A novel acetone sensor utilizing cataluminescence on layered double oxide

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ABSTRACT

This work developed a facile and effective sensor for the determination of acetone, the diabetic biomarker, which was based on cataluminescence (CTL) emission on the surface of layered double oxide (LDO) that is a layered nanomaterial with easy preparation and environmental friendliness. Under the optimized conditions, the linear range of the CTL intensity versus concentration of acetone was 0.1–16 mM with the detection limit of 0.02 mM (S/N = 3). The relative standard deviation (RSD) for 50 repeated measurements of 1.0 mM acetone was 3.6%. Interestingly, there was no or weak response to seven common volatile organic compounds (VOCs), including ethanol, heptanal, ethyl acetate, methanol, formaldehyde, acetic acid and toluene. Furthermore, the proposed CTL sensor was successfully used for sensing acetone in human plasma samples of diabetes patients with a satisfactory recovery. The results demonstrated that the proposed CTL sensor had a promising capability for the sensing of acetone in diabetes diagnosis. The possible CTL mechanism from the oxidation of acetone on the surface of LDO was also discussed.

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1. Introduction

Insulin is a naturally occurring hormone for metabolism and utilization of energy from the ingested nutrients (e.g., sugar and starches). The daily level of insulin is important for the body to function normally [1–3]. Diabetes patients are either unable to generate insulin or the insulin cannot work effectively [4]. Additionally, the medical reports show that a large amount of acetone is generated and acetone concentration is found to elevate by about two degrees of magnitude in the plasma of diabetic patients [5–7]. Hence, acetone is generally regarded as an important biomarker of diabetes or accessorial tool for diabetes diagnosis [8–16]. The commonly analytical techniques for determining acetone for diabetes diagnosis are based on derivatization techniques or mass spectrometry (MS) in conjunction with separation techniques, such as high-performance liquid chromatography (HPLC), gas chromatography (GC) [8–11]. However, the above-mentioned detection methods for acetone often suffer from some disadvantages, such as sophisticated procedures, bulky equipment and low detection sensitivity. In addition, the various types of acetone sensors based on different sensing principles have been fabricated due to their simplicity,

precision and convenience. However, the reported acetone sensors are either poorly selective or inadequately sensitive [12–16].

Cataluminescence (CTL) is a kind of chemiluminescence (CL) during the catalytic oxidation of combustible gases on the surface of solid catalysts in an atmosphere containing oxygen [17,18]. In recent years, the applications of nanomaterial-based CTL to the construction of gas sensors for a variety of volatile organic compounds (VOCs) have attracted considerable attention owing to their advantages of stable intensity, low-cost devices, high sensitivity, and rapid response [19–23]. To the best of our knowledge, there is only one report on CTL determination for acetone in human plasma samples; however, it suffered low selectivity as it was also sensitive to other compounds besides acetone (e.g., methanol, ethanol and formaldehyde) [24]. To improve the selectivity toward acetone, ionic liquids-based headspace solid-phase microextraction technology was used to extract acetone before the CTL detection. Therefore, more efforts should be devoted to the development of a highly sensitive and selective acetone sensor-based CTL.

Layered double hydroxides (LDHs) are an interesting class of inorganic layered solid host matrices with structurally positively charged layers, interlayer balancing anionic species and water molecules [25]. Recently, calcination products of LDHs, known as layered double oxide (LDO), have been paid more attention as catalysts or catalyst precursors owing to their larger surface area, non-toxicity and high chemical stability [26–28]. It has been

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reported that LDO can exhibit stronger catalyzed activity toward aldol condensation of acetone that its LDH counterparts as a result of abundant basic sites [29–32]. Such improvements in catalytic properties are welcome to explore novel applications in sensors.

In the work, calcined Mg/Al- CO_3 LDHs (Mg/Al-LDO) were used as a novel sensing nanomaterial for preparing acetone sensor. Strong CTL emission was generated by the catalytic oxidation of acetone on the surface of LDO. The analytical characteristics were evaluated by the examination of CTL emission from trace acetone on the sensor. The proposed CTL sensor was highly sensitive and selective toward acetone with short response time and good stability. It enabled us to quantify the acetone levels without any sample pretreatments. Validation of the proposed method was checked by determining acetone in human plasma samples of diabetic patients. To the best of our knowledge, this is the first example to employ LDO as CTL sensing nanomaterial for the detection of acetone.

