PD Research Report for the 2015 year

Name（Research group）Li Wang

（Tamai Research Group, Graduate School of Science and Technology）

Research Theme　半導体ナノ微粒子系の多励起子素過程の解明と光応答分子システムへの応用

Research Period　September, 20th, 2015 ~ March, 31st, 2016

The semiconductor nanostructures are promising to provide multiexciton generation for the phtoswitchable systems. Metal nanostructures are good candidates as electron acceptors with attachment of semiconductor nanoparticles. They also represent unique optical properties and localized surface enhancements of electrical fields. In semiconductor and metal hybrid nanosystems, metal components may influence exciton dynamics by charge separation or electric near-field enhancement.[1,2] My interesting is simulation of the optical properties of metal nanostructures for designation of new type hybrid nanosystems. For example, Pd and Ag/Pd/Ag sandwich nanoplates represent tunable localized surface plasmon resonance (LSPR) from near infrared to visible region, which can be alternative materials of normal Au nanostructures. The ultrafast dynamics of Pd and Ag/Pd/Ag sandwich nanoplates represent a continuous variation of the coherent acoustic phonon vibration with increasing the contents of Ag. The origin of the vibration was assigned to phonon oscillation from tip to tip or from edge to edge of the nanoplates. With numerical simulation of eigenfrequency and LSPR by Comsol multiphysics, the results of deformation of nanoplates and LSPR shift can be used for the explanation of the process of coherent acoustic phonon vibration. For this purpose, I simulated the extinction spectra and the structure vibration of Pd and Ag/Pd/Ag sandwich nanoplates.

The models of Pd and Ag/Pd/Ag sandwich nanoplates are designed according to TEM results as shown in Figure 1. The length/height of Pd nanoplates are estimated to be (27.0 ± 2.3)/(1.8 ± 0.4) nm. Random distribution of Ag nanoparticles on the plane of Pd nanoplates (probably on both upper and bottom sides) is observed in the TEM images of Ag/Pd/Ag A (Figure 1b), which are prepared with the least Ag contents. With increasing Ag contents, the brightness of TEM images is enhanced for Ag/Pd/Ag J (Figure 1c), which are prepared with more Ag contents. The structural schematics for the three typical species are plotted in Figure 1d, which are used as the geometries in the simulation by Comsol Multiphysics. The content ratios of Ag and Pd for all the Ag/Pd/Ag sandwich nanoplates are obtained from inductively coupled plasma mass spectrometry (ICP-MS). Hence, the thickness of Ag shell is

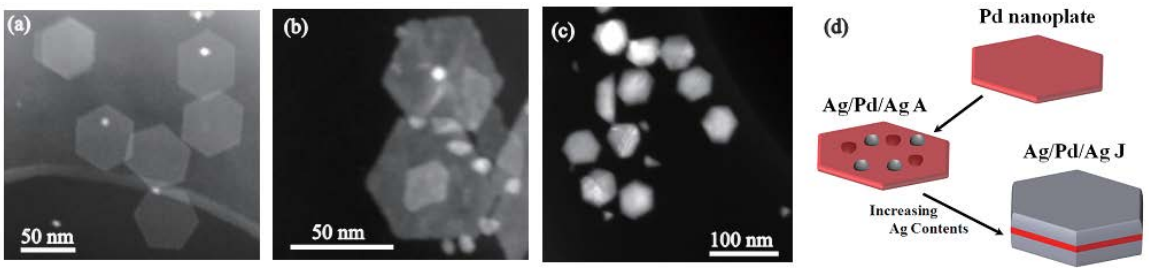

Figure 1. TEM images of Pd nanoplates (a) and Ag/Pd/Ag sandwich nanoplate with two different Ag contents (b and c for the samples labeled with Ag/Pd/Ag A and Ag/Pd/Ag J in the text).Schematics of hexagonal Pd nanoplates, Ag/Pd/Ag A (Ag nanoparticle decorated on both upper and bottom planes of Pd nanoplates), and Ag/Pd/Ag J (thick Ag shell coated on both planes of Pd nanoplates) (d).

estimated to be 1.9, 2.9, 3.6, 4.3, 4.7, 8.0, 10.0, 10.5, 13.5, 21.0, and 25.0 nm, respectively. With increasing Ag content, the eleven Ag/Pd/Ag sandwich nanoplates are labeled as Ag/Pd/Ag A, B, C, D, E, F, G, H, I, J, and K, correspondingly.

