

# Building Interfacial Nanostructures by Size-Controlled Chemical Etching

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**Abstract** Development of soft chemical processes for the synthesis of interfacial architectures with well-defined structural nano-motifs organized over large areas in two dimensions is an important branch of nanotechnology. The present study deals with the fabrication of gold nanostructures using size-selective chemical etching of continuous gold films on glass support with titanium and chromium adhesive layers. In this process, which is called self-passivated surface etching, a gold film is etched in the presence of citric acid, resulting in gold nanostructures adhering to the metal support. The size-controlled chemical dissolution of gold is driven by a competing reaction between self-organized passivation of surface nano-motifs by citric acid shells and soft etching by a nonoxidative composition containing hydrochloric acid and hydrogen peroxide in water. According to these results, the presence of a chemically stable adhesive layer (titanium), citric acid in solution, and agitation are critical factors to be considered. However, the nature of the adhesive layer is the most influential factor. The following technique presents a simple method for the rapid fabrication of a nanostructured gold substrate that has the ability to support both propagating and localized surface plasmon resonances simultaneously.

**Keywords** Interfacial nanostructures · Chemical etching · Thin films · Gold nanostructures · Surface plasmon resonance

## Introduction

Gold nanostructures have generated a great deal of interest due to their size-dependent electronic, optical, and catalytic properties, particularly with respect to their assembly on surfaces. Novel technologies used to obtain patterned metal films on insulating substrates extend the capability to form advanced materials for modern optoelectronic devices, especially those based on surface plasmon resonance phenomena. Such surface architectures in particular can be used as transduction elements in sensors for medical diagnostics and environmental monitoring [1–4]. Development of more sensitive and informative sensor platforms is generally based upon the amplification of sensitivity by increasing the number of analyte binding sites. This goal can be realized by an enhancement of the sensor surface area using both nanostructuring of substrate as well as increasing the overlap of the sensitive area and the space occupied by an evanescent wave. Another approach is to combine both the propagating (p-SPR) and localized surface plasmon resonance (l-SPR) excitations at the same interface. In either case, the creation of an advanced plasmonic material with a patterned surface is the desired outcome.

Both propagating and localized surface plasmon excitations are electromagnetic waves coupled to charge fluctuations, and are pinned to the interface between a metal and a dielectric [1, 5, 6]. On a patterned surface, the optical field excites a surface plasmon polariton (SPP)—an optically active mixture of surface plasmon and optical fields. If an SPP wave is reflected between barriers, it will interfere with itself and form a standing wave, localizing the surface plasmon polariton. In short, the p-SPR is a traveling wave, propagating along the interface shared with a dielectric, whereas the l-SPR is a localized field confined to metallic

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nanoparticles and other nanostructures. Localization occurs around features with sharp asperities; for example, within truncated spherical cavities or balls [6]. These structures are shown to be crucial by providing the control needed to bring the two types of plasmons into resonance with one another, and observe how they interact. One reason for the combining of different plasmonic excitations for sensor applications is the possibility of separating the responses from different distances to the surface. For instance, the I-SPR has a much shorter decay length of the evanescent field (~10–20 nm) compared to the p-SPR (~100–200 nm). The instrumentation needed to monitor such structures can be easily adapted from the conventional SPR-spectrometers. Angle-resolved spectroscopy allows p-SPR and I-SPR modes to be distinguished from each other, since I-SPR is independent from the incident angle of the excitation light and sample orientation. So, in spite of the fact that there exists many methods for obtaining SPP-specific nanostructured surfaces (e.g., nanoporous gold membranes [5], metallic structures with nanovoids [6] etc.), the search for novel techniques to form optically active metal structures containing embedded truncated metal voids or particles is ongoing. One reason for this is the necessity of simple fabrication technologies for laboratory use supported by the creation of ultrathin interfacial nanostructures possessing the features of both planar metal films that exhibit p-SPR excitations, and nanofeatured metals that exhibit I-SPR excitations.

Here, we consider a simple chemical technique for the fabrication of a nanostructured substrate that provides the ability to support both propagating and localized surface plasmon resonances simultaneously. Generally, such optically active gold structures can be considered as a rough, high curvature, yet continuous gold membrane. Classical examples are porous gold foils, metallic structures with nanovoids or nanoballs [5–8]. Porous materials can be manufactured by different methods based on a binary  $A_xB_{1-x}$  alloy; a porous structured metal A can be achieved by solving out the less inert component B (Au–Zn [9], Au–Ag [10, 11], Au–Cu [12]). The classical approach for the fabrication of metallic structures with nanovoids is based upon a mechanical block of surface in the colloidal lithography method [7]. The most popular techniques to obtain island-like structures formed upon continuous film are based on thermal sputtering [1], various lithographic techniques [13–15], photo-stimulated chemical deposition [16]. There are also various approaches that involve chemical binding between nanoparticles and functionalized surfaces [17], in particular those that use microwave radiation [18]. In the following work, we propose a one-step chemical procedure for the fabrication of a surface with nanoelements that uses a continuous metal film on an insulating substrate as rough workpiece. In this process, which is called self-passivated surface etching (SPSE), a