2. Experimental

2.1. Reagents

All reagents were of analytical grade and used without further purification. All solutions were prepared with deionized water (18.2 MU cm, Milli Q, Millipore, Barnstead, CA, USA). Analytical grade chemicals including $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, acetone, ethanol, ethyl acetate, methanol, formaldehyde, acetic acid, toluene, Na_2CO_3 , and NaOH were purchased from Beijing Chemical Reagent Company (Beijing, China). Heptanal and 2,4-dinitrophenyl-hydrazine (DNPH) were purchased from Tokyo Chemical Industry Co., Ltd. HPLC grade acetonitrile was purchased from Merck KGaA (Darmstadt, Germany). CaO was purchased from Fuchen Chemical Reagent Company (Tianjin, China). Mesityl oxide and bromothymol blue (BTB, wt 0.04%, water-soluble) were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). A 200 mM stock solution of acetone was freshly prepared by diluting 75 μL of acetone into 5.0 mL of deionized water. A 0.17 g mL^{-1} $\text{Ca}(\text{OH})_2$ solution was freshly prepared by reaction of CaO with deionized water.

2.2. Apparatus

The powder X-ray diffraction (XRD) measurements were performed on Bruker (Germany) D8 ADVANCE X-ray diffractometer equipped with graphite-monochromatized $\text{Cu/K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The 2θ angle of the diffractometer was stepped from 5° to 75° at a scan rate of $10^\circ/\text{s}$. The particle sizes and external morphology of the samples were observed on a transmission electron microscope (TEM, Tecnai G220, FEI Company). The CTL detection was conducted on an IFFM-E flow injection chemiluminescence analyzer (Ruimai, Xian, China). The CTL spectrum of this system was measured with high-energy cutoff filters from 400 to 640 nm between the CTL cell and the photomultiplier tube (PMT). The resultant gases produced by catalytic oxidation of acetone on the surface of LDO nanoparticles were collected in HPLC grade acetonitrile and then introduced into a Thermo Trace 1300-ISQ GC/MS system (Thermo, USA) equipped with a TR-5MS column (30 m, 0.25 mm i.d., and 0.25 μm film thickness) for the analysis of the reaction products. Control experiments were performed using a Waters 1525 HPLC connected to an UV/visible detector (Waters 2489). A Sun-Fire C18 column (4.6 mm $\times$ 150 mm, 5.0 μm particle size) was used at room temperature. The LDO was calcined at 450°C in SX2-5-12 muffle (Boxun, Shanghai, China). Acetone was delivered by the air carrier gas (supplied by a pump, Beijing Zhongxing Huili Co. Ltd., Beijing, China). The heater controller (Hongbao Electric Co. Ltd., Beijing, China) was used to provide heat for the ceramic rod.

2.3. Synthesis of Mg–Al LDO

The Mg–Al- CO_3 LDHs with different Mg/Al molar ratios were prepared by the coprecipitation method. The precipitation process was taken under low supersaturation conditions at constant pH (10.0). Typically, for the synthesis of interlayer carbonate hydroxide sample with a Mg/Al molar ratio of 3, the salt solution including $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.045 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.015 mol) was made in 60 mL of deionized water. Then, the mixed solution (60 mL) containing NaOH (0.108 mol) and Na_2CO_3 (0.0075 mol) was prepared. The two solutions were added dropwise to a 250 mL four-necked flask under vigorous stirring at room temperature while the pH value kept 10.0. The resulting white precipitate was continually stirred for 24 h at 60°C . The products were centrifugated, washed with degassed and deionized water for three times, dried *in vacuo* at 65°C for 24 h and ground to a fine powder. The resulting solid powder was calcined at 450°C for 3 h before the CTL analysis.

