

Article pubs.acs.org/ac

Ratiometric Cataluminescence for Rapid Recognition of Volatile Organic Compounds Based on Energy Transfer Process

Jiaxi Hu,[†] Lichun Zhang,[†] Hongjie Song,[†] Jianyu Hu,[†] and Yi Lv^{*,†,‡}

[†]Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China

*Analytical and Testing Center, Sichuan University, Chengdu 610064, China

S Supporting Information

ABSTRACT: Recognition of volatile organic compounds (VOCs) is a hot topic full of challenge from the perspective of environmental protection and human security. Here, we developed a novel ratiometric cataluminescence (RCTL) method for fast identification and detection gas compounds at various concentrations based on the energy transfer process, by the means of introducing rare earth ions codoped metal oxide into cataluminescence (CTL) sensor system to work as sensing material. When the prepared stick-like Y_2O_3 :Eu³⁺,Tb³⁺ is exposed to kinds of analytes, different energy transfer process take place to emit two new signals at the characteristic wavelength of Tb^{3+} (I_{Tb}) and Eu^{3+} (I_{Eu}), which is available for us to identify miscellaneous gaseous compounds rely on the ratio of I_{Tb} to I_{Eu} (I_{Tb}/I_{Eu}). To confirm the feasibility of the proposed method, seven kinds of gas compounds, including homologous series and even structural



isomers, were investigated and successfully distinguished in a wide range of concentrations. Besides, further discussion of the CTL sensing and recognition mechanism in this paper has facilitating effects on exploring reactive intermediates and explaining the essential principle of catalytic oxidation process.

Volatile organic compounds (VOCs), chemicals that exist in the air as a form of gaseous states at room temperature, will bring about adverse health effects to human body on account of their special odor, toxicity, irritation, and carcinogenicity. More seriously is that immune system, digestive system, and nervous system function could be destroyed once severely exposed to VOCs.¹ Now, therefore, detection and recognition of VOCs forced to be a hot issue demanding prompt solution from a standpoint of environmental protection and human security. During the past decades, considerable effort has been dedicated to developing a series of methods for the detection and identification of gaseous samples, including chromatography/mass spectrometry (GC/MS), inductively coupled plasma mass spectrometry (ICPMS), bioinspired artificial olfactory systems, gas sensors, and so on. Among others, advantages of rapid response, good economic benefits, and low background make sensor technique, especially cataluminescence-based gas sensor, to be one of the most promising recognition methods. Except for specific recognition of unknown analyte with superior selectivity,^{2-5°} cataluminescence (CTL) gaseous sensing technology is also capable of realizing quantification and recognition of various simple or complex chemicals.^{6,7}

Cataluminescence, an interesting phenomenon, refers to the heterogeneous catalytic reaction occurs on the surface of solid catalytic materials accompanying by luminescence emission.⁸ During the course of conventional CTL reaction, the emitted light is derived from the deactivation of active intermediates from excited states back to ground states.⁹ Specific to diverse gaseous compounds, the generated active intermediates are characteristic, which is considered to be the cornerstone of identifying different VOCs. Put it another way, in contact with analytes, the CTL sensing systems bring about particular response pattern toward a certain sample. Many splendid CTLbased analysis strategies for gaseous recognition were set up on that premise. For instance, Zhang's group first developed a CTL imaging sensor array system⁶ and further to make it successfully apply to actual detection.¹⁰ Based on these pathbreaking works, researchers devoted permanent efforts to establishing novel analysis strategies utilizing less sensing unit to reach better stabilities and reproducibility, such as closed reaction cell system,¹¹ cyclic chemiluminescence system,¹² transient cataluminescence analysis method,¹³ and so on. While based on some rare earth ion doped materials, especially lanthanide ions, there always involves one more energy transfer process from the original intermediates to the rare earth ions, in which the luminescence produced by more reason for excited rare earth ion, leading to the change in the premium wavelength.¹⁴ So that we expect that if double rare earth ions are doped into the base catalyst to respond toward the measured gaseous, both of the rare earth ions are tend to accept the energy released from the original excited

```
Received: February 1, 2019
Accepted: March 14, 2019
Published: March 14, 2019
```

Analytical Chemistry

intermediate. Under the circumstance, the premium wavelength changes to the characteristic wavelength of the rare earth ions to obtain two new peaks in CTL spectrum, which magnify the discrepancy of the original active intermediates versus diverse VOCs, thereby making it possible for us to identify the analytes using the ratio of the signals under the characteristic wavelength of the rare earth ions based on the different energy transfer abilities of the original excited intermediates. Therefore, a novel ratiometric cataluminescence (RCTL) analysis method was established for gas discrimination based on a single element of rare earth ions codoped compounds.

