Highly tapered pentagonal bipyramidal Au microcrystals with high index faceted corrugation: Synthesis and optical properties

Gangaiah Mettela¹, Radha Boya¹, Danveer Singh², G. V. Pavan Kumar² & G. U. Kulkarni¹

¹Chemistry and Physics of Materials Unit and DST Unit on Nanoscience, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P. O., Bangalore 560 064, India, ²Photons and Optical Nanoscopy Laboratory, Department of Physics and Chemistry, Indian Institute of Science Education and Research (IISER), Pune – 411008, India.

Focusing light at sub-wavelength region opens up interesting applications in optical sensing and imaging beyond the diffraction limit. In the past, tapered Au wires with carved gratings have been employed to achieve nanofocusing. The fabrication process however, is expensive and the obtained wires are polycrystalline with high surface roughness. A chemical synthetic method overcoming these hurdles should be an attractive alternative. Here, we report a method to chemically synthesize Au microcrystals (~10 µm) bearing pentagonal bipyramidal morphology with surface corrugations assignable to high index planes. The method is a single step solid state synthesis at a temperature amenable to common substrates. The microcrystals are tapered at both ends forming sharp tips (~55 nm). Individual microcrystals have been used as pick and probe SERS substrates for a dye embedded in a polymer matrix. The unique geometry of the microcrystal also enables light propagation across its length.

One-dimensional (1D) metal nanostructures have gained importance over the last decade due to their interesting optical properties such as tunable absorption from visible to near infrared region¹ and Raman scattering³. They exhibit distinct surface plasmon features, transverse and longitudinal, associated with their dimensionality⁴ which is routinely observed with Ag and Au nanowires⁵. Apart from nanowires, there are other quasi 1D structures namely bipyramids or nanorice, bulged in the center and tapered at the ends⁶, which have been the focus of recent research on anisotropic structures. For instance, Liu et al. have reported the synthesis of Au bipyramids with lengths of ~120 nm prepared in a highly acidic medium⁶. Zheng et al. have synthesized Au nanorice (50–70 nm) bound by high index planes and utilized them for carbon monoxide oxidation⁷. Additionally, Au bipyramids have been employed in varied applications such as dampening of acoustic vibrations⁸ and dielectric sensing⁹. Au nanostars with sharp tips have shown superior surface enhanced Raman spectroscopy (SERS) activity⁹ and plasmon mediated sensing¹¹. Odom and co-workers have shown the photothermal response of the Au nanopyramids with sharp tips¹². Nanorice-like structures have been reported in the case of Ag as well¹³. Recently, star-fruit shaped Au nanorods of lengths up to ~1 µm have been reported by Vgderman and co-workers¹⁴. However in such cases¹⁵, the structures obtained are usually not beyond ~1 µm (for a comprehensive survey of the current literature on bipyramids, see Supplementary Table S1 online). For many applications such as optical nano-focusing¹⁶,¹⁷, it is desirable to have nanowire-like lengths, i.e., typically few micrometers but with the aforementioned special morphology. This explains the reason why many have resorted to using lithography methods to obtain large metal anisotropic structures such as pyramids and grooved structures required in nanophotonic applications¹⁸. In this article, we report the synthesis and microscopy characterization of pentagonal bipyramidal structures of Au which are typically ~10 µm long. We also demonstrate how individual microcrystals can be employed as SERS substrates and optical waveguides.

Anisotropic structures of Au reported in the literature are usually obtained via solution phase synthesis, upon reduction of metal ions stabilized with a suitable surfactant, in the presence of Ag(I) ions⁶,⁹. The latter is understood to play a key role in producing high index planes resulting in interesting morphologies¹⁰,¹¹. Nevertheless, these are seed-mediated multistep reactions²² employing high concentrations of surfactants²³ or highly acidic conditions²⁴ to control the growth. The method, presented in this article, makes use of Ag(I) but not in solution phase. It is
essentially a simple, single step solid state synthesis on a flat substrate, in which a precursor, i.e., a mixture of Au(III) and Ag(I) stabilised by tetraoctylammonium bromide (ToABr) named as AuAgToABr, is subjected to thermolysis on a hot plate in air, to produce long corrugated pentagonal bipyramidal microcrystals.

