were analyzed. The samples were prepared by respectively adding various concentrations benzene and ammonia into clean air. The results are shown in Table 3. The recoveries of 97.1%~102.2% for benzene and 97.6%~103.1% for ammonia showed that the method of determining benzene and ammonia in air is reliable.

Table 3 Analysis results of benzene and ammonia in air samples

Sample number	Actual concentration (mg/m^3)		Testing concentration (mg/m^3)		Recovery(%)	
	Benzene	Ammonia	Benzene	Ammonia	Benzene	Ammonia
1	5.00	5.00	5.11	4.88	102.2	97.6
2	15.00	15.00	14.57	15.15	97.1	101.0
3	20.00	20.00	20.10	20.62	100.5	103.1
4	25.00	25.00	25.45	24.91	101.8	99.6
5	30.00	30.00	30.55	29.43	101.8	98.1
6	35.00	40.00	34.96	39.44	99.9	98.6
7	40.00	50.00	40.62	50.87	101.6	101.8
8	45.00	60.00	44.61	61.38	99.1	102.3
9	50.00	70.00	51.11	69.56	102.2	99.4
10	60.00	80.00	60.95	79.23	101.6	99.0

5. Conclusions

The present results demonstrated the feasibility to design a high performance gas sensor based on sole nano-material $Bi_4SnV_2O_{13}$ for simultaneously determining benzene and ammonia in air at two wavelengths by utilizing their cross sensitivity that used to be thought of intractable defect. The experimental conditions, under which the algebraic sum rule is applicable to the CTL intensities of benzene and ammonia in air, were determined. The method was successfully applied in analysis of benzene and ammonia in artificial air samples. This study provided a credible method for monitoring multi-component gas that is different from the past methods of multiple gas sensors array [34, 41, 42, 47].

Acknowledgements

This work was supported by Beijing Natural Science Foundation (Grant No.2152013), Key Projects of Science and Technology Plan from Beijing Municipal Education Commission of China (KZ201311417038), State 863 Projects (2014AA022002), National International Cooperation Projects (2014DFA61040) and Research Base Projects (Z141109004414002).

References

[1] M. Mascelloni, J.M. Delgado-Saborit, N.J. Hodges, R.M. Harrison, Study of gaseous benzene effects upon A549 lung epithelial cells using a novel exposure system, Toxicol. Lett. 237 (2015) 38–45.

[2] G. De Palma, M. Manno, Metabolic polymorphisms and biomarkers of effect in the biomonitoring of occupational exposure to low-levels of benzene: State of the art, Toxicol. Lett. 231 (2014) 194–204.

[3] N.T. Phan, K.H. Kim, Z.H. Shon, E.C. Jeon, K. Jung, N.J. Kim, Analysis of ammonia variation in the urban atmosphere, Atmos. Environ. 65 (2013) 177-185.

[4] Y.H. Choi, J.H. Kim, B.E. Lee, Y.C. Hong, Urinary benzene metabolite and insulin resistance in elderly adults, Sci. Total Environ. 482-483 (2014) 260-268.

[5] Q.J. Geng, Q.J. Guo, C.Q. Cao, Y.C. Zhang, L.T.Wang, Investigation into photocatalytic degradation of gaseous ammonia in CPCR, Ind. Eng. Chem. Res. 47 (2008) 4363-4368.

[6] F. Wang, C. Li, W. Liu, Y. Jin, Oxidative damage and genotoxic effect in mice caused by subchronic exposure to low-dose volatile organic compounds, Inhal. Toxicol. 25 (2013) 235–242.

[7] R.W. Stahlhut, E. van Wijngaarden, T.D. Dye, S. Cook, S.H. Swan, Concentrations of urinary phthalate metabolites are associated with increased waist circumference and insulin resistance in adult U.S. males, Environ. Health Persp. 115 (2007) 876–82.

[8] K.C. Miranda-Filho, G.L.L. Pinho, W. Wasielesky Jr., A. Bianchini, Long-term ammonia toxicity to the pink-shrimp Farfantepenaeus paulensis, Comp. Biochem. Phys. C 150 (2009) 377-382.