Sensing material not only play the most critical role to response toward the tested analytes with regard to CTL-based sensor system, but also is the foundation of the proposed method. Rare earth compounds, with premium properties of reliable optical applications and enhanced catalytic performances, have broad application value in the fields of electricity, magnetism, biomedical, optics, and catalytic.^{15–18} Particularly, in virtue of the extraordinary spectroscopic properties and luminescent dynamics deriving from unique 4f electrons, lanthanide ions are pervasive in the application for biochemical. Along with introducing rare earth ions into nanomaterial to act as sensing unit in CTL sensors, enhancement of luminescence signals and high efficiency could be obtained, which has been demonstrated by many researchers.¹⁴ It was proved by Zhang's group¹⁹ that among various ions doped ZrO₂ nanomaterials, Eu³⁺ or Tb³⁺ could trigger energy transfer process to produce new peaks. In addition, Y2O3 with advantages of favorable optical and electrical properties and superior catalytic performance have broad application in many fields,^{17,20} including CTL sensor systems.²¹ Thus, rare earth ions Eu^{3+} and Tb^{3+} codoped Y_2O_3 material was synthesized to verify the proposed hypothesis in our experiments. The strongest emission bands of Tb³⁺ and Eu³⁺ originated from ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ (~545 nm) and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (~620 nm), respectively, are supposed to be the critical wavelength,^{22,23} under which the ratio of their intensities were used to characterize the different gases. Note that the two wavelengths are so far apart that two peaks barely overlap. As a result, the rare earth ions codoped compound of Y2O3:Eu3+,Tb3+ was used for the mentioned novel RCTLbased methodology.

In this work, we developed a novel RCTL-based analysis strategy for the simultaneous detection and recognition of VOCs upon Eu, Tb codoped Y₂O₃, which provided new thoughts for CTL-based gas sensor armed with only single sensing elements to achieve gas identification. The stick-like Y₂O₃:Eu³⁺,Tb³⁺ nanomaterial was synthesized by simple hydrothermal method performing rapid response and extraordinary catalytic activity, and was first introduced into CTLbased sensing system. As a proof-of-principle work, catalytic oxidation reactions of different kinds of VOCs, containing homologous series or even structural isomers, were studied upon the Y_2O_3 :Eu³⁺,Tb³⁺ to verify the hypothesis. In addition, for the purpose of well understanding, the mechanism of the established new analysis method, CTL behavior and reaction process of ethyl ether, acetaldehyde and isobutanol were further investigated, which also produce the enormous pushing action to explore and explain the essential principle of luminescence process and catalytic oxidation reaction.

EXPERIMENTAL SECTION

Chemicals. All reagents were of analytical grade and no further purification is required. $Y(NO_3)_3 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$, and Tb_4O_7 were purchased from Adamas Reagent Co., Ltd. NaOH, nitric acid, acetone, butanone, acetaldehyde, butanal, isopropanol, isobutanol, and ethyl ether were obtained from Chengdu Kelong Chemical Reagent Company (China). Deionized water was obtained from a Milli-Q water purification system (Ulupure Co. Ltd., Chengdu, China).

Sample Preparation of Pure Y₂O₃ and Eu, Tb Doped Y_2O_3 . A hydrothermal method was adopted to synthesize a series of powder samples with the chemical composition of $Y_{(2-x-y)}O_3:xEu^{3+},yTb^{3+}(x = 0 \sim 0.12, y = 0 \sim 0.12)$, where Y atoms occupations were considered to be replaced by rare earth atoms. According to each stoichiometric amount of Eu_2O_3 , Y_2O_3 , $Y_{1.94-x}O_3$: xEu^{3+} , 0.06 Tb³⁺ (x = 0, 0.03, 0.06, 0.09, 0.12), $Y_{1.94-y}O_3:0.06Eu^{3+}, yTb^{3+}$ (x = 0, 0.03, 0.06, 0.09, 0.12), raw materials of nitrate of Y, Eu, and Tb were added into proper amount of deionized with continuous stirring until dissolved completely, respectively. Then, mix the above solutions together and dropwise add 10% NaOH solution until pH \sim 11, accompanied by stirring for 30 min. The resultant suspension was followed by transferring into Teflonlined stainless-steel autoclave and temperature was kept at 140 °C for 12 h. After reacting and cooling naturally to room temperature, the resulting products were collected by washing and centrifuging with distilled water and absolute ethanol several times, and were dried in air at 60 °C for 24 h. Finally, the required oxidation products were obtained via calcining at 600 °C for 4 h.

Characterization. The crystal structures of Y_2O_3 , Eu_2O_3 , and $Y_{2-x-y}O_3$: xEu^{3+} , yTb^{3+} ($x = 0 \sim 0.12$, $y = 0 \sim 0.12$) were carried out utilizing an X'Pert pro X-ray diffractometer (XRD, Philips) equipped with Cu K α_1 ($\lambda = 1.5406$ Å) radiation. Step scan mode was employed in the 2θ range of $10 \sim 80^{\circ}$ with a step size of 0.02° and counting time of 0.12 s for each step (scan rate was 10° per min). The sizes and surface morphologies of the as-prepared material $Y_{1.88}O_3$:0.06Eu³⁺,0.06Tb³⁺ were investigated by scanning electron microscopy (SEM, Hitachi, S3400). Transmission electron microscopy (HRTEM) images was performed on a transmission electron microscope (Tecnai G2F20 S-Twin, FEI Co., Hillsboro, OR) at an accelerating voltage of 200 kV. Shimadzu QP2010 GC/MS instrument was used for the mechanism research.

