Selective Functionalization and Spectral Identification of Gold Nanopyramids

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This paper reports the selective functionalization of gold nanopyramids and spectral identification of their orientation on a surface. Facile asymmetric functionalization of the nanopyramids with different thiol-terminated ligands was achieved by controlling the etching conditions of the nanopyramidal template. We confirmed this differential modification by attaching gold colloids to either the inner or outer surfaces of the Au nanopyramids using hybridized DNA. Significantly, we have also demonstrated that the relative orientation of the nanopyramids can be identified by measuring their scattering spectra only. This unique capability of these three-dimensional, asymmetric particles enables their orientation to be determined in condensed media without the need for direct and destructive imaging tools.

Designing nanoparticles with multiple functionalities is an important problem requiring simultaneous control over composition, size, shape, and surface chemistry at the molecular level. The latter is especially important for assembling particles into hierarchical structures that exhibit new properties.[1,2] In this regard, gold nanoparticles are ideal building blocks for constructing multifunctional systems because (1) their surfaces can be easily modified with thiolated and carbodithioate ligands,[3,4] (2) they can be prepared in a wide range of sizes and shapes,[5] (3) their shape controls their optical properties,[6] and (4) wavelengths in the visible and near-infrared (NIR) regions incident on these particles can be converted to heat.[7] Based on these properties, gold particles have shown promise in biomedical applications[8] such as optical imaging probes and phototherapeutic agents.[9] One overarching challenge in functionalizing nanoparticle surfaces, however, is the placement of different molecules at specific locations on a single nanoparticle. Spherical gold colloids have been asymmetrically functionalized with different thiolated molecules to direct the organization of particles into assembled structures,[2,10,11] as well as preferential functionalization of the ends of gold nanorods based on electrostatic attractive interactions.[12] Here we demonstrate an approach to create single material nanoparticles with multiple surface functionalities. Gold nanopyramids were selectively functionalized with chemical and biological molecules to create particles with distinct regions of hydrophobicity and hydrophilicity. These anisotropic nanoparticles scattered visible and NIR light with distinct spectral characteristics, which was then used to determine the relative orientation of the pyramids on a surface.

Gold nanoparticles are typically prepared either by chemical approaches or nanofabrication techniques. Synthetic methods enable the growth of a wide variety of metal nanoparticle shapes, including prisms,[13] stars,[14] rods,[15] and cages,[16] because reaction conditions such as temperature, surfactants, and precursors can be independently controlled.[5] Although solution-based methods are easily scalable, large distributions in particle shape and size and difficulty in selectively functionalizing specific locations of particles are clear disadvantages. Fabrication approaches can overcome these limitations because precisely defined lithographic templates can be used to determine nanoparticle size, shape, and orientation on a surface.[17,18] In addition, top-down approaches can readily produce nanoparticles with complex, three-dimensional shapes. Moreover, the surfaces of fabricated structures are surfactant-free and can be easily modified with specific functionality.

Using templates of arrays of etched pits in single crystalline silicon (100), we previously reported a procedure to generate pyramidal shells with base diameters ranging from 80 to 300 nm and with tips as small as 2 nm.[18] These particles are relatively monodisperse, can be composed of multiple different materials, and have flat outer surfaces because the e-beam deposited material molds directly against atomically smooth silicon (111) faces. This template-based nanofabrication method can readily be combined with self-assembling molecules to create multi-functional nanoparticles with either nonselective or selective chemical and/or biological functionality (Scheme 1).

To bind molecules uniformly to the surfaces of the gold pyramids, we released the pyramids from their silicon templates by sonication and etching and dispersed them into aqueous solutions. Pyramids were made hydrophobic by functionalization with alkanethiols (such as 1-octadecanethiol (ODT)) and hydrophilic by modification with thiolated single stranded (ss) DNA (A = 5′ HS-$(CH_2)_6$-$(A)_{10}$ ATC CTT TAC AAT ATT - 3′). Not surprisingly, scanning electron microscopy (SEM) images could not distinguish between bare gold pyramids and functionalized ones (Figure 1a−c). To verify the monolayer assembly of **A** on the surfaces of the gold pyramids, we exploited the molecular recognition inherent to DNA. 13-nm gold colloids surrounded by complementary DNA (A' = 5′ HS-

