Electronic Supplementary Information

Three-dimensional Defocused Orientation Sensing of Single Bimetallic Core-Shell Gold Nanorods as Multifunctional Optical Probes

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This document contains detailed experimental methods and additional supplementary figures (Fig. S1 to S11).

Experimental Methods

1. Materials and Sample Preparation

Bimetallic AuNRs (Pt-AuNR, Pd-AuNR) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Bare AuNRs (no metals) were purchased from Nanopartz (Loveland, CO, USA). For bare AuNRs, two absorption peaks appear at 516 and 700 nm in the UV-Vis absorption spectrum, which was collected with a Varian Cary 300 UV-Vis spectrophotometer. The 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. A sample was prepared by spin casting the mixture on the well-cleaned glass slide. The concentration of AuNRs deposited on the gold film surface was controlled to be 1 μm^{-2} in order to facilitate single AuNR characterization and to minimize inter-particle SPR coupling resulting in the spectral shift. Then, a 22 mm × 22 mm No. 1.5 coverslip (Corning, NY) was covered on the glass slide for single particle measurements under optical microscopy.

2. Scattering-Based Dark-Field Microscopy Imaging of Single AuNRs

The sample glass slide was placed onto the microscope stge. The DF images of AuNRs under randomly-polarized white light illumination were obtained by using a motorized rotary stage from Sigma Koki (SGSP-60YAM) coupled to the fine-adjustment knob on the microscope. The motor was controlled by Intelligent Driver, CSG-602R (Sigma Koki). We scanned in the z-direction with a vertical step size of ~40 nm. We employed a Nikon Plan Fluor 100× 0.5-1.3 oil iris objective and a Nikon DF condenser for taking DF images for AuNRs. 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.

3. Single Particle Scattering Spectroscopy

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.

4. Simulation of Scattering Image Patterns of AuNRs

We used the simulation program developed by Enderlein and Böhmer.[1] The program is designed to calculate the characteristic intensity distribution from an emitter with three perpendicular emission dipoles of different emission strength. It has been widely used to determine the spatial orientation of single dye molecules.[1, 2] The simulation program is a special Matlab based utility with a graphics user interface (GUI) for easy calculation. This program allows us to calculate exactly the defocused (or focused) images of single molecules. For using the GUI, one should download the files from the website (http://www.joerg-enderlein.de/imagingOfSingleMolecules.html).

The parameters that can be input are: the numerical aperture of the objective lens, magnification of imaging, extent of defocusing (or defocusing distance in micrometers), κ and R. For defining the emission strength ratios of the three independent dipoles (Fig. 2), we input the parameter κ and R into the program. The ratio κ defines the ratio of the emission strength of the b- to the c-dipole (transverse dipoles, Fig. 2) as shown below.

$$I_b / I_c = (1-\kappa)/(1+\kappa)$$

In this study the emission strength of the b-dipole is assumed to be same as that of the c-dipole. In addition, the ratio R defines the emission strength of the a-dipole (or longitudinal dipole) to the combined b and c dipoles (or transverse dipoles) as shown below.

$$R \times I_a + (1-R) \times (I_b + I_c)$$

When R is 1, we only have the contribution from a-dipole (longitudinal dipole) to the image patterns. However, the other two transverse dipoles (b and c) start to contribute to the image patterns with decreasing the ratio R. That is, lower R values indicate more contributions from the two transverse dipoles. Therefore, we were able to calculate the scattering patterns of a AuNR by adjusting the important parameters.