RCTL signals were measured based on 0.03 g sensing material via a BPCL ultraweak luminescence analyzer (Institute of Biophysics, Academia Sinica, Beijing, China) equipped with a photomultiplier tube (Hamamatsu, Japan). And 0.1 s per spectrum was set as the data integration time of BPCL ultraweak luminescence analyzer, and -800 V served as the working voltage of photomultiplier tube. Besides, CTL gas sensor, containing injection system, reaction system and detection system, were prepared as our previous works.¹³

RESULTS AND DISCUSSION

Structure and Morphology of $Y_{2-x-y}O_3:xEu^{3+},yTb^{3+}$ Catalysts. The identifications of crystal structure and purity of isomorphic $Y_{2-x-y}O_3:xEu^{3+},yTb^{3+}$ samples were confirmed by X-ray powder diffraction analysis with the typical X-ray diffractograms of the 2θ range $10 \sim 80^\circ$. XRD patterns of a



Figure 1. (a) XRD patterns of nanomaterials of $Y_{1,94-x}O_3:0.06Eu^{3+},xTb^{3+}$ ($x = 0 \sim 0.12$). (b) XRD patterns of nanomaterials of $Y_{1,94-x}O_3:xEu^{3+},0.06Tb^{3+}$ ($x = 0 \sim 0.12$). (c) The linear evolution for the unit cell volume versus the Tb proportion of the $Y_{1,94-x}O_3:0.06Eu^{3+},xTb^{3+}$ ($x = 0 \sim 0.12$). (d) The linear evolution of the unit cell volume vs the Eu proportion for the $Y_{1,94-x}O_3:xEu^{3+},0.06Tb^{3+}$ ($x = 0 \sim 0.12$).



Figure 2. Comparison of CTL spectra on the surface of (a) pure Y_2O_3 , (b) mixture of Y_2O_3 and Eu_2O_3 (Eu:Y = 0.06:1.94), (c) $Y_{1.94}O_3:0.06Eu^{3+}$, and (d) $Y_{1.88}O_3:0.06Eu^{3+},0.06Tb^{3+}$. Experiment condition: injection volume, 1 μ L; working temperature, 280 °C; flow rate, 300 mL min⁻¹.

series of codoped Y_2O_3 materials with different doping ratios of rare earth ions, including $Y_{1.94-y}O_3:0.06Eu^{3+},yTb^{3+}$ (x = 0, 0.03, 0.06, 0.09, 0.12) and $Y_{1.94-x}O_3:xEu^{3+},0.06Tb^{3+}$ (x = 0, 0.03, 0.06, 0.09, 0.12), were displayed in Figure 1a,b. Each diffractogram of the representative sample was indexed and conformed with that of standard cubic Y_2O_3 (JCPDS: No. 41-1105) only accompanied by a slight shift in the peak positions, demonstrating that the crystal structures were not altered significantly after doping rare earth ions. It can be deduced that Eu^{3+} and Tb^{3+} ions substitute for Y^{3+} ions to occupy their sites in the $Y_{2-x-y}O_3:xEu^{3+},yTb^{3+}$ samples with the essential conditions of comparable ionic radii and identical valency. With the reason that the ionic radii of Eu^{3+} (0.947 Å) and Tb^{3+} (0.923 Å) ions were subtle larger than that of Y³⁺ (0.9 Å), there will be an extension of lattice and a slight increase in lattice parameters, resulting in that the diffraction peaks shift to lower angle in according with Bragg's Law.^{24,25} Besides, specific results of lattice parameters and cell unit density of the as-synthesized Y₂O₃:xEu³⁺,yTb³⁺ were listed in Table S1. In our experiment, under the condition of fixing the doping concentration of Eu³⁺ (Tb³⁺) at 6%, the volume of unit cell will increase linearly as an addition of the Tb³⁺(Eu³⁺) concentration with a range of 0~0.12 in units of 0.03, as presented in Figure 1c,d. Besides, we also synthesized pure Y₂O₃ and Eu₂O₃ for the latter experiments, whose XRD patterns are shown as Figure S1. EDS pattern of Y_{1.88}O₃:0.06Eu³⁺,0.06Tb³⁺ is also

4862

Article



Figure 3. CTL intensities comparison of seven kinds of VOCs on the surface of (a) $Y_{1.94-x}O_3:0.06Eu^{3+}, xTb^{3+}$ ($x = 0.03 \sim 0.12$) and (b) $Y_{1.94-x}O_3:xEu^{3+}, 0.06Tb^{3+}$ ($x = 0.03 \sim 0.12$). Experiment condition: injection volume, 1 μ L; working temperature, 280 °C; flow rate, 300 mL min⁻¹.

supplied in Figure S2, which further proved that Eu³⁺ and Tb³⁺ ions were doped into Y_2O_3 successfully. And the result of the EDS illustrated that the atomic ratio of Tb to Eu to Y was around 1.1:1.1:34, which identify with that added in the synthesis process. In addition, SEM and TEM techniques were used to reveal the morphology of $Y_{1.88}O_3$:0.06Eu³⁺,0.06Tb³⁺. It can be seen from Figure S3a-c that the uniform stick-like morphology of $Y_{1.88}O_3$:0.06Eu³⁺,0.06Tb³⁺ was obtained by a new and simple hydrothermal method. Moreover, the HRTEM image is displayed in Figure S3d, in which the lattice fringe of sample was clearly observed. The interplanar distance is 0.306 nm, corresponding to the (222) planes of $Y_{1.88}O_3$:0.06Eu³⁺,0.06Tb³⁺.

