Shape-Controlled, Single-Crystal Gold Surface Nanostructures.

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ABSTRACT:

Size, shape and crystallinity play a critical role in the wavelength-dependent optical responses and plasmonic local near-field distributions of metallic nanostructures. While their enhanced local fields can drive new and useful chemical and physical processes, the ability to fabricate shape-controlled single-crystal metal nanostructures and position them precisely on substrates for device applications represents a significant barrier to harnessing their greater potential. Here, we describe a novel electroless deposition process in the presence of anionic additives that yields additive-specific, shape-controlled, single-crystal plasmonic Au nanostructures on Ag(100) and Au(100) substrates. Deposition of Au in the presence of SO$_4^{2-}$ ions results in the formation of smooth Au(111)-faceted square pyramids that show large surface enhanced Raman responses. The use of halide additives such as Cl$^-$ and Br$^-$ that interact strongly with (100) facets produces highly textured hillock-type structures characterized by edge and screw-type dislocations (Cl$^-$), or flat platelet-like features characterized by large area Au(100) terraces with (110) step edges (Br$^-$). Use of additive combinations provides structures that comprise characteristics derived from each additive including new square pyramidal structures with dominant Au(110) facets (SO$_4^{2-}$and Br$^-$). Finally we demonstrate that this bottom-up electroless deposition process, when combined with top-down lithographic patterning methods, can be used to position shape-controlled, single-crystal Au nanostructures with precise location and orientation on surfaces. We anticipate that this approach will be employed as a powerful new tool to tune the plasmonic characteristics of nanostructures and facilitate their broader integration into device applications.

Metal nanostructures support collective electron oscillations that can localize spatially-extended electromagnetic (EM) waves. These metal-supported surface plasmons (SPs) alter the phases and amplitudes of EM excitations, providing a means to manipulate light at the nanometer scale, trap their enhanced local fields within designer nanocavities, or leverage their decay into hot carriers to drive new chemical and physical phenomena. SPs have found applications in energy harvesting, photocatalysis, sensors, and engineered metamaterials, where they can display negative refractive index, enable flat optics, and prove sub-wavelength resolution imaging capability. The confinement of quantum emitters to nanometer scale plasmonic cavities can lead
to light-matter interactions in the strong coupling limit\(^9\) and could provide a source of single-photon emitters, all-optical transistors, and new quantum information processing applications\(^{10}\).

Noble metal nanostructures have been a primary focus of many efforts in these areas due to their large charge carrier densities and responses that span the infrared through visible spectral ranges. However, their utility for many of these applications is limited by difficulties in precisely controlling the positions, shapes and orientations of noble metal nanostructures into well-defined device geometries that can be readily integrated into manufacturable platforms. Improved control over surface chemistry to overcome these limitations represents a major challenge in the field, with significant potential technological benefit.

The solution phase synthesis of metal nanocrystals enables the fabrication of nanostructures of well-defined size, shape and composition\(^{11}\). The use of specific chemical interactions between solution additives and growing nucleation centers can alter facet-dependent reduction rates to provide specific shape selectivity. The preferential adsorption of these shape control agents leads to facet-dependent differential growth kinetics resulting in structures that display unique, size- and shape-dependent optical and electronic properties\(^{12-15}\). However, despite exquisite control in the production of these crystalline nanostructures, they are in solution, isolated from each other by the use of capping agents to enhance their stability and prevent their aggregation into larger structures. In this form, it is difficult to assemble, locate and address these nanoparticles with either light or electricity, preventing them from incorporation into devices that exploit their local field enhancements.

