Sensors and Actuators B 222 (2016) 300–306

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Cataluminescence gas sensor for ketones based on nanosized $NaYF_4$:Er

Jie Tang, Hongjie Song, Binrong Zeng, Lichun Zhang*, Yi Lv

Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China

ARTICLE INFO

Article history:
Received 13 April 2015
Received in revised form 4 August 2015
Accepted 11 August 2015
Available online 20 August 2015

Keywords:
$NaYF_4$
Gas sensor
Cataluminescence
Ketones
Dope

ABSTRACT

A novel gas sensor toward ketones based on cataluminescence generated on the surface of nanosized $NaYF_4$:Er was developed. The sensing materials $NaYF_4$:Er was synthesized by a simple hydrothermal method and characterized by powder X-ray diffraction, scanning electron microscope and energy dispersive X-ray spectroscopy. The effect of Er^{3+} doping concentration and crystallinity of $NaYF_4$:Er on the CTL intensity were studied. When the Er^{3+} doping concentration reaches 20%, the materials show excellent sensing characteristics for ketones. Under the optimal experimental conditions, as represented by the acetone and butanone, the gas sensor has fast responses (3 s) and relatively low work temperature (250 °C). The linear range of cataluminescence intensity versus concentration were 2.388–143.28 μg mL^{-1} for acetone and 2.45–49.0 μg mL^{-1} for butanone, with a detection limit (signal-to-noise ratio is 3) of 1.7 μg mL^{-1} and 0.7 μg mL^{-1}, respectively. Foreign 11 substances in common have little interference which indicates the high selectivity of the CTL sensor for ketones.

1. Introduction

Volatile organic compounds (VOCs) are usually emitted as a result of human activities and always used in industrial and domestic activities [1,2]. More seriously, some VOCs are directly harmful (carcinogenetic, nervously paralyzed, uncomfortable, etc.) and cause some social destructions such as ozone hole destruction, green house effect and so on [3]. As one of volatile organic compounds, ketones are the most common reagent in biological chemistry and frequently used as solvent and polymer in industry and pharmaceutical production, especially acetone and butanone. People may develop a headache, fatigue, and even narcosis when the concentration of acetone is high in the air. Acetone levels in diabetic patients' blood and spittle are higher than those of healthy people [4]. A certain concentration of butanone had some stimulative on our eyes and throat. Therefore, it is desirable to establish a sensing platform for on-site and real-time monitoring of ketones.

Recently, scientists have been committed to explore more analytical methods for detection of ketones, such as semi-automated enzymic assay [5], HSCC-UV-IMS [6], high-performance liquid chromatography [7] and dual-wavelength detection [8], etc. All of these techniques inherit merits of high performance and sensitivity for trace acetone, while they meet the intrinsic defects that online monitor the contamination in actual locale is hard to achieve. Hence, it is necessary to seek stable, simple and portable sensors for ketones. Cataluminescence (CTL) is CL generated on the surface of solid catalysts during the catalytic oxidation of organic vapors in an atmosphere containing oxygen. Due to the stable intensity, simple implementation, high sensitivity, and rapid response, CTL gas sensors have received significant research attention. Since 1990, Nakagawa et al. [9,10] have poured much endeavor on the CTL studies and established a series of gas sensing systems. They developed a series of CTL gas sensors with bulk γ-Al_2O_3 as sensing materials to determine vapors of ethanol, butanol [11]. In the last decades, the application of nanomaterials has greatly driven the development of CTL analysis owning to their high surface areas, good adsorption characteristics, high catalytic activity [12,13]. Both Zhang et al. [14,15] and Zhu et al. [16,17] have been engaged in development of a series of different catalytic nanomaterials for CTL gas sensors. In 2002, Zhang et al. [18] firstly utilized nanosized TiO_2 as sensing material to design an acetone and ethanol CTL sensor. After that, various nanomaterials have been attracted widespread attention in the field of catalysis. More recently, Zhang et al. [19] using different nanomaterials assembled a catalytic optical chemo-sensor array for the CTL discrimination of ethanol, hydrogen sulfide, and trimethylamineon. Besides, our group is also devoted to expanding the range of application of nanomaterials in developing CTL sensors [20–22]. Through controllable synthesis of catalysts with special uniform morphologies and doping method, our group has explored great many CTL sensors with better selectivity, high sensitivity, and fast response. For example, we have controllably synthesized Mn_3O_4 micro-octahedra and hexagonal nanoplates with excellent CTL sensing characteristics for acetone [23]. Recently Y-doped

* Corresponding author. Tel.: +86 28 85412398; fax: +86 28 85412398.
E-mail address: zhanglichun@scu.edu.cn (L. Zhang).

http://dx.doi.org/10.1016/j.snb.2015.08.048
0925-4005/

metal-organic framework-5 synthesized by a simple solvothermal method was used as a CTL material to detect isobutanol [24].

With special properties, reliable optical applications and enhanced catalytic performances, rare earth compounds were widely used in electric, magnetic, optical, and catalytic fields [25]. Furthermore, originating from unique 4f electrons of rare earth ions, doping rare earth ions into materials inherits special properties such as reliable optical applications and enhanced catalytic performances. For instance, the CTL at 620 nm from Eu^{3+} doped in nanosized ZrO_2 shows 72 times higher sensitivity than the CTL at 460 nm from excited intermediates in the ethanol sensor [26]. Similarly, Eu^{3+}-doped YVO_4 used as a CTL catalyst can improve sensitivity to detect ethanol [27], and γ-Al_2O_3 activated with Dy^{3+} was obtained with high sensitivity for hydrocarbon CTL gas sensors [28]. In consequence, rare earth ions are attractive to extensively apply in CTL to develop highly sensitive and selective sensors. In this work, we have synthesized $NaYF_4$ nanocrystals doped with different concentrations Er^{3+} to improve the CTL sensing properties. A strong CTL emission could be observed when ketones vapor was delivered through the surface of the nanomaterials. Sensing tests showed that the proposed CTL sensor possessed not only good stability and high sensitivity, but also short response time and excellent selectivity to ketones.