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SCHEME 1 : Nonselective and Selective Functionalization of Gold Pyramidal Shells[a]
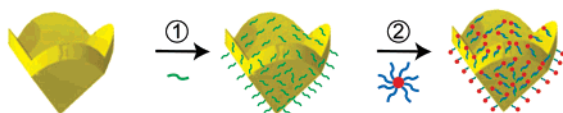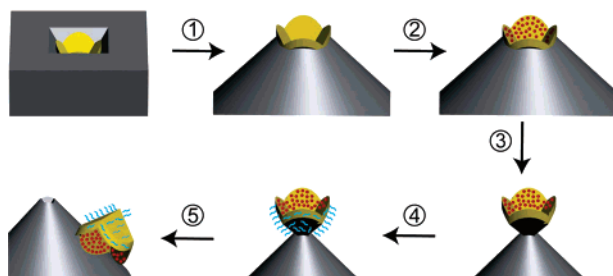
a Free-standing gold nanopyramids can be decorated uniformly by (1) assembling thiolated single-stranded DNA to their surfaces and (2) hybridizing to its complement attached to gold colloids. Template-bound pyramids can be differentially modified by (1) etching the silicon template; (2) functionalizing the inner surfaces with one molecule; (3) exposing the outer faces by etching the template; (4) functionalizing with a different molecule; and (5) releasing the pyramids.
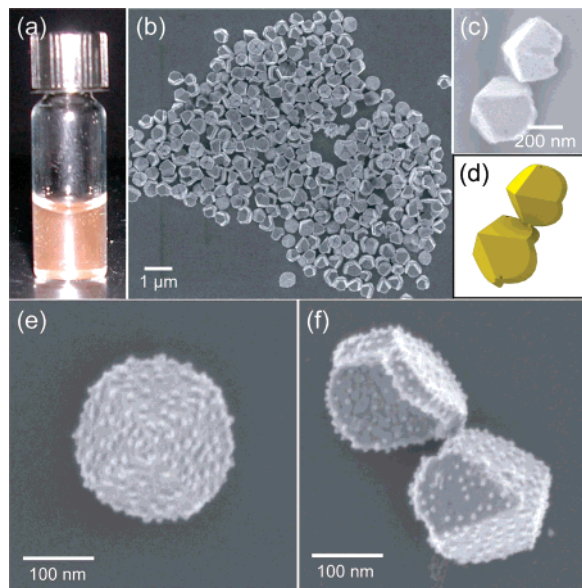

Figure 1. (a) Suspensions of gold pyramids functionalized with ODT. (b) SEM image of pyramids in (a). (c,d) SEM image and graphical image of pyramids with different orientations. (e,f) Pyramids functionalized with gold colloids via DNA linkages.

(CH$_2$)$_6$- (A)$_{10}$ AAT ATT GTA AAG GAT - 3′) were prepared by following well-established procedures[19] and then attached to the surfaces of the pyramids by hybridizing **A** to **A**′. In this way, we could test the viability of the DNA attached to the pyramids (**A**) as well as use the gold colloids as visualization markers. SEM images revealed that the colloids were uniformly assembled on the inner and outer surfaces of gold pyramids (Figure 1e,f). Heating suspensions of pyramids decorated with colloids above the melting temperature ($T_m = 59$ °C) of the DNA duplex resulted in gold pyramids functionalized only with **A**. The gold colloids could be reassembled on the pyramids by decreasing the temperature below T_m to rehybridize **A**′ with **A**.
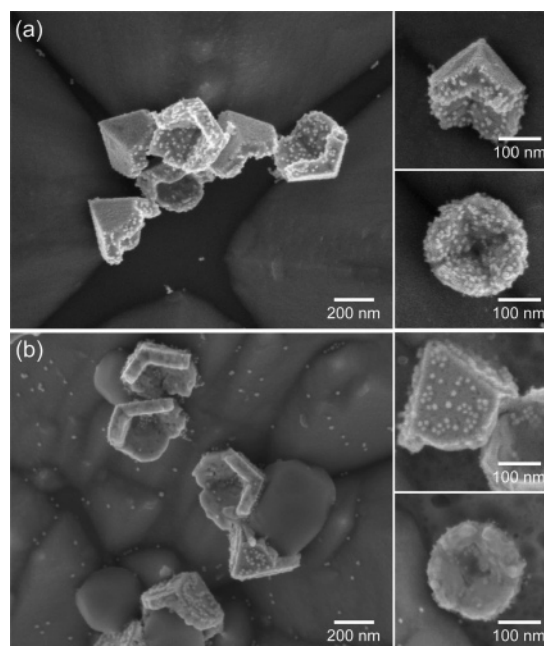

Figure 2. Gold pyramids with amphiphilic character. (a) SEM images of gold pyramids selectively functionalized with DNA on the inner surfaces (visualized by colloids) and ODT on the outer ones. (b) SEM images of pyramids with ODT on the inside and DNA on the outside.