The background, which led to this recipe, is interesting. Recently, some of us reported the synthesis of single crystalline Au microplates by the thermolysis of Au(III) stabilised with ToABr (AuToABr) (see Supplementary Fig. S1 online)24. Similar attempts with AgToABr led to AgBr (see Supplementary Fig. S2 online), as Ag-Br formation is thermodynamically more favourable than of Ag-Ag25. We considered it interesting to examine if Ag(I) will have an influence on Au(III) reduction to form alloy nanostructures. We therefore prepared mixed precursors (AuAgToABr) by phase transferring Au(III) and Ag(I) ions simultaneously from aqueous to organic medium i.e., toluene (see Methods and Supplementary Fig. S3 online). Upon drop coating a mixed precursor (75:25 of Au(III):Ag(I)) on a Si substrate and thermolyzing in air (see schematic in Fig. 1a), there were no plate-like structures but instead micron sized long structures and symmetric 3D particles were obtained along with AgBr particles. The latter could be washed away by treating with liquor ammonia (see Supplementary Fig. S4 online). The focus of the present study is on the long micron sized anisotropic structures.

Results
Optimization of synthesis conditions. As shown in the scanning electron microscopy (SEM) image in Fig. 1b, the obtained structures are 10 ± 2 μm long. The central diameter was found to be in the range, 0.9–1.15 μm with a typical aspect ratio of ~7 (see histogram in Fig. S5). The magnified images in Figs. 1c, d and e bring out the interesting morphology of the long structures. They are tapered on both sides, from the center to the tips and the tapering is not smooth but corrugated. The tips are sharp with a radius of curvature of ~55 nm and a tip angle of ~30° (Figure 1d). The contiguous corrugated features appear akin to folded fingers (Figure 1e). A side view reveals that the corrugated steps are approximately arranged in a pentagonal symmetry (Figure 1f) along the long axis. We term these interesting structures as micron sized corrugated pentagonal bipyramids (μ-CPBs). Atomic force microscopy (AFM) topography image (Figure 1g) shows a well-defined stepped surface which is reflected in the height profile shown in Fig. 1h. The width of the steps varied from ~180 nm at the tip to ~675 nm at the center. The surface roughness on the flat regions of μ-CPB was minimal i.e., ~1.5 nm (see Supplementary Fig. S6 online). It is of considerable importance to have minimal surface roughness to alleviate the loss in light propagation studies18.

The morphology of μ-CPBs and their relative population to other 3D particles depend on the Au(III):Ag(I) ratio in the precursor as well as on the thermolysis temperature (Fig. 2). Elongated structures were observed when Au(III):Ag(I) = 90:10 ratio was employed (Fig. 2a). They appear as dumbbells with pentagonal symmetry with flattened smooth edges; and the average length was found to be ~3 μm. The average length increased to ~3.5 μm with 80:20 of Au(III):Ag(I) and the elongated structures (see Fig. 2b) resembled

Figure 1 | SEM images and surface characterization of μ-CPBs. (a) Schematic illustrating the synthesis of μ-CPBs. SEM images of μ-CPBs prepared at 135°C for 75:25 of Au(III):Ag(I) – (b) low magnification, (c) single μ-CPB, (d) magnified view of the tip and (e) side facets marked in (c). (f) High resolution image of the pentagonal symmetry at the tip. (g) AFM topography image of the stepped surface of a μ-CPB and (h) height profile along the line drawn in (g).
closely μ-CPBs obtained with the 75:25 ratio (Fig. 1c). The surface morphology was found to be sensitive in this concentration region (see Fig. 2c–e). At 50:50, the pentagonal bipyramids possess small length (1.5 μm) with smooth surface (Fig. 2f). From the above experiments, it is clear that 75:25 of Au(III):Ag(I) produced the longest particles (μ-CPBs) with well-developed corrugations. It is noteworthy that the μ-CPBs produced in this study are distinct from the nanorice/bipyramidal particles reported in the literature26,5,7, the latter being typically sub-μm in length. As μ-CPBs are few micrometers in length, they can be easily visualized and manipulated under a conventional optical microscope (see Supplementary Fig. S7 online) unlike the nanorice/bipyramidal particles.

