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In situ, Real-time Environmental SEM Imaging System Development for Water Splitting Reaction Using a Dynamic Light Illumination System

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Photocatalysis plays a crucial role in water splitting reaction to generate the hydrogen, and particularly as catalysis which can reduce contamination. To date, this catalytic behavior has been studied by mathematical approaches and designed by computer simulation at the nanoscale. Although the determination of the active site is important to improve the catalytic function, direct observation of activity sites e.g. electron microscope has rarely been performed because of the vacuum conditions inside an electron microscope, *in situ* observation of photocatalysis behavior which requires liquid, light and dynamic controllability of the atmosphere still remains challenging. Therefore, it is desirable to develop a new electron microscopy in which we can change the environment under illumination of light with atmospheric pressure.

To achieve environmental observations in an electron microscope (EM), a gas injection system, closed cell system and an inverted microscopy open specimen chamber with membrane support have been developed[1], [2]. Regarding electron microscopy in liquid, a closed environmental cell system has been demonstrated e.g. utilizing graphene and a MEMS (Micro Electro Mechanical Systems) enclosed cell[3]. First, *in situ* observation in liquid requires a solid membrane to prevent from the liquid boiling. Besides its advantage of hands on operation by using open air chamber; severe surface conditions require an enclosable system to keep the specimen into non-reactive gas. Thus, a closed cell system which can dynamically change environment on demand is desired. Especially, as for the case of water splitting material, severe surface condition of catalyst requires the non-active gas/liquid enclosure. Thus, we first developed the dynamic gas - liquid exchanging system with enclosed circuit. Furthermore, light illumination system is integrated to the gas/liquid cell system for the first time.

In our previous study, the environmental gas cell system successfully demonstrated dynamic environmental observation under atmospheric pressure[4]. Si_3N_4 thin MEMS made film allowed us to perform high resolution observation approximately several tens nm under atmospheric pressure. In this study, a bespoke feed through flange of two gas - liquid pass lines is integrated with an optical fiber which allows dynamic illumination of the laser light in the EM specimen chamber as shown in Figure 1. Fiber optics is introduced to the bottom of the environmental cell chamber. End of the optics is coupled with the optical lens to achieve the highly effective light illumination to the specimen while avoiding leak from the cell by gas tight sealing. These gas/liquid line and optical fiber are designed to be flexible and coupled with compact cell unit. This allows us to tilting the cell unit by SEM specimen stage to achieve perfect bubble removing to visualize bubble from water splitting. Cell unit with these lines are illustrated in Figure 2a. Laser lighting system is employed as a lighting source with 405 nm wavelength as the reactive wavelength range of this photocatalysis. As shown in Figure 2b, Focusing and alignment system is integrated to the laser generation system to control the 200mW laser power and maintain accurate illumination to perform the optimal light illumination. The detailed study from aspects of photocatalytic and crystallography will be published elsewhere.

In conclusion, a new environmental cell system with optical illumination system is developed. Live imaging which dynamically changing the gas/liquid species of atmospheric pressure can clearly identify the nanoscale morphology changes. This light illumination system to visualizing photocatalytic behaviour inside of the vacuum chamber will be utilized for the study of catalytically active site investigation by nanoscale [5], [6].

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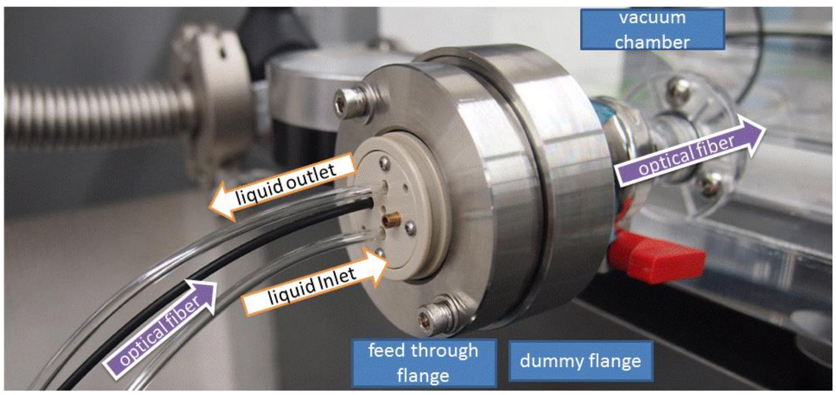

Figure 1. Feed through flange with vacuum chamber: Bespoke feed through flange allows us to dynamically introducing the gas to the environmental cell throughout inlet tube and outlet tube. Optical fiber is also integrated for the first time for laser illumination on the specimen inside of the environmental cell. Transparent vacuum chamber is employed to show these gas and optical lines.

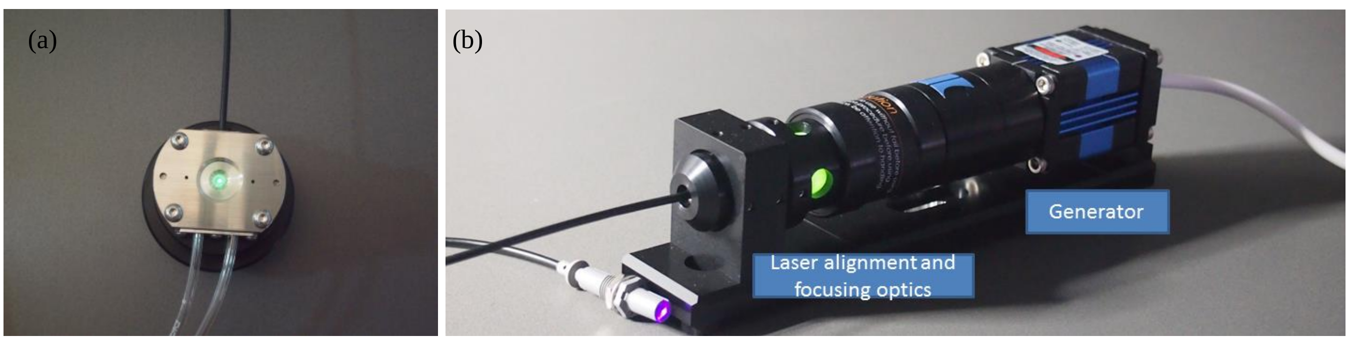

Figure 2. (a) Environmental liquid cell system with optical fiber and gas-liquid lines: Green light is introduced to the fiber optics to show where the thin MEMS membrane window exists.
(b) Laser illumination system: generator is integrated with focusing - alignment optics (unit with yellow window).

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