Supplementary Material for PCCP

Electronic Supplementary Information

Tunable depolarized light scattering from gold and gold/silver nanorods

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Experimental section

(a) Reagents

For sample preparation, the following reagents were used: hexadecyltrimethylammonium bromide (CTAB, 96%; Fluka), benzyldimethylhexadecylammonium chloride (BDACH, 99%; Sigma-Aldrich), silver nitrate ($AgNO_3$, Reakhim Co.; Russia), tetrachloroauric acid ($HAuCl_4$, >99%, Sigma-Aldrich), isoascorbic acid (IAA, >99%; Fluka), sodium borohydrate (96%, Sigma-Aldrich), polyvinylpyrrolidone (PVP, 12 PF; BASF), sodium saline of polyacrylic acid (PAA, 35%, Mw = 15,000; Sigma-Aldrich), sodium hydroxide, hydrochloric acid (Reakhim Co., Russia), and glycerol (reagent grade; ECROS, Russia). All chemicals were used as received. Milli-Q grade water was used in all preparations.

(b) Gold rod synthesis

Au NRs with diameters of about 10 to 12 nm were synthesized by a seed-mediated growth method [1], with minor modifications in the concentrations of some reagents and in the reaction protocols. First, gold seed particles are prepared by adding aqueous sodium borohydride (10 mM, 0.1 mL) to a mixed aqueous solution of CTAB (0.1 M, 1 mL) and $HAuCl_4$ (10 mM, 0.025 mL). For preparation of NRs with an aspect ratio of about 4 (PR wavelengths from 800 to 830 nm), 1 mL of 4 mM $AgNO_3$, 2.5 mL of 10 M $HAuCl_4$, 0.5 mL of 80 mM IAA, 0.5 mL of 1M HCl, and 0.5 mL of gold seed solutions are sequentially added to 50 mL of 0.1 M CTAB solution. Nanorods are allowed to grow overnight without stirring at 30 °C.

For preparation of NRs with a higher aspect ratio (about 5.2; PR wavelength of 970 nm), 1 mL of 4 mM $AgNO_3$, 2.5 mL of 10 M $HAuCl_4$, 0.5 mL of 80 mM IAA, 0.5 mL of 1M HCl, and 0.09 mL of gold seed solutions are sequentially added to 50 mL of a mixed surfactant solution

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(0.055 M CTAB and 0.07 M BDAC). Nanorods are allowed to grow overnight without stirring at 30 °C. In what follows, the NR samples are designated NR-800, N830, and NR-970.

(c) Separation of gold NRs

For elimination of by-product particles from as-prepared samples, a separation procedure should be applied [2, 3]. Here, we use the protocol described in Ref. [4]. Briefly, the following solutions are prepared first: n[g] glycerol + m[g] 100 мM CTAB, where n = 1, 2,..5 and m = 9, 8,…5. A 10-mL nanorod solution is centrifuged for 7 min at 13,500 g. Then, 9.6 mL of supernatant liquid is removed, and the sediment is stratified over the stepwise density gradient of glycerol (from 50% to 10%; step, 10%) at 2 mL each step density, in a rotary tube with a total volume of 15 mL. These tubes are centrifuged (30 min, 4,000 g), and the upper part of the first layer is used for further experiments (Fig. 1S). After separation, the selected fraction is centrifuged for 30 min at 12,000 g and then is redispersed in 0.1 M CTAB.