2. Experiment

2.1. Reagents and material

All chemicals were of analytical grade or better and were used as received without further purification. Sodium fluoride, yttrium oxide (Y_2O_3), erbium oxide (Er_2O_3), sodium hydroxide, ethanol and oleic acid are supplied by Chengdu Kelong Chemical Reagent Co. Ltd. (Chengdu, China). All aqueous solutions were prepared using ultrapure water (Mill-Q, Millipore, 18.2 MΩ resistivity).

2.2. Preparation of materials

$NaYF_4$:Er were synthesized according to previously reported method with some modifications [29]. In a typical synthesis process for $NaYF_4$:Er (20%), a mixture of 0.113 g Y_2O_3 and 0.0383 g Er_2O_3 (n_Y:n_{Er} = 80:20) was dissolved in hot nitric acid (65 °C) to acquire $Ln(NO_3)_3$, and the solvent was evaporated after 6 h reaction. 7 mL of NaF aqueous solution (1 mol/L) and 1 mL of $Ln(NO_3)_3$ aqueous solution was added to the mixture of NaOH (1.2 g), ethanol (8 mL), deionized water (4 mL), and oleic acid (20 mL), and the solution was thoroughly stirred. Subsequently, the milky colloidal solution was transferred to a 50 mL teflon-lined autoclave, which was heated at 180 °C for 24 h. The final products were collected by means of centrifugation, washed with ethanol and deionized water for several times. After dried in vacuum at 80 °C for 4 h. $NaYF_4$ nanocrystals doped with different concentrations of Er^{3+} were prepared by the same procedure except for varying the amount of Er_2O_3.

2.3. Characterization

The crystal phase of $NaYF_4$:Er was identified by the powder X-ray diffraction (XRD, Philips Analytical, Netherlands) with a plumbaginous-monochromatized Cu $K_{\alpha1}$ (λ = 1.5406 Å) radiation. The morphology of the samples was inspected using scanning electron microscopy (SEM, JSM-5900LV) at an acceleration voltage of 20 kV. And Energy-dispersive X-ray spectroscopy (EDS) was obtained on the same instrument to determine the elemental compositions of $NaYF_4$:Er.

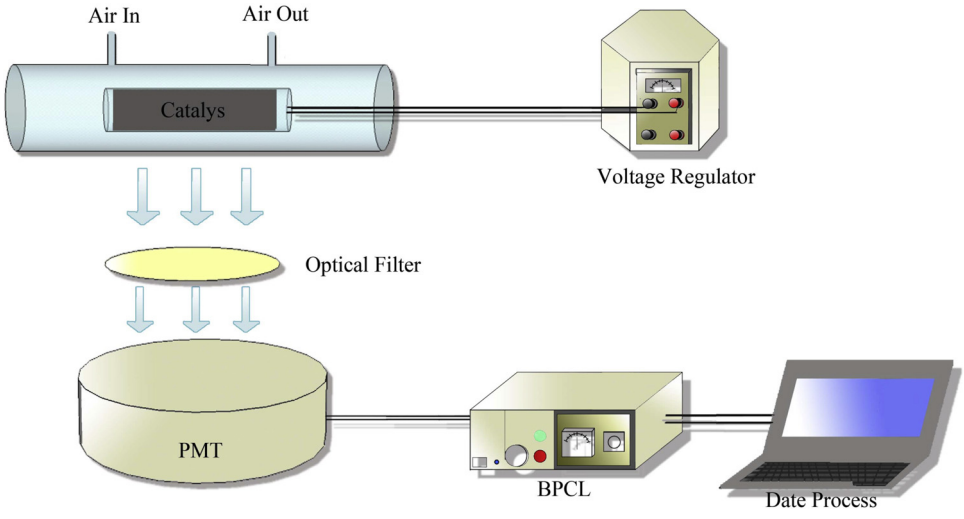
2.4. CTL sensing measurements

The schematic diagram of the CTL gas sensor was shown in Scheme 1. About 0.03 g $NaYF_4$:Er, which was calcined in a muffle furnace at 400 °C, were coated on a ceramic heating rod which was put in a quartz tube (i.d. = 10 mm and length = 100 mm). VOCs vapors were introduced into the sensing system by air flow, and the consequent CTL emission was recorded by a BPCL ultra-weak luminescence analyzer (BP-II, Institute of Biophysics, Academia Sinica, Beijing, China). The temperature of the heating rod was controlled by a digital controller and the flow rate of air was adjusted by a precision flow meter.

3. Results and discussion

3.1. Characterization

All $NaYF_4$ nanocrystals doped with different concentrations Er^{3+} were obtained consisting of a majority of cubic phase and a small amount of hexagonal phase, as demonstrated by the XRD pattern in Fig. 1. All diffraction peaks of the samples matched very well with cubic phase (JCPDS 39-0723) and hexagonal phase (JCPDS 16-0334). No other impurity peaks (e.g. Er_2O_3) were detected. The EDS spectrum in Fig. 2a clearly revealed the presence of Er and other elements, which means that Er^{3+} were successfully doped into $NaYF_4$ nanocrystals.



Scheme 1. Schematic diagram of the CTL sensing system.