A CL Mode Detector for Rapid Catalyst Selection and Environmental Detection Fabricated by Perovskite Nanoparticles

FEI TENG,*†‡ TONGGUANG XU,* TANG TENG,§ SHUHUI LIANG,* BULGEN GAUGE,* JIE LIN,* WENQING YAO,* RUILONG ZONG,* YONGFA ZHU,*‡‡ AND YOUFEI ZHENG‡

Department of Chemistry, Tsinghua University, Beijing 100084, P.R. China, College of Environmental Science and Technology, Nanjing University of Information Science and Technology, Nanjing 210044, P.R. China, Department of Information Science, Suzhou Institute of Trade and Commerce, Suzhou 215009, P.R. China

Received November 13, 2007. Revised manuscript received January 17, 2008. Accepted February 25, 2008.

La$_1-x$Sr$_x$MnO$_3$ (x = 0, 0.2, 0.5, 0.8) nanoparticles were synthesized and their chemiluminescence (CL) and catalytic properties of CO oxidation were determined. We mainly investigated the influences of filter band length, flow rate of gas, test temperature, catalyst compositions, and particle size on CL intensities and catalytic activities of the catalysts. The catalysts were characterized by means of XRD, TEM, N$_2$ adsorption isotherm, CO-TPD, and O$_2$-TPD, etc. It was found that the strong CL response signals occurred over these perovskites nanoparticles; and that CL properties of the catalysts were well correlated with the reaction activities. These nanoparticles can be used to fabricate a stable gas detector due to a high activity and stability of perovskite structure. CL mode could be a rapid and effective method for the selection of new catalysts from thousands of materials, as well as for the detection of environmental deleterious gases.

Introduction

Chemiluminescence (CL) is defined as the emission of electromagnetic radiation (usually in the visible or near-infrared region) produced by a chemical reaction, in which the resulting molecular species are excited to the electronic excited states. While the exited molecular species fall to their ground states, a weak light is released. For a solid catalyst, CL generally results from the interaction between gas and solid surface, which has been studied for decades. In 1976, CL phenomenon was first reported by Breyssse et al. (1). They observed that during catalytic oxidation of CO on ThO$_2$ surface, a weak catalytic luminescence phenomenon has occurred. This luminescence mode was defined as “catalytic luminescence (CTL)”. At that time, however, the CTL phenomenon has not attracted attention to researchers.

Since the 1990s, nanoparticles have attracted widespread attention because of their potential applications in various fields, such as catalysis (2, 3), chemical and biochemical sensing (4, 5), and biological imaging (6, 7). Nanoparticles have been extensively researched due to their high reactivities. Nanoparticles have provided new avenues to expand the analytical applications of this CL detection mode. McCord et al. found that the interaction of porous silicon and sodium hydroxide could result in an intense CL, which suggested that CL could be generated on the surface of nanoparticles (8). The direct CL reactions of gold nanoparticles with bis(4,6-trichlorophenyl)oxalate and hydrogen peroxide have also been examined but not yet applied in analysis (9–11). The different organic vapors can be discriminated from the different CL responses in the presence of the nanoparticles. Many investigations have indicated that CL property of nanoparticles would be promising for new applications (12, 13). So far, CL properties of noble metals-based nanoparticles have been researched extensively. Since these noble metals are scarce and expensive, it is desirable to research CL properties of inexpensive materials.

Recently, CL properties of several single-oxide nanoparticles have been studied by some researchers. Zhu et al. (14) first researched CL of organic vapor over different nanoparticles, including MgO (28 nm), TiO$_2$ (20 nm), Al$_2$O$_3$ (18 nm), Y$_2$O$_3$ (90 nm), LaCoO$_3$:Sc$^{3+}$ (50 nm), and SrCoO$_3$ (25 nm). Rakow et al. (15) reported that the nanoparticles are potentially suitable for processing as a chip-mounted sensor array. Nakagawa et al. (16) have manufactured a γ-Al$_2$O$_3$ sensor to detect ethanol, aceton, and carboxyl acid, which utilize the combustibility of these chemicals on this solid. Okabayashi et al. (17) have also manufactured a Dy-doped γ-Al$_2$O$_3$ sensor used for hydrocarbon gases. Zhang et al. (14, 18–20) have designed the highly selective CL sensors for ethanol, aldehyde, ammonia, sulfureted hydrogen, and butyl ketone. They reported that ZrO$_2$ nanoparticles-based sensor for ethanol has no response to hexane, cyclohexane, ethylene, hydrogen, ammonia, and nitrogen oxides. While Tb was doped, the sensitivity of Tb-ZrO$_2$ sensor can be enhanced as high two level as that of the undoped one. They have also manufactured MgO-Al$_2$O$_3$ (4:1 mol ratio) nanosensor, which has a high selectivity to butyl ketone (21). Nevertheless, the structure–stability of the single oxides is generally not good enough to use under severe conditions. Especially at high temperatures, single oxides are easy to sinter or to transform to other crystalline phases, resulting in the decrease of sensitivity. The highly stable CL sensors are still challenged by the structure properties of materials which limit their practice applications. It is well-known that perovskites (ABO$_3$) are one of the most active and stable catalysts for the removal of pollutants (CO, NO, and hydrocarbon), and perovskites as solid oxidants have been extensively researched in environmental catalysis (22). Up to now, nevertheless, CL properties of gases on perovskites have been scarcely researched.