2.4. CTL measurements

The CTL system was shown in Fig. S1. By diluting 200 mM acetone stock solution with deionized water, a series of acetone working solutions were freshly obtained. A LDO suspension was prepared by diluting LDO powder in deionized water, then it was coated onto the cylindrical ceramic heater (inner diameter = 5 mm, length = 8 cm, Shanghai Anting Factory, Shanghai, China), which was then put into a quartz tube (diameter = 1 cm, length = 10 cm, Institute of Chemistry, Chinese Academy of Science, Beijing, China). A series of acetone solutions (50 μL) were injected into a 2.0 mL gasification chamber, the gas would be conducted into a close reaction cell by air carrier gas. The CTL signals were monitored by a PMT adjacent to the CTL quartz tube. The data integration time of the CTL analyzer was set at 1 s per spectrum, and a work voltage of 900 V was used for the CTL detection. The signal was imported to the computer for data acquisition.

2.5. Sample pretreatment

Whole blood samples from diabetic patients were obtained from China–Japan Friendship Hospital, Beijing, China. The sealed centrifuge tube was used to collect blood samples by a heparin-containing syringe. To minimize the loss of acetone, whole blood samples were stored at -20°C and thawed at 4°C just before analysis. After the plasma samples were obtained via centrifugation at 5000 rpm for 5 min, it was analyzed immediately by the proposed CTL sensor.

3. Results and discussion

3.1. LDO-triggered acetone CTL

The TEM image and the representative XRD pattern of LDO with the Mg/Al ratio of 4 indicated that the LDH layer collapsed into small pieces with a higher crystallinity after calcination. Additionally, to obtain the CTL response profile of acetone on the surface of LDO, different concentrations of acetone were injected into the air carrier with a flow rate of 400 mL min^{-1} at 300°C working temperature. The curves 1, 2 and 3 of Fig. 1 denoted the results for different acetone concentrations of 10 mM, 20 mM and 30 mM, respectively. We could observe that the CTL signals increased with an increase in the concentration of acetone. For the three concentrations of acetone, the signals rapidly increased from the baseline to the maximum value within around 3 s after sample injection, indicating that the proposed sensing mode exhibited a rapid response to different concentrations of acetone.

Fig. 1. CTL response profiles of different concentrations of acetone. Conditions: acetone concentration, 10 mM, 20 mM and 30 mM, respectively; reaction temperature, 300 °C; air flow rate, 400 mL min⁻¹.

3.2. Mg to Al molar ratios

It has been reported that the Mg/Al ratio of LDO has a great effect on its catalytic performances [33]. Note that the large values of Mg/Al ratio (e.g., Mg/Al molar ratio = 5, 6) can lead to a high density of Mg octahedra in the LDH sheet, facilitating the formation of Mg(OH)₂ or MgCO₃ [34]. In this study, the effect of LDO with Mg/Al molar ratios varying from 2 and 4 on the CTL intensity was investigated. The results showed that the CTL intensity of LDO with the Mg/Al molar ratio of 4 was strongest. This might due to the increasing basic sites of LDO when the Mg/Al ratio was from 2 to 4, facilitating the proceeding of the CTL reaction [29]. Therefore, the LDO with the Mg/Al molar ratio of 4 was used throughout this study.

3.3. CTL reaction temperature

The working temperature for CTL reaction was still an important factor in the reaction rate of the catalytic oxidation reaction. The CTL intensity for acetone improved with the increased temperature owing to the higher conversion of acetone on LDO at higher temperature [35]. However, higher temperature (above 300 °C) could result in partly desorption of LDO on the ceramic rod. Therefore, 300 °C was selected as the optimal temperature in this work.

3.4. Flow rate of carrier gas

The acetone vapor and the selected catalyst would have a proper contact time with a proper flow rate [21]. Therefore, the effect of carrier gas flow rate on the CTL intensity was examined in the range of 150–750 mL min⁻¹ (Fig. 2). The CTL intensity of acetone increased gradually with increasing the air flow rate in the range of 150–400 mL min⁻¹. However, when the flow rate was higher than 400 mL min⁻¹, the CTL intensity decreased due to the fact that the reaction time between acetone and catalyst would possibly not be sufficient. Therefore, 400 mL min⁻¹ was chosen as the optimal flow rate for the subsequent studies.

