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**GREEN LUMINESCENCE EMITTED FROM ADSORBED OXYGEN
AURORA HAS APPEARED ON THE SURFACE OF MATERIALS?!**

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INTRODUCTION

Anomalous initial peaks in CL intensity-time curves have been reported by many investigators for different materials, i.e., salad oil (1), polymers (2-4), and nitrocellulose (5). The characteristic CL peak disappeared when a sample was reheated after being cooled down to ambient temperature in nitrogen. The most authors have attributed the CL peaks to the decomposition of hydroperoxides formed by autoxidation during storage in air. Activation energy for the CL peaks was reported to be 75.6 kJ mol⁻¹ (2), which is apparently lower than expected values (>100 kJ mol⁻¹) for the decomposition of organic hydroperoxides. We found that cellulose filters continued to emit weak luminescence for longer than 1 week in flowing nitrogen when they were heated at around 100°C. Light emission mechanism for the characteristic CL peaks is still debated. In photoluminescence study of organic compounds such as filter paper and powder milk, we found green light emission spectra and then succeeded in taken colour pictures like green aurora with high sensitive colour CCD camera. Observed green light emission may imply that significant amount of oxygen may exist on the surface of organic materials with oxygen-containing functional groups (-OH, -COOH, and -ONO₂). Those adsorbed oxygen may act as a strong oxidizer for organic materials when they are heated even in an inert atmosphere because the energy of desorption would be partially transferred to desorbed oxygen molecules (i.e., hot oxygen). Reported low activation energies for chemiluminescence of organic materials will be interpreted as the bond dissociation energy of oxygen bonds (weak covalent bonds) between oxygen molecules and neighbouring oxygen atoms of oxygen-containing functional groups in organic materials. Importance of oxygen adsorbed onto the surface of materials can not be overemphasised in chemiluminescence and photoluminescence.

MATERIALS AND METHODS

Materials

Filter Papers used in this study were obtained from Advantec (Japan). 18-8 stainless cell was a standard cell with a diameter of 50 mm provides by Tohoku

Electronic Industrial (TEI) (Japan). Powder milk measured is the product of Morinaga Milk Industry Co. (Japan).

Apparatus and Procedure

Luminous intensity-time curves and spectra of test samples stimulated thermally and photochemically were measured with a chemiluminescence spectrometer CLA-FS1. Colour photos of the photoluminescence of samples settled in a cell with a diameter of 50 mm were taken with a high sensitive colour camera CL-Cube employing an ultra high sensitive colour CCD camera of Bitran Co., Japan. Both types of the apparatus are available from the Tohoku Electronic Industrial Co., Japan. The black light has power of $240 \mu\text{W cm}^{-2}$ and wavelength of 365 nm. In order to obtain a spectrum for steep decay photoluminescence curves, a sample was irradiated with the NUV light for 5 seconds outside the apparatus and then the sample chamber was pushed back into the apparatus. Luminescence measurement was started normally 5 seconds after the end of irradiation under a predetermined cutoff filter. The measurements were repeated for 20 filters. Latest model of the CLA-FS1 makes the spectrum measurement a simple process.

RESULTS AND DISCUSSIONS

A filter paper was heated in temperature ranging from 90°C to 120°C in a flowing nitrogen of 60 ml/min. The exhibited anomalous initial peak in the CL curves as can be seen Fig. 1. The initial peak disappears when it was heated again after being cooled down to room temperature. Luminous intensities after the peak decayed exponentially. Thus, kinetic analysis of the luminescence peak decay was conducted as follows; (1) decay curves after the peak were plotted in logarithmic fashion against time resulting in straight lines with different slopes, (2) the slopes of the straight lines were plotted against reciprocal absolute temperatures as depicted in the right figure in Fig. 1. The Arrhenius plot gave activation energy of 29 kJ mol^{-1} for the initial decay parts.