References

1. M. Böhmer and J. Enderlein, *J. Opt. Soc. Am. B*, 2003, **20**, 554-559.

2. M. A. Lieb, J. M. Zavislan and L. Novotny, *J. Opt. Soc. Am. B*, 2004, **21**, 1210-1215.

Supplementary Figures

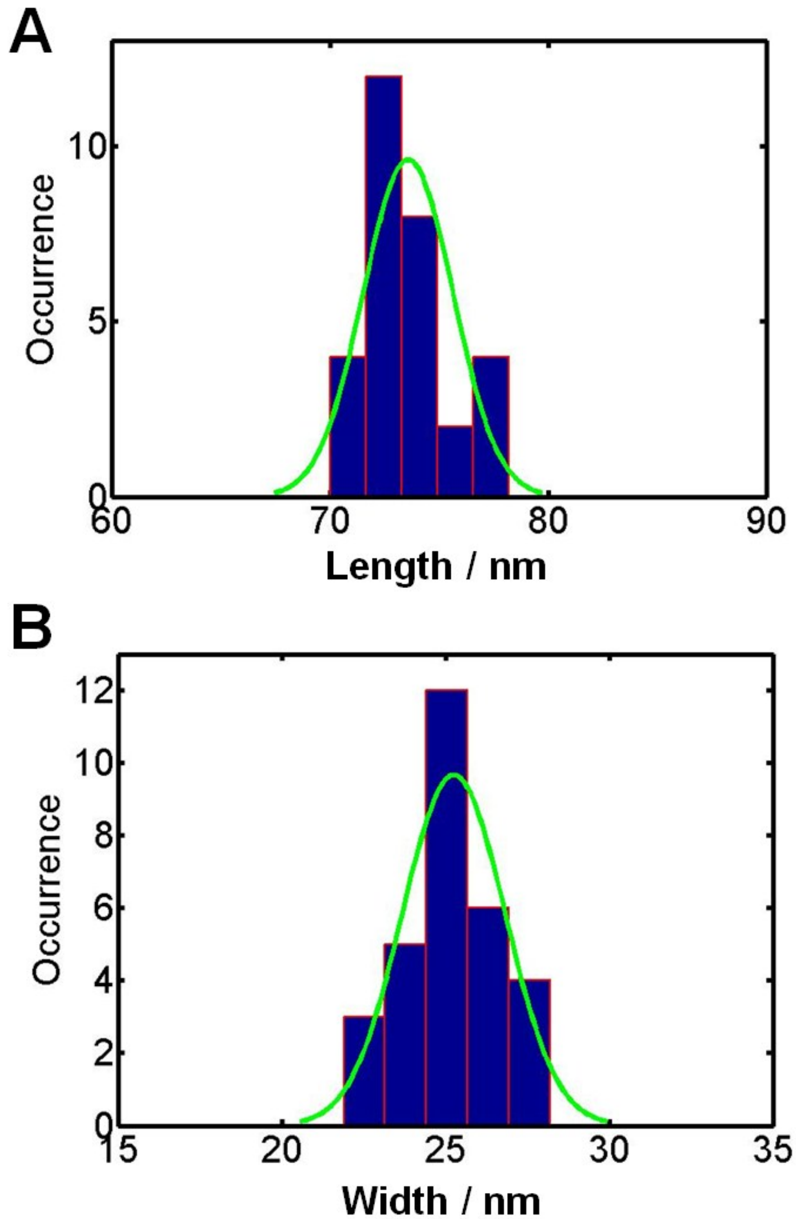

Fig. S1 Size distribution of bimetallic AuNRs. The average length and width are 73.6(±2.14) nm and 25.3(±1.56) nm, respectively.