Besides the metal content, thermolysis temperature was found to be a crucial parameter for controlling the structure of μ-CPBs. The histogram in Fig. 2g shows the relative yields of μ-CPBs and 3D particles at various thermolysis temperatures (μ-CPBs) yield is above 45% at all temperatures. The thermogravimetric analysis indicates that there is no weight loss below 135°C and the precursor decomposition is rapid above 170°C (see Supplementary Fig. S8 online). The length and morphology of μ-CPBs are influenced by the rate of precursor decomposition; slower the decomposition, longer the μ-CPBs. At 135°C and 155°C, we observed long μ-CPBs with sharp tips (see Fig. 1 and 2h respectively), while short pentagonal bipyramids with blunt tips and smoother surfaces are seen at higher temperatures (see Fig. 2i and j). The ones observed at 175°C (see Fig. 2i) are bipyramids which possess similar morphology as at higher temperatures (see Fig. 2i and j). The ones observed at 175°C (see Fig. 2i and j) and 250°C (see Fig. 2f) resemble the nanorods morphology reported in the literature6. Thus, higher growth kinetics does not seem to permit the formation of well corrugated surface. A higher reduction rate at elevated temperatures leads to large number of nucleation sites and in turn, a large number of smaller particles.

Structure of μ-CPB. In order to understand the structure of the μ-CPBs in detail, high resolution X-ray diffraction (XRD), SEM and transmission electron microscopy (TEM) analysis have been performed. The μ-CPBs are highly crystalline as evident from the XRD pattern. The intensity of the (220) peak was found to deviate from the standard JCPDS data (65–2870) by 44% (see Supplementary Fig. S4 online), as <110> is the preferred growth direction. Low magnification TEM image (Figure 3a) shows the corrugated surface of a μ-CPB. Electron diffraction (ED) pattern collected from the tip showed two sets of spots (see Fig. 3b), hexagonal and rhombus patterns overlapping each other. These correspond to the Au FCC lattice viewed along the <111> and <110> zone axes, respectively. The ED pattern from the center of μ-CPB also shows two sets of spots indexable to <112> and <001> zone axes (see Fig. 3c). Similar ED patterns have been observed in the case of penta-twinned Au, Ag and Cu nanorods27. This indicates that the μ-CPBs possess a penta-twinned structure grown along the <110> direction. When high resolution TEM (HRTEM) was performed at the tip, the observed spacing between the fringes was ~2.36 Å corresponding to a d-spacing of Au(111) (see Fig. 3d). Figure 3e shows HRTEM image collected from the region of the side facets of μ-CPBs (indicated as e in Fig. 3a). The d-spacing was ~2.07 Å corresponding to Au(200). The zig-zag ridges cannot be the (100) planes as the latter are atomically flat. The values of the angles at the ridges point to plausible existence of high-index planes. From the TEM image (Fig. 3f), the angles subtended by the surface planes of the adjacent ridges are measured to be 147.7° and 146.8°, which are in close agreement with expected angular relation for the (730) and (112) zone axes (see Supplementary Table S2 online). To further confirm the assignments, one may refer to the projection angles in edge-on orientation along the <110> axis (see Supplementary Table S2 online and Fig. 3g). Considering the ridges to be extraneous growth from the atomically flat (100) planes, the measure edge-on projection angles indicate that the ridges are (hk0) (see Supplementary Tables S2 and S3 online and Figs. 3f, 3g) (where h>1 and k ≥ 1) type high-index planes. Based on the above results, the growth direction of the μ-CPBs is considered to be <110> while the side facets are (100). The tips are enclosed with stable (111) facets, in agreement with the reported literature on Au nanorice27. Figure 3h shows a highly magnified SEM image of a
μ-CPB with various planes and growth directions assigned, based on ED and HRTEM analysis. The surface composition of μ-CPBs was examined using core-level spectroscopy (see Supplementary Fig. S9 online). Interestingly, the surface was found to be almost entirely made of Au(0), Ag(0) being negligible.

