

## Plasmonic resonance tuning of Pd nano-dimer arrays using hydrogen absorption

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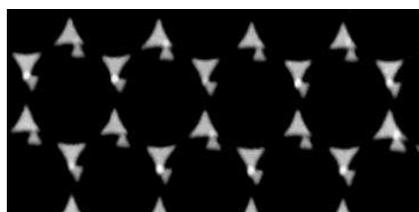
### [Introduction]

Metal nanostructures of coinage metals such as gold, silver, and copper are known to exhibit strong plasmon resonances. Many attempts have been made to increase the sensitivity of spectroscopy and the efficiency of photochemical reactions using plasmon resonances on coinage metal nanostructures. On the other hand, plasmonic property of transition metals such as platinum or palladium, which have a much wider application in modern industries, has not been studied much because of their rather weak plasmon resonances. The weak resonance of transition metals is due to the strong mixture of d-electrons with sp-electronic states. However, this electronic structure also leads to unique properties of these metals such as catalytic activity. Hence, there is a possibility to design a functional plasmonic device using transition metals. In the present work, we demonstrate dynamic tuning of plasmon resonances on palladium nano-dimer arrays, which is controlled via hydrogen absorption into the Pd nanostructures.

### [Experimental]

Pd nano-dimers were fabricated on a glass substrate using angle-resolved nanosphere lithography (AR-NSL). Briefly, a monolayer of polystyrene-beads with diameter of 350 nm was formed on the substrate as a shadow mask for vacuum deposition of Pd. After double angle evaporation of Pd, the polystyrene monolayer was removed so that the array of Pd-dimers was formed. Figure 1 shows a typical AFM image of the Pd dimer array. A number of pairs of Pd nano-triangles aligned two-dimensionally on the substrate.

Plasmon resonances of the arrays were measured in-situ by optical transmission measurements with and without hydrogen gas flow.



400 nm

Figure 1. Typical AFM image of the Pd nano-dimer array.

### [Results and Discussions]

Figure 2 shows polarization-dependent extinction spectra of the Pd-dimer array. When the incident light was polarized along the short axis of the dimers, a plasmon resonance peak appeared around 500 nm, which was similar to that of the Pd-monomer. On the other hand, when polarized along the long axis of the dimers, a very broad plasmon resonance appeared around 600 nm. The peak shift for the long axis can be explained by plasmon coupling between two adjacent Pd nano-triangles.

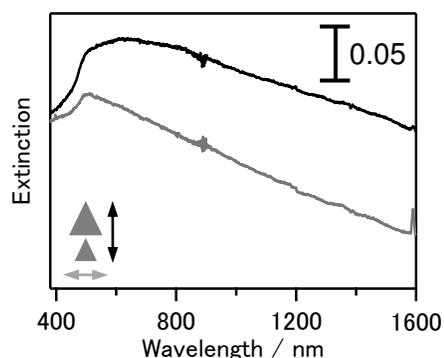


Figure 2. Extinction spectra of the Pd nano-dimer array, measured under polarization parallel and perpendicular to the dimer axis

Spectral variation of the Pd nano-dimer array was measured in-situ with and without hydrogen gas flow. Figure 3a shows temporal variation of the extinction of the dimer long axis at 600 nm under 3% hydrogen gas flow. One can clearly see that the plasmon resonance became weaker in the presence of hydrogen and quickly recovered to the original resonance intensity under the nitrogen gas flow. The magnitude of the variation was about 1.5 times larger for the dimer long axis than for the short axis. In a similar manner, we measured the extinction variation under hydrogen gas flow of various concentrations. As shown in Fig. 3b, the magnitude of the hydrogen-induced resonance variation exhibited a significant dependence on the hydrogen concentration. According to the phase diagram of palladium-hydrogen system, the concentration dependence of the resonance variation was very similar to that of the phase transition from metallic palladium to palladium hydrate, indicating that the hydrogen-induced variation of the plasmon resonance was mainly ascribed to the phase transition of Pd nanostructures.

In conclusion, we have dynamically controlled the plasmon resonance of Pd nano-dimers by hydrogen absorption, which was never expected in conventional plasmonic systems of coinage metals.

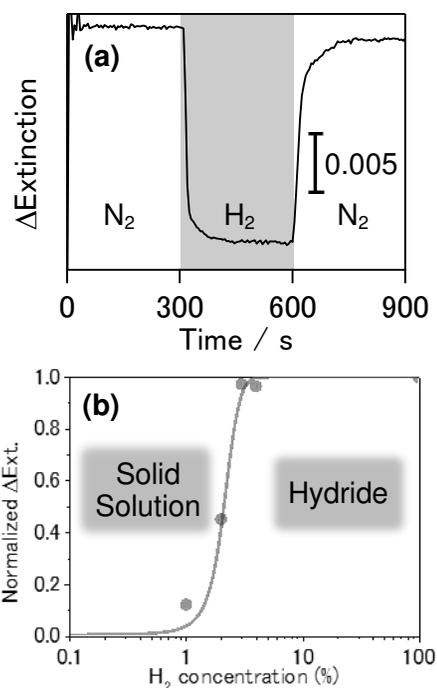


Figure 3. (a) Time-course of the extinction of the long axis of Pd nano-dimer array at 600 nm with and without 3% hydrogen gas flow. (b) Hydrogen concentration dependence of the extinction variation at 600 nm.