We have recently described an alternative approach to crystalline noble metal nanostructures that is compatible with current device fabrication protocols\(^{16}\). The method employs green, electroless chemistry that is scalable to the wafer level and enables the fabrication of ultrasmooth, epitaxial, single crystal noble metal films that are ideal for the subtractive manufacture of nanostructure through ion beam milling, and additive crystalline nanostructure via lithographic patterning to provide single crystal features and large area metamaterial arrays. While noble metals are characterized by inherent optical absorption losses that are exacerbated by their tendency to form polycrystalline structures when deposited by conventional physical vapor deposition methods, our single crystal metal nanostructures limit resistive and optical absorption losses and demonstrate improved thermal and mechanical stability compared to polycrystalline structures. The capability of fabricating nanoscale plasmonic materials with control over size, shape, crystallinity, and substrate location would provide a new level of control to create next generation nanoscale technologies. Here, we describe the use of shape control strategies typically employed in the solution phase synthesis of nanocrystals to impart shape control to surface nanostructure, expanding the toolkit for controlling metal surface texture with nanoscale level precision.
Under highly alkaline conditions, the deposition of Au from aqueous solutions of HAuCl$_4$ onto Ag(100)/Si(100) single crystal substrates proceeds by reduction of AuCl$_4^-$ ions, and leads to the formation of ultrasmooth, epitaxial, single-crystal, thin Au(100) films (Fig. 1a). The deposition of gold in the presence of SO$_4^{2-}$ anions alters the resulting Au film morphology significantly (Fig. 1b). Scanning electron microscopy (SEM) of this textured film shows that the film is comprised of small (sub-100 nm) faceted features that show a general square pyramidal shape preference. Attempts to remove or dislodge these structures by repeated sonication and solvent cleaning were unsuccessful, indicating they are an integral component of the surface structure and have not been formed by nucleation in solution followed by deposition onto the substrate. Closer inspection indicates that the facets are smooth and oriented with respect to the underlying substrate, lending support to this view (Fig. 1c).

Figure 1. The effect of sulfate anion on single crystal Au deposition. a) Top-view SEM of a smooth, epitaxial, single crystal Au film deposited through alkaline electroless deposition of a HAuCl$_4$ solution onto a Ag(100)/Si(100) single crystal substrate. b) Tilt view SEM of a Au-nanopyramid textured Au film grown as in a) but with the incorporation of 0.25 M NaSO$_4$ in the deposition bath. c) Expanded view of b) highlighting the strong square pyramidal shape preference, the common orientation of square pyramids with respect to the underlying substrate, and the smooth facets of the nanostructures.

The single crystal Ag(100)/Si(100) substrates used in this work are formed by thermal evaporation of Ag onto H-terminated Si(100) wafers. The wafer is carefully split into smaller 1x1 cm$^2$ substrates by ready fracture of the wafer along its family of (011) crystalline planes$^{17,18}$ (M1-0302 SEMI standards). The crystal substrate on which the Au growth begins is Ag(100) with substrate edges oriented in the family of <110> directions. The orientation preference of the nanopyramids is observed to be such that the square bases of the pyramidal structures are aligned parallel to the edges of the substrate. This orientation preference suggests that the pyramid facets are the (111) family of crystal planes. The growth of Au films in the presence of higher sulfate concentrations (0.50 M and 0.75 M) was also investigated. The results of these studies (Fig. S1) show the same shape preference with modest differences in crystallite size and surface density.

High resolution transmission electron microscopy (HRTEM) reveals that the square pyramidal structures are monocrystalline and oriented as described above. Fig. 2a shows a high angle
annular dark field scanning TEM image of two adjacent nanostructures of nominal 40 nm dimension that appear triangular in cross-section. Elemental mapping (Fig. 2b) shows that the structures are Au in composition and sit atop a thin layer of Au formed on the Ag(100)/Si(100) single crystal substrate. TEM measurements of the nanocrystallite facet angles relative to the (100) substrate suggests that the observed square pyramidal structures display their (111) facets, consistent with the expected angle of 54.7° between the (100) and (111) crystal planes of face-centered-cubic (fcc) metals (Fig. 2c). This is confirmed through HRTEM measurements (Fig. 2d) that display the single crystal nature of the square pyramidal crystallites as well as their orientation with respect to the underlying single crystal substrate, through direct observation of the crystallite lattice planes.