3.5. Highly selectivity toward acetone

The selectivity of CTL sensors is important for their real analytical applications. In this proposed system, we interestingly found that LDO nanoparticles showed an excellent selectivity toward acetone by testing the other seven kinds of common VOCs under the same experimental conditions with the concentration

Fig. 2. Effect of flow rate of carrier gas on the CTL intensity. Conditions: acetone concentration, 10 mM; reaction temperature, 300 °C.

of 1.0 mM. These VOC species included ethanol, heptanal, ethyl acetate, methanol, formaldehyde, acetic acid and toluene. As shown in Fig. 3, the above-mentioned seven common VOCs exhibited no or very weak CTL signals, indicating that the present gas sensor may be used to sense acetone with high selectivity. There are some causes to contribute to high selectivity toward acetone: (1) the medium-strength basic sites of LDO nanoparticles could exhibit its highly catalytic performances in the conversion of acetone into CTL emitting species because the aldol condensation of acetone occurs mainly on basic sites [29,31]; (2) in comparison to the other compounds tested, the carbon–oxygen double bond in acetone is easily cleaved, facilitating the proceeding of aldol condensation; and (3) the aldol condensation of acetone could easily take place in lower operation temperatures, but the other compounds tested in aldol condensation reactions own slow reaction rate in lower temperatures [32]. In addition, note that the concentration of acetone in diabetes patients is much higher than those of the other compounds tested [10,24]. Therefore, the CTL on the surface of LDO nanoparticles exhibited highly selective recognition toward acetone under the optimal conditions.

3.6. Analytical characteristics

Under the optimum experimental conditions, the CTL intensity was increased with an increase in the concentration of acetone (e.g., 500 mM). However, the CTL intensity was proportional to the concentration of acetone in the range from 0.1 to 16 mM. The regression

Fig. 3. Selectivity of CTL sensor toward acetone based on LDO nanoparticles. Conditions: VOC concentration, 1.0 mM; reaction temperature, 300 °C; air flow rate, 400 mL min⁻¹.

Fig. 4. Two linear regions between CTL intensity and acetone concentration. Conditions: reaction temperature, 300 °C; air flow rate, 400 mL min⁻¹.

equation was $\Delta I = 6.3878C - 4.5723$ ($R^2 = 0.991$), where ΔI was the relative CTL intensity and C was the concentration of acetone, respectively (Fig. 4). The detection limit for acetone ($S/N = 3$) was 0.02 mM, and the CTL response profile of acetone at the limit of detection was shown in Fig. S2. In addition, the stability of the proposed CTL sensor was carried out by continually injecting 50 μ L of 1.0 mM acetone into the sensor chamber for 50 times under the optimum conditions, the relative standard deviation (RSD) was 3.6%, indicating an acceptable stability. After several months, the CTL intensity was approximately 96% of its initial value. Therefore, the present sensor showed a good long-term reproducibility.

Table 1
Assay results of acetone in human plasma samples.

Samples	CTL method ^a (mM)	HPLC–UV method ^a (mM)	Added (mM)	Found ^a (mM)	Recovery (%)
Plasma 1	1.32 $\pm$ 0.07	1.21 $\pm$ 0.09	1.00	2.30 $\pm$ 0.05	104
			2.00	3.21 $\pm$ 0.08	97
Plasma 2	0.91 $\pm$ 0.04	0.97 $\pm$ 0.03	1.00	1.96 $\pm$ 0.09	103
			2.00	2.97 $\pm$ 0.03	102

^a Mean $\pm$ SD of three measurements.

3.7. Real samples

It is reported that acetone level in plasma of normal donors is below 0.008 mM, which is lower than the 0.02 mM detection limit in the proposed method [9]. In order to evaluate the applicability and reliability of the proposed method, it was applied for the determination of acetone in human plasma samples of diabetes patients. The pretreated plasma samples were analyzed immediately. Acetone in human plasma samples was well quantified using a standard addition method, and the results were shown in Table 1, which were in good agreement with those obtained by the accepted HPLC–UV detection method for acetone [24]. To evaluate the accuracy of this method, the recovery of known amounts of acetone added to the human plasma samples were tested. The good recoveries of acetone obtained ranged from 97% to 104%, indicating the good accuracy of the proposed method. These satisfactory results demonstrated the reliability of the present method for detecting acetone in real samples.