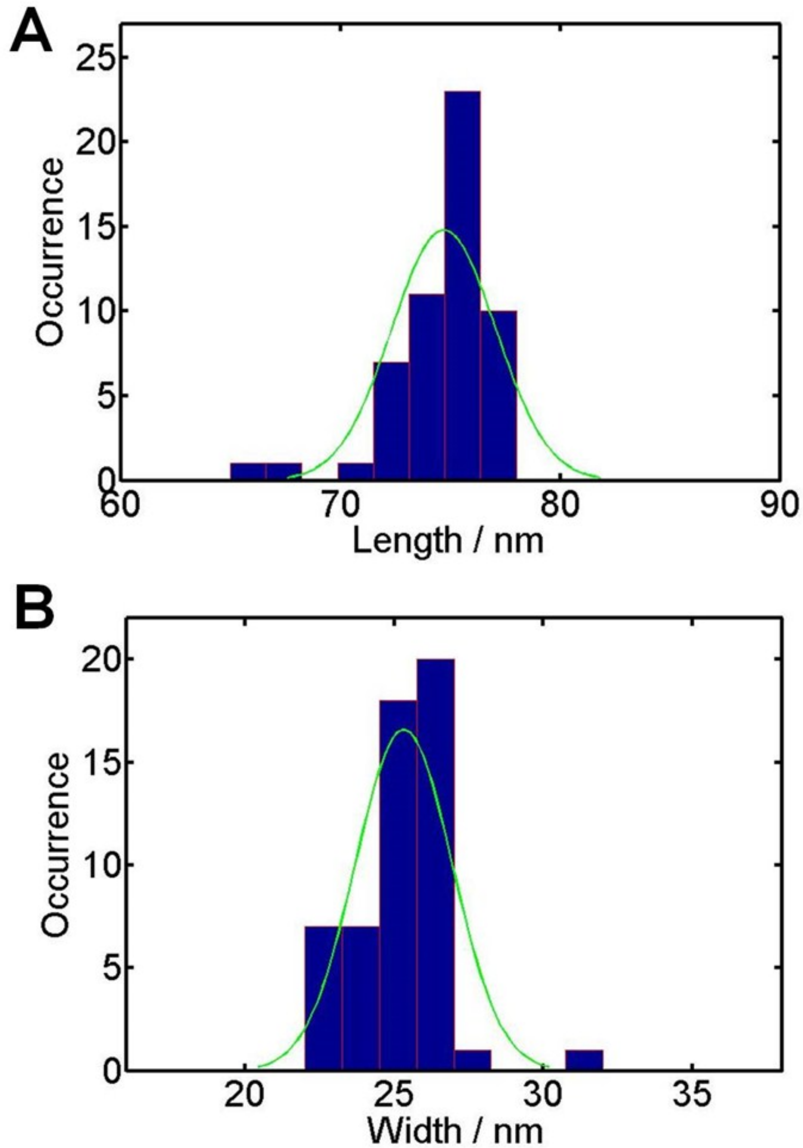

Fig. S2 Size distribution of bare AuNRs. The average length and width are 73.7(±3.38) nm and 25.4(±1.65) nm, respectively.

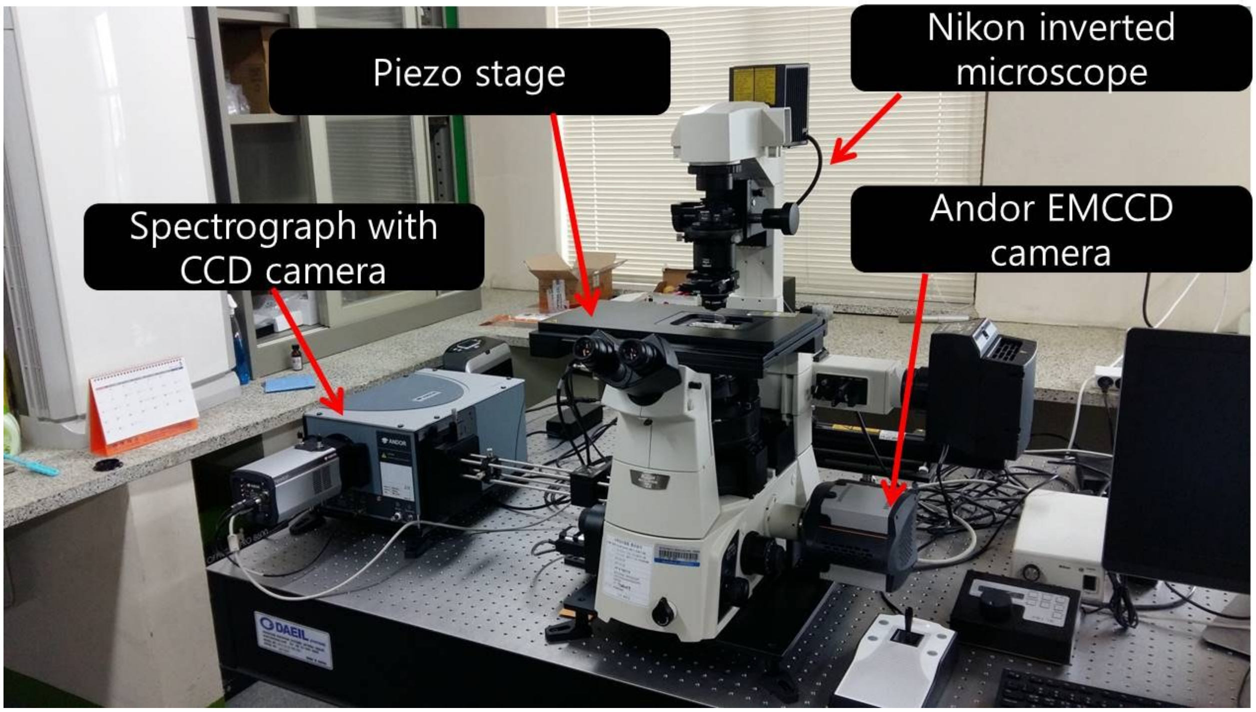

Fig. S3 Experimental setup for single particle microscopy and spectroscopy.