Figure 2 a) High angle annular dark field scanning TEM image of two adjacent nanopyramids, b) elemental mapping of a) with Ag in red and Au in green, c) bright field TEM image of the two nanopyramids, d) HRTEM of the nanopyramid on the left in c).

Under the alkaline conditions employed for Au deposition, the silver substrate and subsequent growing gold film are strongly influenced by adsorbed hydroxide species and by anionic additives capable of interacting with the substrate. The growing gold film evolves by the gradual appearance of step edges and the growth of minor facets as deposition proceeds on the original and available (100) substrate facet. The facet-dependent relative reduction rates then determine the resulting film morphology. The growth of Au in highly alkaline conditions gives rise to smooth epitaxial Au films (Fig. 1a), implying that lateral growth along the family of <011> directions is more rapid than growth on other crystal facets (vide infra). However, the presence of SO$_4^{2-}$ anions has a profound effect on the resulting film morphology, giving rise to shape selective growth. The mechanism for square pyramidal shape preference can be understood in
terms of an interaction between sulfate anions and the Au(111) facets of the evolving monocrystalline Au film. As step edges and minor (111) facets begin to form, SO$_4^{2-}$ anions adsorbed at these sites stabilize them and reduce the rate of their further growth relative to other low index (e.g. (110) and (100)) facets. As film growth proceeds, larger growth rates on the readily available (100) and minor (110) facets lead eventually to their disappearance, and a film surface structure defined by larger area (111) facets. Thus, strong interaction between SO$_4^{2-}$ anions and Au(111) crystal facets serve as an effective blocking mechanism to lower reduction rates on growing (111) facets. Evidence of growth in the families of <011> and <010> directions (parallel to the surface) and (110) planes (angled 45° with respect to the surface) can also be observed during film growth and lead to expansion of the nanopyramids from the edges of their square bases, leading ultimately to the merging of neighbouring nanostructures and the formation of larger square pyramids.

The interaction between SO$_4^{2-}$ anions and Au(111) facets has previously been investigated via in situ infrared spectroscopy, in situ scanning tunneling microscopy (STM) and DFT calculation\textsuperscript{19-22}. While these studies have focused on acidic electrolytes, they provide compelling evidence for SO$_4^{2-}$ anion interaction with the Au(111) facet, displaying well-ordered sulfate adlayers in which sulfates are bound at 3-fold hollow sites of the (111) facets via three oxygen atoms, stabilized by water molecules that bridge adjacent adsorbed sulfate anions. Similarly ordered adlayer structures of sulfate and phosphate on Au(100) surfaces have been reported in in situ STM studies of Au(100) by Kolb and co-workers, but suggest that they require the presence of H$_3$O$^+$ ions for their stabilization\textsuperscript{23,24}. We investigated the plasmonic response of these nanostructured Au films via surface enhanced Raman scattering (SERS). Plasmonic local field enhancements are known to enhance scattering efficiencies nonlinearly and are used here as a measure of plasmonic activity. Figure 3 illustrates the SERS response of two typical Raman marker molecules, benzoic acid (BA) and Rhodamine 6G (R6G). Films of BA and R6G were prepared by dip coating gold substrates from 20 or 10 mM solutions, respectively, and the SERS responses were obtained from a Renishaw (Invia) Raman microscope/spectrometer using a 785 nm diode laser source. Raman marker films were deposited both on smooth monocrystalline gold and on the nanostructured gold films described above. Also shown in Fig. 3 is the Raman response of a silicon wafer - typically used as an alignment and signal optimization reference for these tools - under identical illumination and spectrum collection conditions. The gold films comprised of nanopyramids demonstrate significant SERS enhancement compared to the monocrystalline gold films and provide signal levels comparable to those obtained from the silicon reference. While it is not the focus of this manuscript and no attempts have been made to optimize the SERS response from these
nanostructured films, the nanopyramid substrates provide SERS responses comparable to those reported for Au nanoparticles\textsuperscript{25-27} and may provide an alternative approach to the production of SERS substrates. Integrating sphere absorption measurement of the nanostructured film in the absence of an overlayer (Fig. S5) shows broadband (500-1000 nm) absorption ranging from 40-20\%, which will be shifted to longer wavelengths in aqueous media or upon adsorption of analyte species. The oxidation-resistant gold nanostructured film is cost-effective, cleanable, and reusable, and shows plasmonic response over a wide range of wavelengths, making this approach a new potential broadband SERS platform.