3.8. Possible mechanism of the CTL reaction

To study the CTL mechanism of the acetone sensor, GC/MS was carried out to detect the reaction products of the catalytic oxidation of acetone on the surface of LDO nanoparticles. Acetonitrile was used to collect the tail gases. GC/MS data demonstrated the production of the traces of mesityl oxide during the CTL reaction (Fig. 5a), and there were no other products detected. These results were in agreement with our previous work [29]. In addition, we found that the CTL intensity of 1.0 mM mesityl oxide was the same as that of 2.0 mM acetone, which may be attributed to the fact that the aldol condensation of two acetone molecules can generate one molecule mesityl oxide [32]. The CTL spectrum of the present CTL system was measured using a series of high-energy cutoff filters from 400 to 640 nm. It could be clearly seen from Fig. 5b that the maximum emission wavelength for the present CTL system was about 550 nm, meaning that the emissive species for the observed CTL was carbon dioxide molecules in the electronic excited state (CO_2^*) rather than the excited state of mesityl oxide. Next, CO_2^* could produce photoemissions when returning to its ground states [36]. On the other

Fig. 5. (a) GC/MS chromatograms of the tail gas from the catalytic oxidation of acetone. (b) CTL spectrum of acetone vapor on the surface of LDO. Inset: Mass spectrum of the GC peak at 2.4 min (mesityl oxide). Conditions: acetone concentration, 10 mM; reaction temperature, 300 °C; air flow rate, 400 mL min⁻¹.

hand, the final oxidation products of acetone were confirmed by using BTB (pH indicator) and $\text{Ca}(\text{OH})_2$ solutions. As shown in Fig. S3, an obvious color change from blue (at $\text{pH} \geq 8$) to green (at $\text{pH} 6\text{--}7$) of 0.01 wt% BTB aqueous solution could be seen when the tail gases were injected, indicating the generation of CO_2 . After the acetone oxidation products were captured in $\text{Ca}(\text{OH})_2$ solution, it was found that the clear solution turned to turbid. These results were in agreement with our previous work [29]. Based on the above results, the possible mechanism of the acetone CTL was as follows. When acetone vapor passed through the surface of the ceramic heaters, the aldol condensation of acetone happened in the presence of O_2 . The produced mesityl oxide could easily further be oxidized to CO_2^* in the presence of LDO nanoparticles. Finally, CO_2 in the electronic excited state could produce photoemission when it returned to its ground states.

4. Conclusions

In summary, LDO nanoparticles are easily prepared and environmentally friendly. For the first time, we have demonstrated the feasibility to design a CTL sensor for the quantitative analysis of acetone by using LDO nanoparticles as catalysts. The proposed acetone CTL sensor exhibited highly selective and sensitive recognition toward acetone with satisfactory stability and simplicity. Combined with its simple apparatus and its long-term stability, the implementation of the proposed sensor has been applied for the sensing of acetone in human plasma samples of diabetes patients. The development of sensor arrays for gas mixture recognition should be explored through tuning different kinds of LDO.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2014.08.064>.

