Nanonecklaces assembled from gold rods, spheres, and bipyramids†

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Gold nanorods, nanospheres, and bipyramids have been assembled using glutathione and cysteine into three types of necklace structures, which might be useful for the fabrication of nanoscale photonic, electronic, and optoelectronic devices.

Gold nanoparticles exhibit rich surface plasmon properties. Reproducible chemical methods have been developed to prepare Au nanoparticles of well-controlled sizes and shapes.[1–3] The next major challenge is to assemble these nanoparticles across different length scales into devices of desired functions and properties. For example, it has been demonstrated that electromagnetic energy can be guided along chains of Au nanoparticles through surface plasmon coupling.[4] To date, such sub-wavelength plasmonic waveguides have mainly been fabricated using electron beam lithography, which limits their integration with other optical and/or electronic components.

Gold nanorods possess transverse and longitudinal surface plasmons, with the latter tunable from the visible to infrared spectral regions.[3] It has been shown that Au nanorods can be end-to-end assembled using bio-recognition systems, such as biotin–streptavidin and antigen–antibody.[5] These biomolecules have high binding specificity, but are currently expensive. The end-to-end assembly of Au nanorods has also been demonstrated in acetonitrile–water mixture (4 : 1 v/v) using mercaptocarboxylic acid, cysteine, and glutathione.[6] However, this assembly process must be carried out under extremely strict conditions, as the presence of a large proportion of acetonitrile often induces aggregation of Au nanorods, at least according to our own observations.

Glutathione is the most abundant thiol species in cells, with an intracellular concentration of 1–10 mM and extracellular level of <10 μM.[7] It has gained much attention due to its vital biological functions. It can keep the cysteine thiol group in proteins in the reduced state and protect DNA and RNA from oxidation. It has been suggested that aging is directly correlated with reduced intracellular glutathione concentrations. Previous investigations have found that glutathione can serve as triggers for drug release both *in vitro* and in cell cultures from Au nanoparticle carriers.[8]

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Here we report a feasible approach for the linear assembly of Au nanorods using glutathione and cysteine in aqueous solutions without the addition of organic solvents. Because the coupled longitudinal plasmon between linearly assembled Au nanorods is red-shifted relative to that of isolated ones,[9] the glutathione-induced assembly of Au nanorods might provide an opportunity for simultaneous glutathione-triggered cell imaging and drug release. We have further applied this assembly approach to the creation of necklace structures composed of Au nanorod–nanosphere and bipyramid–nanosphere pairs. The nanorod–nanosphere necklace structures could be used to fabricate single-electron transistors by laying down electrodes on the nanorods,[10] while such devices have typically been made by fortuitously trapping nanoparticles between prefabricated electrode gaps. In addition, because the electric field in the gap between closely spaced nanorods,[9] and especially bipyramids,[11] due to their higher curvature, is largely enhanced at the plasmon wavelength, our necklace structures could be used to amplify a variety of optical signals.

Previously reported procedures of a seed-mediated growth in aqueous cetyltrimethylammonium bromide (CTAB) solutions were used for the preparation of Au nanorods,[12] nanospheres,[13] and bipyramids.[14] For Au nanorod assembly, calculated volumes of 0.01 M glutathione were added into nanorod solutions so that the resulting mixture solutions had the same total volume of 4 mL and contained varying concentrations of glutathione. The mixture solutions were shaken and then kept in an isothermal bath at 45 °C for >5 h. To prepare samples for transmission electron microscopy (TEM) observation, copper grids coated with lacey Formvar and stabilized with carbon were immersed horizontally into the mixture solutions for 1–2 h and then taken out carefully. They were dried in air before TEM observation.