As we know, the catalyst selection is generally carried out by the determination of reaction activity. Generally, this determination mode is needed to construct expensive reaction equipments, and time-consumed and tedious. It is needed to design a new and rapid mode of catalyst selection. CL mode is one of the most useful methods, because the determination mode of CL can be performed within a few minutes and no expensive reaction equipment is needed. To the best of our knowledge, most of previous research about CL properties of micro- or nanosized particles have focused...
on CL applications in analysis (8, 18, 29). CL applications in catalysis have not been reported, and few studies have revealed the essence correlations between catalytic reaction and CL mechanism (24).

In this research, we reported, for the first time, CL properties for CO over perovskite La_{1−x}Sr_xMnO_3 (x = 0, 0.2, 0.5, 0.8) nanoparticles. The effects of filter band length, flow rate of gases, test temperature, catalyst compositions, and particle size on CL intensity of CO were investigated, and the essence correlation between CL and catalytic reaction of the catalyst was elucidated.

**Experimental Section**

**Chemicals.** In this work, all chemicals, including La(NO_3)_3·6H_2O (A.R.), Sr(NO_3)_2 (A.R.), Mn(NO_3)_2·2H_2O (A.R.), KOH (A.R.) and Citric acid (CA) (A.R. C_6H_8O_7·H_2O, MW = 210), were purchased from Beijing Chemicals Company of China and used as received.

**Synthesis of La_{1−x}Sr_xMnO_3 Nanoparticles (50 nm).** La_{1−x}Sr_xMnO_3 (x = 0, 0.2, 0.5, 0.8) nanoparticles were prepared by a coprecipitation method, in which the molar ratios of Sr/La/Mn were kept at (1−x)/x/1. Under ultrasonic agitation, the mixed solution of metals nitrates was mixed with KOH, while the final pH value of the mixture was adjusted to pH 9. The solids were separated by centrifugation, washed with deionized water, and dried at 80 °C overnight in an oven. The solids were then calcined at 700 °C for 5 h under flowing air.

**Synthesis of La_{0.8}Sr_{0.2}MnO_3 Nanoparticles (20 nm).** La_{0.8}Sr_{0.2}MnO_3 nanoparticles were prepared by a citrate method (25). The mixture solution was prepared by dissolving nitrates and citric acid (CA) in deionized water, in which the molar ratios of Sr/La/Mn/CA were kept at 0.8/0.2/1/4. The resulting solution was evaporated at 80 °C, and completely dried at 80 °C overnight in an oven. The obtained spongy material was crushed and calcined at 600 °C for 5 h under flowing air.

**Synthesis of La_{0.6}Sr_{0.4}MnO_3 Particles (≥ 100 nm).** The large La_{0.6}Sr_{0.4}MnO_3 particles were obtained by a solid state reaction. The metals nitrates were ground and mixed homogeneously and then calcined at 1000 °C for 2 h under flowing air.

**Characterization of the Nanoparticles.** The sample was characterized by XRD (Rigaku D/MAX-RB X-ray powder diffractometer), using graphite monochromatized Cu Kα radiation (λ = 0.154 nm), operating at 40 kV and 50 mA. The patterns were scanned from 10° to 70° (2θ) at a scanning rate of 1° min⁻¹. A nitrogen adsorption isotherm was performed at −196°C on a Micromeritics ASAP2010 gas adsorption analyzer. The sample was degassed at 250°C for 5 h before the measurement. Surface area was calculated by the BET (Brunauer–Emmett–Teller) method. The morphology of the catalyst was observed on a TEM (JEOL 200CX) instrument with an accelerating voltage of 200 kV. The powders were ultrasonically dispersed in ethanol, and then deposited on a thin amorphous carbon film supported by a copper grid.