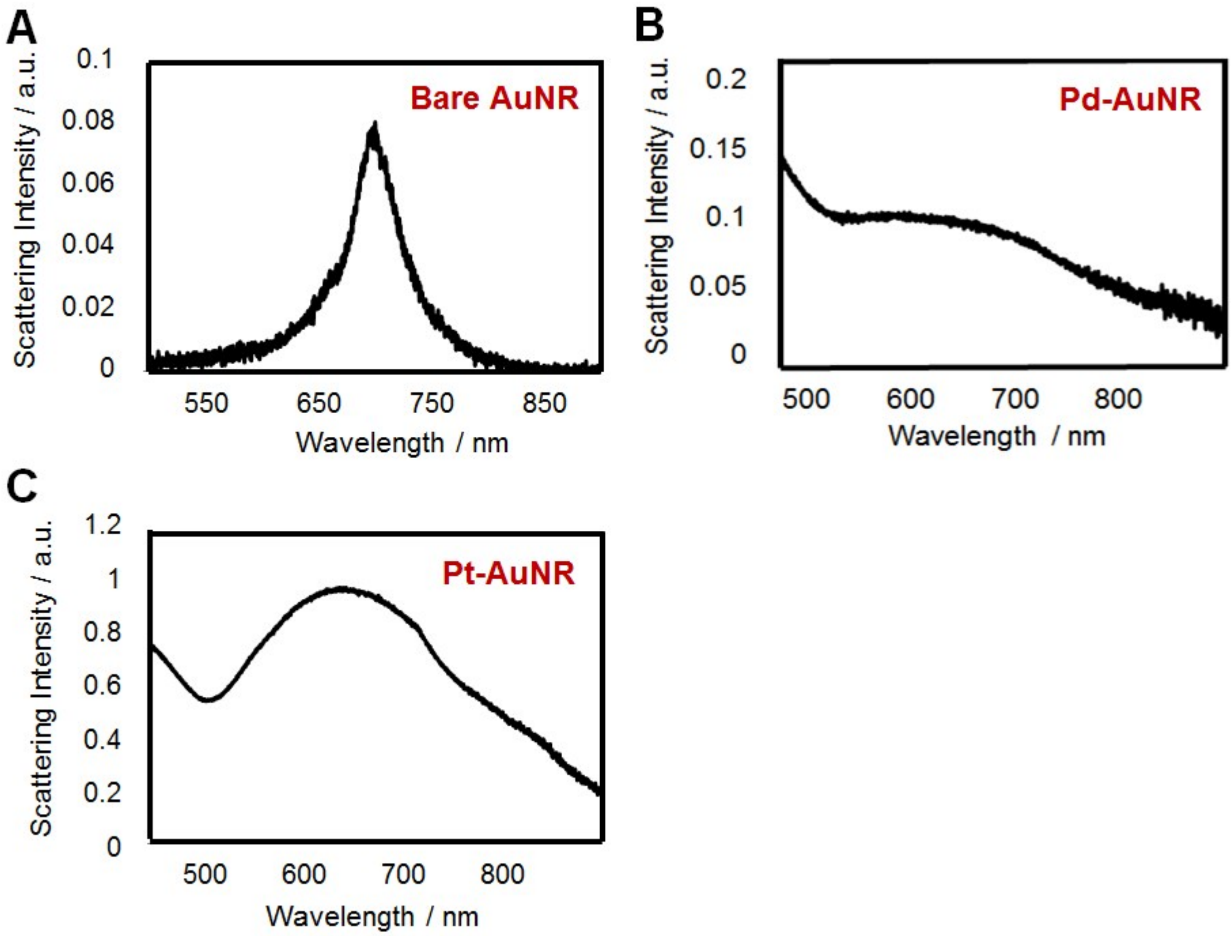

Fig. S4 Single particle scattering spectra of (A) bare AuNR, (B) Pd-AuNR, and (C) Pt-AuNR. The strong plasmon damping is observed for the hybrid bimetallic AuNRs with the much increased LSPR linewidth.