Fig. 1a shows the extinction spectral change (Hitachi U-3501 UV-Visible/NIR spectrophotometer) of Au nanorods after the addition of varying amounts of glutathione. The longitudinal plasmon wavelength of the nanorods is centered at 778 nm. After the addition of glutathione, the intensity of the longitudinal plasmon peak is significantly reduced, and concomitantly a new peak at 948 nm is formed, which becomes stronger and stronger (Fig. 1b). A clear isosbestic point is observed at 850 nm, suggesting the presence of two types of Au nanorods in the solutions. One is isolated nanorods and the other is assembled ones. In addition, the transverse plasmon peak centered at 520 nm remains approximately unaffected during the spectral change. These observations indicate that Au nanorods are end-to-end assembled through glutathione. The new plasmon peak in the extinction spectra results from the longitudinal plasmon coupling.[9] The assembly of Au nanorods is unambiguously confirmed by TEM imaging (FEI CM120). Before the addition of glutathione, Au nanorods are

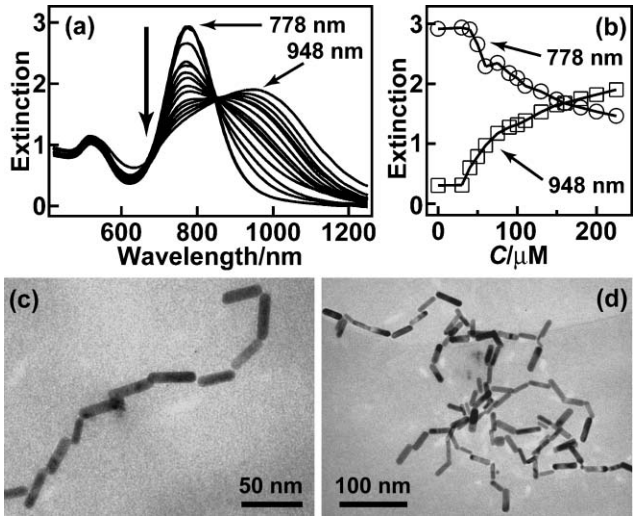

Fig. 1 (a) Extinction spectra of Au nanorod solutions upon the addition of glutathione at 0, 30, 40, 50, 60, 75, 90, 100, 110, 130, 150, 160, 180, 200, and 225 μM, respectively. (b) Extinction changes at wavelengths of 778 and 948 nm. (c) TEM image of Au nanorods assembled into a chain. (d) TEM image of Au nanorods end-to-end assembled into branched chains. The sample for TEM observation was prepared with glutathione concentration at 150 μM. The concentration of Au nanorods in the solutions is estimated to be 0.6 nM.[15]

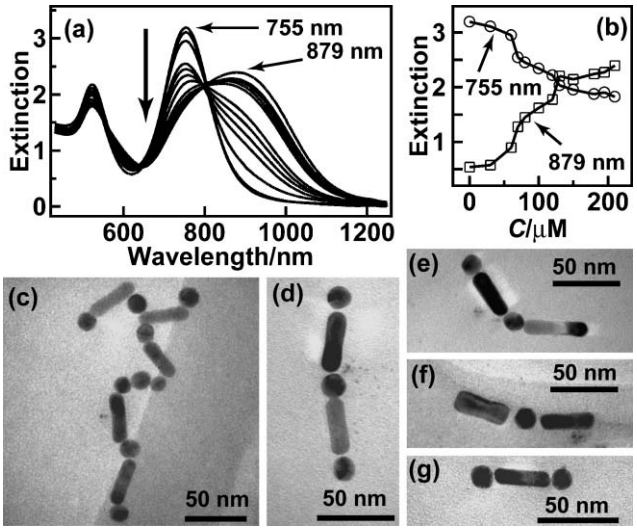

Fig. 2 (a) Extinction spectra of Au nanorod–nanosphere mixture solutions upon the addition of glutathione at 0, 30, 60, 70, 80, 100, 120, 130, 150, 180, 195, and 210 μM, respectively. (b) Extinction changes at the wavelengths of 755 and 879 nm. (c)–(g) TEM images of Au nanorods and nanospheres assembled into chain structures. The sample for TEM observation was prepared with glutathione concentration at 150 μM. The concentrations of Au nanorods and nanospheres are estimated to be 0.8 and 1.0 nM, respectively.[15]

randomly distributed (ESI†, Fig. S1). In the presence of glutathione, they are preferentially assembled in an end-to-end fashion to form linear and branched chains (Fig. 1c, 1d, and ESI†, Fig. S2). An average of multiple TEM images indicates that 98% of Au nanorods are end-to-end linked with other nanorods (ESI†, Table S1).