**Chemiluminescence (CL) Experiments.** The CL detection system employed in this work is shown in the literature (14). The detect system consists of a CL-based sensor, a digital programmable temperature controller of the sensor, and an optical detector. The CL sensor was made by sintering a 0.2 mm thick layer of the catalyst powder on a cylindrical ceramic heater of 5 mm in diameter. Typically, 0.03 g of catalyst powders were mixed with absolute ethanol to prepare a paste, and the paste was coated on the surface of the heating tube; and then it was heated in an oven at 110°C for 24 h and heated at 500°C for 1 h in air to form a coating. In order to accurately control the thickness, the same procedure was repeated. The obtained sensor was set in a quartz tube of 12 mm (i.d.) through which air at atmospheric pressure flows at a constant rate. A certain volume pulse of CO was injected into the air flow. The sample gas can flow only through the outside of the ceramic heater because this ceramic tube is solid. The temperature of the sensor was controlled by a digital temperature controller. The CL intensity at a certain wavelength was measured by a photon-counting method with a BPCL ultrawake chemiluminescence analyzer (BPCL, Chemiluminescence analyzer made by Biophysics Institute of the Chinese Academy of Science). In the experiment, the optical filters with different wavelength (from 400 to 750 nm) were used. Before each test, the catalyst sensor was heated at 500°C for 1 h in air to avoid the influence of previous absorbates.

**Catalytic Reaction Experiments.** The oxidation of CO was carried out in a conventional flow system at atmospheric pressure. A 0.1 g aliquot of catalyst was loaded in a quartz reactor (inner diameter: 5 mm), with quartz beads packed at both ends of the catalyst bed. The thermal couple was placed in the catalyst bed to monitor the reaction temperature since CO oxidation is an exothermic reaction. Before each run, the catalyst was flushed with air (200 mL min⁻¹) at 500°C for 1 h in order to remove the previous absorbates from the catalyst surface, and then cooled to 30°C. A gas mixture of 2 vol.% CO and 98 vol.% air was fed to the catalyst bed at a certain flowing rate of 200 mL min⁻¹. The inlet and outlet gas compositions were analyzed by an online gas chromatograph with a GDX-403 GC-column (1.5 m x 4 mm) at 100°C and a hydrogen flame ionization detector (FID).

**Results**

XRD, TEM, and BET Results of La_{1−x}Sr_xMnO_3 Nanoparticles. Figure 1 gives XRD patterns of La_{1−x}Sr_xMnO_3 samples by the coprecipitation method. All the diffraction peaks can
La$_{0.8}$Sr$_{0.2}$MnO$_3$ catalyst has the strongest CL intensity. The CL intensities were tested using eight filters with different band lengths of light. La$_{0.8}$Sr$_{0.2}$MnO$_3$ nanoparticles at different test conditions, such as flowing rate of gases ($F$), test temperature ($T$), CO concentration ($C$), and band length of filter ($\lambda_{filter}$). The effect of flowing rate of gases on CL intensity of La$_{0.8}$Sr$_{0.2}$MnO$_3$ catalyst was investigated (see Figure S2, Supporting Information). It can be observed that CL intensity first increased with flowing rate ($F \leq 320$ mL min$^{-1}$), and then it reached a maximum at $F \geq 320$ mL min$^{-1}$ This directly means that the catalytic reaction, which produces the luminescent molecules, is controlled by a diffusion process at lower flowing rates; but the catalytic reaction is controlled by a surface reaction process at higher flowing rates. In the diffusion-controlled process, the adsorbrates on the catalyst surface reacted rapidly once the reacting molecules reached the catalytic surface, and the mass-transfer process dominated the whole process. In the surface reaction-controlled process, nevertheless, the mass transfer of reacting molecules from bulk to catalyst surface is quick and the surface reaction dominates the whole process. The effect of CO concentration on CL intensity of La$_{0.8}$Sr$_{0.2}$MnO$_3$ catalyst was researched (see Figure S3 and Table S2, Supporting Information). A good linear correlation between CL intensity and CO concentration can be observed in the concentration range (5.0–320.0 $\mu$g mL$^{-1}$), and the detection limit of CL sensor for CO has been determined as low as 0.5 $\mu$g mL$^{-1}$. This means that CL properties of the catalyst should be determined at a constant concentration of CO. Figure S4 in the Supporting Information shows the temperature dependent CL intensity over La$_{0.8}$Sr$_{0.2}$MnO$_3$ catalyst. CL intensity increased with test temperature and reached a high value. It is clear that the test temperature has a significant influence on CL intensity. This is because CO conversion increased with the temperature. It is important for CL determination to maintain a constant test temperature. Figure S5 in the Supporting Information gives CL intensities of La$_{0.8}$Sr$_{0.2}$MnO$_3$ nanoparticles, which were tested using eight filters with different band lengths (400–750 nm). La$_{0.8}$Sr$_{0.2}$MnO$_3$ nanoparticles show the highest CL intensity with a 640 nm filter, indicating that the generated weak lights in CO oxidation centered near 640 nm. From above, CL properties of the catalysts should be determined under the same conditions in order to obtain the correct results.