**Growth mechanism.** The growth of μ-CPBs is indeed interesting. A μ-CPB has two growth modes namely along the longitudinal axis and the lateral growth leading to the observed corrugation (five-fold stars stacked along the longitudinal growth direction). These aspects were investigated by arresting the growth of μ-CPBs at different time periods by simply removing the substrate from the hot plate and examining under SEM. Initially, we discuss the growth along \(\langle 110\rangle\) direction. The thermolysis carried out for 30 min gave rise to nearly spherical particles in the range, 25–30 nm (see Supplementary Fig. S10 online). The particles may have definite facets which is however not clearly visible in the SEM images owing to their small size. The facets become visible once the particles grew beyond 100 nm (time of thermolysis, 60 min). At this point, the particle is essentially a multiply twinned decahedron (MTD) (see Fig. 4b and its schematic in Fig. 4a) which is one among the known stable polyhedrons in this size regime. It has ten \(\{111\}\) facets, five \(\{100\}\) facets and two possible growth directions, \(\langle 110\rangle\) i.e., along the particle axis and also along five equivalent \(\langle 112\rangle\) directions across the particle side faces as shown in Fig. 4a. Anisotropic particle growth is mainly due to the differences in the growth rates on different crystallographic facets. For FCC metals, the surface energy of different facets is as follows, \(\gamma_{\langle 111\rangle} < \gamma_{\langle 100\rangle} < \gamma_{\langle 110\rangle}\). The \[110\] and [211] faces have surface energies of 0.0991 and 0.0908 eV/Å\(^2\) respectively. Hence a faster growth along the \(\langle 110\rangle\) direction is expected. The growth rate along the \(\langle 112\rangle\) direction comes next. There is another contributing factor for the anisotropic structure of the μ-CPB. MTD is viewed as an association of five tetrahedral units, sharing an edge. The angle expected between two tetrahedral units is 70.53°. When five such tetrahedrons are stacked in a face-to-face orientation, there will be an angular gap of 7.35° to fill in. It therefore causes strain at the corners, which in turn induces anisotropic growth of μ-CPBs. MTD may act as a seed for further growth and this aspect is discussed in detail in the literature in relation to Au/Ag anisotropic structures. In the given reaction mixture, the following reactions are expected where the described redox potentials are with respect to the standard hydrogen electrode (SHE).

\[
\begin{align*}
\text{Ag}(0) & \rightarrow \text{Ag}(I) + e^- \quad E_0 = -0.8 \text{ V} \quad (1) \\
\text{Ag} + \text{Br}^- & \rightarrow \text{AgBr} + e^- \quad E_0 = 0.3 \text{ V} \quad (2) \\
\text{Au}(\text{III}) + 3e^- & \rightarrow \text{Au}(0) \quad E_0 = 0.99 \text{ V} \quad (3)
\end{align*}
\]

Following equations 1 and 2, Ag(0) oxidizes to Ag(I) and generates an electron. Au ions get reduced by accepting the electrons according to equation 3. It is therefore not surprising that no
significant Ag3d signal was observed in X-ray photoelectron spectrum (XPS) (see Supplementary Fig. S9 online).

As shown in Fig. 4c, nanoparticles obtained at 120 min thermolysis appear like elongated decahedrons. Similar structures are addressed as nanorice in the literature. They have a typical length of ~150 nm and an aspect ratio ~2. In the subsequent growth, the aspect ratio of the decahedron increased by many folds (see Fig. 4d corresponding to 150 min thermolysis). In stage 4d, the nanoparticles became tapered with a large curvature. The intense electric field corresponding to 150 min thermolysis appear like elongated decahedrons. Similar structures are also an important contributing factor. At higher temperatures, rugated surfaces. Ultra-slow precursor decomposition at 135°C is also an important contributing factor. At higher temperatures, the differences in the growth rates in different directions may be small. The ten {111} facets at the tip remain almost unaffected from the seed decahedron to μ-CPBs as the growth on these planes is thermodynamically unfavorable. The longitudinal growth along the growth axis is relatively rapid whereas the side facets i.e., {100} are adsorbed with Ag which acts as a surfactant and thus the growth is inhibited.

While Ag actively participates in the Au μ-CPBs growth, it does not become part of it (see Supplementary Fig. S9 online). Following the Hume–Rothery rules\textsuperscript{39}, one would expect an alloy formation, as Ag has similar lattice parameters. Not quite surprisingly, Au–Ag alloy bipyramids (40–90 nm) have been reported in the literature starting with HAUCl₅, AgNO₃ and polyvinylpyrrolidone (PVP) as a capping agent\textsuperscript{38}. In the present method, clearly, Au and Ag though exist in atomic intimacy, did not form an alloy. The reason for this unusual behavior is that the Au and Ag precursors separate themselves into different domains as the solvent evaporates from the mixed precursor, prior to thermolysis. This became apparent from XRD patterns and polarizing microscopy images (see Supplementary Fig. S13 online) collected from the precursor film, which showed AuToABr and AgToABr crystallizing in individual domains. This may be an additional parameter contributing to the observed highly anisotropic growth.