![Figure 3. SERS spectra obtained from a) BA-coated Au nanopyramids, BA-coated monocrystalline Au(100) film and a silicon wafer reference sample, b) R6G-coated Au nanopyramids, R6G-coated monocrystalline Au(100) film and a silicon wafer reference sample.](image)

We have also examined the role of other anionic electrolyte additives on the growth of single crystal gold films (Figure 4). The use of chloride anions in the alkaline electroless deposition bath (Fig. 4a-b) gives rise to surface nanostructure reminiscent of that obtained with sulfate anions (Fig. 4d), but with important differences. Fig. 4a shows that the dominant surface features that result from Cl\textsuperscript{-} addition are also square pyramidal structures with dominant Au(111) features.
However, the pyramidal structures appear to be much larger in dimension (typically 2-5 μm) compared to those resulting from SO₄²⁻ addition, and their Au(111) features appear to have a well-developed texture that is common to all structures, differing dramatically from the smooth facets that result from sulfate addition. Fig. 4b shows an enlarged top view SEM image of a single Au pyramid deposited in the presence of chloride anions. The structure is formed with textured facets that appear to result from a platelet-growth morphology in which the edges of smooth growing Au layers possess defects that drive further deposition to occur discontinuously and with a slightly skewed orientation with respect to underlying gold layers. The results are structures possessing highly granular facets that display a helical character. This morphology can be understood in terms of the formation of edge- and screw-type lattice dislocations induced by chloride ion interactions with the growing gold surface. Such lattice defects often lead to the growth of spiral-like structures and can be explained by a kink-limited growth model in which the growth of crystalline layers is affected by the presence of (here Cl⁻) additives. As the kinks and step edges are formed, their growth kinetics are modified through energetically favorable interaction with additive ions, stabilizing these dislocations, limiting further growth of low index

![Figure 4. Growth of single crystal Au films under the influence of different anionic additive species.](image)

Top-view SEM image of a Au film grown under the influence of a) 0.25 M Cl⁻, b) expanded top-view SEM of one of the structures identified in a). Top-view SEM images of a Au film grown under the influence of c) 0.75 M Br⁻, d) 0.25 M SO₄²⁻, e) 0.25 M Cl⁻ and 0.25 M SO₄²⁻, and (f) 0.25 M SO₄²⁻ and 0.25 M Br⁻.
facets, and eventually leading to textured structures comprising higher index Au facets. To the best of our knowledge, this type of growth behavior has not previously been observed through chloride addition, however, the use of chloride ions in conjunction with Ag⁺ has been implicated in the growth of concave cubic gold nanocrystals with high-index facets.

Halide adsorption on the (100) and (110) facets of fcc metals is expected to differ significantly from that on (111) facets, where the hexagonal symmetry of halide adlayers is expected to mimic the underlying surface symmetry. Strong adsorbate-metal interactions between halides and (100) surfaces is thought to arise from their preferred four-fold hollow adsorption sites. Due to weaker relative repulsive interactions between adsorbed ions and the higher coordination of the adsorbed ions with the surface metal atoms, halide adsorbates are more strongly bound in these sites than in the three-fold hollow sites on (111) surfaces. Preferential halide adsorption on Au(100) facets can give rise to slow and/or discontinuous growth on (100) surfaces, impeding the deposition of smoothly faceted structures, explaining, at least in part, the structures resulting from chloride additive deposition.

