EVALUATION OF PHOTO-CATALYTIC REACTIONS BY USING MINIATURIZED QCM ARRAY

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Abstract: This paper reports a real-time measurement of photo-catalytic reactions by using miniaturized quartz-crystal microbalance (QCM) array. The QCM used here was miniaturized and integrated by using microfabrication techniques. Two QCM's were located close to each other and one of the QCM's was used as a reference sensor for the accurate and independent determination of mass change effects and environmental change effects. Frequency change induced by ultra violet (UV) irradiation was cancelled well by this method. The minimum detectable frequency change under the irradiation was below 1 Hz. This method enabled us to measure a photo-decomposition of a representative detergent on a TiO_2-coated QCM at the resolution of pico-gram range in real time.

Key words: QCM, Photo-catalytic reactions, Pollutants

1. INTRODUCTION

The photo-catalytic materials attract attention because it can decompose organic pollutants. Photo-catalytic activity has been evaluated by degradation of dye on photo-catalytic materials [1]. The disadvantage is that it requires a dye molecule. For evaluating the decomposition of organic pollutants, an alternative method which can be applied to any kinds of organic materials are demanded.

Quartz crystal microbalance (QCM) is one of the alternatives to evaluate photo-catalytic reactions without dye molecules. Because of the piezoelectric properties, QCM shows frequency changes during UV irradiation. Therefore, the mass change effects caused by the photo-catalytic reactions have been measured under low intensity UV irradiation [2]. The other solution reported is stopping the irradiation during the frequency measurements [3].

We have been developing a QCM based evaluation method. The QCM was miniaturized and integrated by using microfabrication techniques [4]. Two QCM's are located close to each other and one of the QCM's was used as a reference sensor for correcting environmental change effects .

In this report, we attempted to evaluate photo-catalytic reactions of a representative detergent by using the developed method.

2. EXPERIMENTAL

2.1 Experimental set-up

Figure 1(a) shows the experimental set-up for evaluating photo-catalytic reactions. Dual QCM was used for this evaluation. In this study, we used a new type of QCM developed by our laboratory [5]. The electrode configuration of the QCM is shown in figure 1 (b). The exciting electrodes are located on one side. Therefore, the QCM is suitable for spin coating and for packaging. The resonant frequency is about 17 MHz and the mass sensitivity is about 60 pg/Hz. The TiO_2-coated QCM array was prepared by three times spin coating of a TiO_2 sol solution. Commercially available photo-catalytic TiO_2 sol solution (ISHIHARA SANGYO, ST-K211) was used in this study. The QCM array was heated at 573 K for 1 hour. After an irradiation of UV light, the surface of QCM shows super-hydrophilic wettability. Therefore, the TiO_2 thin film has photo-catalytic ability [6].

Before the evaluation with the QCM array, we measured the frequency response under UV irradiation. UV light from a high-pressure mercury lamp (HAMAMATSU, LC5) was irradiated uniformly. Here, infrared cut-off filter (HAMAMATSU, A7028-03) was used for reducing thermal effects.

Figure 2 shows an example of the frequency response. The environmental change effects induced by such as UV irradiation, gradual temperature change are corrected well by the referenced QCM. For example, the difference in resonant frequency between Ch1 and Ch2 was about 0.2 Hz for 6 mW/cm^2. The intensity shown here was measured in the UV-A and UV-B ranges. The frequency change induced by the UV irradiation was measured by placing a pinhole on the one of the QCM's. Figure 3 shows the examples of the frequency responses. The resulting frequency change versus irradiation intensity of UV light exhibits a linear relationship as shown in figure 4. In this study, the ratio of frequency response to irradiation intensity was about 4 Hz/mWcm^{-2} .

Then, one of the QCMs' was coated with cast organic film. Methylene blue (MB) film or sodium dodecylsulphate (SDS) film was used as the organic film. These organic materials were dissolved in distilled water, and coated on the electrode surface of QCM by using a micro syringe. All measurements were carried out under room temperature.