Energy Transfer Ability of Rare Earth lons Doped Y₂O₃ Catalysts. In order to explore the discrepancy of energy transfer properties, CTL spectral curves of VOCs, acquired by several optical filters with wavelength ranged from 400 to 640 nm, were investigated on the surface of different materials, including pure Y_2O_3 , mixture compound of Y_2O_3 and Eu_2O_3 (atomic ratio of Eu:Y = 0.06:1.94), single-doped material of Y_{1.94}O₃:0.06Eu³⁺ and codoped material of $Y_{1.88}O_3: 0.06Eu^{3+}, 0.06Tb^{3+}$. From Figure 2a,b, CTL spectra upon the mixture compound primarily displayed the characteristic wavelength of their own intermediates and extremely weak peaks of the Eu³⁺ characteristic wavelength at around 620 nm, compared with that on pure Y2O3. While the spectral curves based on the doped material of $Y_{1,94}O_3:0.06Eu^{3+}$ showed the dramatically strong peaks at the Eu³⁺ characteristic wavelength of 620 nm, accompanied by an almost disappeared original peak, as seen from Figure 2c. And multipeaks appeared in the CTL spectra for each VOC on the codoped material of $Y_{1.88}O_3$:0.06Eu³⁺,0.06Tb³⁺, as employed in Figure 2d. To be specific, positions of two main new peaks produced in the CTL spectra were at characteristic wavelength of Tb³⁺ of 545 nm and Eu³⁺ of 620 nm, and another new peak at 490 nm was assigned to the second characteristic wavelength of Tb³⁺. Hence, it can be concluded that high-efficiency energy transfer processes from the original intermediates to rare earth ions are able to occur only based on rare earth ion doping materials. Furthermore, different intensities at the wavelength of 545 and 620 nm or even disparate ratios of the two intensities were acquired for diverse VOCs on Y_{1.88}O₃:0.06Eu³⁺,0.06Tb³⁺, which lay a foundation for recognizing various VOCs.

CTL Properties of VOCs upon Rare Earth Doped Y_2O_3 Catalysts. Owing to a positive correlation between catalytic activity of materials and conversion of reaction,²⁶ total CTL signals were measured to select premium sensing material. Based on various codoped materials of as-synthesized $Y_{2-x-y}O_3:xEu^{3+},yTb^{3+}$ (x = 0~0.12, y = 0~0.12), various VOCs, including acetone, butanone, butanal, isobutanol, isopropanol, ethyl ether, and acetaldehyde, were introduced into the sensor independently by the carrier gas to measure the CTL intensity, as presented in Figure 3. The results displayed that each catalyst was able to response to the VOCs with certain strength, among which the Y_{1.88}O₃:0.06Eu³⁺,0.06Tb³⁺ showed superior behavior toward most of the VOCs than the others, so that it was selected to carry out the subsequent experiments and verify the hypothesis mentioned previous. For the sake of superior performance of the catalyst toward VOCs, condition optimization of experiment should be done at the beginning. As shown in Figure S4, the optimum condition turned out to be 300 mL min⁻¹ for the air flow rate and 280 °C for the reaction temperature, which were also used for the following experiments.

Identification of VOCs. On the basis of the assumption mentioned before, $Y_{2-x-y}O_3:xEu^{3+},yTb^{3+}$ contains two energy acceptors to receive the energy released from the original excited intermediates to generate excited rare earth ions of Tb^{3+*} and Eu^{3+*}, which are supposed to emit signals at the wavelength of 545 and 620 nm, respectively,¹⁹ during the deactivation of excited species to the ground states. And the ratios of $I_{\rm Tb}/I_{\rm Eu}$ are characteristic for different VOCs. In order to confirm the feasibility and capacities to differentiate the compounds based on the proposed novel analysis method, various concentrations of different VOCs were introduced into the sensing system individually to conduct further investigation. The results of the CTL response curves of various VOCs at five concentrations under 545 and 620 nm were illustrated in the left side of Figures 4 and S4, in which three parallel experiment results were offered to reflect the repeatability and reliability of the proposed method. It could be calculated to obtain the values of $I_{\rm Tb}/I_{\rm Eu}$ for various VOCs, which are different from each other. What counts is that the $I_{\rm Tb}/I_{\rm Eu}$ value was not correlated with the concentration for a given analyte under certain conditions, which makes this method to be efficient and practical for us to detect and recognize different compounds at varies concentrations. From the results of experiment, VOCs with various types (e.g.: butanone $(I_{\rm Tb}/I_{\rm Eu} = 1.33)$ and isobutanol $(I_{\rm Tb}/I_{\rm Eu} = 0.75))$, homologous series (e.g.: acetone $(I_{Tb}/I_{Eu} = 1.74)$ and butanone $(I_{\rm Tb}/I_{\rm Eu} = 1.33))$, or even structural isomers (e.g.: butanone ($I_{Tb}/I_{Eu} = 1.33$) and butanal ($I_{Tb}/I_{Eu} = 0.95$)) can be successfully identified utilizing the analysis method.

