Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Characterizing Optical Properties of Single Palladium-Coated Core-Shell Gold Nanorods as Multifunctional Orientation Probes

So Young Lee[1] and Ji Won Ha[1*]

[1]Advanced Nano Bio Imaging and Spectroscopy (ANBIS) Laboratory, Department of Chemistry, University of Ulsan, 93 Daehak-Ro, Nam-Gu, Ulsan 44610, South Korea

[*]To whom correspondence should be addressed.

J. W. Ha

Phone: +82-52-259-2347

Fax: +82-52-259-2348

E-mail: jwha77@ulsan.ac.kr

This document contains the experimental details and additional supplementary figures (Fig. S1 to S4).

Experimental Methods

Sample Preparation and Characterization. Pd-AuNRs with an average size of 25 nm × 73 nm were purchased from Sigma-Aldrich (St. Louis, MO, USA) The Pd-AuNR colloid solution was first diluted with 18.2-MΩ pure water to a proper concentration. The diluted solution was then sonicated for 15 min at room temperature. Samples were prepared by spin casting the solution on the pre-cleaned glass slide. Then, a 22 mm × 22 mm No. 1.5 coverslip (Corning, NY) was covered on the glass slide. In this study, the concentration of Pd-AuNRs on the glass surface was controlled to be ~1 μm^{-2} in order to facilitate single particle characterization and to minimize inter-particle SPR coupling resulting in the spectral shift. Structural characterization was carried out using a transmission electron microscope (TEM) (H-8100, Hitachi, JAPAN).

Dark-field Microscopy and Single Particle Spectroscopy. DF microscopy imaging was performed under a Nikon inverted microscope (ECLIPSE Ti-U) in this study. In DF mode, the microscope utilized a Nikon Plan Fluor 100× 0.5-1.3 oil iris objective and a Nikon DF condenser. An Andor $iXon^{EM}$+ CCD camera (iXon Ultra 897) was employed to record DF images of Pd-AuNRs. The collected images were analyzed with Image J. Furthermore, DF scattering spectra were acquired with an Andor spectrometer (SHAMROCK 303i, SR-303I-A) and an Andor CCD camera (Newton DU920P-OE). When taking a spectrum, the scanning stage moved the sample to the desired location so that only the scattered light from the selected location was collected by the objective. The scattered light was directed to the entrance of the spectrometer, dispersed by a grating (300 l/mm, center wavelength: 700 nm), and detected by the Newton CCD camera. The background was measured at a region without any particles. Data analysis was performed with specially designed Matlab programs.

Differential Interference Contrast Microscopy. Differential interference contrast (DIC) microscopy was used with a Nikon inverted microscope (ECLIPSE Ti-U) in this study. DIC microscopy consists of a set of two Normarski prisms, two polarizers, and a quarter-waveplate (Fig. S4). The samples were illuminated through an oil immersion condenser (numerical aperture (NA) = 1.4), and, after passing through the sample, the signals were collected by a Plan Apo oil-immersion objective (100×, NA = 1.4). A bandpass filter with central range of 660 nm (full width at half maximum: ± 5 nm) was obtained from Thorlabs (Newton, NJ, USA) and inserted into the microscope's beam path to illuminate the samples in our study. A rotational study was carried out at 660-nm excitation by rotating the rotational stage by 10° per step for single Pd-AuNRs. When we rotated, the fixed Pd-AuNRs were positioned in different orientations. An Andor iXon^{EM}+ CCD camera (iXon Ultra 897) was employed to record highly detailed DIC images of Pd-AuNRs. The collected DIC images were analyzed with Image J.

Orientation-dependent DIC Images of Single Pd-AuNRs. In DIC microscopy the incident beam is split into two orthogonally polarized beams in the two bright and dark polarization directions by the first Nomarski prism (Fig. S4). These two beams are separated by a certain distance (usually a few hundred nanometers) along the shear direction. When two beams pass through the specimen, they generate image contrasts for optical path length gradients in the specimen. Therefore, each of the two orthogonally polarized beams generates an independent intermediate image. One such image is shifted laterally by ~100 nm and then overlapped with the other to generate the final interference image. For anisotropic shape of Pd-AuNRs, the two intermediate images are different because the two illumination beams are

phase-delayed to different extents, depending on the orientation of the Pd-AuNR relative to the two polarization directions. Therefore, the DIC images of Pd-AuNRs appear as diffraction-limited spots with disproportionate bright and dark parts and they show different bright and dark intensities depending on the Pd-AuNR orientation. For example, the darkest (or brightest) intensity is observed when the longitudinal axis of a Pd-AuNR lying flat to the surface is parallel to the dark (or bright) polarization axis. The bright and dark intensities are changed periodically as a function of the orientation angle φ and the intensities from bright and dark polarization directions are anti-correlated for single Pd-AuNRs.