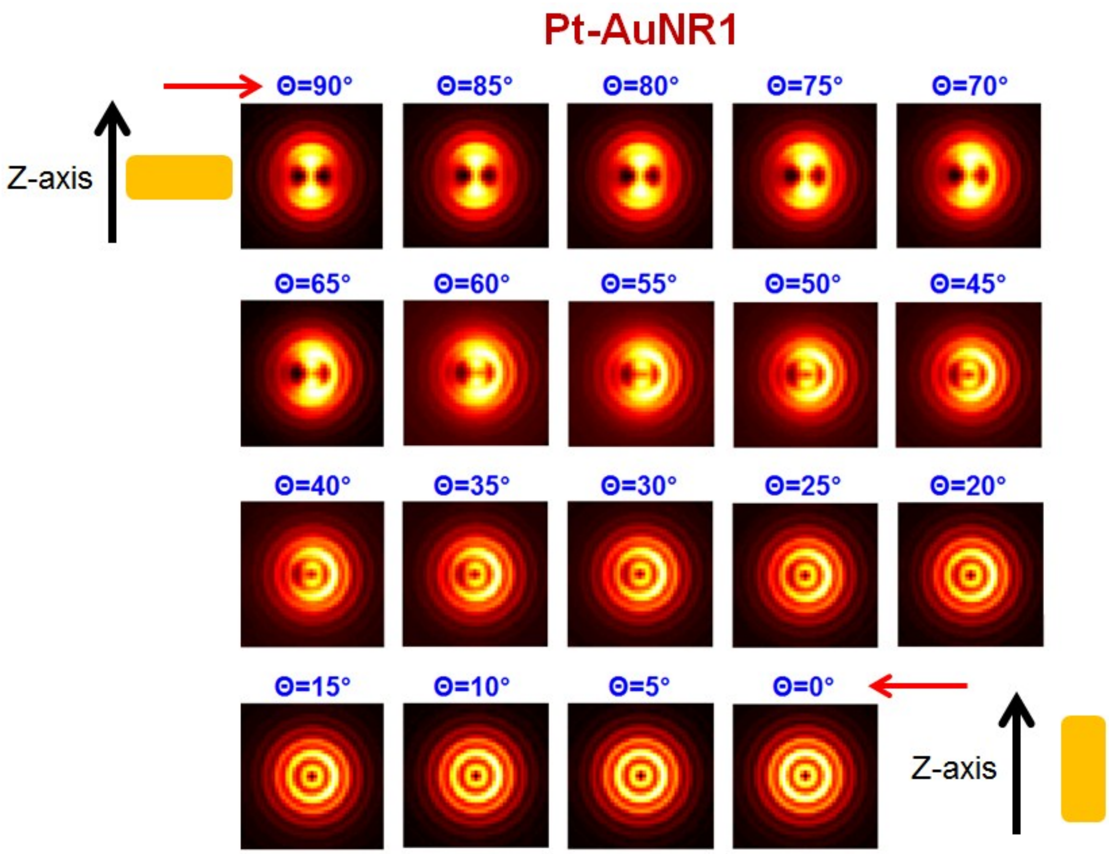

Fig. S5 The simulated characteristic scattering patterns of a Pt-AuNR by varying the polar angle θ from 0° to 90°.

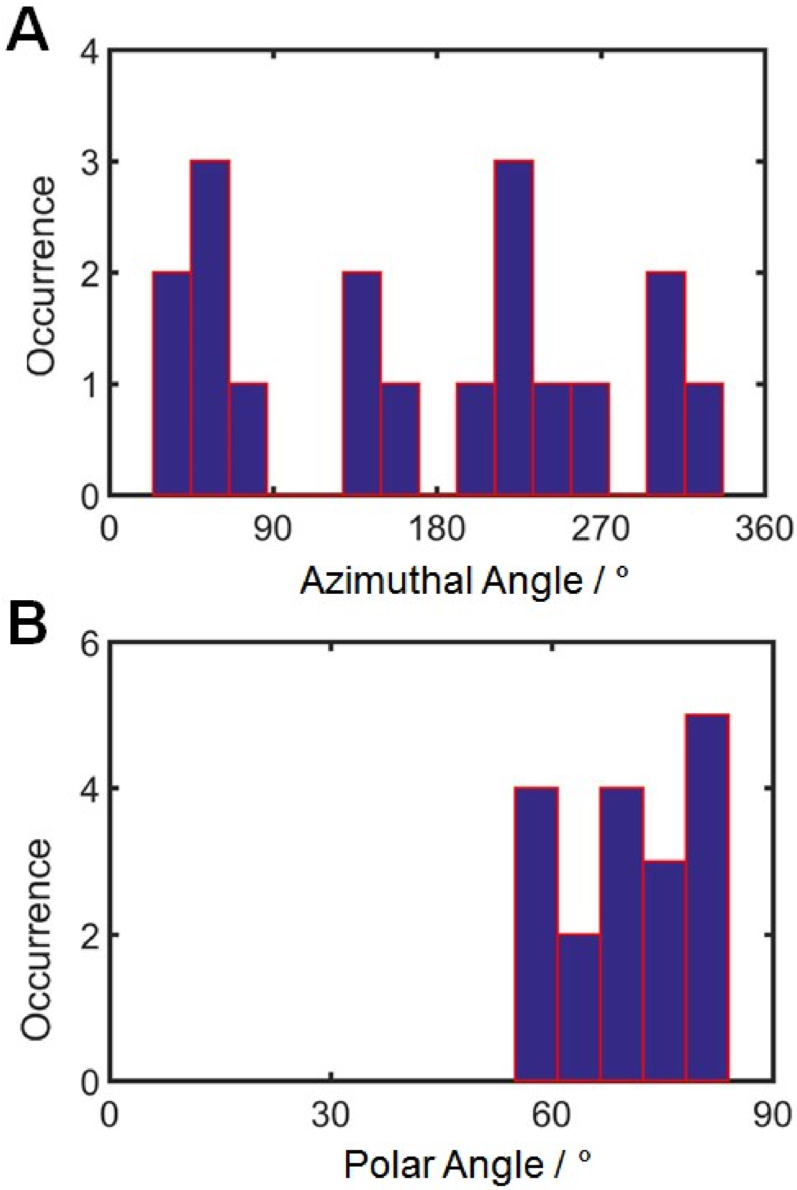

Fig. S6 The histograms of (A) azimuthal and (B) polar angles for 20 Pd-AuNRs measured in this study. The azimuthal angles were randomly distributed between 0° and 360°, while the polar angles were distributed between 60° and 90°.