Simultaneously, quantitative analysis of these VOCs also can be achieved by this sensing system as presented in the right side of Figures 4 and S4, in which either correlation curves of



Figure 4. CTL response curves of actone, butanoe, butanal and isobutanol at 545 and 620 nm vs five concentrations on the basis of $Y_{1.88}O_3$:0.06Eu³⁺,0.06Tb³⁺ material. (left) Calibration curves for I_{Tb} intensity at 545 nm and I_{Eu} intensity at 620 nm of various gas compounds based on the $Y_{1.88}O_3$:0.06Eu³⁺,0.06Tb³⁺ material. (right) Experiment condition: working temperature, 280 °C; flow rate, 300 mL min⁻¹.

545 and 620 nm was employed to quantify the initial concentration of the measured analytes. By the way, as shown in Figure S5, total intensity detected without optical filters also can be used to realize quantitative analysis, which exhibited higher sensitivity and wider linear range. And the specific value of $I_{\rm Tb}/I_{\rm Eu}$, linear range, and the limit of detection of seven kinds of VOCs were listed in Table 1.

Possible Mechanism. When referring to the mechanism of distinguishing VOCs by the ratios of $I_{\rm Tb}/I_{\rm Eu}$, take ethyl ether, acetaldehyde, and isobutanol as model examples to specifically explore. GC-MS experiments were carried out to prove and speculate the possible intermediates in the catalytic oxidation reaction for the three analytes. Accompanied by carrier gas with the flow rate as low as possible to prevent the

Table 1. Data of Confidence Interval ($\alpha = 0.05$) for $I_{\rm Tb}/I_{\rm Eu}$, Linear Range, and the Detection Limit of Seven Kinds of VOCs

VOCs	confidence interval of $I_{\rm Tb}/I_{\rm Eu}~(\alpha = 0.05)$	linear range $(\mu g m L^{-1})$	detection limit $(\mu g m L^{-1})$
acetone	1.74 ± 0.03	5.98-203.50	0.094
butanone	1.33 ± 0.07	3.12-128.86	0.050
butanal	0.95 ± 0.06	4.38-140.40	0.059
isobutanol	0.75 ± 0.03	3.58-229.14	0.18
isopropanol	2.08 ± 0.08	2.62-78.54	0.63
ethyl ether	0.59 ± 0.04	4.76-428.10	0.53
acetaldehyde	1.58 ± 0.15	28.49-522.27	0.21

air bubbles from taking the exhaust away, the gaseous products of the measured VOCs were collected by DMF solution for a certain time to ensure that the samples were sufficient for detection. Then the collected residual compounds were introduced into the Shimadzu QP2010 GC/MS instrument to analyze. It has already been proved that the intermediates of the ethyl ether and acetaldehyde were CH3CHO* and CH₃CH=CHCHO*, respectively, by many researchers,^{27,28} which is also in accord with our results of GC-MS experiment as shown in Figure 5a,b. Aimed at the products of the catalytic oxidation of ethyl ether and acetaldehyde, except for the undecomposed reactants, CH₃CHO and CH₃CH=CHCHO were detected and found at 1.641 and 3.178 min, respectively. Even so, our group have demonstrated that multifarious intermediates were possible to produce in the catalytic oxidation process of ethyl ether by theoretical calculation.²⁹ As for isobutanol, from the Figure 6a, double peaks of the CTL kinetic curve on pure Y₂O₃ might be generated from the producing of two or more intermediates during the course of the catalytic oxidation reaction, which emitted two signals with the energy release during the deactivation of two excited species to the ground states. Moreover, CTL signals at different wavelength were recorded with optical filters in Figure 3a. It could be speculated that multiple peaks of the CTL spectrum correspond to the presence of multiple excited species at different wavelength. In addition, the concrete products were further verified by GC-MS experiment as presented in Figure 5c. Except for the undecomposed reactant isobutanol (2.703 min), another five products of the catalytic oxidation of isobutanol were found to be CO_2 (1.595 min), $CH_2 = C(CH_3)_2$ (1.694 min), $CH_3 COCH_3$ (1.883 min), epoxy isobutane (2.157 min), and CH₂=C(CH₃)CHO (2.220 min). Based on the fundamental organic chemistry knowledge, the catalytic reaction pathway might be carried out as Figure 6b. In consequence, the most probable intermediates

for isobutanol were considered to be $CH=C(CH_3)-CHO^*$ and CO_2^* with the reason of the high yields and more general forms of intermediates.