By virtue of such contributing factors at play, remarkably large multiply twinned particle (MTP) structures (Au μ-CPBs) have thus been observed which stand out from the known anisotropic structures till date. The MTP structures reported in literature are usually nanoparticles with decahedron or slightly elongated rice morphology else nanowires with five-fold tapered ends. The μ-CPB particles reported here are unique in that the tips are made of MTP structure recorded on an individual μ-CPB shown in Fig. 5a, consists of intense peaks at 1000, 1023, 1070 and 1576 cm⁻¹, all assignable to various vibration modes in ring breathing, C-H bending, C-S stretching and C=C bond respectively of the aromatic ring\textsuperscript{42}. The Raman enhancement factor (G) calculated based on the peak intensity at 1576 cm⁻¹ is found to be 2.4 × 10⁶ for TP. In the spectrum shown in Fig. 5b, the peaks are assignable to R6G

**Figure 4 | Investigation of growth of μ-CPBs.** (a) Schematic of decahedron with facets and growth directions marked. (b–f) FESEM images of typical μ-CPBs collected at different time periods during thermolysis at 135°C. (g) Schematic depicting growth along <112> directions involving Ag(I) deposition on Au facets and galvanic displacement of Ag(0) by Au(I) from the surrounding molten precursor. This process eventually leads to the fivefold star shape as seen along the <110> direction.

SERS, pick and probe measurements. The corrugated surface of the μ-CPB prompted us to use them as SERS substrates. For this purpose, thiophenol (TP) (1 mM) and Rhodamine 6G (R6G) (1 mM) were used as Raman probe molecules. The Raman spectrum of TP recorded on an individual μ-CPB shown in Fig. 5a, consists of intense peaks at 1000, 1023, 1070 and 1576 cm⁻¹, all assignable to various vibration modes in ring breathing, C-H bending, C-S stretching and C=C bond respectively of the aromatic ring\textsuperscript{42}. The Raman enhancement factor (G) calculated based on the peak intensity at 1576 cm⁻¹ is found to be 2.4 × 10⁶ for TP. In the spectrum shown in Fig. 5b, the peaks are assignable to R6G
vibrational modes; peak at 614 cm\(^{-1}\) corresponding to C-C-C stretching mode and the peaks at 1355 and 1509 cm\(^{-1}\) stand for the C-C stretching.\(^{31}\) Enhancement factor (also known as G-factor) is estimated to be \(5.8 \times 10^6\) based on the peak at 614 cm\(^{-1}\).

Since µ-CPBs are sharp objects, we tried pick and probe technique for molecules using single µ-CPB. A polymer (PVP) film containing probe molecules (R6G) was chosen, which was gently scratched with a µ-CPB mounted on a Cu wire using a micromanipulator (see Supplementary Fig. S14 online and Figs. 5d–g). A small amount of R6G-PVP blend was thus picked up on the µ-CPB tip. The spectrum collected from the tip of µ-CPB (see Fig. 5c) is relatively noisy and the peaks are broadened due to the inhomogeneous environment\(^{22}\) of the analyte molecules on the µ-CPB surface. The number of adsorbed R6G molecules on the tip estimated based on the area of µ-CPB tip came out to be \(\sim 2700\). The above experiment illustrates the possibility of using µ-CPBs in sensitive SERS based detection. Unlike conventional plasmonic nano-crystals, these microcrystals exhibit broad plasmonic spectral features and have excitations at both visible and infra-red wavelengths (see Supplementary Fig. S15 online). Further, they host nanoscale topographic features in the form of ridges which form interesting sites for adsorption of molecules. Indeed, such confined nano-volumes act as plasmonic hot-spots where large electric fields can build up giving rise to enhanced light-molecule interaction such as SERS.

**Light propagation.** The µ-CPBs were investigated for light propagation as they have corrugated, grating-type surface with minimal roughness at each step as well as tapered ends resembling tapered V-grooves\(^{44}\). These structural features are important because the tips can facilitate localized optical fields while the corrugations on the surface facilitate effective conversion of free photons to surface plasmons with minimal scattering loss\(^{50}\). With this hindsight, we tested the plasmon assisted light propagation properties of Au µ-CPBs. Figure 6a shows the dark-field optical image of an isolated Au µ-CPB. Upon focusing a 632.8 nm (2 µm diameter) laser beam on one end of the Au µ-CPB (Figure 6b), we observed out-coupling of light at the distal end of the microstructure. This clearly indicated that the µ-CPB acts as a plasmonic waveguide. The incidence of visible light at one end of the structure causes the conversion of momentum of free photons into that of propagating plasmon polariton within the microstructure. This propagating plasmon reaches the distal end of the µ-CPB where again the plasmon polaritons are back-converted into free photons (see Figs. 6b and c).