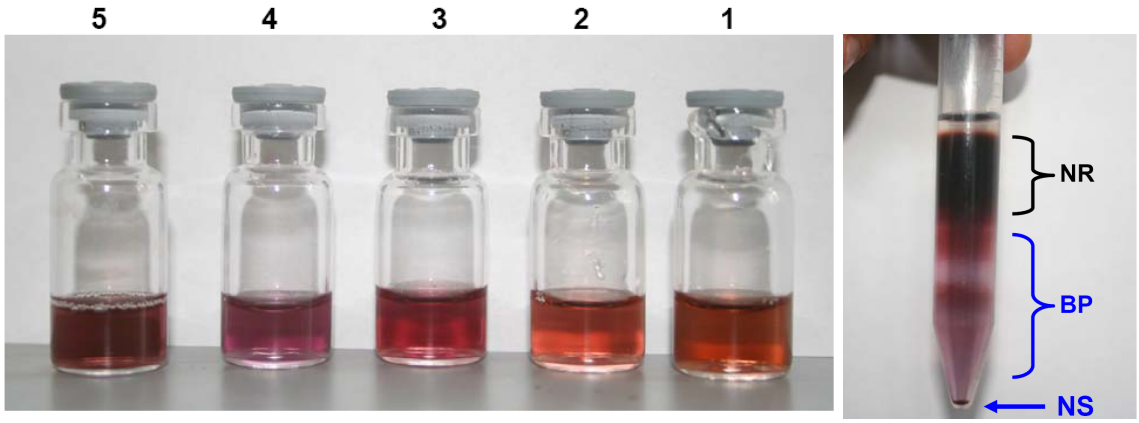

Fig. 1S. (Color online). Separation of the NR-800 sample in a stepwise glycerol gradient. Upper fraction 1 contains mainly NRs; the next color bands (2–5) correspond to byproduct particles (BP). Note that upper fractions 2 and 3 have extinction spectra close to that of major fraction 1 (PR bands near 780 to 800 nm), whereas the spectrum of bottom fraction 5 corresponds to byproducts with a PR band near 540 nm. The arrow points to the dark sediment of colloidal gold particles (nanospheres NS).

(d) Synthesis of Au/Ag core shell NRs

Au/Ag NRs were fabricated with by a two-step method [5], by reducing silver sodium on the Au NR surface with IAA in a PVP water solution under alkalic conditions, as described in detail elsewhere [6]. Briefly, 0.8 mL of separated gold NRs in 0.1 M CTAB is diluted in 4 mL of 1 wt % aqueous PVP. To this mixture, different amounts of 1 mM $AgNO_3$ (0.02 to 0.9 mL), 0.1 M IAA (0.01 to 0.5 mL), and 0.1 M NaOH (0.02 to 1 mL) are added at a constant molar ratio

between $AgNO_3$, IAA, and NaOH. Raising the pH initiates the coating reaction and leads to a color change within a few minutes (Fig. 2S).

Fig. 2S. Changes in colloid colors with an increase in the mass ratio m_{Ag}/m_{Au} from 0 (left) to 1.14 (right). The initial sample is NR-800.

(e) Sample characterization and optical measurements. Transmission electron microscopy **(**TEM) images were obtained with a Libra-120 transmission electron microscope (Carl Zeiss, Germany; Fig. 3S).