As mentioned above, various intermediates could generate during a course of the catalytic oxidation of a compound,³⁰ which could be the sufficient condition of the following formula: $aA \rightarrow bB^* + cC^*$ (B* and C* stand for the intermediates generated from the catalytic reaction of compound A). It is widely known that the chemiluminescence (CL) efficiency (φ_{cl}) is equal to the product of chemical reaction efficiency (φ_r) and luminescence efficiency (φ_f) , which represent the percentages of excited molecules and the molecules in the reaction, as well as luminescent molecules and excited molecules, respectively.³¹ And the intensity of CL (I_{cl}) is positively correlated with the reaction rate and CL efficiency, which can be expressed as $I_{cl} = \varphi_{cl} \cdot dc/dt$. In this work, energy transfer procedure introduces a parameter of energy transfer efficiency ($\varphi_{\rm ET}$), meaning the percentage of excited rare earth ions and excited molecules, so that the expression of CL intensity could be regarded as $I_{cl} = \varphi_{cl} \cdot \varphi_{ET} \cdot dc_A / dt$. In detail, the whole procedure can be divided into three steps as follow.

First step is catalytic oxidation process, which can be expressed as

$$aA \xrightarrow{[0]} bB^* + cC^* \tag{1}$$

$$c_{\mathrm{B}*} = \alpha_{\mathrm{B}*}c_{\mathrm{A0}} \tag{2}$$

$$c_{\mathrm{C}*} = \alpha_{\mathrm{C}*}c_{\mathrm{A0}} \tag{3}$$

(a, b and c are the stoichiometric numbers of reactant A, product B*, and product C*, respectively. α_{B^*} and α_{C^*} represent conversion rate of the reactant. c_{B^*} and c_{C^*} represent the concentration of intermediates B* and C* generated at some point, and c_{A0} represents the initial concentration of compound A.)

Second step is energy transfer process,³² which can be expressed as

$$B^* + Eu^{3+} \to B + Eu^{3+*}(\varphi_{B1})$$
 (4)

$$B^* + Tb^{3+} \to B + Tb^{3+*}(\varphi_{B2})$$
 (5)

$$C^* + Eu^{3+} \to C + Eu^{3+*}(\varphi_{C1})$$
 (6)

$$C^* + Tb^{3+} \to C + Tb^{3+*}(\varphi_{C2})$$
 (7)

or

$$B^{*} + Eu^{3+} + Tb^{3+} \to B + Eu^{3+*}(\varphi_{B1}) + Tb^{3+*}(\varphi_{B2})$$
(8)



Figure 5. GC chromatogram of the reaction products generated from the catalytic oxidation of (a) ethyl ether, (b) acetaldehyde, and (c) isobutanol upon the $Y_{1.88}O_3:0.06Eu^{3+}, 0.06Tb^{3+}$ material.

Article



Figure 6. (a) CTL response kinetic curve of isobutanol upon the $Y_{1.88}O_3: 0.06Eu^{3+}, 0.06Tb^{3+}$ material. (b) Possible catalytic oxidation process of isobutanol.

$$C^* + Eu^{3+} + Tb^{3+} \to C + Eu^{3+*}(\varphi_{C1}) + Tb^{3+*}(\varphi_{C2})$$
(9)

 $(\varphi_{B1}, \varphi_{B2}, \varphi_{C1}, \text{ and } \varphi_{C2}$ represent the energy transfer efficiency from B* to Eu³⁺ and Tb³⁺, as well as C* to Eu³⁺ and Tb³⁺, respectively).

Third step is luminescence process, which can be expressed as

$$\operatorname{Eu}^{3+*} \to \operatorname{Eu}^{3+}(K_{\operatorname{Eu}}) \tag{10}$$

$$\mathrm{Tb}^{3+*} \to \mathrm{Tb}^{3+}(K_{\mathrm{Tb}}) \tag{11}$$

($K_{\rm Eu}$ and $K_{\rm Tb}$ represent the luminescent efficiency of Eu³⁺* and Tb³⁺*).

Since the characteristic wavelength of Tb^{3+} and Eu^{3+} are 545 and 620 nm, respectively,³³⁻³⁵ the CL intensity under 545 and 620 nm represent the luminescent signal generated by the energy transferred from intermediates to Tb^{3+} and Eu^{3+} , respectively.

under 545 nm:
$$I_{\rm Tb} = K_{\rm Tb}(\varphi_{\rm B2} dc_{\rm B*}/dt + \varphi_{\rm C2} dc_{\rm C*}/dt)$$

$$= K_{\rm Tb}(\varphi_{\rm B2} d\alpha_{\rm B*} c_{\rm A0}/dt + \varphi_{\rm C2} d\alpha_{\rm C*} c_{\rm A0}/dt)$$

$$= K_{\rm Tb}(\varphi_{\rm B2} \alpha_{\rm B*} + \varphi_{\rm C2} \alpha_{\rm C*}) dc_{\rm A0}/dt$$
(12)

under 620 nm: $I_{\text{Eu}} = K_{\text{Eu}}(\varphi_{\text{B1}} dc_{\text{B*}}/dt + \varphi_{\text{C1}} dc_{\text{C*}}/dt)$

$$= K_{\rm Eu}(\varphi_{\rm B1} d\alpha_{\rm B*} c_{\rm A0}/dt + \varphi_{\rm C1} d\alpha_{\rm C*} c_{\rm A0}/dt)$$
$$= K_{\rm Eu}(\varphi_{\rm B1} \alpha_{\rm B*} + \varphi_{\rm C1} \alpha_{\rm C}) dc_{\rm A0}/dt$$
(13)