The use of bromide ions (Br⁻) in the solution-phase synthesis of shape-controlled nanocrystals is well known, where strong Br⁻ ion interaction with the family of (100) crystalline facets leads to their stabilization, and a range of resulting shape-controlled structures. Fig. 4c displays the effects of Br⁻ on the electroless deposition of gold on Ag(100) single crystal substrates. The SEM image displays a largely flat surface collage comprised of (100) terraces with little to no structure normal to the surface and many step edges, indicating film evolution primarily through lateral growth. This motif is consistent with strong adsorption of bromide anions to the top (100) facet limiting the development of minor (111) facets and driving growth along the families of <110> and <010> in-plane directions. Inspection of Fig. 4c shows indications of facet edges oriented both parallel and 45° to the frame of the figure, however, they are oriented predominantly in the family of <110> directions, parallel to the frame of the figure. The development of pronounced (110) step edges suggests that while bromide interacts strongly with (100) facets, it appears to interact more strongly with the family of (110) edges.

Gold deposition in the presence of additive mixtures provides an additional means of tailoring surface nanostructure. Figure 4e displays a plan view SEM image of Au film deposition in the presence of both sulfate and chloride anions. Interestingly, the resulting nanostructures display elements of Au deposition observed from each additive. The dominant structural motif is the appearance of square pyramidal structures as observed for sulfate additive-based growth (Fig. 4d). However, unlike the pyramids formed from sulfate additives alone which are characterized by smooth (111) facets, the presence of chloride additives appears to impart additional texture to the (111) facets, as one might anticipate based on Figs 4a-b. Further, the use of other
additive combinations can provide nanostructure facet selection as illustrated in Fig. 4f, where the combination of sulfate and bromide ions is employed during gold deposition. The presence of sulfate anions again favors the appearance of oriented square pyramidal nanostructures through the stabilization of (111) facets to enable out-of-plane Au nanostructure growth. However, the orientation of the pyramidal facets in this case is rotated 45° with respect to those observed from the sulfate additive alone (Fig. S2). The additional presence of bromide in the deposition bath gives rise to the growth of square pyramidal nanostructures comprised dominantly of (110) facets. Consistent with the observation of bromide-induced in-plane growth in the absence of sulfate (Fig. 4c), bromide appears to interact preferentially with the growing (110) out-of-plane facets as well. Thus, this combination of additives results in relative facet growth rates such that (111) > (100) > (110).

The presence of anionic additives in the deposition bath during alkaline epitaxial electroless deposition represents a new strategy to control single crystal surface nanostructure. The range and complexity of interactions that can affect nanostructure growth in these systems is significant and can include the facet-dependent interactions between anionic additives and the growing single crystal metal, and facet-dependent anion-anion interactions within anionic adlayers. The use of anionic additives can further complicate the deposition chemistry through formation of mixed Au³⁺-based complex ions, whose facet-dependent reduction potentials will differ from those of Au(OH)₄⁻ ions. Other possible complications include the potential for metal ion reduction via additive anions as opposed to OH⁻ ions, as we have previously assumed in the absence of additives. Nevertheless, shape-controlled single crystal surface nanostructure can be achieved through differential growth kinetics on the growing facets of monocrystalline metal substrates, providing the capability of fabricating nanoscale plasmonic materials with control over size, shape, crystallinity, and substrate location.