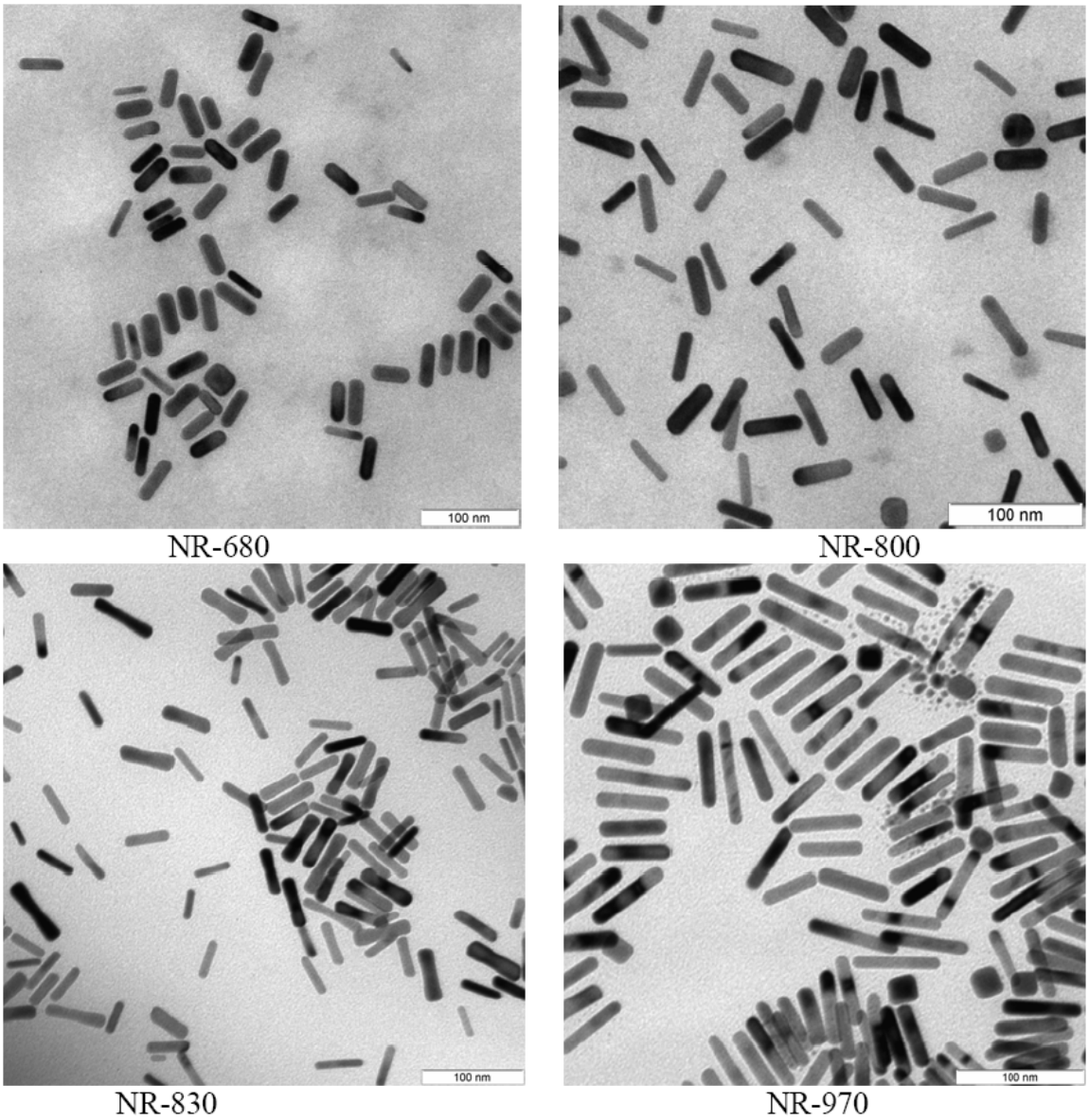

Fig. 3S. TEM images of Au nanorods NR-680, NR-800, NR-830, and NR-970.

Energy dispersive X-ray (EDX) spectra were measured with an attachment to a Tescan MIRA II LMU scanning electron microscope (Czech Republic). With the microscope operating in the reflection scanning or transmission mode, we selected a small (about 200 x 200 nm) area on the TEM grids and recorded EDX spectra from this area (Fig. 4S).

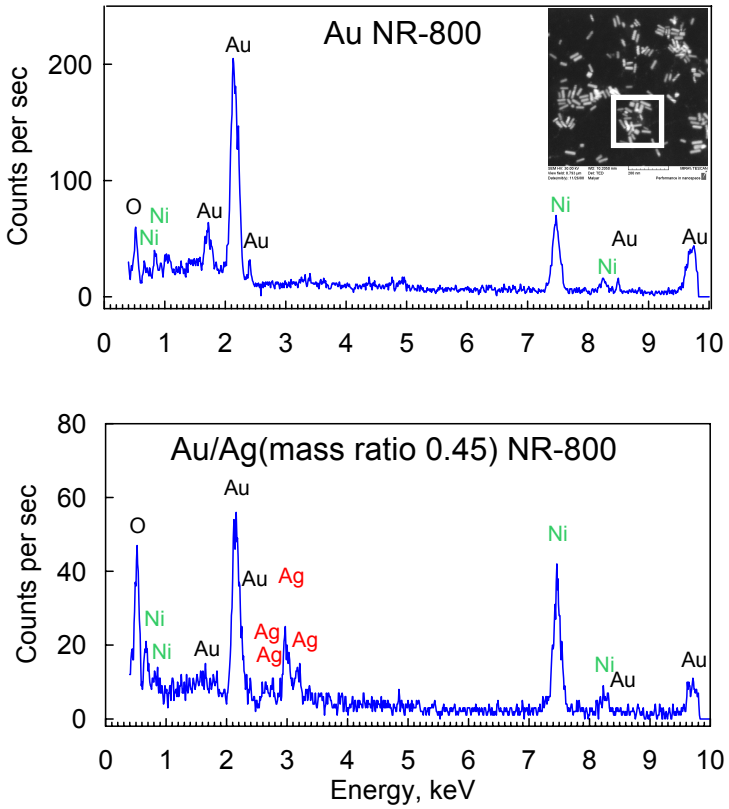

Fig. 4S. EDX spectra of initial Au NR-800 particles and core/shell Au/Ag NRs with the ratio $m_{Ag}/m_{Au} = 0.45$. The inset shows a scanning electron microscopy image and a selected part from which EDX spectra were collected.