**Effect of Test Conditions on CL Intensities of La$_{0.8}$Sr$_{0.2}$MnO$_3$ Nanoparticles.** Typically, we determined CL intensities of La$_{0.8}$Sr$_{0.2}$MnO$_3$ nanoparticles at different test conditions, such as flowing rate of gases ($F$), test temperature ($T$), CO concentration ($C$), and band length of filter ($\lambda_{filter}$). The effect of flowing rate of gases on CL intensity of La$_{0.8}$Sr$_{0.2}$MnO$_3$ catalyst was investigated (see Figure S2, Supporting Information). It can be observed that CL intensity first increased with flowing rate ($F \leq 320$ mL min$^{-1}$), and then it reached a maximum at $F \geq 320$ mL min$^{-1}$ This directly means that the catalytic reaction, which produces the luminescent molecules, is controlled by a diffusion process at lower flowing rates; but the catalytic reaction is controlled by a surface reaction process at higher flowing rates. In the diffusion-controlled process, the adsorbrates on the catalyst surface reacted rapidly once the reacting molecules reached the catalytic surface, and the mass-transfer process dominated the whole process. In the surface reaction-controlled process, nevertheless, the mass transfer of reacting molecules from bulk to catalyst surface is quick and the surface reaction dominates the whole process. The effect of CO concentration on CL intensity of La$_{0.8}$Sr$_{0.2}$MnO$_3$ catalyst was researched (see Figure S3 and Table S2, Supporting Information). A good linear correlation between CL intensity and CO concentration can be observed in the concentration range (5.0–320.0 $\mu$g mL$^{-1}$), and the detection limit of CL sensor for CO has been determined as low as 0.5 $\mu$g mL$^{-1}$. This means that CL properties of the catalyst should be determined at a constant concentration of CO. Figure S4 in the Supporting Information shows the temperature dependent CL intensity over La$_{0.8}$Sr$_{0.2}$MnO$_3$ catalyst. CL intensity increased with test temperature and reached a high value. It is clear that the test temperature has a significant influence on CL intensity. This is because CO conversion increased with the temperature. It is important for CL determination to maintain a constant test temperature. Figure S5 in the Supporting Information gives CL intensities of La$_{0.8}$Sr$_{0.2}$MnO$_3$ nanoparticles, which were tested using eight filters with different band lengths (400–750 nm). La$_{0.8}$Sr$_{0.2}$MnO$_3$ nanoparticles show the highest CL intensity with a 640 nm filter, indicating that the generated weak lights in CO oxidation centered near 640 nm. From above, CL properties of the catalysts should be determined under the same conditions in order to obtain the correct results.