In order to quantify the performance of µ-CPBs as plasmon waveguides, we calculated the propagation loss in the structure. Propagation loss \(\alpha\) is given by\(^{46}\)

\[
\alpha = \left( -10 \times \log\left(\frac{1}{e}\right)/L_0 \right) = 4.343/L_0
\]

where \(L_0\) is the propagation length, calculated using the formula

\[
I(x) = I_0 \times \exp\left(-x/L_0\right)
\]

where \(I_0\) is the incident intensity, \(I(x)\) is the intensity out-coupled light at distance \(x\) from the incident spot. For the Au µ-CPB of length 8.8 µm shown in Fig. 6a, the calculated propagation loss was 2.32 dB/µm. The propagation loss in the microstructure is both radiative and ohmic. The nanoscale ridges may scatter the plasmon resulting in photon emission. One way to overcome the losses is to use smooth bipyramid-like structures (Fig. 2a), and further taper them down with a focused-ion beam or possibly by a chemical recipe. This will facilitate nano-tapered, single crystalline, low-loss plasmonic structures that can be utilized for efficient optical waveguiding. It is to be noted that ridges in our geometry do have an advantage as...
they can act as potential hot-spots. Therefore, molecules confined to these ridges are subject to large electric fields. This can be further harnessed for sensitive detection of molecules at ultra-low concentrations. Furthermore, these microcrystals with controllable nanoscale features can be easily accessed and probed using far-field optical microscopy techniques. This is a major advantage when one needs to interface such structures with biological entities such as cells and tissues.

**Discussion**

In conclusion, µ-CPBs were synthesized using a simple solid state synthesis route (i.e., unaided by any solvent). The current method is versatile in that it is a single step synthesis and can be carried out on almost any flat substrate that can withstand 130 °C with almost no organic impurities in the final product. The growth of µ-CPBs can be halted or resumed at any time, by simply turning on and off the hot plate. The µ-CPBs being long enough can be easily observed during an ordinary optical microscope. Although the µ-CPBs are entirely made of Au, the presence of (AgBr)− ion in the reaction medium seems to play a key role in tuning the shape of the anisotropic particles. Shape and size of the µ-CPBs can be tailored by varying the mole ratio of Au(III) and Ag(I) in the precursor as well as by the thermolysis temperatures. The µ-CPBs serve as excellent SERS substrates. The efficiency of the tip of a µ-CPB was studied in a “pick and probe experiment.” The tip carrying only 2700 R6G molecules produced a near-field enhanced gas sensing in a single tailored nanofoxc. Nat. Mater. 10, 631–636 (2011).

