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Advances in nanomaterial-assisted cataluminescence and its sensing applications

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ABSTRACT

Cataluminescence (CTL) emitted on the surface of solid materials during a catalytic reaction is a very interesting phenomenon, which gives a novel, powerful tool for chemical analysis. Nanomaterial-assisted CTL is a promising transduction principle for gas sensing, and its main features of high sensitivity and long lifetime are also favorable for developing a wide array of analytical devices. This review summarizes advances in nanomaterial-assisted CTL methodologies, including the working mechanism, exploration of sensing materials, innovations in strategy and instrumentation, new types of CTL-based sensing system, and their application to analysis of complex gases and volatile organic compounds. Finally, we discuss some critical challenges and prospects in this field.

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1. Introduction

Chemiluminescence (CL) detection is a powerful tool for chemical analysis for its advantages of low or even no natural background, high sensitivity, rapidity, and simple instrumentation. CL emission can occur in gas, liquid, or solid phases, further facilitating and widening its scope of analytical applications. Undoubtedly, CL has attracted much attention of researchers for its potential applications in analytical chemistry. The increasing popularity of CL for chemical analysis is apparent from the literature, although most efforts are in solution-based measurement {e.g., Lin and Lu [1–4], Aslan and Geddes [5], Giokas and Vlessidis [6], Wang [7], Ju [8], and Lv et al. [9].

While liquid-phase CL has shown great potential application in food analysis [10,11], pharmaceutical analysis [12], immunoassay [4,6,8], DNA analysis [4,8], and other biological analyses [7,13,14], gas-phase CL plays an important role in measuring and monitoring gaseous or volatile components in the atmospheric environment [15–19]. Since 1970, various CL methods for atmospheric NO analysis have been established and some recommended for environmental air monitoring. Traditionally, the study of gas-phase CL has been limited to measurement of ozone-induced CL systems, including nitric oxides, olefin, volatile sulfur compounds, and vaporized arsenic [20–22]. It is necessary to develop new CL systems to meet the ever-expanding monitoring needs of a wide variety of species in gases.

Cataluminescence (CTL) is CL emitted on the surface of solid materials during a catalytic reaction. In 1976, Michèle Breysse et al. [23] observed CTL emission during the catalytic oxidation of carbon monoxide on the surface of thoria. This luminescence is ascribed to light emission during catalysis in an atmosphere containing oxygen and the CTL intensity depends linearly on the rate of the catalytic reaction, which implies that carbon monoxide in the air can be detected continuously by measurement of the CTL emission from the surface of thoria. This phenomenon can be applied to the CTL-based gas sensors. Generally speaking, there are two gas-detection modes in gas sensors: one utilizing changes in sensor materials by interaction with gases, and the other utilizing signals obtained from the gas itself. The latter is favorable in view of the stability of the gas sensor. CTL methodology uses this approach. The CTL response is fast, reproducible and proportional to the concentration of the analytes of the order of ppm in air.

Since 1990, Nakagawa and co-workers [24–31] have poured much endeavor into CTL studies and established a series of gas-sensing systems. As seen from Table 1, they proposed and established CTL gas sensors with bulk γ-Al_2O_3 or γ-Al_2O_3:Dy^{3+} as sensing materials to determine vapors (e.g., ethanol, butanol, acetone, and *n*-butyric acid) and fragrance vapors (e.g., lemon and orange). Since then, CTL-based gas sensors have been reported by many academic groups {e.g., Zhang's, Zhu's, Cao's, Lu's and ours (as discussed in Sections 2–6, and Tables 2 and 3)}.

In recent years, we were particularly interested in CTL-based sensing. As a novel CL method to design gas sensors, CTL brings many advantages, such as high sensitivity, fast response and long-term stability. Furthermore, nanomaterials bring great opportunities for advances in CTL sensors (e.g., miniaturization and portability). Meanwhile, CTL can dramatically expand the range of detectable gas species by using catalysts in detection of gases or vapors continuously without any consumption of sensor substance by measuring CTL from the catalyst surface. Accordingly, CTL is a promising transduction principle for gas sensing, and its main features of high sensitivity and long lifetime are also favorable for developing a wide array of analytical devices. We summarize the advances in nanomaterial-assisted CTL methodologies. We provide the reader with an overview of CTL-based methodologies improved and reported in recent years, emphasizing the working mechanism, sensing materials, innovation in instrumentation, and versatility in applications.

2. Working mechanism of cataluminescence

Since CTL is generated in the course of a catalytic reaction, clear explanation of the CTL working mechanism could help in optimization of reaction conditions and design of better catalysts as sensing materials, thus improving the performance of CTL sensors. Nakagawa and co-workers [17] have done a lot in clarifying the CTL mechanism in both theoretical and experimental aspects by investigating the relationship between CTL intensity and rate of catalytic oxidation.

As CTL emission is observed in the course of catalytic oxidation, the overall reaction process must be considered in order to describe the working mechanism of the CTL-based sensor. Fig. 1A shows the catalyst layer to depict the simplified overall reaction processes involving CTL emission on a CTL-based gas sensor.

Generally, the CTL process at the surface of the solid catalyst is regarded as a heterogeneous catalytic reaction, which undergoes five stages:

1 gas molecules R (reactant) and O (oxygen) diffuse from the outer gas phase and reach the catalyst surface;
2 gas molecules are chemisorbed to form R_{ad} and O_{ad} at the catalyst surface, and, at a certain temperature, parts of them are desorbed to the gas phase again;
3 chemisorbed R_{ad} and O_{ad} react to produce chemisorbed RO_{ad} at the surface;
4 the product RO is desorbed from the surface; and,
5 RO diffuses off to the gas phase.

Table 1
Cataluminescence (CTL)-based sensing system of gases or vapors

Instrumentation and strategies	Gases or vapors	Catalysts	Temp. (°C)	LOD	Ref.
- CTL-based sensor - Periodic temperature cycles & algebraic sum rule (by solving simultaneous equations)	Discrimination of mixed odor vapors (e.g., ethanol, butanol, acetone, *n*-butyric acid, xylene)	γ-Al_2O_3	450	~1 ppm	[24–27]
- CTL-based sensor - a spectroscopic image system	Recognition of organic vapor (e.g., ethanol, butanol, acetone, MEK, xylene, butyric acid)	γ-Al_2O_3	440~530	–	[28]
- CTL-based sensor - Doping the catalyst	Hydrocarbon gas (methanol, ethylene, *iso*-butane)	γ-Al_2O_3: Dy^{3+}	450	0.2 ppm	[29]
- CTL-based sensor - Temperature-programmed CTL glow curve and principal component analysis (PCA)	Discrimination of fragrance vapors of lemon and orange (e.g., linalool, citral, limonene, *a*-pinene)	γ-Al_2O_3-Dy_2O_3 mixture	100~700	0.1~1 ppm	[30]
- Two CTL sensors - Temperature-programmed sensing	Identification of 11 types of gases (methanol, ethanol, 1-propanol, 1-butanol, acetone, pinene, linalool, diacetyl, *n*-butyric acid ethyl ester, acetic acid *n*-amyl ester, *n*-nonyl aldehyde)	γ-Al_2O_3 γ-Al_2O_3: Dy^{3+} $CaCO_3$: Dy^{3+} ZrO_2: Dy^{3+}	100~450	~1 ppm	[31,32]