$$\begin{split} I_{\rm Tb}/I_{\rm Eu} &= K_{\rm Tb}(\varphi_{\rm B2}\alpha_{\rm B^*} + \varphi_{\rm C2}\alpha_{\rm C^*}) {\rm d} t_{\rm A0}/{\rm d} t/K_{\rm Eu}(\varphi_{\rm B1}\alpha_{\rm B^*} + \varphi_{\rm C1}\alpha_{\rm C^*}) {\rm d} t_{\rm A0}/{\rm d} t\\ &= K_{\rm Tb}(\varphi_{\rm B2}\alpha_{\rm B^*} + \varphi_{\rm C2}\alpha_{\rm C^*})/K_{\rm Eu}(\varphi_{\rm B1}\alpha_{\rm B^*} + \varphi_{\rm C1}\alpha_{\rm C^*}) \end{split}$$
(14)

Under certain conditions, α , φ , and K are constant, so that the value of $I_{\rm Tb}/I_{\rm Eu}$ should also be constant, which is consistent with the results of our experiment that $I_{\rm Tb}/I_{\rm Eu}$ is independent with the initial concentration of compound A. It also can be inferred from the eq 14 that the ratio of $I_{\rm Tb}/I_{\rm Eu}$ depends on the types and proportion of the intermediates (B* and C*) produced in the catalytic oxidation reaction.

CONCLUSIONS

Broadly speaking, we established a novel RCTL analysis method based on energy transfer to determine and distinguish various VOCs at different concentrations on the surface of

stick-like rare earth ions (Eu, Tb) codoped Y₂O₃ that was the first time to be introduced into CTL sensors. On the basis of Y₂O₃:Eu³⁺,Tb³⁺, the energy transfer process was involved in the whole catalytic reaction to produce the excited species of Tb³⁺* and Eu³⁺* that will emit two signals at 545 and 620 nm, respectively, to return back to ground states, which make it possible for us to determine different compounds with homologous series and even structural isomers on the grounds of the ratio of $I_{\rm Tb}/I_{\rm Eu}$. The proposed strategy provides researchers diverse CTL behavior from single sensing material by taking advantage of energy transfer mechanism. It should be expected that the application of rare earth ions codoped compounds in CTL area could be a new trend to realize the identification of more complex analytes or even gas mixture via introducing more rare earth ions into the host nanomaterial or establishing sensor array with analogous codoped compounds containing different types and ratios of rare earth ions. Furthermore, the discussion and exploration of the mechanism in this paper contribute to investigating reactive intermediates and explaining catalytic oxidation process.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.anal-chem.9b00592.

Lattice parameters of the prepared $Y_{2-x}O_3:xEu^{3+},yTb^{3+}$ ($x = 0 \sim 0.12$, $y = 0 \sim 0.12$) (Table S1); XRD patterns of pure Y_2O_3 and Eu_2O_3 (Figure S1); EDS pattern of $Y_{1.88}O_3:0.06Eu^{3+},0.06Tb^{3+}$ (Figure S2); SEM, TEM, and HRTEM patterns of $Y_{1.88}O_3:0.06Eu^{3+},0.06Tb^{3+}$ (Figure S3); optimization of flow rate and temperature (Figure S4); CTL response curves and calibration curves of isopropanol, ethyl ether, and acetaldehyde under 545 and 620 nm (Figure S5); calibration curves of acetone, butanone, butanal, isobutanol, isopropanol, ethyl ether, and acetaldehyde (Figure S6) (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: lvy@scu.edu.cn. Tel./Fax: +86-28-8541-2798.

ORCID

Yi Lv: 0000-0002-7104-2414

Notes

The authors declare no competing financial interest.

Analytical Chemistry

ACKNOWLEDGMENTS

The National Natural Science Foundation of China is gratefully acknowledged (Nos. 21874094 and 21675113). This work is also supported by the Science and Technology Department of Sichuan Province (19YYJC2423) and the Fundamental Research Funds for the Central Universities. Prof. Yingying Su and Dr. Shuguang Yan from Analytical and Testing Center, Sichuan University, are gratefully thanked for technical assistance.