The experimental absorption spectra of Pd and Ag/Pd/Ag nanoplates are shown in Figure 2a. The peak position and full width at half maximum (FWHM) of plasmon band for all the nanoplates are summarized in Figure 2c. The simulation of extinction spectra for Pd and Ag/Pd/Ag nanoplates are plotted in Figure 2b and are summarized in Figure 2d. The simulation spectrum is in a good agreement with experimental data for uncoated Pd nanoplates dispersed in water. After $AgNO_3$ solution was gradually added for growth of Ag shell, the LSPR peak is red-shifted to 1143 nm for Ag/Pd/Ag A owing to the plasmonic percolation behavior.[3] However, the simulated spectrum for the model of Ag/Pd/Ag A is almost no shift from pure Pd nanoplate (data is not shown here). With further adding Ag contents, the LSPR peak begins blue shift and finally reaches to 460 nm for Ag/Pd/Ag K. With increasing the thickness of Ag shell from 2 to 25 nm, the simulated spectra are also blue shifted from 654 to 452 nm and FWHM becomes narrower from 170 to 95 nm, correspondingly.

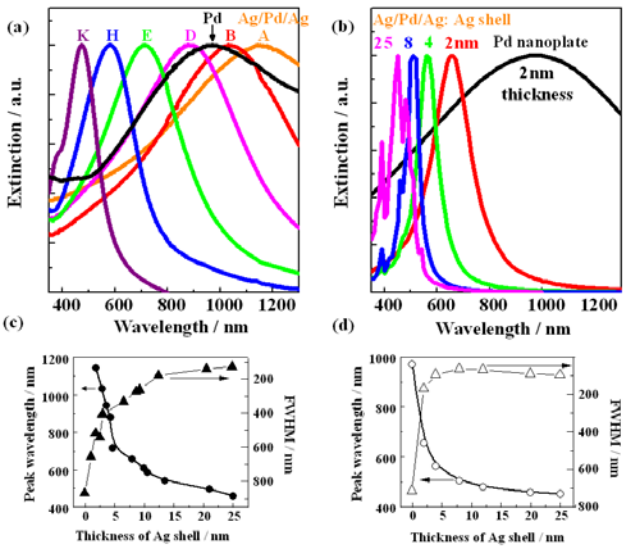

Figure 2. Experimental extinction spectra and the corresponding peak wavelength and full width at half maximum (FWHM) of Pd and Ag/Pd/Ag nanoplates (a and c). Simulation extinction spectra of Pd and Ag/Pd/Ag nanoplates with 2, 4, 8, 12, 20, and 25 nm Ag shell thickness (b and d).

The shift of LSPR of Pd and Ag/Pd/Ag sandwich nanoplates corresponding to the structure deformation induced by laser irradiation is still in progress. The data will helpful for understanding the size variation in the process of coherent acoustic phonon vibration of metal nanostructures.

Publications:

1**)** L. Wang, Y. Tian, T. Okuhata, and N. Tamai, "Charge Transfer Dynamics and Auger Recombination of CdTe/CdS Core/Shell Quantum Dots", *J. Phys. Chem. C* **2015**, 119, 17971−17978

2) L. Wang, T. Sagaguchi, and N. Tamai, "Coherent acoustic phonon vibration of Pd and Ag/Pd/Ag sandwich nanoplates", (In draft)

Reference:

(1) Okuhata, T.; Kobayashi, Y.; Nonoguchi, Y.; Kawai, T.; Tamai, N. Ultrafast Carrier Transfer and Hot Carrier Dynamics in PbS-Au Hybrid Nanostructures. *J. Phys. Chem. C* **2015**, *119*, 2113-2120.

(2) Masuo, S.; Kanetaka, K.; Sato, R.; Teranishi, T. Direct Observation of Multiphoton Emission Enhancement from a Single Quantum Dot Using AFM Manipulation of a Cubic Gold Nanoparticle. *Acs Photonics* **2016**, *3*, 109-116.

(3) Chen, H.; Wang, F.; Li, K.; Woo, K. C.; Wang, J.; Li, Q.; Sun, L.-D.; Zhang, X.; Lin, H.-Q.; Yan, C.-H. Plasmonic Percolation: Plasmon-Manifested Dielectric-to-Metal Transition. *ACS Nano* **2012**, *6*, 7162-7171.