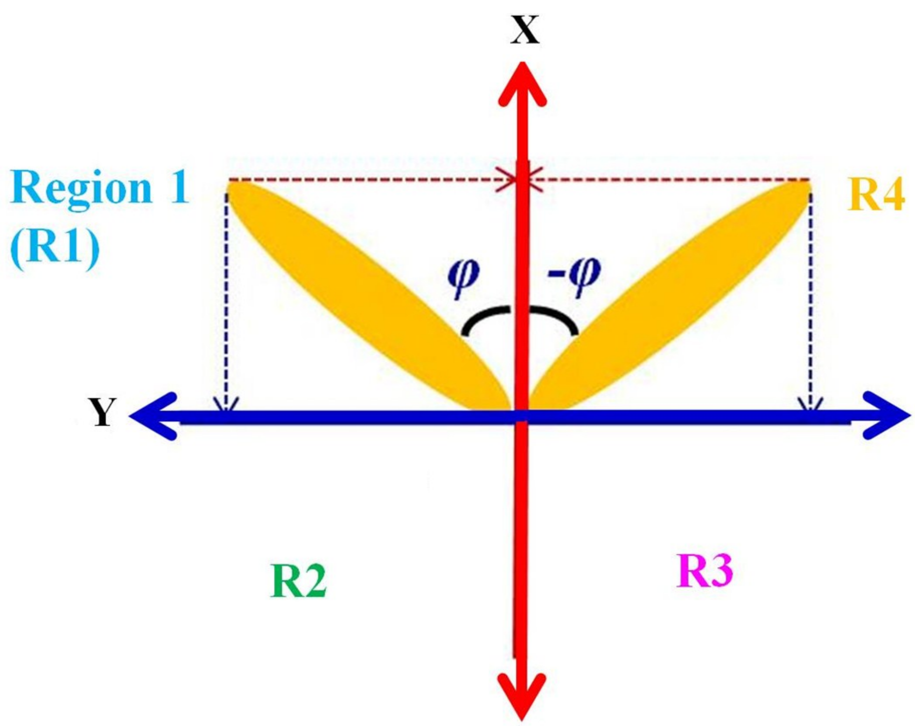

Fig. S7 Schematic diagram to show angular degeneracy generally considered a major limitation of polarization-based techniques in single particle rotational tracking. The angular degeneracy is resulted from the 2-fold optical symmetry of a AuNR relative to the x-axis (red-arrow). We cannot distinguish the orientation angle between φ and -φ with the respect to x- axis.