Here, we demonstrate this control by employing a combination of the “bottom-up” growth of shape-controlled single crystal gold nanostructures with “top-down” electron beam lithography (EBL) patterning methods to yield a single crystal Au nanostructured metamaterial array. Under the prevailing alkaline deposition conditions, hydroxide ions can act as both a shape control agent through facet-dependent Au-hydroxide ion interactions, as well as the reducing agent required to convert the Au(III)-based Au(OH)₄⁻ complex ions to Au. Unrestricted growth on planar Ag(100) and Au(100) substrates (Fig. 1a) proceeds through a 2-dimensional, rapid in-plane growth mechanism in the family of <110> directions, to yield ultrasmooth single crystal Au(100) films. Laterally restricted growth results in deposition normal to the surface, dictated by the (much slower) relative rates of deposition on the (111) and (100) facets. Fig. 5a shows a top view SEM image of a single crystal Au metamaterial array formed by epitaxial electroless deposition onto an EBL-patterned Au(100) surface containing a 700 nm period, square array of 250 nm diameter cylindrical pores formed by patterning a 200 nm thick film of PMMA electron beam
Fig. 5b illustrates the faceted, single crystal nature of the individual pillars, comprised of a flat-top (100) facet and (111)-faceted side walls. The shape of the resulting structures suggests that the effects of the hydroxide ion are to impart relative facet-dependent growth rates, $R_{\text{facet}}$, such that $R_{110} \gg R_{100} > R_{111}$. With rapid lateral growth limited by the pore side walls, the nanopillar shape is dictated by growth in the $<100>$ direction that is more rapid than in the $<111>$ direction, leading eventually to the disappearance of the (100) facet and the prevalence of (111) facets. Note that the order of facet-dependent growth rates correlates well with the relative order of hydroxide ion adsorption energies on the three low-index Au surfaces $\text{Au}(110) > \text{Au}(100) > \text{Au}(111)$, suggesting that the rate of $\text{Au(OH)}_4^-$ reduction is limited by its adsorption to the gold surface through its hydroxide ligands and/or that surface bound hydroxide plays a key role in the detailed reduction mechanism. Use of other additives or additive combinations provides a mechanism to alter these relative growth rates through blocking mechanisms or modified reduction mechanisms and therefore, to drive alternative crystalline facet structure as demonstrated in Figure 4.

In summary, we have demonstrated the deposition of shape-controlled single crystal Au surface nanostructures via solution deposition through the use of anionic additives. The method is scalable and environmentally friendly with appropriate choice of additives. Additive selection determines the facet-dependent Au deposition rates and can be used to tailor surface nanostructure shape and texture. In combination with conventional patterning methods, we have also demonstrated the ability to deposit a large area array of shape-controlled, single
crystal Au nanopyramids, with precise positioning, demonstrating a new level of control in the
design and fabrication of nanometer scale noble metal-based structures. We anticipate that this
approach will be exploited for the fabrication of high quality, single-crystal plasmonic, photonic,
and electronic structures, where the advantages of reduced optical absorption and resistive
losses, and shape-dependent, tailored local near-fields are desired.

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SUPPORTING INFORMATION

Shape-Controlled Growth of Single Crystal Gold Surface Nanostructures

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Single crystal silver Ag(100) substrate preparation:

Ag(100) deposition was carried out using a Kurt J. Lesker Company PVD-75 thermal evaporation tool with a base pressure of <2 × 10⁻⁷ Torr. Ag (99.99% Kurt J. Lesker Company) was evaporated from an alumina coated tungsten wire basket. The substrate was heated via a backside quartz lamp and the temperature was monitored with a K type thermocouple attached to the backside of the sample chuck assembly. Deposition was carried out at a substrate temperature of 360 °C and a rate of 3 Å s⁻¹. Prior to Ag deposition, substrates were immersed in either dilute HF acid solutions (10:1 with de-ionized water), or similarly diluted commercial buffered oxide etch solutions (BOE, CMOS Grade, J.T. Baker Inc.), to remove the native oxide layer from the surface of the silicon wafer. All activities, prior to characterization of the films, were carried out under class 100 clean room conditions or better.