[9] N. Baimatova, J.A. Koziel, B. Kenessov, Quantification of benzene, toluene, ethylbenzene and o-xylene in internal combustion engine exhaust with time-weighted average solid phase microextraction and gas chromatography mass spectrometry, Anal. Chim. Acta 873 (2015) 38–50.

[10] J. Langejuergen, M. Allers, J. Oermann, A. Kirk, S. Zimmermann, Quantitative detection of benzene in toluene- and xylene-rich atmospheres using high-kinetic-energy ion mobility spectrometry (IMS), Anal. Chem. 86 (2014) 11841-11846.

[11] M. Tobiszewski, S. Tsakovski, V. Simeonov, J. Namieśnik, Multivariate statistical comparison of analytical procedures for benzene and phenol determination with respect to

their environmental impact, Talanta 130 (2014) 449–455.

[12] S. Zimmermann, F. Gunzer, Simultaneous detection of benzene and toluene using a pulsed ion mobility spectrometer, Sens. Actuators, B 188 (2013) 106-110.

[13] F.L. Meng, H.H. Li, L.T. Kong, J.Y. Liu, Z. Jin, W. Li, Y. Jia, J.H. Liu, X.J. Huang, Parts per billion-level detection of benzene using SnO_2/graphene nanocomposite composed of sub-6nm SnO_2 nanoparticles, Anal. Chim. Acta 736 (2012) 100-107.

[14] S.T. Hobson, S. Cemalovic, S.V. Patel, Preconcentration and detection of chlorinated organic compounds and benzene, Analyst 137 (2012) 1284-1289.

[15] B.M. Jayawardane, I.D. McKelvie, S.D. Kolev, Development of a gas-diffusion microfluidic paper-based analytical device (μPAD) for the determination of ammonia in wastewater samples, Anal. Chem. 87 (2015) 4621-4626.

[16] I. Timofeeva, I. Khubaibullin, M. Kamencev, A. Moskvin, A. Bulatov, Automated procedure for determination of ammonia in concrete with headspace single-drop micro-extraction by stepwise injection spectrophotometric analysis, Talanta 133 (2015) 34-37.

[17] K. Kolacinska, R. Koncki, A novel optoelectronic detector and improved flow analysis procedure for ammonia determination with Nessler's reagent, Anal. Sci. 30 (2014) 1019-1022.

[18] T. Fu, Silver sulfide-based sensor for the selective determination of ammonia at room temperature, Electrochim. Acta 121 (2014) 168-174.

[19] W.L. Yang, A.N. Zhu, J.B. Zhang, Y.J. Zhang, X.M. Chen, Y. He, L.M. Wang, An inverse dispersion technique for the determination of ammonia emissions from urea-applied farmland, Atmos. Environ. 79 (2013) 217-224.

[20] H. Chen, H.F. Li, J.M. Lin, Determination of ammonia in water based on chemiluminescence resonance energy transfer between peroxymonocarbonate and branched NaYF 4:Yb3+/Er3+ nanoparticles, Anal. Chem. 84 (2012) 8871-8879.

[21] W. Sha, S.W. Ni, C.H. Zheng, Development of cataluminescence sensor system for benzene and toluene determination, Sens. Actuators, B 209 (2015) 297–305.

[22] V.S. Vaishnav, S.G. Patel, J.N. Panchal, Development of ITO thin film sensor for detection of benzene, Sens. Actuators, B 206 (2015) 381–388.

[23] C. Murugan, E. Subramanian, D. P. Padiyan, Enhanced sensor functionality of in situ

synthesized polyaniline–SnO_2 hybrids toward benzene and toluene vapors, Sens. Actuators, B 205 (2014) 74-81.

[24] D. Rithesh Raj, S. Prasanth, T.V. Vineeshkumar, C. Sudarsanakumar, Ammonia sensing properties of tapered plastic optical fiber coated with silver nanoparticles/PVP/PVA hybrid, Opt. Commun. 340 (2015) 86-92.

[25] X.G. Li, N. Chen, S.W. Lin , J. Wang, J.W. Zhang, NiO-wrapped mesoporous TiO_2 microspheres based selective ammonia sensor at room temperature, Sens. Actuators, B 209 (2015) 729-734.