Prior to their release in solution, pyramids fabricated within templates had inner surfaces exposed and outer surfaces embedded in silicon. We have taken advantage of this step in the fabrication procedure to achieve differential modification of the inner and outer surfaces of the pyramid as well as to create asymmetrically functionalized particles with amphiphilic character (Scheme 1). To generate hydrophilic inner surfaces, gold pyramids embedded within templates were first functionalized with **A** (and then again with **A**′-colloids). To form hydrophobic outer surfaces, the silicon substrate was partially etched using an anisotropic wet etch[18] to expose the outer surfaces of the pyramids, which was subsequently immersed in a 10 mM solution of ODT for 12 h to achieve monolayer coverage (Figure 2a). Importantly, the DNA was still viable after etching the silicon template because the density of gold colloids on the inner surfaces remained similar before and after etching. We also created pyramids with hydrophobic interiors and hydrophilic exteriors by functionalizing the inside with ODT and the outside with **A** (Figure 2b). The presence of a few colloids on the ODT functionalized surface can be attributed to nonspecific adsorption. Hence, pyramids with different amphiphilicity can be designed simply using a template-based fabrication method.

Correlating the orientation and spectral characteristics of single nanopyramids is not only important for understanding how anisotropic particles interact with light but is also critical for their prospects in applications using differentially modified pyramids. Noticeably, when dispersed on a surface, the pyramids exhibited two different orientations: (1) tip pointing up (and away from the surface) or (2) tip pointing down (and touching the surface). Because arrays of aligned gold pyramids embedded in PDMS films exhibit orientation-dependent optical properties at visible and near-infrared (NIR) wavelengths,[20] we anticipated that the properties of individual pyramids might behave similarly. Dark field spectroscopy was performed on isolated pyramids dispersed onto transparent substrates (indium tin oxide on glass) patterned with markers so that the scattering spectra
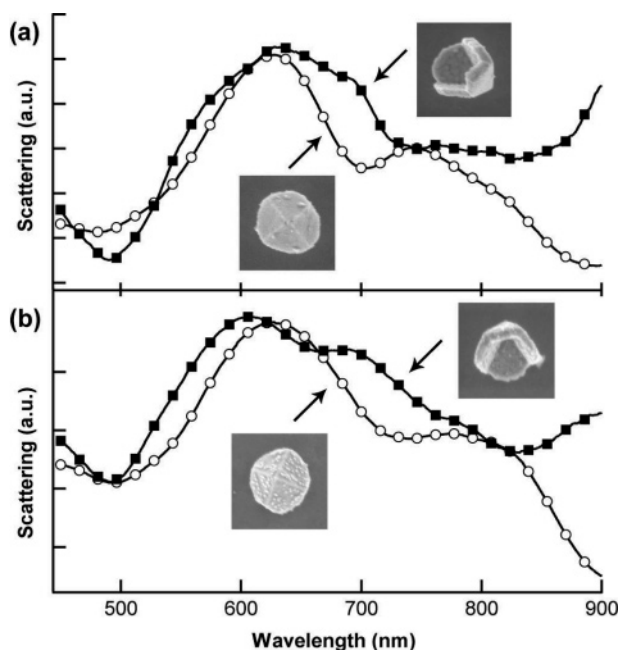
Figure 3. Orientation-dependent optical properties of gold pyramids. Scattering spectra of (a) individual pyramids with two different orientations and (b) pyramids functionalized with gold colloids. The sizes of the SEM images are 600 nm × 600 nm.

could be matched to specific particles whose orientations were determined by SEM.[21]

Figure 3a reveals that gold pyramids with tips pointing up supported a surface plasmon resonance at 610 nm and a secondary peak around 750−800 nm. Pyramids with tips pointing down exhibited a broad peak at 630 nm and stronger scattering at longer wavelengths in the NIR. Gold pyramids decorated with colloids exhibited similar properties to those of bare pyramids (Figure 3b), which indicates that the larger scattering cross-section of the pyramids dominates the optical response for this assembled system.