**Effect of Test Conditions on CL Intensities of La$_{0.8}$Sr$_{0.2}$MnO$_3$ Nanoparticles.** Typically, we determined CL intensities of La$_{0.8}$Sr$_{0.2}$MnO$_3$ nanoparticles at different test conditions, such as flowing rate of gases ($F$), test temperature ($T$), CO concentration ($C$), and band length of filter ($\lambda_{filter}$). The effect of flowing rate of gases on CL intensity of La$_{0.8}$Sr$_{0.2}$MnO$_3$ catalyst was investigated (see Figure S2, Supporting Information). It can be observed that CL intensity first increased with flowing rate ($F \leq 320$ mL min$^{-1}$), and then it reached a maximum at $F \geq 320$ mL min$^{-1}$ This directly means that the catalytic reaction, which produces the luminescent molecules, is controlled by a diffusion process at lower flowing rates; but the catalytic reaction is controlled by a surface reaction process at higher flowing rates. In the diffusion-controlled process, the adsorbrates on the catalyst surface reacted rapidly once the reacting molecules reached the catalytic surface, and the mass-transfer process dominated the whole process. In the surface reaction-controlled process, nevertheless, the mass transfer of reacting molecules from bulk to catalyst surface is quick and the surface reaction dominates the whole process. The effect of CO concentration on CL intensity of La$_{0.8}$Sr$_{0.2}$MnO$_3$ catalyst was researched (see Figure S3 and Table S2, Supporting Information). A good linear correlation between CL intensity and CO concentration can be observed in the concentration range (5.0–320.0 $\mu$g mL$^{-1}$), and the detection limit of CL sensor for CO has been determined as low as 0.5 $\mu$g mL$^{-1}$. This means that CL properties of the catalyst should be determined at a constant concentration of CO. Figure S4 in the Supporting Information shows the temperature dependent CL intensity over La$_{0.8}$Sr$_{0.2}$MnO$_3$ catalyst. CL intensity increased with test temperature and reached a high value. It is clear that the test temperature has a significant influence on CL intensity. This is because CO conversion increased with the temperature. It is important for CL determination to maintain a constant test temperature. Figure S5 in the Supporting Information gives CL intensities of La$_{0.8}$Sr$_{0.2}$MnO$_3$ nanoparticles, which were tested using eight filters with different band lengths (400–750 nm). La$_{0.8}$Sr$_{0.2}$MnO$_3$ nanoparticles show the highest CL intensity with a 640 nm filter, indicating that the generated weak lights in CO oxidation centered near 640 nm. From above, CL properties of the catalysts should be determined under the same conditions in order to obtain the correct results.
Here, (g) and (ads) refer to gas phase and adsorbed states. The authors suggested that Co and O sites act as adsorption and activation centers for CO and O₂, respectively. It is considered that the lattice oxygen does not participate in complete combustion and that the adsorbed oxygen species alone are responsible for the total oxidation reaction (37). However, Rao et al. (38) have proposed that the lattice oxygen of perovskite participate in CO oxidation. A full consensus has not been reached so far on the main aspects which determine the catalytic behavior of perovskites. In our opinion, we think that the adsorbed oxygen could play a key role in CO oxidation because CO oxidation proceeded in a low temperature in which the lattice oxygen may less active. This needs further research. In our catalyst, Mn ions act as active centers for CO chemisorption. CO and Mn sites function as Lewis base and Lewis acid sites, respectively (39). The interaction between Mn ions and CO molecules can be modeled by crystal field theory. CO 5σ electrons and empty 2π* orbitals can coordinate with d orbitals and d electrons of Mn ions, respectively. CO 5σ electrons donate electrons to coordinate with MnO₆ species possessing empty eg (dz²) orbitals. The empty 2π* orbitals of CO molecules show some P orbital properties. Therefore, the t₂g (dxy, dyz, or dxz) electrons of Mn ions can hold to the empty 2π* orbitals of CO, forming feedback π bond. It not only increases the coordination bond strength (Mn—CO) but also decreases the bond strength of C—O. In conclusion, CO chemisorbed on Mn site reacted with the adsorbed oxygen to form CO₂. We could assume that the catalyst with a larger number of Lewis acid sites may favor for CO chemisorption, leading to a faster oxidation rate. The adsorption of reacting molecules on the catalyst played in an important role in CO oxidation. Therefore, it is necessary to research the adsorption behaviors of reacting molecules on the catalysts.