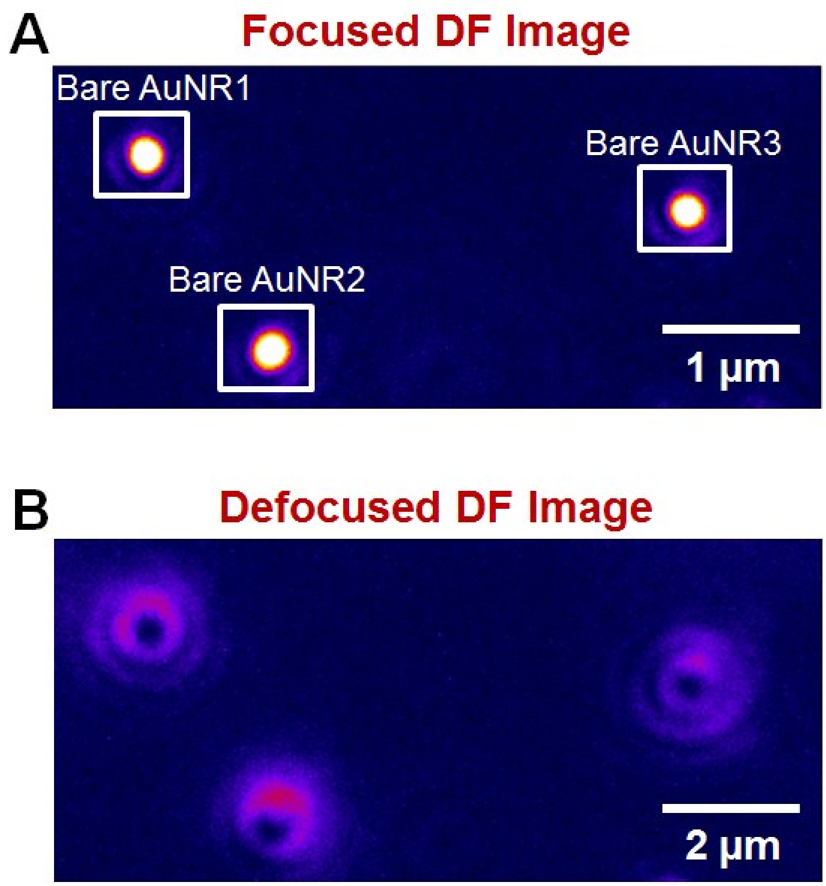

Fig. S8 (A) Focused DF image of bare AuNRs. (B) Defocused DF image for the same AuNRs at the defocusing distance of ~1 µm.

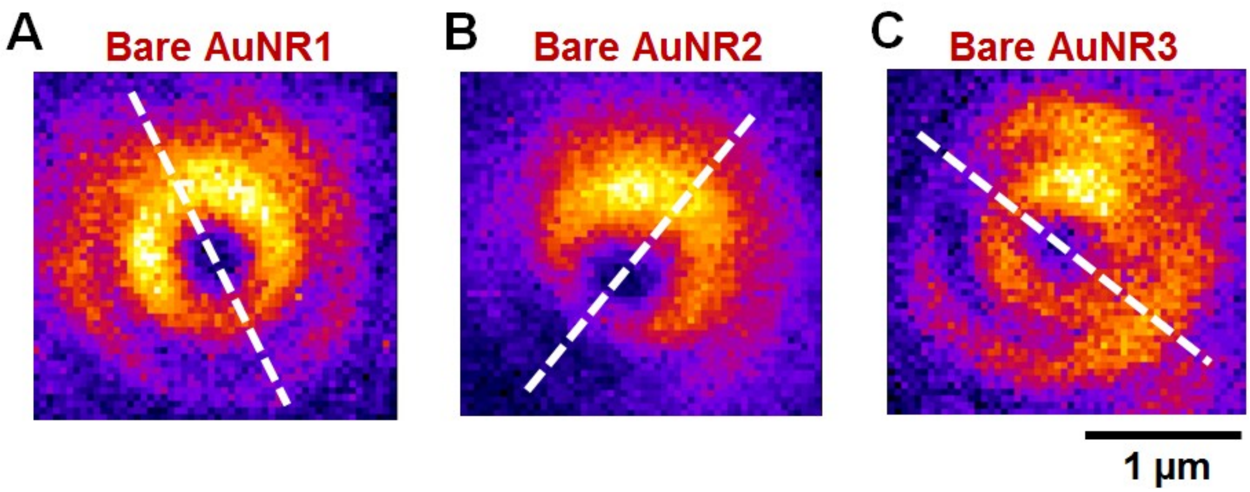

Fig. S9 Enlarged defocused scattering images of three AuNRs highlighted with a white square in Fig. S8.