References

- [1] N. Cheung, P. Mitchell, T.Y. Wong, Diabetic retinopathy, *Lancet* 376 (2010) 124–136.
- [2] M. Kitada, Z.Y. Zhang, A. Mima, G.L. King, Molecular mechanisms of diabetic vascular complications, *J. Diabetes Investig.* 1 (2010) 77–89.
- [3] M. Brownlee, Biochemistry and molecular cell biology of diabetic complications, *Nature* 414 (2001) 813–820.
- [4] R.J. McCrimmon, C.M. Ryan, B.M. Frier, Diabetes and cognitive dysfunction, *Lancet* 379 (2012) 2291–2299.
- [5] M.P. Kalapos, On the mammalian acetone metabolism: from chemistry to clinical implications, *Biochim. Biophys. Acta* 1621 (2003) 122–139.
- [6] M.W. Savage, K.K. Dhataria, A. Kilvert, G. Rayman, J.A.E. Rees, C.H. Courtney, L. Hilton, P.H. Dyer, M.S. Hamersley, Joint British Diabetes Societies guideline for the management of diabetic ketoacidosis, *Diabet. Med.* 28 (2011) 508–515.
- [7] M. Veciana, Diabetes ketoacidosis in pregnancy, *Semin. Perinatol.* 37 (2013) 267–273.
- [8] S. Fujii, T. Maeda, I. Noge, Y. Kitagawa, K. Todoroki, K. Inoue, J.Z. Min, T. Toyo'oka, Determination of acetone in saliva by reversed-phase liquid chromatography with fluorescence detection and the monitoring of diabetes mellitus patients with ketoacidosis, *Clin. Chim. Acta* 430 (2014) 140–144.
- [9] L. Dong, X.Z. Shen, C.H. Deng, Development of gas chromatography–mass spectrometry following headspace single-drop microextraction and simultaneous derivatization for fast determination of the diabetes biomarker, acetone in human blood samples, *Anal. Chim. Acta* 569 (2006) 91–96.
- [10] N. Li, C.H. Deng, N. Yao, X.Z. Shen, X.M. Zhang, Determination of acetone, hexanal and heptanal in blood samples by derivatization with pentafluorobenzyl hydroxylamine followed by headspace single-drop microextraction and gas chromatography–mass spectrometry, *Anal. Chim. Acta* 540 (2005) 317–323.