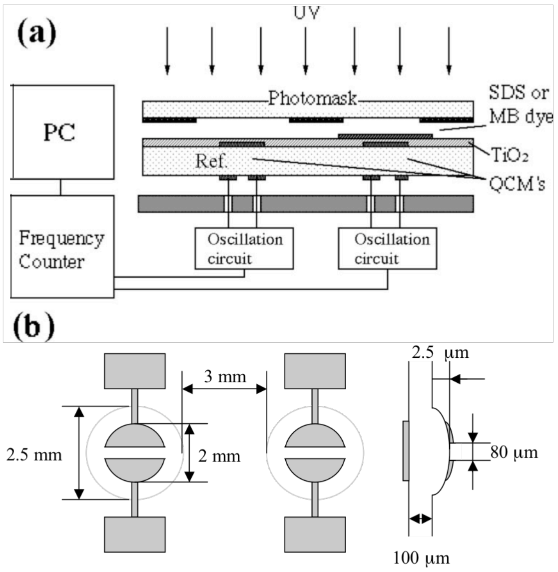

Fig. 1: The experimental set-up for the evaluation of photo-catalytic reactions (a) and the electrode configuration of dual QCM (b).

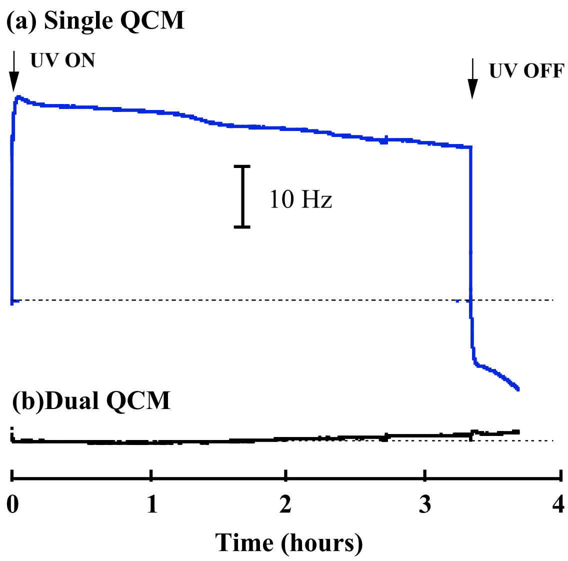

Fig. 2: An example of the correction of environmental influences on the resonant frequency by using the referenced QCM. (a) Frequency response of a single QCM. (b) Frequency response of a dual QCM. Irradiation power of UV is about 6.5 mW/cm^2.

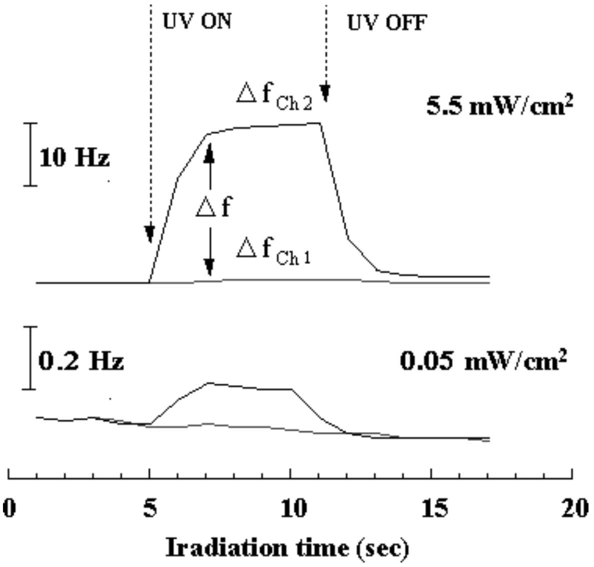

Fig.3: Frequency responses under the UV irradiation.