Determining the Orientation Angle of Single Pd-AuNRs. In DIC microscopy we can estimate the orientation of Pd-AuNRs from their focused DIC image patterns. There are two methods to determine the orientation angle of single Pd-AuNRs in the focal plane. First, the DIC image patterns of a Pd-AuNR lying flat to the surface are periodically changed as a function of orientation angle. Therefore, we can simply estimate the orientation angle of Pd-AuNRs from their characteristic orientation-dependent DIC image patterns. For example, the totally bright intensity suggests that the orientation angle of a Pd-AuNR is close to 90°, meaning the long axis of a Pd-AuNR is parallel to the bright polarization direction. Second, the DIC polarization anisotropy based on the intensity analysis can also enable us to determine the spatial orientation of single Pd-AuNRs.

Calculation of the orientation angle φ from the DIC polarization anisotropy *P*. Two orthogonal intensities from bright and dark polarization directions are obtained in DIC microscopy. The DIC bright intensity of a Pd-AuNR is proportional to the fourth power of the sine of the orientation angle φ between the long axis of a NR and the dark axis. In

addition, the DIC dark intensity is proportional to the fourth power of the cosine of the orientation angle φ. Therefore, the normalized bright and dark intensities ($I_{B,N}$, $I_{D,N}$) as a function of the orientation angle φ can be written as

$$I_{B,N}(\varphi) = sin^4(\varphi)$$

$$I_{D,N}(\varphi) = cos^4(\varphi)$$

DIC polarization anisotropy P is defined as

$$P = \frac{I_{B,N} - I_{D,N}}{I_{B,N} + I_{D,N}}$$

Therefore, the polarization anisotropy P can be rewritten as

$$P = \frac{sin^4(\varphi) - cos^4(\varphi)}{sin^4(\varphi) + cos^4(\varphi)}$$

The orientation angle φ can be expressed in terms of P and the following relationship for the orientation angle φ as a function of P is finally obtained.

$$\varphi = \text{acos}\left(\sqrt{\frac{A - \sqrt{A^2 - 2A}}{2}}\right),\ P < 0$$

$$\varphi = \text{acos}\left(\sqrt{\frac{A + \sqrt{A^2 - 2A}}{2}}\right),\ P > 0$$

where A is defined as (P-1)/P.