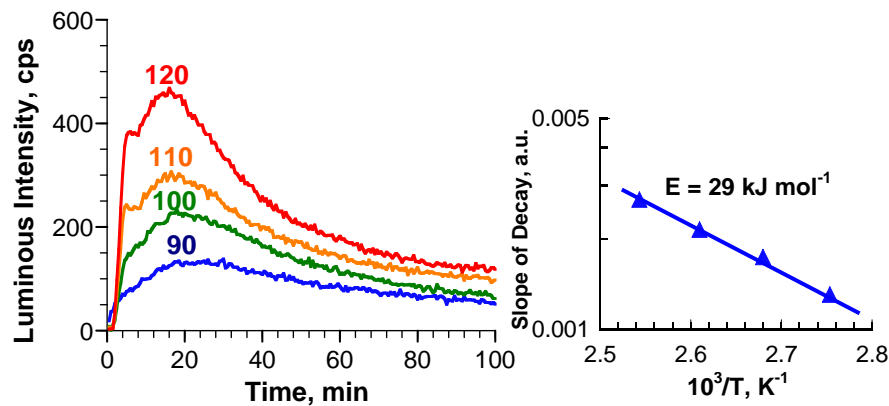


Figure 1 (Left) Typical CL curves for filter paper heated at different temperatures in nitrogen. (Right) The Arrhenius plot of the slope after the CL peak against reciprocal temperatures provided activation energy of 29 kJ mol^{-1} .

Activation energy for the second slow decay curves of the filters paper was obtained to be 50 kJ mol^{-1} . Both of these values are very low compared to the reported activation energies for the thermal decomposition of organic hydroperoxides which is ranging from 96 kJ mol^{-1} to 116 kJ mol^{-1} (6).

In order to clarify the CL curves of filter paper observed in nitrogen atmosphere we also adopted photoluminescence. A photoluminescence curve of filter paper measured in nitrogen is depicted in Fig. 2. The photoluminescence curve exhibited exponential decay having a radiative lifetime of about 3 seconds. The luminescence spectrum is also plotted in Fig. 2 where logarithm of luminous intensities were plotted against wavelength. The emission spectrum showed characteristic triangle having a peak in the range of 480-520 nm.

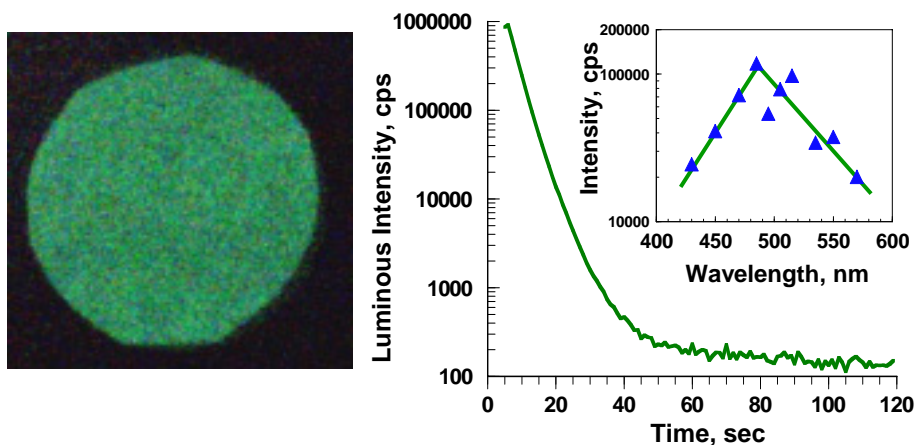


Figure 2 (Right) Photoluminescence curve of filter paper irradiated with NUV (365 nm) light and the emission spectrum. (Left) photo of green-coloured filter paper taken with CL-Cube.

The emission band of 480 nm has been assigned to transition of electronically excited oxygen molecules to the ground state as follows ($[^1\Delta_g + ^1\Sigma_g^+] \rightarrow 2\ ^3\Sigma_g^-$). This type of oxygen emission is known as one-photon two-molecule process, where two electronically-excited oxygen molecules emit light in the collision. Observed band spectra shown in upper right figure of Fig. 2 suggest that the green luminescence from filter paper. Evidently, bluish green photo was obtained as can be seen in left figure of Fig. 2. It will be natural to draw an analogy between green light emission from the surface of paper and green aurora caused by atomic oxygen in the upper atmosphere (7).

