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# Evolution of biogenic amine concentrations in foods through their induced chemiluminescence inactivation of layered double hydroxide nanosheet colloids

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ABSTRACT

Turn-on/off fluorescence and visual sensors through hydrogen bonding recognition have been clearly established in the literature. There is apparently no good reason to disregard hydrogen bonding-induced inactivation of chemiluminescence (CL). In this work, serving as novel CL catalyst and CL resonance energy transfer acceptor (CRET), layered double hydroxide (LDH) nanosheet colloids can induce a significant increase in the CL intensity of bis(2,4,6-trichlorophenyl) oxalate (TCPO)–$H_2O_2$ system. On the other hand, biogenic amines can selectively inhibit the CL intensity of the LDH nanosheet-TCPO–$H_2O_2$ system as a result of inactivation of photoluminescence LDH nanosheets through the displacement of O–H···O bonding by O–H···N bonding. In addition, histamine is used as a common indicator of food spoilage, and it is found that the CL intensity is linear with histamine concentration in the range of 0.1–100 μM, and the detection limit for histamine ($S/N=3$) is 3.2 nM. The proposed method has been successfully applied to trace histamine evolution of spoiled fish and pork meat samples, displaying a time-dependent increase in the biogenic amines levels in such samples.



## 1. Introduction

Food safety is closely related to common people's health (Butler, 2012). The World Health Organization and Centers for Disease Control and Prevention announce that there are approximately 76 million cases of foodborne illness in the United States each year, leading to 325,000 hospitalizations and 5,000 deaths (Laury et al., 2009; Lee et al., 2012; Popkin et al., 2012). In developing countries, the current number of the reported cases exceeds the expected value (Lee et al., 2012). Therefore, intricate standards are required to ensure that food is safe to consume in a bid to halt the increasing incidence of food poisoning (Engelseth, 2013; Hammond and Dubé, 2012). Biogenic amines are frequently found in raw and fermented foods in a wide variety of food products, and the presence of high levels of biogenic amines in foods is indicative of microbial spoilage. An excessive oral intake of biogenic amines is frequently responsible for a number of diseases and certain tumors (Castagnolo et al., 2011; Márquez et al., 2013; Sánchez-Jiménez et al., 2013). Therefore, biogenic amines might serve as a useful indicator of food quality and hygiene (Chen and Chen, 2013; Erim, 2013). It is important to exploit a reliable and highly sensitive sensor for rapid screening of biogenic amines. Currently available methods for determining biogenic amines are generally based on high-performance liquid chromatography (HPLC) precolumn or postcolumn derivatization with high extinction coefficients or high fluorescence yields because biogenic amines exhibit no native absorbance and fluorescence (Erim, 2013; Oguri et al., 2002). However, such approaches are time-consuming, and thus not suitable for routine use. Accordingly, the development of an inexpensive, rapid and easy method for determining biogenic amines would be highly desirable (Zhao et al., 2010).

The process of forming and breaking hydrogen bonding could generate some wondrous phenomenon. Recently, hydrogen bonding-promoted covalent modifications that are particularly useful in small molecular self-assembly and turn-on/off fluorescence and visual probes (Ai et al., 2009; Jo and Lee, 2009; Jo et al., 2013). For example, Lee group has designed a turn-on fluorescence probe of cyanide in water based on electrophile activation of latent fluorophores through remote hydrogen bonding (Jo and Lee, 2009; Jo et al., 2013); Lu and co-authors have taken advantage of the color change of gold nanoparticles induced hydrogen bonding recognition to develop a visual sensor for melamine in raw milk and infant formula (Ai et al., 2009). As an competitive optical technique, the chemiluminescence (CL) technique exhibites stable intensity, simple implementation, high sensitivity, and rapid response (Na et al., 2006; Liu et al., 2010; Wang et al., 2007). Therefore, there is apparently no good reason to disregard hydrogen bonding-induced activation/inactivation of CL.

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Layered double hydroxides (LDHs) are an interesting class of inorganic layered matrices in nanoscale space with structurally positively charged layers and interlayer balancing anionic species and water molecules (Rives et al., 2013). The high charge density of LDH layers and anionic species result in strong interlayer electrostatic interactions between sheets. In 2005, Sasaki and co-workers successfully achieved the delamination of many highly crystallized LDHs into well-defined nanosheets with formamide via the strong hydrogen bonding effect between carbonyl groups of formamide and hydroxyl groups of the LDH host (Li et al., 2005). It is well-known that amino groups are characteristic hydrogen bonding donors. Typically, the hydrogen bonding strength of O–H···N is stronger than O–H···O (Taylor and Kennard, 1984). Taking inspirations from naturally occurring, we may anticipate that amino groups can be easily attached to hydroxyl groups in comparison to carboxyl groups, which is able to recognize biogenic amines.

Here, we observed that O–H···O bonding between formamide and LDH nanosheets could lead to strong blue photoluminescence of the exfoliated LDH nanosheets under UV lamp at 365 nm at room temperature. On the other hand, biogenic amines can inactivate photoluminescence LDH nanosheets through the displacement of O–H···O bonding by O–H···N bonding. In addition, LDH nanosheet colloids were found to enhance bis(2,4,6-trichlorophenyl) oxalate (TCPO)–$H_2O_2$ CL system (Fig. 1). In such case, LDH nanosheets served dual functions in the CL enhancement: CL catalyst and CL resonance energy transfer (CRET) acceptor. Finally, the LDH nanosheet-TCPO–$H_2O_2$ CL system has been successfully applied to trace evolution of biogenic amine in spoiled fish and pork meat samples with simplicity, selectivity and sensitivity.