REFERENCES

- (1) Rakow, N. A.; Suslick, K. S. Nature 2000, 406, 710-713.
- (2) Zhang, Z. Y.; Zhang, C.; Zhang, X. R. Analyst 2002, 127, 792-796.
- (3) Wu, L. Q.; Zhang, L. C.; Sun, M. X.; Liu, R.; Yu, L. Z.; Lv, Y. Anal. Chem. 2017, 89, 13666–13672.
- (4) Li, L.; Deng, D. Y.; Huang, S. X.; Song, H. J.; Xu, K. L.; Zhang, L. C.; Lv, Y. Anal. Chem. **2018**, 90, 9598–9605.
- (5) Song, H. J.; Zhang, L. C.; He, C. L.; Qu, Y.; Tian, Y. F.; Lv, Y. J. Mater. Chem. 2011, 21, 5972–5977.
- (6) Na, N.; Zhang, S. C.; Wang, S.; Zhang, X. R. J. Am. Chem. Soc. 2006, 128, 14420–14421.
- (7) Na, N.; Liu, H. Y.; Han, J. Y.; Han, F. F.; Liu, H. L.; Ouyang, J. Anal. Chem. **2012**, *84*, 4830–4836.
- (8) Tang, F.; Guo, C. A.; Chen, J.; Zhang, X. R.; Zhang, S. C.; Wang, X. H. *Luminescence* **2015**, *30*, 919–939.
- (9) Zhang, L. C.; Song, H. J.; Su, Y. Y.; Lv, Y. TrAC, Trends Anal. Chem. 2015, 67, 107–127.
- (10) Wu, Y. Y.; Na, N.; Zhang, S. C.; Wang, X.; Liu, D.; Zhang, X. R. Anal. Chem. **2009**, 81, 961–966.
- (11) Zhang, R. K.; Cao, X. A.; Liu, Y. H.; Chang, X. Y. Anal. Chem. **2011**, 83, 8975–8983.
- (12) Zhang, R. K.; Hu, Y. F.; Li, G. K. Anal. Chem. 2014, 86, 6080–6087.
- (13) Xu, H. L.; Li, Q. Y.; Zhang, L. C.; Zeng, B. B.; Deng, D. Y.; Lv, Y. Anal. Chem. **2016**, 88, 8137–8144.
- (14) Zhou, Q.; Zhang, L. C.; Fan, H. Y.; Wu, L.; Lv, Y. Sens. Actuators, B 2010, 144, 192-197.
- (15) Kratsch, J.; Roesky, P. W. Angew. Chem., Int. Ed. 2014, 53, 376–383.
- (16) Li, L. J.; O'Farrell, E. C.; Loh, K. P.; Eda, G.; Ozyilmaz, B.; Castro Neto, A. H. *Nature* **2016**, *529*, 185–189.
- (17) Serrano, D.; Karlsson, J.; Fossati, A.; Ferrier, A.; Goldner, P. Nat. Commun. 2018, 9, 2127.
- (18) Liu, C. Y.; Hou, Y.; Gao, M. Y. Adv. Mater. 2014, 26, 6922–6932.
- (19) Zhang, Z. Y.; Xu, K.; Baeyens, W. R. G.; Zhang, X. R. Anal. Chim. Acta 2005, 535, 145–152.
- (20) Wakefield, G.; Holland, J.; Dobson, P.; Hutchison, J. Adv. Mater. 2001, 13, 1557–1560.
- (21) Zhang, L. C.; Hou, X. L.; Liu, M.; Lv, Y.; Hou, X. D. Chem. -Eur. J. 2011, 17, 7105-7111.
- (22) Shang, M. M.; Li, G. G.; Kang, X. J.; Yang, D. M.; Geng, D. L.; Lin, J. ACS Appl. Mater. Interfaces 2011, 3, 2738–2746.
- (23) Cooper, D. R.; Capobianco, J. A.; Seuntjens, J. Nanoscale 2018, 10, 7821–7832.
- (24) Li, K.; Fan, J.; Mi, X. Y.; Zhang, Y.; Lian, H. Z.; Shang, M. M.; Lin, J. Inorg. Chem. **2014**, *53*, 12141–12150.
- (25) Zhang, M.; Farid, M. A.; Wang, Y.; Xie, J. L.; Geng, J. L.; Zhang, H.; Sun, J. L.; Li, G. B.; Liao, F. H.; Lin, J. H. *Inorg. Chem.* **2018**, 57, 1269–1276.
- (26) Wang, X.; Na, N.; Zhang, S. C.; Wu, Y. Y.; Zhang, X. R. J. Am. Chem. Soc. 2007, 129, 6062-6063.
- (27) Zhang, L. J.; Wang, S.; Lu, C. Anal. Chem. 2015, 87, 7313–7320.
- (28) Zhang, L. J.; Wang, S.; Yuan, Z. Q.; Lu, C. Sens. Actuators, B 2016, 230, 242-249.

- (29) Hu, J.; Xu, K. L.; Jia, Y. Z.; Lv, Y.; Li, Y. B.; Hou, X. D. Anal. Chem. **2008**, 80, 7964–7969.
- (30) Yang, P.; Ye, X. N.; Lau, C.; Li, Z. X.; Liu, X.; Lu, J. Z. Anal. Chem. 2007, 79, 1425–1432.
- (31) Wang, F.; Lin, J.; Wang, H. Y.; Yu, S. S.; Cui, X. Q.; Ali, A.; Wu, T.; Liu, Y. *Nanoscale* **2018**, *10*, 15932–15937.
- (32) Strieth-Kalthoff, F.; James, M. J.; Teders, M.; Pitzer, L.; Glorius, F. Chem. Soc. Rev. 2018, 47, 7190–7202.
- (33) Li, S. W.; Zhang, X.; Hou, Z. Y.; Cheng, Z. Y.; Ma, P. A.; Lin, J. Nanoscale **2012**, *4*, 5619–5626.
- (34) Peng, D.; Wu, X.; Liu, X.; Huang, M. J.; Wang, D.; Liu, R. L. ACS Appl. Mater. Interfaces 2018, 10, 32859–32866.
- (35) vuojola, J.; Lamminmaki, U.; Soukka, T. Anal. Chem. 2009, 81, 5033–5038.