

## Cathode Luminescence Spectroscopy of Gold Nanoparticle Catalyst in Gas Environments

Takayuki Tanaka<sup>1,2</sup>, Naoki Yamamoto<sup>1,2</sup>, Kunio Takayanagi<sup>1,2</sup>

<sup>1</sup> Department of Physics, Tokyo Institute of Technology, 2-12-1-H-51, Oh-okayama, Meguro-ku, Tokyo 152-8551, Japan

<sup>2</sup> Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency, K's Gobancho, 7, Gobancho, Chiyoda-ku, Tokyo 102-0076, Japan

Gold nanoparticle on TiO<sub>2</sub> (Au/TiO<sub>2</sub>) [1–5] and Cu-doped TiO<sub>2</sub> [6] are promising for application to low temperature CO oxidation (2CO+O<sub>2</sub>→2CO<sub>2</sub>) catalyst [1–5] and visible light-sensitive photocatalyst [6], respectively. It is proposed that their catalyses are excited by negatively charged O<sub>2</sub> molecule (O<sub>2</sub><sup>-</sup>) [1–6], which is proposed to be generated by Au-O<sub>2</sub>-Ti co-bonding [4], interstitial Ti ion [3, 7] and Cu dopant [6]. We studied the effect of adsorbed O<sub>2</sub> (O<sub>2</sub><sup>-</sup>) in Au/TiO<sub>2</sub> catalyst, from the change of electronic states by gas adsorption.

Specimens of Au/TiO<sub>2</sub> were prepared in a vacuum chamber. The TiO<sub>2</sub> (rutile) crystals were annealed at 1170 K for 1 hour and gold was deposited subsequently on the TiO<sub>2</sub> at room temperature to form nanoparticles. The Au / TiO<sub>2</sub> specimen was mounted on a gas-injection holder for experiments of bright field scanning transmission electron microscopy (BF-STEM) and cathode luminescence (CL).

The Au/TiO<sub>2</sub> specimen was observed by STEM. Figure 1 (a) shows a typical BF-STEM image of Au/TiO<sub>2</sub>. Figure 1 (b) shows the corresponding spectrum map of CL (CL map) at 404 nm. The CL map was drawn from CL spectra, which were simultaneously acquired with the STEM image of Fig. 1 (a). The CL map is colored by the CL intensity at 404 nm. As the thickness of TiO<sub>2</sub> increased, intensity of CL spectrum was inclined to increase in Fig. 1 (b). The peak wavelength depended on the local position of Au/TiO<sub>2</sub>. In the Au/TiO<sub>2</sub> region of Fig. 1 (a), the peak wavelengths were 400 ~ 490 nm. The wavelength of λ~410 nm corresponds to band gap energy of TiO<sub>2</sub> (3.0 eV).

Figure 2 (a) showed a “mean CL spectrum”, which was acquired in condition of no gas exposure. The “mean CL spectrum” was averaged in a region of an Au/TiO<sub>2</sub> specimen. The peak wavelength of the mean CL spectrum was 393 nm. The mean CL spectrum changed by O<sub>2</sub> exposure of 1x10<sup>-4</sup> Pa. The change from the spectrum of Fig. 2 (a) to that of the O<sub>2</sub> exposure, called “O<sub>2</sub> spectrum” hereafter, was shown by purple curve in Fig. 2 (b). The O<sub>2</sub> spectrum showed new broad peaks, which ranged from 350 ~ 390 nm. The broad peaks included signals below λ=410 nm, correspondent to band gap energy of TiO<sub>2</sub>. On the other hand, the mean CL spectra did not change by CO exposure of 1x10<sup>-4</sup> Pa. The CO spectrum of 1x10<sup>-4</sup> Pa, defined as the change from the spectrum of Fig. 2 (a), did not have new peaks, as shown by green curve in Fig. 2 (b). Spectrum of co-exposure of CO and O<sub>2</sub> at each partial pressure of 1x10<sup>-4</sup> Pa, as shown by red curve in Fig. 2 (b), was similar to the O<sub>2</sub> spectrum of 1x10<sup>-4</sup> Pa. It is found that the changes of mean CL spectra by gas exposure depend on partial pressure of O<sub>2</sub>. The new peaks below λ=410 nm by O<sub>2</sub> exposure are thought to be the resonance state of O<sub>2</sub> adsorption (O<sub>2</sub><sup>-</sup>). The change by CO exposure of 1x10<sup>-4</sup> Pa was not almost detected.