[26] Z.F. Zhu, J. J. Lu, M. I. G. S. Almeida, Q.S. Pu, S.D. Kolev, S.R. Liu, A microfabricated electroosmotic pump coupled to a gas-diffusion microchip for flow injection analysis of ammonia, Microchim. Acta 182 (2015) 1063-1070.

[27] C. Chen, L.X. Cai, B. Tan, Y.J. Zhang, X.D. Yang, J. Zhang, Ammonia detection by using flexible Lewis acidic sites in luminescent porous frameworks constructed from a bipyridinium derivative, Chem. Commun. 51 (2015) 8189-8192.

[28] M. Breysse, B. Claudel, L. Faure, M. Guenin, R.J. Williams, T. Wolkenstein, Chemiluminescence during the catalysis of carbon monoxide oxidation on a thoria surface, J. Catal. 45 (1976) 137–144.

[29] Q.H. Wang, B. Li, Y.H. Wang, Z.X. Shou, G.L. Shi,Sensitive and selective cataluminescence-based sensor system for acetone and diethyl ether determination, Luminescence 30 (2015) 318-324.

[30] W. Sha, S.W. Ni, C.H. Zheng, Development of cataluminescence sensor system for benzene and toluene determination, Sens. Actuators, B 209 (2015) 297-305.

[31] B.R. Zeng, L.C. Zhang, X.Y. Wan, H.J. Song, Y. Lv, Fabrication of α-Fe_2O_3/g-C_3N_4 composites for cataluminescence sensing of H_2S, Sens. Actuators, B 211 (2015) 370-376.

[32] Z.H. Li, W. Xi, C. Lu, Hydrotalcite-supported gold nanoparticle catalysts as a low temperature cataluminescence sensing platform, Sens. Actuators, B 219 (2015) 354-360.

[33] L.C. Zhang, H.J. Song, Y.Y. Su, Y. Lv, Advances in nanomaterial-assisted cataluminescence and its sensing applications, TrAC, Trends Anal. Chem. 67 (2015) 107-127.

[34] B. Liu, H. Kong, A. Luo, A cataluminescence-based vapor-sensitive sensor array for discriminating flammable liquid vapors, Talanta 121 (2014) 43-49.

[35] L. Zhang, Y. Chen, N. He, C. Lu, Acetone cataluminescence as an indicator for evaluation of heterogeneous base catalysts in biodiesel production, Anal. Chem. 86 (2014) 870-875.

[36] J. Chen, X. Cao, R. Xing, L. Xu, Y. Liu, J. Zeng, A sensor system for identifying ether vapors based on extracting two-stage cataluminescence signals, Acta Chim. Sinica 71 (2013) 1421-1428.

[37] X. Jiao, L. Zhang, Y. Lv, Y. Su, A new alcohols sensor based on cataluminescence on nano-CdS, Sens. Actuators, B 186 (2013) 750-754.

[38] H. Xia, R. Zhou, C. Zheng, P. Wu, Y. Tian, X. Hou, Solution-free, in situ preparation of nano/micro CuO/ZnO in dielectric barrier discharge for sensitive cataluminescence sensing of acetic acid, Analyst 138 (2013) 3687-3691.

[39] C. Kang, F. Tang, Y. Liu, Y. Wu, X. Wang, A portable gas sensor based on cataluminescence, Luminescence 28 (2013) 313-317.

[40] R. Zhang, X. Cao, Y. Liu, X. Chang, Development of a simple cataluminescence sensor system for detecting and discriminating volatile organic compounds at different concentrations, Anal. Chem. 85 (2013) 3802-3806.

[41] S. Li, J. Zheng, W.Zhang, J.Cao, S.Li, Z. Rao, Molecular recognition and quantitative analysis of xylene isomers utilizing cataluminescence sensor array, Analyst 138 (2013) 916-920.

[42] B. Li, J. Liu, G. Shi, J. Liu, A research on detection and identification of volatile organic compounds utilizing cataluminescence-based sensor array, Sens. Actuators, B 177 (2013) 1167-1172.

[43] J. Liu, Y. Zhang, Y. Yuan, W. Zuo, A nano-Co_3O_4-based low temperature cataluminescence sensor for the detection of gaseous ethyl ether, Acta Chim. Sinica 71 (2013) 102-106.