Figure S6 (see Supporting Information) shows CO-TPD profiles of CO on La₁₋ₓSrₓMnO₃ catalysts. A significant portion of CO desorbed as a form of CO₂ in the processes, so the adsorption amount of CO on the catalyst amounts to the total desorption amounts of both CO₂ and CO. In the range of 100–600 °C, five to six desorption peaks of CO₂ peaks, as well as two to five peaks of CO, can be observed. It is clear that the intensity, number and distribution of peaks over these catalysts are different. The CO or CO₂ peak intensity of the Sr-doped catalysts is stronger than that on LaMnO₃. The quantitative analysis results (see Table S4, Supporting Information) showed that the total CO adsorption amount on the parent LaMnO₃ is smaller than those on the Sr-doped ones. At x = 2, the total CO adsorption amount is largest. The results indicate that there may be more active centers on La₁₋ₓSrₓMnO₃ catalysts due to the Sr doption. It has been reported that the partially substituting of low-valence ion for La can result in the formation of anion or oxygen vacancies (23, 32–34). The Sr doption may improve the adsorption properties of reacting molecules on the
catalysts. The sorption is directly related to CO catalytic reaction over La$_{1-x}$Sr$_x$MnO$_3$ nanoparticles. La$_{0.8}$Sr$_{0.2}$MnO$_3$ catalyst is expected to have more defects, corresponding to a larger number of Lewis acid sites. The oxygen vacancies can be confirmed by O$_2$–TPD profiles (see Figure S7 and Table S5, Supporting Information). It is generally accepted that the desorption peaks of oxygen at lower temperatures result from the oxygen adsorbed on the catalyst surface (designated α-oxygen), and the desorbed amount of α-oxygen can be referred to surface oxygen vacancies; and the desorption peaks of oxygen at high temperatures can be referred to lattice oxygen or bulk oxygen (related to the reduction of Mn ion) (designated β-oxygen). As shown in Figure S6. There are two oxygen-desorption peaks, respectively. α-oxygen peak at about 480 °C corresponds to the desorption of the oxygen chemically adsorbed on oxygen vacancies. β-oxygen peak in the range of 700–800 °C might be attributed to the lattice oxygen associated with the redox of B ions. Compared with the undoped LaMnO$_3$, the desorbed amounts of α-oxygen increase slightly, implying that oxygen vacancies increase, but the peaks areas of β-oxygen varied inconsistently. Based on the above information, we could infer that the oxygen defects increased due to the Sr dopant. These results confirmed that the Sr dopant increased the adsorption of oxygen. In our experiment, La$_{0.8}$Sr$_{0.2}$MnO$_3$ had the maximum oxygen vacancies. It may be that $x = 0.2$ is the appropriate doping amount. This needs research further.

Breysse et al. have proposed a mechanism of recombination radiation based on ThO$_2$ (1). CO is chemisorbed to form the CO$^+$ ion; O$_2$ is dissociated and chemisorbed to form the O$^-$ ion. This means that the chemisorbed CO forms a positively ionized surface state (the surface donor state) accompanied by the localized hole, and the chemisorbed oxygen forms a negatively ionized surface-state (the surface acceptor state) accompanied by the localized electron. Surface reaction between these chemisorbed species will occur to form the chemisorbed CO$_2$. The chemisorbed CO$_2$ accompanied by the localized electron and hole is a chemisorption surface state bound to an exciton. The desorption of CO$_2$ is accompanied by annihilation of the exciton, and luminescence is emitted by recombination of electron and hole. Over our perovskite catalysts, it is possible gases from the adsorption and catalysis reaction may be more complicated and different from the former. However, many researchers have proposed that the CL mechanism is luminescence from the excited species produced in catalytic oxidation (40, 41). The exothermal chemical reaction produces energy enough to induce the transition of an electron from its ground-state to an excited electronic state. This electronic transition is often accompanied by vibrational and rotational changes in the molecule. CL is observed when the electronically excited product relaxes to its ground-state with emission of photons (42). Based on the above (40–44), the CL reaction can be represented with the following formula:

$$\text{CO}_2(\text{ads}) + \text{energy} \rightarrow \text{CO}_2(\text{ads}) \rightarrow \text{CO}_2 + \text{hv} \quad (\text{vi})$$

In our work, it was accepted that CO$_2$ was the luminescence species. While CO molecules were oxidized on the catalyst surface, an amount of energy was released, which would be absorbed by CO$_2$ molecules. As a result, CO$_2$ molecules would jump from ground-state up to electronic excited state (*CO$_2$). While the electronic excited *CO$_2$ molecules decayed to the ground state, a CL was generated. CL intensity is linearly proportional to the produced CO$_2$ concentration. It is clear that CL spectra are closely correlated with the catalytic reaction, in which the conversion of CO into CO$_2$ is directly related to the catalytic properties of the catalysts. The easier the catalytic reaction, the more CO$_2$ molecules were formed. As a result, the CL intensity is stronger. The activity and CL represent the same process. It is reasonable that CL spectra can be used to quantitatively evaluate a given catalytic reaction.