Au (nanopyramid) growth under influence of sulfate ions (SO₄²⁻):

The deposition bath was made by dissolving 0.355 g Na₂SO₄ salt in 10 ml of 1.0 M pre-made NaOH solution to achieve a 0.25 M SO₄²⁻ concentration. A 1 x 1 cm² Ag(100) substrate is placed facing up in a beaker containing the NaOH- SO₄²⁻ solution. A volume of 500 μL 0.0025 M HAuCl₄ solution is pipetted into the mixture and then the beaker is placed in a water bath. The temperature of the water bath is kept constant at 60°C for the duration of the deposition (typically 2 hours), without the need of stirring the mixture. After deposition, the sample is removed from the reaction solution, and washed thoroughly by distilled water for 2 minutes followed by sonication in isopropanol alcohol (IPA) for 1 minute and rinsed again with distilled water for 1 minute and then dried by a flow of filtered air.

The growth of Au at higher concentrations of SO₄²⁻ (0.5 M and 0.75 M) was also investigated with the same duration and deposition temperature. Figure S1 illustrates the top view SEM images of the Au nanocrystallites grown under the influence of 0.5 M and 0.75 M SO₄²⁻, respectively.
Au growth under influence of chloride ions (Cl\(^-\)):

A 0.25 M Cl\(^-\) containing bath is prepared by dissolving 0.146 g of NaCl in 10 ml of 1.0 M NaOH. The Ag(100) substrate (1 x 1 cm\(^2\) in dimension) is placed in the bath and then 500 μL of HAuCl\(_4\) with 0.0025 M concentration is pipetted into the bath. The beaker containing the Au\(^{3+}\)-NaOH-Cl\(^-\) mixture is then placed in a water bath at a temperature of 50°C. The duration of the deposition is 3 hours, during which the temperature is kept constant at 50°C. The sample is then removed from the solution, washed for 2 minutes in distilled water, sonicated in IPA for 1 minute, rinsed with distilled water for 1 minute and then air dried.

Au growth under influence of bromide ions (Br\(^-\)):

A 0.75 M Br\(^-\) containing bath is prepared by dissolving 0.771 g of NaBr in 10 ml of 1.0 M NaOH. The Ag(100) substrate (1 x 1 cm\(^2\) in dimension) is placed in the solution and then 500 μL of HAuCl\(_4\) with 0.0025 M concentration is pipetted into the bath. The beaker containing the Au\(^{3+}\)-NaOH-Br\(^-\) mixture is placed in a water bath that has been heated to 60°C and is maintained at this temperature during the 2 hour deposition period. Finally, the sample is washed for 2 minutes in distilled water, sonicated in IPA for 1 minute, rinsed with distilled water for 1 minute and then air dried.

Au growth under influence of Cl\(^-\) and SO\(_4^{2-}\) ions:

A bath containing 0.25 M Cl\(^-\) ions and 0.25 M of SO\(_4^{2-}\) ions is prepared by dissolving 0.146 g of NaCl and 0.355 g of Na\(_2\)SO\(_4\) in 10 ml of 1.0 M NaOH. The Ag(100) substrate (1 x 1 cm\(^2\) in
Au growth under influence of Br\(^-\) and SO\(_4^{2-}\) ions:

A bath containing 0.75 M of Br\(^-\) ions and 0.25 M of SO\(_4^{2-}\) ions is prepared by dissolving 0.771 g of NaBr and 0.355 g of Na\(_2\)SO\(_4\) in 10 ml of 1.0 M NaOH. The Ag(100) substrate (1 x 1 cm\(^2\) in dimension) is placed in the solution and then 500 μL of HAuCl\(_4\) with 0.0025 M concentration is pipetted into the bath. The beaker containing the solvated ions is then placed in a water bath at a temperature of 60°C. The duration of the deposition is 2 hours during which the temperature is kept constant at 60°C. The sample is then removed from the solution, washed for 2 minutes in distilled water, sonicated in IPA for 1 minute, rinsed with distilled water for 1 minute and then air dried. This process led to the formation of surface nanostructures with Au(110) facets. Figure S2 shows a top-view SEM image of the nanostructures grown in proximity to the edge of the substrate (known with respect to the <110> direction of the Si(100) wafer). On the basis of this image, we are able to assign unambiguously the orientation of the nanostructure angled side walls to be the family of (110) crystalline facets.
Single crystal Au(100) substrate preparation:

A 1 x 1 cm\(^2\) Ag(100) was used as a substrate to grow 200 nm thick single crystal Au(100) electrolessly. The Ag substrate was submerged in 10 mL of 1.0 M NaOH which acted as the deposition bath. Then, 250 \(\mu\)L of 0.025 M of HAuCl\(_4\) solution was added to the deposition bath (10 mL NaOH). The deposition bath was placed in a water bath where its temperature was kept at 70°C for 60 minutes undisturbed to grow 200 nm thick single crystal Au(100) film on the Ag(100) substrate. The sample was then washed with distilled water and sonicated in isopropanol alcohol for 60 s and air dried. Single crystal deposition was confirmed through 2D-XRD and high resolution TEM analysis.

Metamaterial array patterning using electron-beam lithography (EBL):

The metamaterial arrays were made by patterning 500 x 500 \(\mu\)m\(^2\) areas on an electron-sensitive poly(methyl methacrylate) (PMMA) A4 film, which was deposited at 4000 rpm onto a 1 x 1 cm\(^2\) single crystal Au(100) substrate to achieve 200 nm thickness followed by 4 minutes of soft bake at 180°C, using a Raith e-LiNE EBL system. The electron exposure was done at 7 mm working distance, with 20 \(\mu\)m aperture, 20kV extra high tension (EHT) and with an area dose of 200 \(\mu\)C/cm\(^2\). After the patterning exposure, the PMMA was developed in MIBK-IPA 3:1 for 120 s followed by 120 s of IPA rinse (Figure S3).

![Figure S3. Top-view SEM image of patterned arrays with 250 nm pore diameter on PMMA A4 after development.](image-url)
Au growth in nano-patterned arrays:

Growth of periodic crystalline nanostructures was carried out by pipetting 250 μL of 0.025 M HAuCl₄ into 10 ml of NaOH (1.0 M) to prepare the deposition bath and inserting the nano-patterned arrays into the solution. The beaker containing the nano-patterned array was then placed in the 60°C hot water bath for 5 minutes. The sample was then removed, washed for 2 minutes in distilled water, 1 minute with IPA and then placed in acetone for 2 minutes while being sonicated to remove the PMMA mask. After the PMMA lift-off, the sample was rinsed with water and air dried.

Sample preparation for transmission electron microscopy (TEM):

For TEM analysis, a small section of the sample was lifted-out and mounted on a TEM grid. First, a 10 x 1 μm² area was covered with a platinum-based protective layer using focused-ion beam (FIB) induced deposition in an FEI Helios NanoLab 650 FIB/SEM system. Then, the desired section with a volume of 10 x 1 x 5μm³ is carved out using FIB trenching and milling, and mounted on a transport needle followed by transferring and gluing it onto a copper TEM grid. The sample then was FIB thinned down to a thickness of roughly 30-50 nm. Figure S4 shows the scanning-electron microscope (SEM) images of the sample attached to the TEM grid where the area above the black arch shape in the middle of the first image is the thinnest. TEM was performed using a 200 kV FEI Tecnai Osiris S/TEM tool.

Figure S4. SEM images of the sample suspended on the TEM grid, a) SEM side view image of the lifted-out sample and b) SEM image of a zoomed-in region of the sample shown in a).

Nanopyramid surface absorption measurement:

Absorbance of the pyramidal surface nanostructures fabricated by depositing Au under the influence of SO₄²⁻ was measured by placing the sample in an integrating sphere, directing the beam of a broadband light source into the sphere, and illuminating the surface nanostructures
with a spot size of 1 mm in diameter. The scattered photons from the surface were collected by a fiber optic and directed to a spectrometer. The absorption from the surface is shown in Figure S5.

Figure S5. Integrating sphere nanopyramid absorbance measurement. The SERS spectra described in the text were collected with a 785 nm excitation wavelength, where the surface demonstrates up to 20% absorption as can be read from this absorbance spectrum.