1. Murphy, C. J. et al. Anisotropic Metal Nanoparticles: Synthesis, Assembly, and Optical Applications. J. Phys. Chem. B 109, 13857–13870 (2005).
2. Tao, A. et al. Silver Langmuir–Blodgett Silver Nanowires for Molecular Sensing Using Surface-Enhanced Raman Spectroscopy. Nano Lett. 3, 1229–1233 (2003).
3. Yu, Chang, S.-S., Lee, C.-L. & Wang, C. R. C. Gold Nanodisks: Electrochemical Synthesis and Optical Properties. J. Phys. Chem. B 101, 6661–6666 (1997).
4. Yu, X., Xiong, Y., Lim, B. & Shraibak, S. E. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? Angew. Chem. Int. Ed. 48, 103–109 (2009).
5. Kou, X. et al. Growth of Bipyramids with Improved Yield and Their Curvature-Directed Oxidation. Small 3, 2103–2113 (2007).
6. Liu & Guyot-Sionnest, P. Mechanism of Silver(I)-Assisted Growth of Gold Nanodisks and Bipyramids. J. Phys. Chem. B 109, 22197–22200 (2005).
7. Zheng, Y. et al. Facile Synthesis of Gold Nanorod Enclosed by High-Index Facets and Its Application for CO Oxidation. Small 7, 2307–2312 (2011).
8. Pelton, M. et al. Damping of acoustic vibrations in gold nanoparticles. Nat. Nanotechnol. 4, 492–495 (2009).
9. Burgin, J., Liu, M. & Guyot-Sionnest, P. Dielectric Sensing with Deposited Gold Bipyramids. J. Phys. Chem. C 112, 19279–19282 (2008).
10. Rodriguez-Lorenzo, L., Álvarez-Puebla, R. N. A., de Abajo, F. J. G. & Liz-Marzán, L. M. Surface Enhanced Raman Scattering Using Star-Shaped Gold Colloidal Nanoparticles. J. Phys. Chem. C 114, 7336–7340 (2009).
11. Liu, N., Yang, M. L., Hentschel, M., Gieschen, H. & Alivisatos, A. P. Nanoantenna-enhanced gas sensing in a single tailored nanofoxc. Nat. Mater. 10, 631–636 (2011).
12. Hasan, W. et al. Tailoring the Structure of Nanoparticles for Optimal Heat Generation. Nano Lett. 9, 1555–1558 (2009).
13. Liang, H., Yang, H., Wang, W., Li, J. & Xu, H. High-Yield Uniform Synthesis and Nanostructure-Determination of Rice-Shaped Silver Nanocrystals. J. Am. Chem. Soc. 131, 6068–6069 (2009).
14. Vigderman, L. & Zubarev, E. R. Starfruits-Shaped Gold Nanorods and Nanowires: Synthesis and SERS Characterization. Langmuir 28, 9034–9040 (2012).
15. Senapati, D., Singh, A. K. & Ray, P. C. Real time monitoring of the shape evolution of branched gold nanostucture. J. Phys. Chem. L 110, 88–91 (2010).
16. Ropers, C. et al. Grating-coupling of surface plasmons onto metallic tips: A nanofocused light source. Nano Lett. 7, 2784–2788 (2007).
17. Lindquist, N. C., Nagpal, P., Lesufleur, A., Norris, D. J. & Oh, S.-H. Three-Dimensional Plasmonic Nanofocusing. Nano Lett. 10, 1369–1373 (2010).
18. Noginov, M., Krescher, D. & Norris, D. J. Ultrasmooth Patterned Metals for Plasmonics and Metamaterials. Science 325, 594–597 (2009).
19. Kou, X. et al. Growth of Gold Nanorods and Bipyramids Using CTEAB Surfactant. J. Phys. Chem. B 110, 16377–16383 (2006).
20. Ming, T. et al. Growth of Tetrahedral Gold Nanocrystals with High-Index Facets. J. Am. Chem. Soc. 131, 16530–16531 (2009).
21. Personick, M. L., Langille, M. R., Zhang, J. & Mirkin, C. A. Shape Control of Gold Nanoparticles by Silver Underpotential Deposition. Nano Lett. 11, 3394–3398 (2011).
22. Wu, H.-L., Chen, C.-H. & Huang, M. H. Seed-Mediated Synthesis of Branched Gold Nanocrystals Derived from the Side Growth of Pentagonal Bipyramids and the Formation of Gold Nanotriangular Nanocrystals. Nano Lett. 11, 109–114 (2008).
23. Lee, S., Mayer, K. M. & Hafner, J. H. Improved Localized Surface Plasmon Resonance Immunoassay with Gold Bipyramid Substrates. Anal. Chem. 81, 4450–4455 (2009).
24. Radha, B., Arif, M., Datta, R., Kundu, T. & Kulikarni, G. Movable Au microplates as fluorescence enhancing substrates for live cells. Nano Res. 3, 738–747 (2010).
25. deB. Darwent, B. Bond Dissociation Energies in Simple Molecules. http://www.nist.gov/data/ndrs/NSRDS-NBS31.pdf (1970).
26. Zhou, Z.-Y., Tian, N., Huang, Z.-Z., Chen, D.-J. & Sun, S.-G. Nanoparticle catalysts with high energy surfaces and enhanced activity synthesized by electrochemical method. Faraday Discuss. 140, 81–92 (2009).
27. Johnson, C. J., Dujardin, E., Davis, S. A., Murphy, C. J. & Mann, S. Growth and form of gold nanorods prepared by seed-mediated, surfactant-directed synthesis. J. Mater. Chem. 12, 1765–1770 (2002).
28. Elechiguerra, J. L., Reyes-Gasga, J. & Yacaman, M. J. The role of twinning in shape evolution of anisotropic noble metal nanostructures. J. Mater. Chem. 16, 3906–3919 (2006).
29. Tsuji, M. et al. Toward branched platinum nanoparticles by polyl reduction: A role of poly(vinylpyrrolidone) molecules. Colloids Surf. A 317, 23–31 (2008).
30. Kan, C. et al. Gold Microplates with Well-Defined Shapes. Small 6, 1768–1775 (2010).
31. Tsuji, M. et al. Stepwise Growth of Decahedral and Icosahedral Silver Nanocrystals in DMF. Cryst. Growth Des. 10, 296–301 (2009).
32. seo, D. et al. One-Dimensional Gold Nanostructures through Directed Anisotropic Overgrowth from Gold Decahedrons. J. Phys. Chem. C 113, 3449–3454 (2009).
33. Sun, Y. Silver nanowires - unique templates for functional nanostructures. Nano T 2, 1626–1642 (2010).
34. Hassan, H. H., Ibrahim, M. A. M., Rehim, S. S. A. E. & Amin, M. A. Comparative Studies of the Electrochemical Behavior of Silver Electrode in Chloride, Bromide and Iodide Aqueous Solutions. Int. J. Electrochem. Sci. 5, 278–294 (2010).
35. Pérez-Juste, J., Liz-Marzán, L. M., Carnie, S., Chan, D. Y. C. & Mulvaney, P. Electric-Field-Directed Growth of Gold Nanorods in Aqueous Surfactant Solutions. *Adv. Funct. Mater.* **14**, 571–579 (2004).