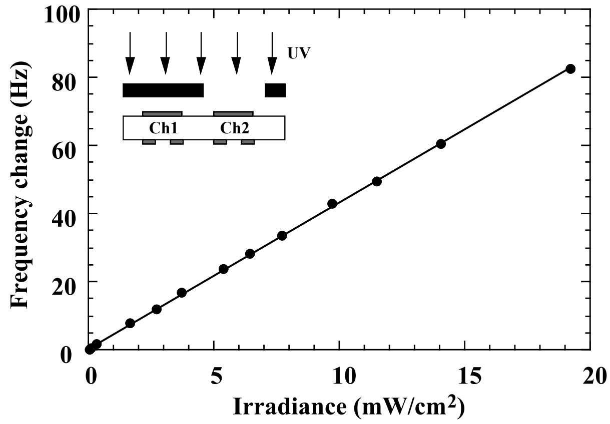

Fig. 4: Frequency changes against the intensity of UV irradiance. The diameter of the pinhole is 3 mm and that of the QCM is 2 mm.

3. RESULTS AND DISCUSSION

Figure 5 shows an example of photo-decomposition measurement for spin-coated thin MB dye film. Here, the irradiation power of UV was about 3 mW/cm^2. As shown in the figure 4(a), it is impossible to evaluate the mass change effects by using a single QCM because the environmental change effects cannot be determined. On the contrary, dual channel QCM developed here can measure the decomposition. The frequency change was 17 Hz and the corresponding mass value was about 1 ng. The frequency drift during the measurement was about 0.2 Hz. If we assumed the minimum detectable response is three times the value, our QCM system has mass sensitivity of 40 pg under UV irradiation. The time needs to decompose the MB dye film on the TiO_2 thin film was approximately 5 hour. This result was coincided with the transmittance measurement [7].

Figure 6 shows the frequency change measured for a cast MB dye film. The evaluation of the photocatalytic reactions is impossible in case of the single QCM. On the contrary, the dual QCM can determine the mass change effects accurately. At first, the frequency decreases were measured and it ranged from 10 to 20 Hz. As described before, the frequency decrease was not measured when the film was coated by spin-coating method. One of the possible reasons is that the photo-catalytic TiO_2 film shows super hydrophilicity by UV irradiation. As the result, the frequency increased by the adsorbed water on the film. It seems that the super-hydrophilicity is influenced by coating method. The other possible reason is that MB dye was oxidized and the mass increased. It is impossible to evaluate these contributions independently from the total frequency change.

Figure 7 shows the frequency change measured for a cast SDS film. The frequency increase caused by the decomposition of the cast SDS film was measured. Single QCM can measure the decomposition of the film qualitatively. However, the accurate determination of the mass change effects is impossible because of the frequency drift. On the contrary, we can measure the accurate determination of the mass change effects by using dual QCM. The frequency decrease was not measured. This means that SDS adsorbed on the surface uniformly. It is expected that SDS would uniformly adsorb on the surface because of its amphipathic property. The frequency change measured is about 67 Hz and this value is close to the theoretically calculated frequency change (c.a. 62 Hz) from mass of the cast film.

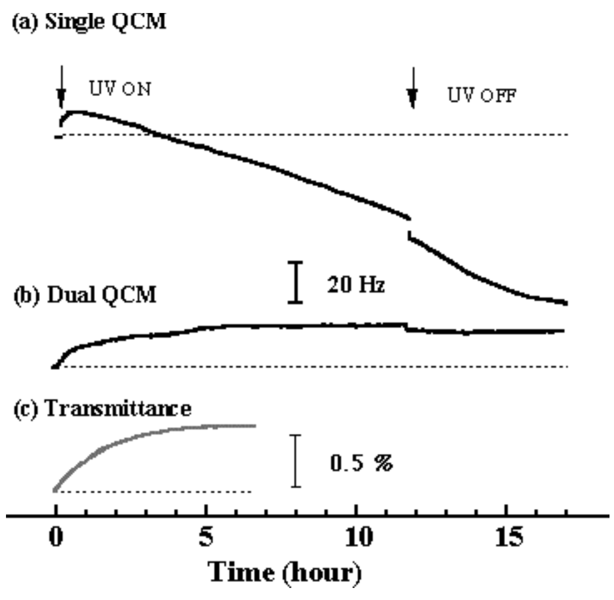

Fig. 4: Measured photo-catalytic reactions by using miniaturized QCM array [7]. The MB dye was spin-coated on the TiO_2 film.