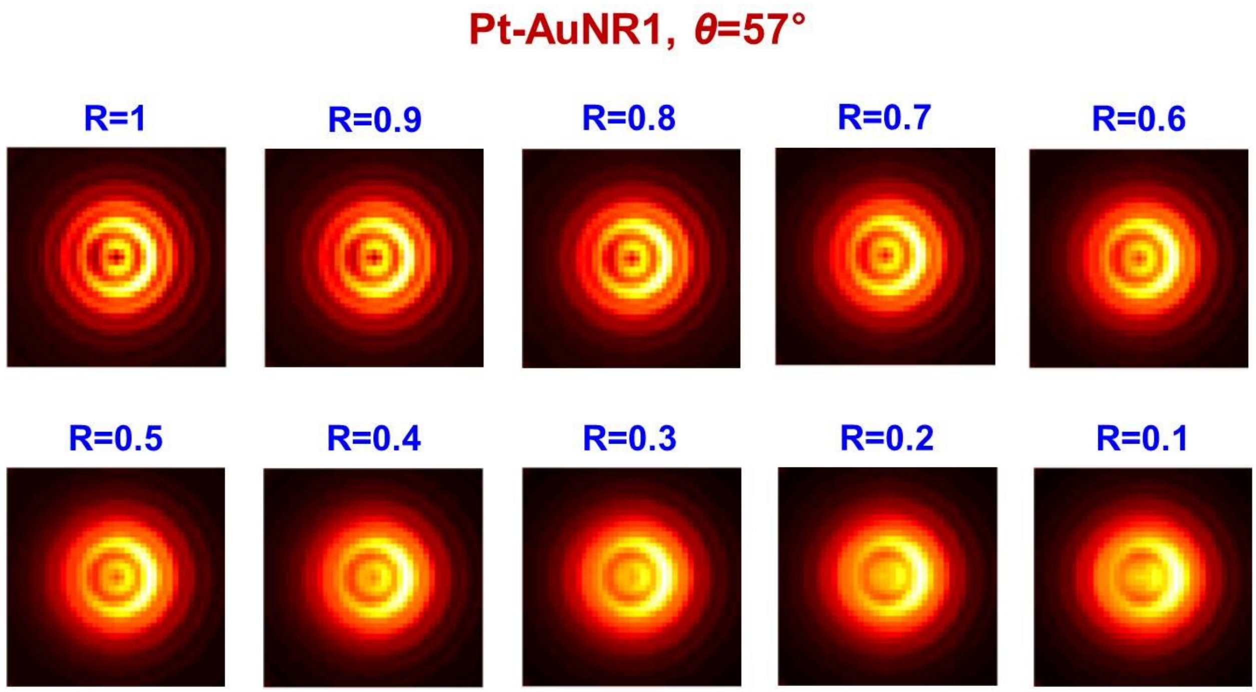

Fig. S10 The simulated defocused scattering patterns of a AuNR by varying the parameter R from 1 to 0.1. In this simulation, the polar angle θ of a Pt-AuNR1 was set to 57°. A solid bright spot at the center of the doughnut-shaped scattering pattern is clearly appeared with decreasing the R value.

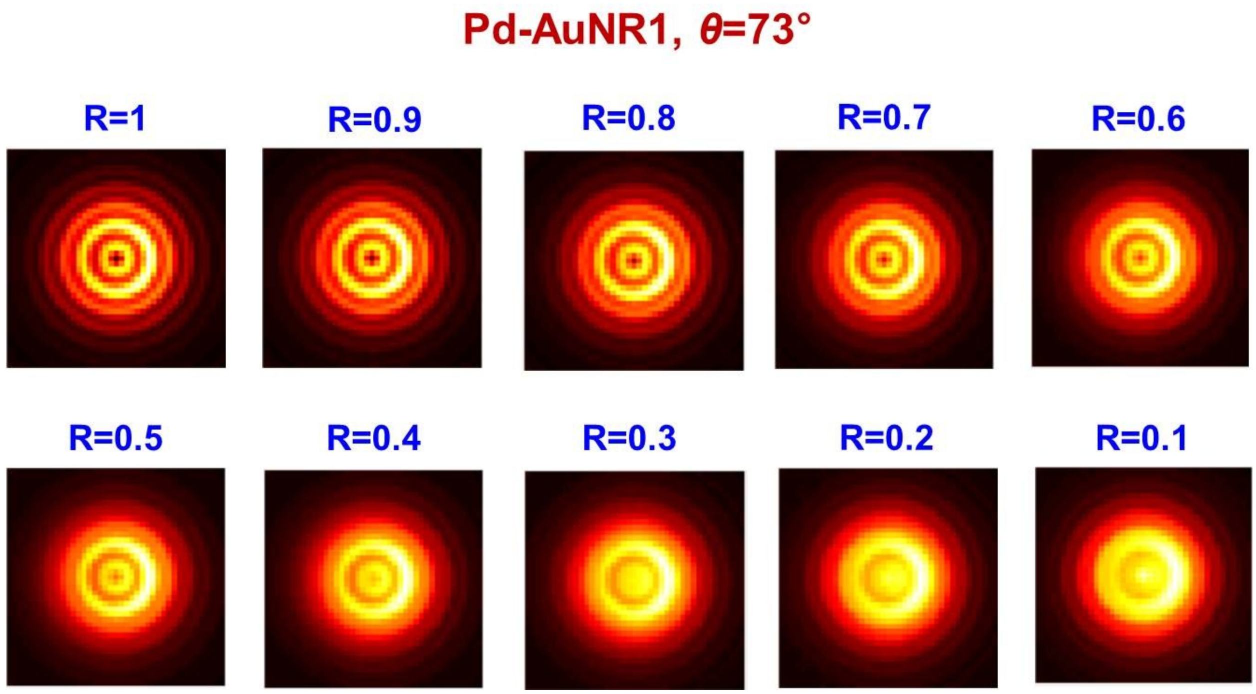

Fig. S11 The simulated defocused scattering patterns of a AuNR by varying the parameter *R* from 1 to 0.1. In this simulation, the polar angle θ of a Pd-AuNR1 was set to 73°. A solid bright spot at the center of the doughnut-shaped scattering pattern is clearly appeared with decreasing the *R* value.