36. Świętrzko, G. W., Ivanova, O. S. & Zamborini, F. P. Twin Plane Decoration of Silver Nanorods with Palladium by Galvanic Exchange at a Controlled Rate. *Langmuir* **27**, 13303–13301 (2011).

37. Raghavan, V. *Materials Science and Engineering: A First Course* Ch. 5 (PHI Learning Pvt. Ltd, New Delhi, 2006).

38. Zhang, X. *et al.* Synthesis and Growth Mechanism of Pentagonal Bipyramid-Shaped Gold-Rich Au/Ag Alloy Nanoparticles. *Langmuir* **23**, 6372–6376 (2007).

39. Gammons, C. H. Hydrothermal synthesis of gold grains with apparent five-fold symmetry. *Can. Mineral.* **34**, 1–8 (1996).

40. Rath, V. Zur Kristallographie des goldes. *Z. Krystallogr.* **1**, 1–17 (1877).

41. Taylor, C. E., Pemberton, J. E., Goodman, G. G. & Schoenfisch, M. H. Surface Enhancement Factors for Ag and Au Surfaces Relative to Pt Surfaces for Monolayers of Thiophenol. *Appl. Spectros.* **53**, 1212–1221 (1999).

42. Wang, D.-Y. *et al.* Silver-Nanoparticle-Conjugated Polypeptide Brushes for Surface-Enhanced Raman Scattering. *J. Phys. Chem. C* **113**, 13498–13504 (2009).

43. Kneipp, K., Kneipp, H. & Bohr, H. Topics in Applied Physics (eds Katrin Kneipp, Martin Moskovits & Harald Kneipp) Vol. **103**, 261–277 (Springer Berlin/Heidelberg, 2006).

44. Beermann, J. *et al.* Localized field enhancements in two-dimensional V-groove metal arrays. *J. Opt. Soc. Am. B* **28**, 372–378 (2011).

45. Wild, B. *et al.* Propagation Lengths and Group Velocities of Plasmons in Chemically Synthesized Gold and Silver Nanowires. *ACS Nano* **6**, 472–482 (2011).

46. Ma, Y. *et al.* Direct measurement of propagation losses in silver nanowires. *Opt. Lett.* **35**, 1160–1162 (2010).

47. Chikkaraddy, R., Singh, D. & Kumar, G. V. P. Plasmon assisted light propagation and Raman scattering hot-spot in end-to-end coupled silver nanowire pairs. *Appl. Phys. Lett.* **100**, 043108 (2012).

48. Radha, B. & Kulkarni, G. A Real Time Microscopy Study of the Growth of Giant Au Microplates. *Cryst. Growth Des.* **11**, 320–327 (2011).

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Author contributions
G.M., R.B. and G.U.K. designed and performed the experiments and also analyzed the data. D.S. and G.V.P.K. performed light propagation experiments. All authors reviewed the manuscript.

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