Extinction spectra were recorded with a Specord BS-250 UV-vis (Analytik Jena, Germany). Differential light scattering spectra were measured with an attachment to a Specord M-40 spectrophotometer (Carl Zeiss, Germany), as described previously [7]. Depolarized light scattering spectra $\Delta_{vh}(\lambda)$ were measured with a homemade setup (Fig. 5S). Details of the setup, its testing with SiO_2 and gold nanospheres, and an estimation of instrumental and multiple scattering effects, have been described elsewhere [4]. The depolarization ratio is calculated by $\Delta_{vh} = (I_{vh} - I_{vh}^0)/(I_{vv} - I_{vv}^0)$, where the photocurrents I_{vh}^0 and I_{vv}^0 are measured for water. Fig. 6S shows an example of the extinction and depolarization spectra for Au/Ag core shell NRs when the gold NR-825 sample was used as a template.

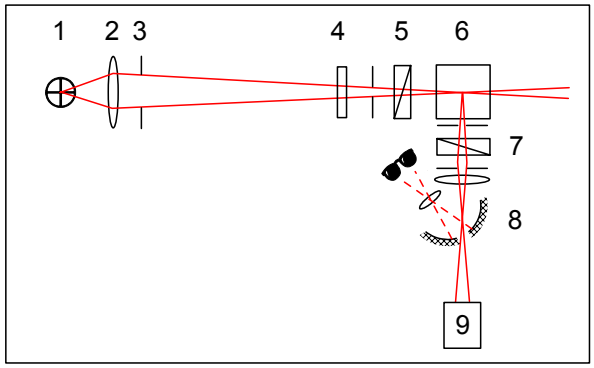

Fig. 5S. The light beam from a halogen lamp (1) travels through an achromatic lens (2), a diaphragm (3), an interference filter (4), and a polarization prism (5), and it focuses near the center of a four-sided quartz cuvette (6). The scattered light is analyzed by using a polarization prism (7) and a detector setup (9) that includes a photomultiplier, a pulse amplifier-discriminator, a pulse counter, and PC software. A spherical mirror with a central pin hole allows for visual control of scattering volume with respect to the pin hole.

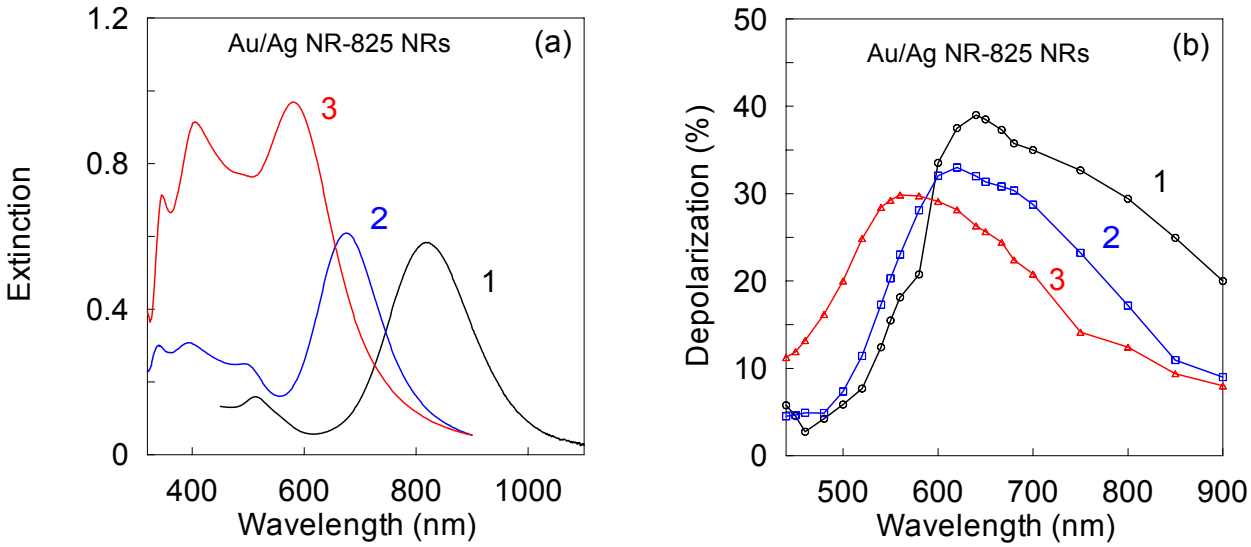

Fig. 6S. Extinction (a) and depolarization (b) spectra of Au/Ag core/shell NRs with the m_{Ag} / m_{Au} ratio = 0 (1, initial gold NR-825 template particles), 0.685 (2), and 1.01 (3).

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