Noticeably, the spectral properties of the gold pyramids with different orientations were quite different in intensity at longer wavelengths (around 800−850 nm). To test whether such spectral differences could be exploited to identify the relative orientation of pyramids on a substrate, which would be unique to this nanoparticle system, we carried out single particle spectroscopy on isolated pyramids dispersed on a substrate. Figure 4a is a dark field (DF) optical image of individual gold pyramids that appeared to scatter light with a uniform, yellowish-orange color. We selected, at random, six of these spots and measured their scattering spectra (Figure 4b), which were then separated into two categories: (1) those whose 600-nm resonance peak dominated and (2) those whose 850-nm features were comparable in intensity to their 600-nm ones. We calculated the ratio of the scattering intensity at 600 and 850 nm and found that they segregated into two sets of bands, which could be used to predict the relative orientation of the pyramids based on the orientation-dependent scattering results in Figure 3. As expected, when we imaged the pyramids with SEM, the correlation between the orientation and signature features in their spectra matched perfectly (Figure 4c,d). Such spectral identification of orientation, without the need for polarized light, has positive implications for identifying how gold pyramids can orient themselves in condensed media without the need for destructive imaging techniques such as electron microscopy.

In summary, we have developed a versatile and flexible method for designing differentially modified gold nanoparticles and demonstrated how their spectra can be used as signatures for identifying their orientation on a surface. Because the surfaces of the pyramids can be tailored and cleaned up within a template, multi-functional particles can now be dispersed into solution without excess ligands (such as unbound DNA). Furthermore, under unpolarized light, the optical properties of individual pyramids can be used to determine their relative orientation. For example, spectral features could be used to indicate the orientation of asymmetrically functionalized pyramids assembled in complex environments such as the surface or within the interior of cells. Differentially modified gold pyramids that absorb and scatter light in the NIR should thus offer intriguing prospects in imaging, targeted delivery, and localized therapeutics.
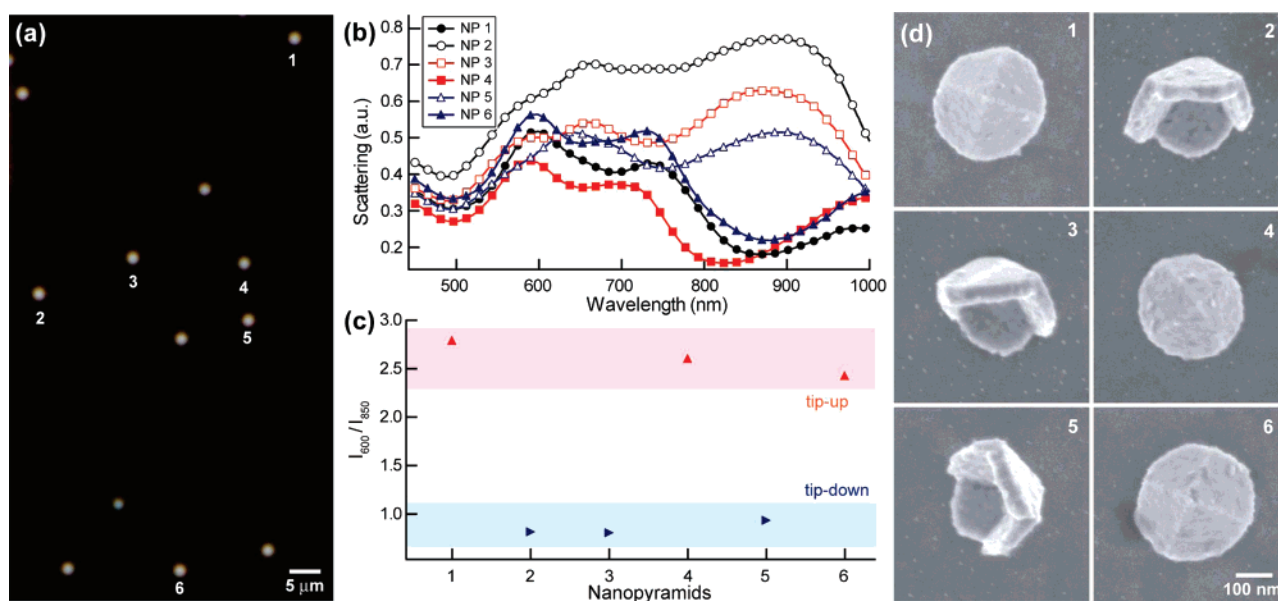

Figure 4. Spectral identification of gold pyramids. (a) DF micrograph of isolated gold pyramids deposited on ITO-coated glass substrates. (b) Scattering spectra of six individual gold pyramids. (c) Ratio of normalized scattering intensity at 600 and 850 nm for each pyramid. The numbering corresponds to those indicated in (a). (d) SEM images of the six pyramids confirming that their relative orientation can be determined only by their optical properties.

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