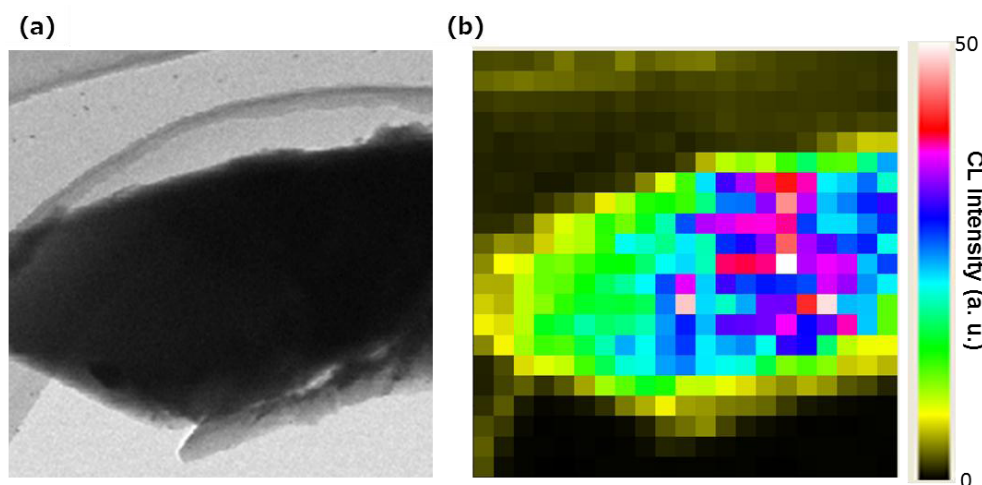
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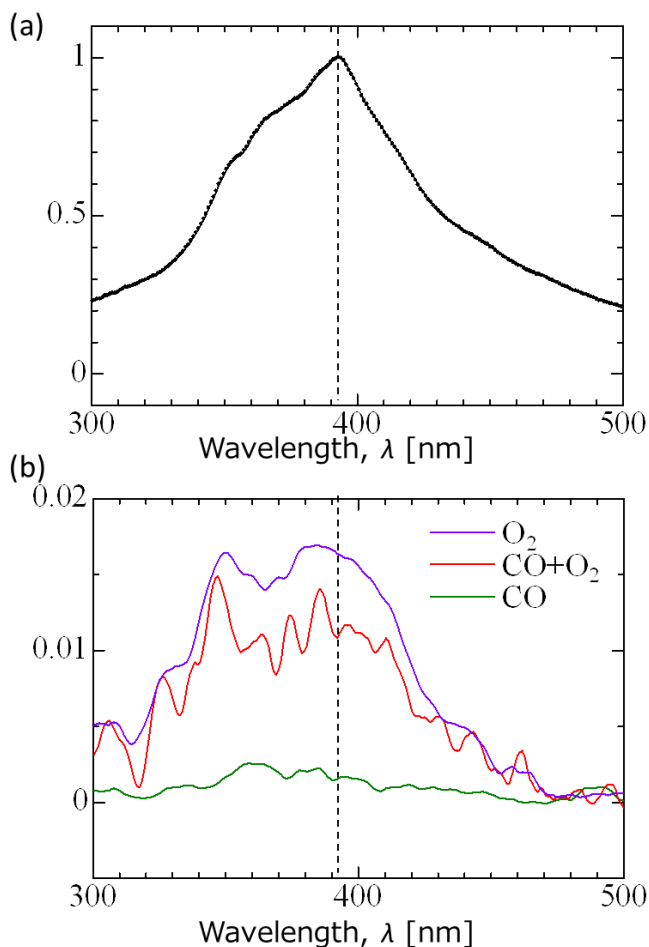
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**Figure 1.** (a) BF-STEM image of Au/TiO<sub>2</sub> specimen (940nm x 940nm) and (b) the corresponding CL Map at 404 nm. The CL map is colored by the CL intensity at 404 nm. As the CL intensity increases, the color changes from black to white.



**Figure 2.** (a) Mean CL spectrum acquired by no gas exposure. Mean CL spectrum is averaged in a region of Au/TiO<sub>2</sub>. (b) Change of mean spectrum from (a) by O<sub>2</sub> exposure of  $1 \times 10^{-4}$  Pa, drawn by purple curve, CO exposure of  $1 \times 10^{-4}$  Pa by green curve and co-exposure of CO and O<sub>2</sub> at each partial pressure of  $1 \times 10^{-4}$  Pa by red curve, respectively.