The end-to-end assembly of Au nanorods using glutathione produces nanorod chains. This assembly approach was also used to create necklace structures composed of alternate Au nanorods and nanospheres. CTAB-capped Au nanospheres with an average diameter of 14 nm were used.[13] Estimated amounts of Au nanorods precipitated by centrifugation were dispersed into the nanosphere solutions so that the particle concentrations of Au nanorods and nanospheres are approximately equal. Because the plasmon peak of the Au nanospheres overlaps with the transverse plasmon peak of the Au nanorods, the plasmon peak of the nanorod–nanosphere mixture solutions at 520 nm is stronger than that of pure nanorod solutions (Fig. 2a). Upon the addition of glutathione at varying concentrations, the longitudinal plasmon peak at 755 nm decreases in intensity and a new plasmon peak appears at 879 nm and becomes increasingly stronger (Fig. 2a and 2b). A clear isosbestic point is present at 800 nm. TEM imaging shows that the presence of glutathione induces the assembly of the Au nanorods and nanospheres (Fig. 2c–2g, and ESI†, Fig. S3, S4). The nanorods are preferentially assembled alternately with the nanospheres instead of among themselves and the assembly occurs preferentially through the ends of the nanorods. On average, 75% of Au nanorods are linked with nanospheres at one or both of their ends and 73% of nanospheres are linked with nanorods (ESI†, Table S1). The new plasmon peak therefore results from the coupling between the longitudinal plasmon of the nanorods and the plasmon of the nanospheres.

The end-to-end assembly approach was further used to create necklace structures composed of alternate Au bipyramids and nanospheres, because bipyramids exhibit larger local electric field enhancement at the ends owing to the sharper curvature.[11] As-prepared bipyramid solutions contain approximately equal concentrations of bipyramids and faceted nanospheres with an average diameter of 45 nm.[14] They were used without the addition of extra Au nanospheres. The extinction spectra show that as the concentration of glutathione in the bipyramid–nanosphere mixture solutions is increased, the longitudinal plasmon peak centered at 782 nm is decreased in intensity and a new peak appears around 902 nm (Fig. 3a and 3b). A clear isosbestic point is present around 825 nm. TEM imaging reveals that the Au bipyramids are preferentially assembled alternately with the nanospheres and that the glutathione-induced assembly occurs preferentially through the ends of the bipyramids (Fig. 3c–3g, and ESI†, Fig. S5, S6). On average, 95% of Au bipyramids are linked with nanospheres at one or both of their ends, and 90% of nanospheres are linked with bipyramids (ESI†, Table S1). The new plasmon peak therefore results from the coupling between the longitudinal plasmon of the bipyramids and the plasmon of the nanospheres. Two shoulder peaks around 690 and 960 nm are also observed at high concentrations of glutathione. These two peaks are probably due to the plasmon coupling between the faceted nanospheres and between the bipyramids, respectively.

We further investigated the effect of the addition of cysteine, glycine, and 3-mercaptopropionic acid on the assembly of Au nanorods, nanospheres, and bipyramids. The extinction spectra taken as a function of the concentration of cysteine (ESI†, Fig. S7) reveal that cysteine can also induce the linear assembly of Au nanorods and bipyramids. On the other hand, the extinction spectra of Au nanorod and bipyramid solutions remain essentially unchanged even if the concentrations of glycine and mercaptopropionic acid are up to 3 mM (ESI†, Fig. S8 and S9).