As described above two different values of activation energy (29 and 50 kJ mol⁻¹) were observed for filter paper heated in inert atmosphere. These experimental facts may suggest that there might exist two different types of adsorbed oxygen: one is weakly adsorbed oxygen molecules between O₂ and O₂ above monomolecular layer and the other is strongly adsorbed oxygen between O₂ and OH groups on the surface of cellulose. When filter paper was heated, weakly adsorbed oxygen molecules could be liberated firstly followed by strongly adsorbed oxygen molecules. These two processes could produce the initial CL peaks. It should be pointed out that the adsorbed oxygen molecules on the surface of filter paper could act as a UV stabiliser because the surface oxygen molecules absorb UV light followed by emission of visible light.

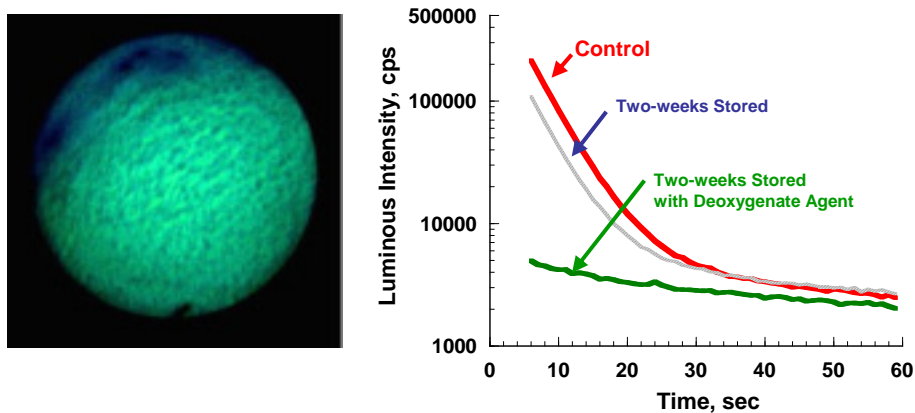


Figure 3 (Right) Photoluminescence curves for powder milks irradiated with NUV light. Control is fresh powder milk. Two glass bottles of powder milk were stored in a refrigerator for two weeks; one bottle contained a package of deoxygenate agent and the other none. (Left) The photo of fresh powder milk.

Left photo in Fig. 3 is for fresh powder milk irradiated with a black light (365 nm) for 5 seconds in air. NUV-irradiated powder milk exhibited bluish green colour like cellulose filter did. Right figure in Fig. 3 shows the photoluminescence curves of powder milks: (1) control (fresh powder milk taken out from a bottle opened), (2) powder milk stored for 2 weeks in a refrigerator after open, and (3) powder milk stored in the refrigerator for 2 weeks containing a small package of deoxygenation agent. Emission decay curve for fresh milk powder is almost similar to that for the milk powder stored for 2 weeks. The initial luminous intensity for powder milk containing a deoxygenated agent in the bottle was significantly lowered to almost 2% of that for control. This is a direct evidence that oxygen molecules are the light-emitting species in the photoluminescence of powder milk because deoxygenated agents can absorb oxygen molecules from materials. All the three emission curves became overlapped above 60 seconds. This may imply that the deoxygenation agent can absorb only weakly adsorbed oxygen but not strongly adsorbed oxygen.

CONCLUSIONS

Adsorbed oxygen molecules on the surface of organic materials play a vital role in chemiluminescence and photoluminescence. Moreover, desorbed oxygen molecules act as a stronger oxidizer rather than atmospheric oxygen because the desorbed oxygen molecules are "hot molecules" partially containing the energy of desorption. The surface-bound oxygen molecules must be considered as significant in any autoxidation of organic materials at ambient air and temperature. Observed

beautiful greenish luminescence from filter paper and powder milk fascinated us totally. Elucidation of the aurora-like luminescence mechanism is in progress.

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