Supplementary Figures

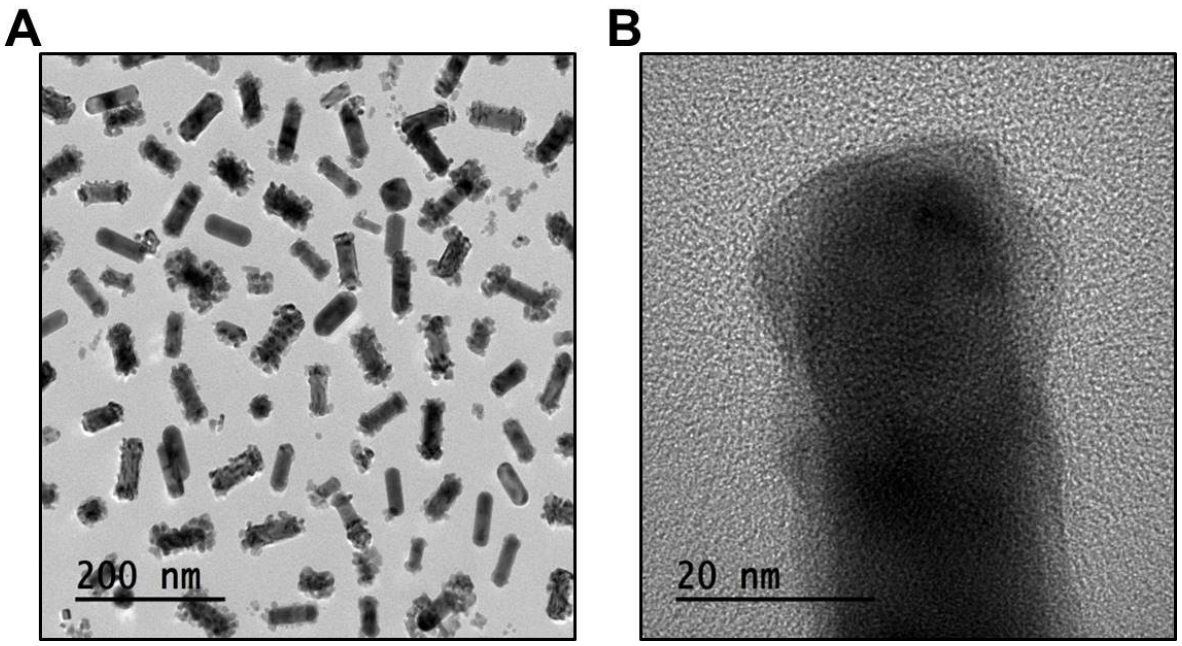

Fig. S1 (A) TEM image of palladium-coated gold nanorods. The average length and width are 73 nm and 25 nm, respectively. (B) Enlarged TEM image of single Pd-AuNR.

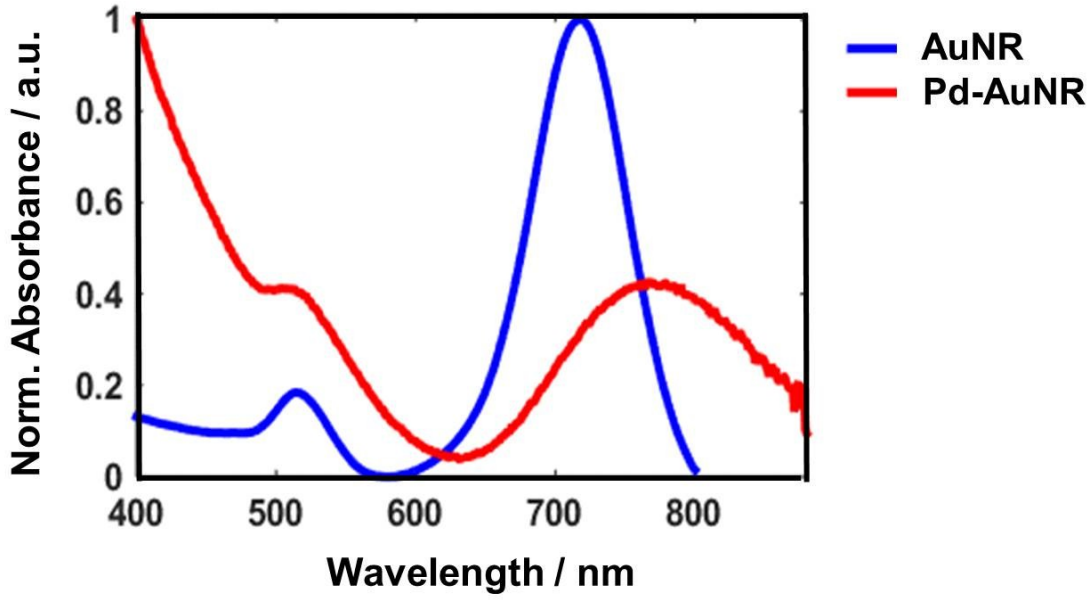

Fig. S2 Normalized UV-Vis absorption spectra of AuNRs (blue) and Pd-AuNRs (red) dispersed in water. The SPR linewidth was increased for the Pd-AuNRs due to strong plasmon damping caused by the Pd metals on the AuNR surface.