CL Detector for Environmental Combustible Gases and Catalyst Selection. We have found that luminescent efficiencies and spectral shapes of the CL are dependent on the kinds of reactants and catalysts. Even if the same luminescent species could be produced from the different combustible gases on a given catalyst, the amounts of the generated luminescent species by different combustible gases are different. Therefore, the same nanomaterial exhibits different intensities of CL upon exposure to different gases. This enables us to discriminate the kind of combustible gas. The compounds within a given chemical class can be still discriminated effectively because the mechanisms and rates of catalytic reactions are dependent on temperature, which leads to different luminescence efficiencies and spectral shapes (26). Even if similar shape were recorded with the sensor for two gases at one temperature, they may be differentiated by different CL intensities at another temperature. The CL sensor system may be useful for analyzing various environmental toxic gases because of the linear characteristics of CL intensity as a function of gas concentration (40). Besides, a variety of highly active catalysts have been pursued for a series of important industrial reactions. Therefore, it has become crucial in the field of catalysis to develop innovative approaches allowing rapid evaluation of the activity by screening a large diversity of catalyst candidates for a specific catalytic reaction. The CL spectral shapes of a compound are different on different nanomaterials. The good correlation between CL and activity indicates that the CL intensity could be applied for the screening of the catalytic activity. Based on the good correlation between CL and catalysis reactions, we have developed a new CL-based detector with multiregions (Figure 6). The new detector can be used for the selection of multiacatalysts at one time. The different catalysts can be coated onto the different regions. CL spectra can be acquired only by adjusting the location of region and the flowing region of reacting gases. The multiregion CL detector is simple and rapid for screening a large number of catalysts. This technique would be potentially applied to explore the new catalysts. As we know, the catalysts are generally selected by testing their activities, in which the complicate and expensive equipment is needed and the test needs a long duration. Especially, while selecting new catalysts from thousands of materials, the procedures are expensive, time-consuming, and laborious. The catalyst selection is still a challenge to researchers. CL determination of catalyst is facile, rapid, and low-cost since CL spectra can be obtained within a few minutes and no complicated and expensive equipment is needed. The CL determination mode can be used as an effective means to select catalysts. Because the perovskite has a high catalytic activity and structure-stability, many combustible molecules may be oxidized completely into CO$_2$. It could be expected that such CL sensor of perovskite nanoparticles could potentially be used to justify other high-temperature combustion reaction (e.g., catalytic combustion of methane). We have also observed that the CL intensity is linearly proportional to the concentration of methane in our research range of 0–2.5 vol.% in air with a detection limit below 0.15 vol.% at 600°C; and that the CL sensor made of La$_{0.8}$Sr$_{0.2}$MnO$_3$ nanoparticles maintained a high stability after running for 48 h at 600°C. However, the CL sensor of single-oxide nanoparticles was not suitable for
high-temperature reaction due to their unstable structure. CL mode is useful to select excellent catalysts for catalytic oxidation reactions. The new catalysts could be useful to eliminate effectively the environmentally toxic gases. The CL responses on catalytic nanomaterials provide abundant optical information which motivates the fabrication of chemical sensor arrays. An intensive effort is currently devoted toward the development of high-throughput screening approaches. The CL reaction is of practical importance for detecting environmental pollutants. We intend to apply this technique to the analysis of explosives and to volatile organic compounds.

In summary, a long-lifetime CL gas sensor can be fabricated using perovskite nanoparticles due to stable crystal structure and high activity. The good correlation between CL and activity indicates that the CL intensity could be applied for the screening of the catalytic activity. CL mode could be a facile and rapid means for the detection of environmentally deleterious gases and the selection of excellent catalysts from thousands of materials.

Acknowledgments
We gratefully acknowledge the research funding supported by National Basic Research Program of China (2007CB613303) and Chinese Postdoctoral Science Foundation (no. 20060390057).

Supporting Information Available
CO- and O2-TPD experiments; CL intensities of La1–xSrxMnO3 at different flowing rate, CO concentration, temperature, band-length filters, and particle sizes; BET areas, particle sizes and size distributions, crystal sizes, CO- and O2-TPD results of La–SrMnO3 catalysts. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited
(9) Zhang, Z.; Cui, H.; Shi, M. Chemiluminescence accompanied by the reaction of gold nanoparticles with potassium perman- 


ES702845Z