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Optical Ozone Sensing by Composite Films of Noble Metals and CdSe/ZnS Quantum Dots

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Abstract
The photoluminescence-based ozone sensitivity of composite films composed of noble metal particles and CdSe/ZnS core-shell quantum dot is investigated. The composite films are prepared by the sputter-deposition of Pt, Au, Pt-Pd alloy or Ag particles onto a glass plate substrate, which is followed by deposition of quantum dots from an organic solution. For comparison, a quantum dot film without any noble metal is prepared. In air, the Pt- , Au- and Pt-Pd alloy-based composite films, and quantum dot-only film emit bright photoluminescence, whereas emission from Ag-based composite film is weak. The composite films and quantum dot-only film show reversible changes in photoluminescence intensity in presence of ozone at the ppm level in air at room temperature. Optical ozone sensitivity, i.e., ozone-induced changes in photoluminescence intensity of quantum dot, are affected by the noble metal particles in the film. When compared with a quantum dot-only film, a composite film composed of Pt or Au shows higher ozone sensitivity by 43% or 27%, respectively. In contrast, the sensitivity of a composite film composed of Pt-Pd alloy particles is lower than that of a quantum dot-only film by 32%. However, the alloy- and Au-based films show quicker recovery of photoluminescence, which is after removal of ozone in the surrounding atmosphere, when compared with quantum dot-only and Pt-based film. These results show a possibility to enhance the optical ozone sensitivity and response/recovery rate of quantum dots by the addition of noble metal particles.

Key words: optical ozone sensor, photoluminescence, quantum dot, noble metal, composite film

Introduction

Utilization of ozone gas is expanding as a strong and clean oxidizing agent for purification of air and water, manufacture of semiconductors, medicines, esthetics and chemicals. However, ozone is harmful to human health when its concentration exceeds a few ppm in air. Therefore, a requirement for the expedient sensing of ozone in air is growing.

Optical sensors have advantages over electronic sensors, such as resistance to electromagnetic noise, safety against fire caused by electric spark, remote/noncontact signal readout, and compatibility with optical fibers and waveguides. We have recently reported that thin films of CdSe-based core-shell quantum dots (QDs) show ozone-induced quenching of photoluminescence (PL) and reversible recovery of PL in pure air [1]. This phenomenon is expected to be used for ozone sensor having advantages over conventional ozone detection techniques [2]. We hypothesize that ozone-induced PL quenching originates from changes in the ratio of radiative to non-radiative carrier recombination processes that were controlled by the degree of non-radiative recombination with surface bound ozone [1].

A potential approach for enhancing ozone sensitivity and response/recovery rate is combined with QDs and other ozone reactive materials. Noble metal (NM) particles including Pt, Au, Pd and Ag are reported to have ozone reactivity such as catalytic activity and reversible adsorption-desorption [3-6].

Therefore, we investigated PL intensity changes of NM-QD composite films and NM-free QD film by ozone gas in air.

Experimental

NM-QD composite films were prepared in the following manner. Small NM particles (NM: Pt, Au, Pt-Pd alloy (Pt/Pd=85/15 (w/w)) or Ag were deposited on a glass plate substrate by dc sputtering method [7]. An organic solution that contained homogeneously dispersed red-emitting CdSe/ZnS core-shell QDs (Invitrogen Q21721MP) was then drop-deposited on the small NM particles. For comparison, NM-free QD film on a glass plate substrate was prepared by drop-deposition of QD.

PL intensity and spectra of QD films with or without NM on glass substrate were measured at 25°C under 1 atm by using a spectrometer [1]. For PL measurements, the sensor film samples were excited with UV light (wavelength = 365 nm). Synthetic air or air containing ozone was introduced into an experimental gas cell [1].

Results and Discussion

In air, the Pt-QD, Au-QD, Pt-Pd-QD and QD-only films emitted bright PL, whereas the PL of Ag-QD film was weaker by one order of magnitude. The peak PL wavelength of these films was constant at 656 nm, irrespective of the presence or absence of 0.5 ppm ozone in air. The stable emission wavelength helps us to rule out any deterioration or agglomeration of QD. These NM-QD composite films and QD-only films showed reversible changes in PL intensity by ozone in air. However, in the Ag-QD film, the signal-to-noise ratio was low due to weak PL.

Figure 1 shows PL intensity response of the Pt-QD, Au-QD, Pt-Pd-QD and QD-only films to 0.5 ppm ozone in air. On exposure to 0.5% ozone in air, all films showed rapid decrease in PL intensity at 656 nm. Decrease of PL intensity after exposure to 0.5 ppm ozone for 12 min were 9%, 13%, 11% and 6% for QD-only, Pt-QD, Au-QD and Pt-Pd-QD films, respectively. Namely, the ozone sensitivity of Pt-QD and Au-QD films were higher than that of QD-only film by 43% and 27%, respectively. High sensitivity to ozone suggests enhanced ozone adsorption by Pt and Au. Ozone sensitivity of the Pt-Pd-QD film was 32% lower than that of NM-free QD film, however, the Pt-Pd-QD film showed fast recovery of PL intensity in air. The low ozone sensitivity and fast PL recovery of the Pt-Pd-QD film are considered to reflect on the catalytic activity of Pd to ozone decomposition [5]. Fast recovery was also observed in the Au-QD film, suggesting quick ozone desorption from Au particles.

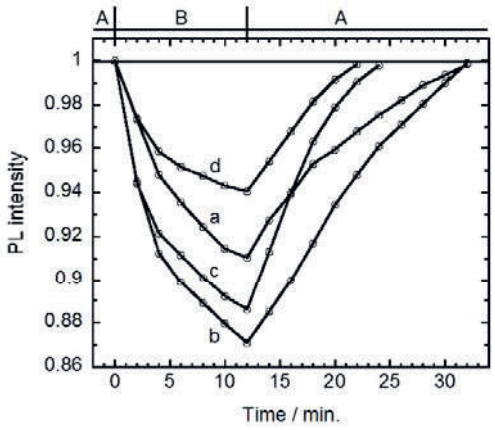

Fig. 1. Time response of PL intensity at 656 nm for (a) a QD-only, (b) a Pt-QD, (c) a Au-QD and (d) a Pt-Pd-QD films to 0.5 ppm ozone in air. A, in air; B, in air containing 0.5 ppm ozone.

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