## 2. Experimental section

### 2.1. Chemicals and materials

Analytical grade chemicals including $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Na_2CO_3$, NaOH, NaCl, $NaNO_3$, HCl, $H_2O_2$, $HClO_4$, acetonitrile, ethyl acetate, acetaldehyde, acetone, acetopheone, benzaldehyde, aniline, and N,N-dimethyl formamide were purchased from Beijing Chemical Reagent Company, and were used without further purification. TCPO, cholamine, 2-phenylethylamine, and putrescine were obtained from Tokyo Chemical Industry Co., Ltd. (Japan). 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) was bought from Tokyo Kasei Kogyo Co., Ltd. (Japan). Histamine, tyramine, spermine, spermidine were obtained from National Institute of Metrology (China). Formamide was purchased from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). Dimethylaminonaphthalene sulfonyl chloride was purchased from J&K Scientific Ltd. A working solution of TCPO was prepared by dissolving the white solids in ethyl acetate, and working solution of $H_2O_2$ was prepared daily by diluting 30% (v/v) $H_2O_2$ in acetonitrile. Water was purified with a Milli-Q purification system (Barnstead, CA, USA).

### 2.2. Apparatus

Scanning electron microscopy (SEM) was measured on Hitachi (Japan) S-4700 field-emission scanning electron microscope. Transmission electron microscopy (TEM) photographs and selected area electron diffraction (SAED) patterns were performed on a Tecnai G220 TEM (FEI Company, USA). The crystal structure and phase purity of resulting powders were evaluated by the powder X-ray diffraction (XRD; Bruker D8 Advance) using Cu/Kα radiation ($\lambda = 1.54$ Å). The patterns were acquired for $2\theta$ range from 5° to 70°. Fourier transform infrared (FT-IR) spectra in a range of 400–4000 $cm^{-1}$ were measured on a Nicolet 6700 FT-IR spectrometer (Thermo, USA) using the KBr pellet technique at a resolution of 4 $cm^{-1}$. $^1H$ NMR spectra of the formamide and LDH nanosheet solution were recorded at room temperature with a 600 MHz Bruker (Germany) spectrometer. UV–vis spectra were measured on a USB 4000 miniature fiber optic spectrometer in absorbance mode with a DH-2000 deuterium and tungsten halogen light source (Ocean Optics, Dunedin). Electronic spin resonance (ESR) measurements were performed on a JES-FA200 spectrometer (JEOL, Tokyo, Japan) at room temperature. Instrument conditions: microwave frequency, 9.75 GHz, power, 12.72 mW, modulation amplitude, 2.01 G, modulation frequency, 100 kHz. 20 μL 0.5 M $H_2O_2$ were added into the mixture of 20 μL of 0.2 M DMPO, 20 μL of LDH nanosheet colloidal solutions or 20 μL of pure formamide. The photoluminescence spectra were obtained using a F-7000 fluorescence spectrophotometer (Hitachi, Japan) at a slit of 5.0 nm with a scanning rate of 1200 nm/min. Steady state and time-resolved fluorescence measurements were performed on an Edinburgh instrument spectrometer using Xe lamp. The quantum yield and lifetime values were obtained from the reconvolution fit analysis (Edinburgh F980 analysis software). The CL intensity versus time profile was conducted on an

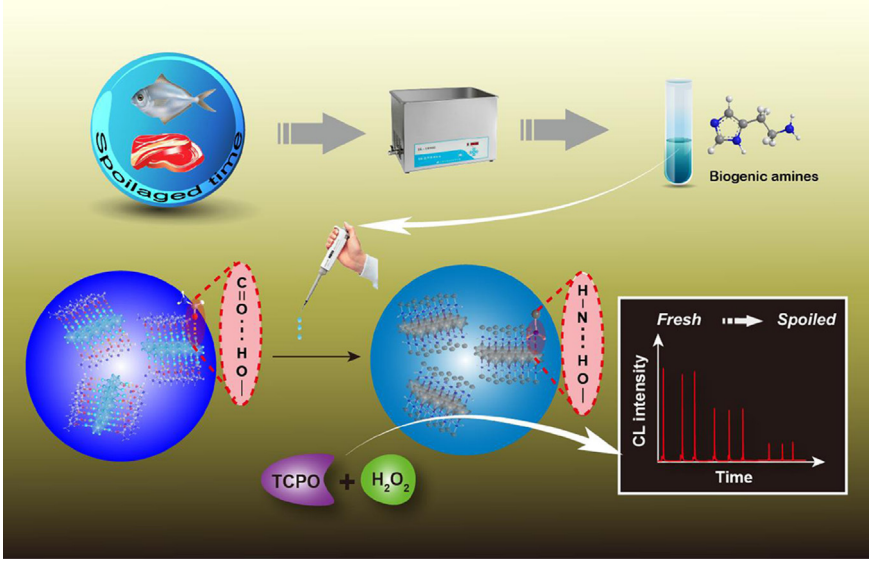


**Fig. 1.** Schematic illustration of CL sensing for biogenic amines evolution of spoiled foods.