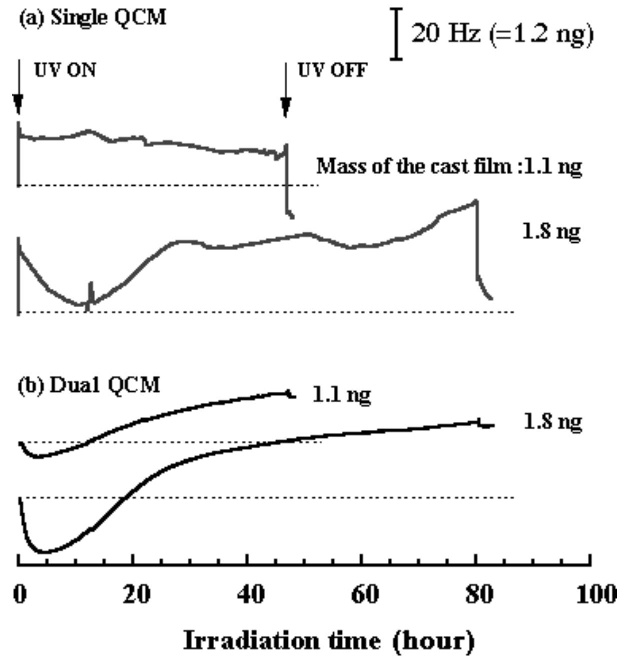

Fig. 6: Measured photo-catalytic reactions of a cast MB dye film on the TiO_2 thin film by using miniaturized QCM array. (a) The frequency changes measured by single QCM. (b) The frequency changes measured by dual QCM.

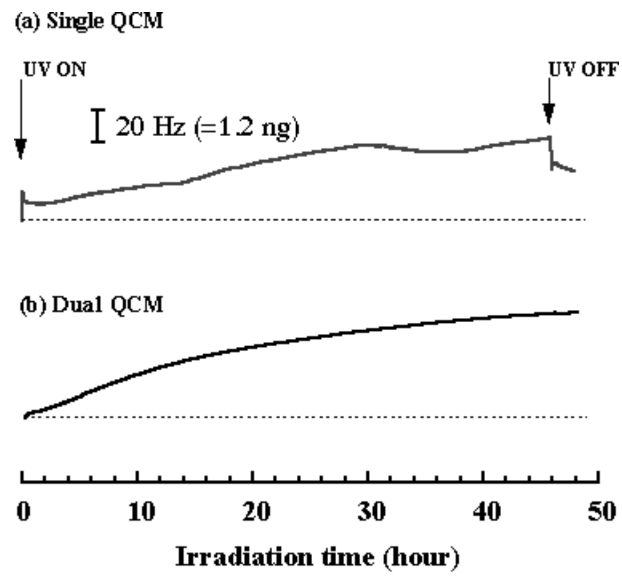

Fig. 7: Measured photo-catalytic reactions of a cast SDS film under the UV irradiation by using miniaturized QCM array. (a) The frequency change measured by single QCM. (b) The frequency change measured by dual QCM.

4. CONCLUSION

Real-time measurements of photo-catalytic reactions were demonstrated by using miniaturized QCM array. Our experiments revealed that coating process is important for the accurate analysis of the decomposition.

Our methodology enabled us to measure the accurate and independent determination of mass change effects from environmental change effects under UV irradiation. The experimental study on the reaction of persistent organic pollutants as to the chemical structures, presence of metal catalysts and on-site measurement under sun-light will be expected in the foreseeable future.

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