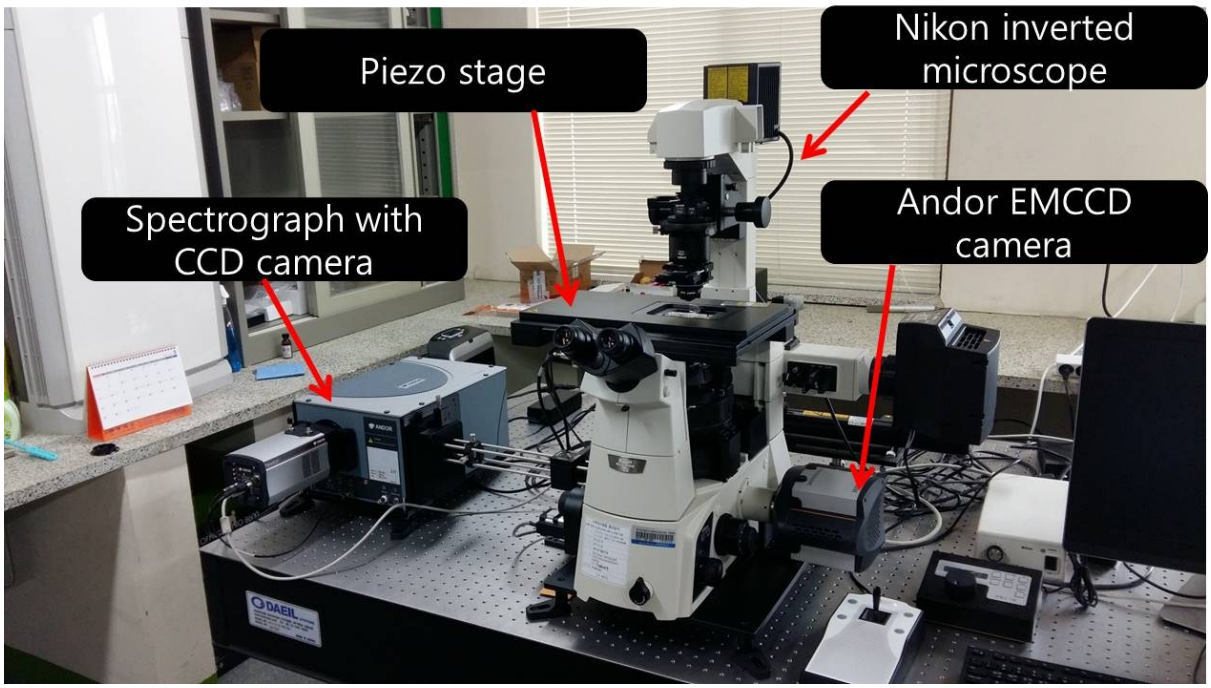

Fig. S3 A photograph of experimental setup for single particle microscopy and spectroscopy.

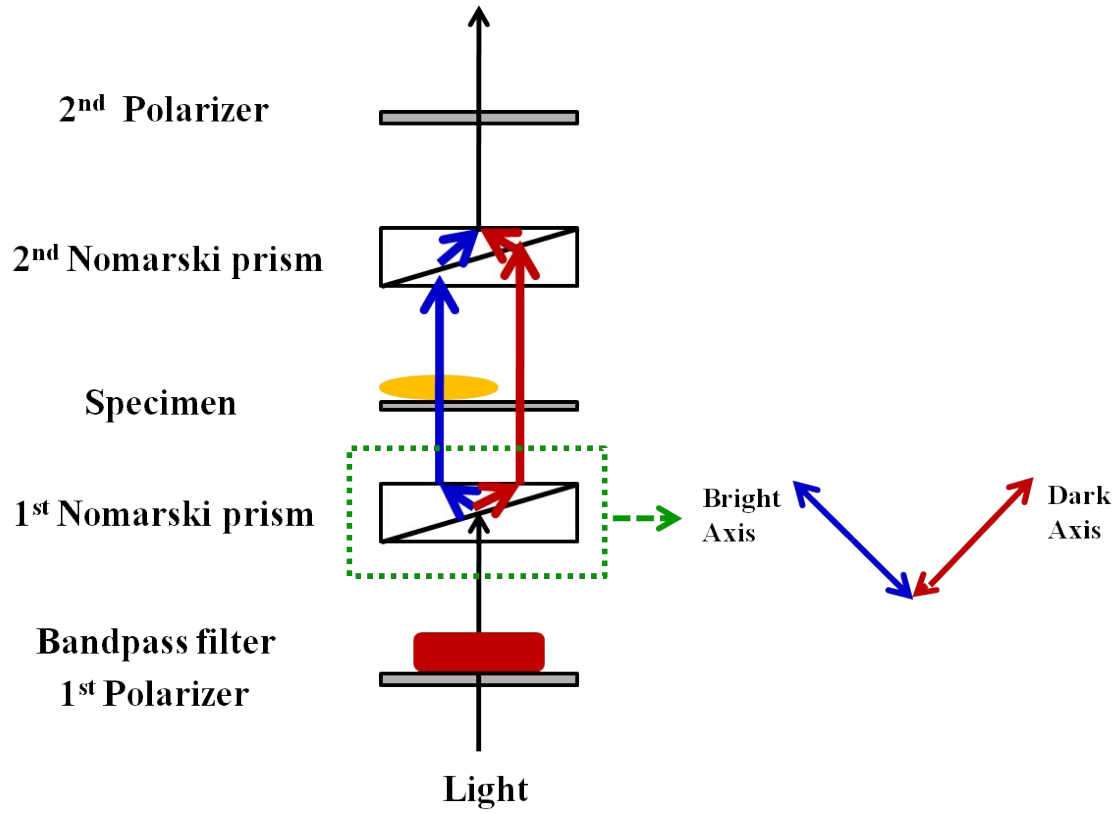

Fig. S4 The working principle of DIC microscopy.