- [11] G.-T. Fan, C.-L. Yang, C.-H. Lin, C.-C. Chen, C.-H. Shih, Applications of Hadamard transform–gas chromatography/mass spectrometry to the detection of acetone in healthy human and diabetes mellitus patient breath, *Talanta* 120 (2014) 386–390.
- [12] S.-J. Choi, I. Lee, B.-H. Jang, D.-Y. Youn, W.-H. Ryu, C.O. Park, I.-D. Kim, Selective diagnosis of diabetes using Pt-functionalized WO_3 hemitube networks as a sensing layer of acetone in exhaled breath, *Anal. Chem.* 85 (2013) 1792–1796.
- [13] P. Sun, Y.X. Cai, S.S. Du, X.M. Xu, L. You, J. Ma, F.M. Liu, X.S. Liang, Y.F. Sun, G.Y. Lu, Hierarchical $\alpha\text{-Fe}_2\text{O}_3/\text{SnO}_2$ semiconductor composites: hydrothermal synthesis and gas sensing properties, *Sens. Actuators B: Chem.* 182 (2013) 336–343.
- [14] M. Righettoni, A. Tricoli, S.E. Pratsinis, Si: WO_3 sensors for highly selective detection of acetone for easy diagnosis of diabetes by breath analysis, *Anal. Chem.* 82 (2010) 3581–3587.
- [15] T.I. Nasution, I. Nainggolan, S.D. Hutagalung, K.R. Ahmad, Z.A. Ahmad, The sensing mechanism and detection of low concentration acetone using chitosan-based sensors, *Sens. Actuators B: Chem.* 177 (2013) 522–528.
- [16] T. Xiao, X.-Y. Wang, Z.-H. Zhao, L. Li, L. Zhang, H.-C. Yao, J.-S. Wang, Z.-J. Li, Highly sensitive and selective acetone sensor based on C-doped WO_3 for potential diagnosis of diabetes mellitus, *Sens. Actuators B: Chem.* 199 (2014) 210–219.
- [17] R.A. Potyrailo, V.M. Mirsky, Combinatorial and high-throughput development of sensing materials: the first 10 years, *Chem. Rev.* 108 (2008) 770–813.
- [18] N. Na, S.C. Zhang, X. Wang, X.R. Zhang, Cataluminescence-based array imaging for high-throughput screening of heterogeneous catalysts, *Anal. Chem.* 81 (2009) 2092–2097.
- [19] R.K. Zhang, X.A. Cao, Y.H. Liu, X.Y. Chang, Development of a simple cataluminescence sensor system for detecting and discriminating volatile organic compounds at different concentrations, *Anal. Chem.* 85 (2013) 3802–3806.
- [20] M.R. Almasian, N. Na, F. Wen, S.C. Zhang, X.R. Zhang, Development of a plasma-assisted cataluminescence system for benzene, toluene, ethylbenzene, and xylenes analysis, *Anal. Chem.* 82 (2010) 3457–3459.
- [21] L. Tang, Y. Li, K.L. Xu, X.D. Hou, Y. Lv, Sensitive and selective acetone sensor based on its cataluminescence from nano- La_2O_3 surface, *Sens. Actuators B: Chem.* 132 (2008) 243–249.
- [22] W. Sha, D.F. Cui, B. Li, Q.H. Wang, Y.H. Wang, C.H. Zheng, A portable embedded drug precursor gas detection and identification device based on cataluminescence-based sensor array, *Sens. Actuators B: Chem.* 200 (2014) 132–139.
- [23] X.Y. Wan, H.J. Song, D. Zhao, L.C. Zhang, Y. Lv, A Y-doped metal-organic framework-based cataluminescence gas sensor for isobutanol, *Sens. Actuators B: Chem.* 201 (2014) 413–419.
- [24] P. Yang, C. Lau, X. Liu, J.Z. Lu, Direct solid-support sample loading for fast cataluminescence determination of acetone in human plasma, *Anal. Chem.* 79 (2007) 8476–8485.
- [25] Q. Wang, D. O'Hare, Recent advances in the synthesis and application of layered double hydroxide (LDH) nanosheets, *Chem. Rev.* 112 (2012) 4124–4155.
- [26] M.-Y. Guan, D.-M. Xu, Y.-F. Song, Y. Guo, $\text{ZnO}/\text{ZnAl}_2\text{O}_4$ prepared by calcination of ZnAl layered double hydroxides for ethanol sensing, *Sens. Actuators B: Chem.* 188 (2013) 1148–1154.
- [27] L. Cui, H.S. Yin, J. Dong, H. Fan, T. Liu, P. Ju, S.Y. Ai, A mimic peroxidase biosensor based on calcined layered double hydroxide for detection of H_2O_2 , *Biosens. Bioelectron.* 26 (2011) 3278–3283.
- [28] Y.J. Lin, Q.L. Fang, B.L. Chen, Perchlorate uptake and molecular mechanisms by magnesium/aluminum carbonate layered double hydroxides and the calcined layered double hydroxides, *Chem. Eng. J.* 237 (2014) 38–46.
- [29] L.J. Zhang, Y.C. 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.
- [30] L. Faba, E. Díaz, S. Ordóñez, Aqueous-phase furfural–acetone aldol condensation over basic mixed oxides, *Appl. Catal. B* 113–114 (2012) 201–211.
- [31] P. Kuśtrowski, D. Sułkowska, L. Chmielarz, A. Rafalska-Lasocha, B. Dudek, R. Dziembaj, Influence of thermal treatment conditions on the activity of hydrotalcite-derived Mg–Al oxides in the aldol condensation of acetone, *Microporous Mesoporous Mater.* 78 (2005) 11–22.
- [32] S. Ordóñez, E. Díaz, M. León, L. Faba, Hydrotalcite-derived mixed oxides as catalysts for different C–C bond formation reactions from bioorganic materials, *Catal. Today* 167 (2011) 71–76.
- [33] D. Tichit, M. Naciri Bennani, F. Figueras, R. Tessier, J. Kervennal, Aldol condensation of acetone over layered double hydroxides of the meixnerite type, *Appl. Clay Sci.* 13 (1998) 401–415.
- [34] H. Yan, M. Wei, J. Ma, D.G. Evans, X. Duan, Plane-wave density functional theory study on the structural and energetic properties of cation-disordered Mg–Al layered double hydroxides, *J. Phys. Chem. A* 114 (2010) 7369–7376.
- [35] J. Hu, K.L. Xu, Y.Z. Jia, Y. Lv, Y.B. Li, X.D. Hou, Oxidation of ethyl ether on borate glass: chemiluminescence, mechanism, and development of a sensitive gas sensor, *Anal. Chem.* 80 (2008) 7964–7969.
- [36] R.K. Zhang, X.A. Cao, Y.H. Liu, X.Y. Chang, A new method for identifying compounds by luminescent response profiles on a cataluminescence based sensor, *Anal. Chem.* 83 (2011) 8975–8983.

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