[44] P. Cai, H. Song, L. Zhang, Y. Lv, Enhanced cataluminescence sensing characteristics of ethanol on hierarchical spheres ZnO, Sens. Actuators, B 173 (2012) 93-99.

[45] G. Shi, B. Sun, Z. Jin, J. Liu, M. Li, Synthesis of SiO_2/Fe_3O_4 nanomaterial and its application as cataluminescence gas sensor material for ether, Sens. Actuators, B 171-172 (2012) 699-704.

[46] Y. Liu, F. Tang, C.J. Kang, X. Cao, Detection of hydrogen sulphide using cataluminescence sensors based on alkaline-earth metal salts, Luminescence 27 (2012)

274-278.

[47] N. Na, H. Liu, J. Han, F. Han, J. Ouyang, Plasma-assisted cataluminescence sensor array for gaseous hydrocarbons discrimination, Anal. Chem. 84 (2012) 4830-4836.

[48] K.W. Zhou, P. Zhang, W. Chen, A gaseous ethanol sensor based on cataluminescence on nanometer composite oxide, Acta Chim. Sinica 68 (2010) 921～925.

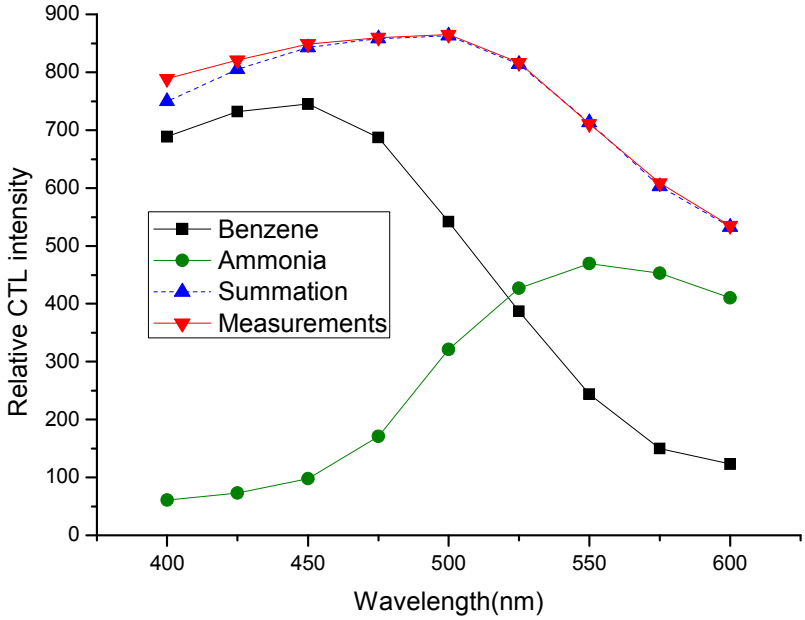
[49] K.W. Zhou, Y. Zhou, Y. Sun, X.J. Tian, Determination of formaldehyde in air utilizing cataluminescence by nanometer composite oxide, Acta Chim. Sinica 66 (2008) 943～946.

[50] K.W. Zhou, X.R. Zhang, Determination of butanone in workshop air utilizing chemiluminescence on nanosized materials, Chin. J. Anal. Chem. 32 (2004) 25-28.

[51] K.W. Zhou, Y.L. Cheng, H.W. Yang, C.X. Gu, Y. Xiao, M.H. Zhao, Simultaneous determination of benzene and formaldehyde in air by cross cataluminescence on nano-$3TiO_2$–$2BiVO_4$, Sens. Actuators, B 202 (2014) 721-726.

[52] K.W. Zhou, H.W. Yang, C.X. Gu, Y.L. Cheng, W.Z. LI, A Gaseous Benzene and Trimethylamine Sensor Based on Cross Sensitivity on Nano $Zr_3Y_2O_9$, Chin. J. Anal. Chem. 42 (2014) 805 ~810.

Graphical Abstract



$$I^{475} = I^{475}_{\text{Benzene}} + I^{475}_{Ammonia} = 131.3C_{Benzene} + 29.3C_{Ammonia} + 55.3$$

$$I^{550} = I^{550}_{Benzene} + I^{550}_{Ammonia} = 33.7C_{Benzene} + 87.7C_{Ammonia} + 106.4$$