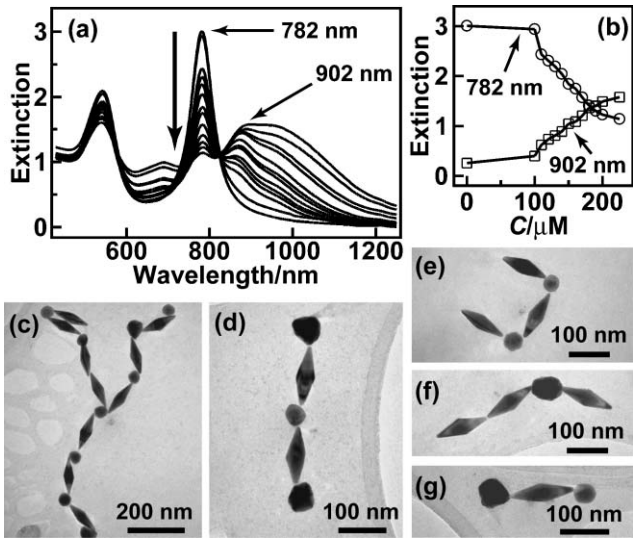

Fig. 3 (a) Extinction spectra of Au bipyramid–nanosphere mixture solutions upon the addition of glutathione at 0, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, and 225 μM, respectively. (b) Extinction changes at the wavelengths of 782 and 902 nm. (c)–(g) TEM images of Au bipyramids and nanospheres assembled into chain structures. The sample for TEM observation was prepared with glutathione concentration at 180 μM. The concentrations of Au bipyramids and nanospheres are estimated to be 0.7 and 0.5 nM, respectively.[15]

Glutathione and cysteine are thiol species containing both carboxyl and amino groups. They are present in the zwitterionic form in the Au nanoparticle solutions with a pH of ~4 (Fig. 4a). We believe that both the thiol group and the zwitterionic form are essential for the linear assembly of the Au nanoparticles. Glycine lacks the thiol group. Mercaptopropionic acid has the thiol group, but lacks the zwitterionic group. Therefore they are not able to induce the linear assembly. In aqueous solutions, Au nanorods and bipyramids are encapsulated in a bilayer of CTAB.[16] Glutathione and cysteine are preferentially bound to the ends of Au nanorods and bipyramids through the thiol group, probably because the CTAB bilayer is less ordered at the highly curved ends than on the smooth sided surfaces. The assembly of Au nanorods and bipyramids at the ends is assisted by the zwitterionic groups through a cooperative two-point electrostatic interaction (Fig. 4b), as also suggested previously by others.[6] In the case of the nanoparticle mixtures, the preferential nanorod–nanosphere and bipyramid–nanosphere assembly instead of nanorod–nanorod, bipyramid–bipyramid, and nanosphere–nanosphere assembly is probably determined jointly by the probability of particle collision and that of being bound together electrostatically per collision.

The work presented herein illustrates a feasible approach for the assembly of nanonecklace structures using glutathione and cysteine. Three types of necklace structures, composed of Au nanorods, nanorod–nanosphere pairs, and bipyramid–nanosphere pairs, have been demonstrated. These linear structures are potentially useful for surface plasmon-based biosensing,[6] electric field-enhanced spectroscopy,[9] and for the fabrication of plasmonic waveguides,[4] photoresponsive switches,[17] and single-electron transistors.[10]

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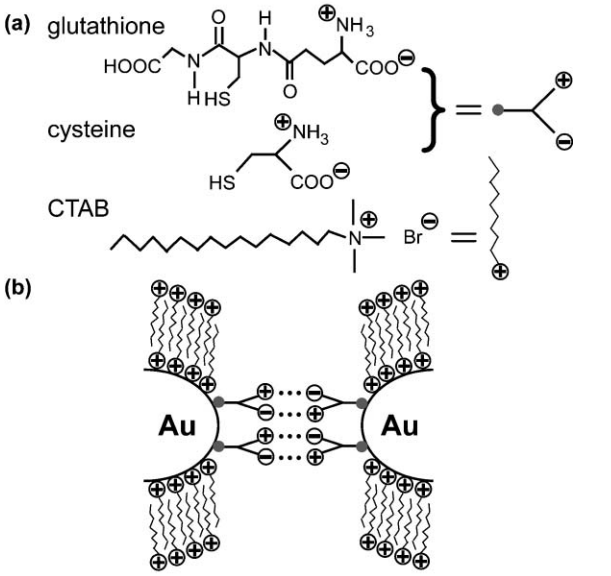

Fig. 4 (a) Molecular structures of glutathione, cysteine, and CTAB. (b) Schematic assembly mechanism.

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