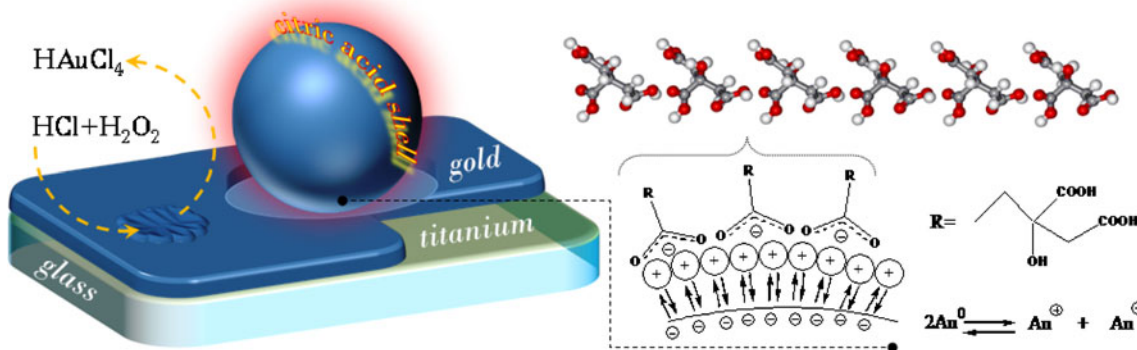
gold film is etched in the presence of a citric acid additive, resulting in gold nanostructures adhering to a continuous gold layer on the support (Fig. 1).

Our approach per se is based on the chemical methods of preparing small gold particles initiated by the pioneer works by Turkevich et al. [19]. The key feature that unites the different procedures used for the chemical synthesis of nanoparticles is the presence in the system of a certain amount of an organic additive whose interaction with the particle surface makes it possible to stabilize nanostructures by slowing down any further growth. It follows that such a coat also hinders the aggregation of nanoparticles [20]. The growth and dissolution of crystals are opposite processes. Therefore, a growth inhibitor of a particular nanoparticle, in principle, will also influence the rate of dissolution of that same size. By this principle, it would be logical to assume that application of soft etchants of gold in the presence of organic stabilizers could slow down dissolving of objects of definite size. The key element of the approach is the arrangement of etching conditions under which the process of gold dissolution occurs. This would be predominantly in such areas in which the sizes are in the range of the required nanostructures. This would enable one to obtain the surface elements in nanometer scale by using continuous gold films as raw stock. In order to verify this interaction, the etching of continuous gold film in the presence of tailored growth inhibitor was systematically investigated. To explore this possibility, it is necessary to show the presence of peculiarities in the interfacial organization specific to nanoscale (e.g., specific absorbance) and their dependence on the parameters of both the etching process and the presence of an adhesive layer. The present work is focused on these issues of building interfacial nanostructures by wet etching.

In this work, we discuss the methodological aspects of wet chemical etching, then introduce experimental data that demonstrates the particularities of etching reactions occurring on the gold transducer surface under different conditions. An analysis of the results in the frame of the proposed model is given, along with a discussion of the driving forces of surface passivation and etching prevention. Finally, some approaches for developing the wet etching methodology, as well as some recommendations concerning application of the proposed procedures for setting up fabrication protocols are discussed.

### Wet Chemical Etching of Gold

In spite of the common opinion of the high chemical inertness of gold and its alloys, a number of ways for the chemical dissolution of this metal have been proposed. Most of them dealt with gold extraction from gold ores



**Fig. 1** General concept of the size-controlled chemical etching of gold surfaces in the presence of citric acid. Scheme illustrates the interfacial equilibrium of gold atoms at the nanostructured surface. Typical

packing of citric acid in crystalline lattice (build on the data from [46] using VieverPro 4.2 (Accelrys Inc.) shown in *right top corner*)

[21]. However, there is very limited information on the problems concerning controlled dissolution of gold under soft conditions.

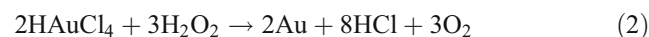
Bearing in mind the objective of our work, the requirement of low rates of dissolution of thin films without application of potentially dangerous chemical reagents assumes a rejection of the techniques involving acid–base compositions, where oxygen (owing to its relatively small size and high electronegativity) stabilizes the atoms of other elements with a high oxidation state. The examples are, in particular, chromium (VII) in  $\text{Cr}_2\text{O}_7^{2-}$  ( $\text{K}_2\text{Cr}_2\text{O}_7$ , bichromate) or sulfur (V) in peroxymonosulphate  $\text{SO}_5^{2-}$  (Piranha etchant). It has been shown earlier that a mixture based on the nonoxidizing components containing HCl and  $\text{H}_2\text{O}_2$  impacts more softly on thin gold films [22]. Therefore, we utilized an as-prepared mixture of distilled water, hydrochloric acid (vol. 37%), and hydrogen peroxide (vol. 30%) as our main etchant.

To determine the optimal modes of gold layer etching, we performed our investigations with thin (50 nm) gold films sputtered through an adhesion layer (thickness of 3 nm) onto (TF1) glass plates. The ratio between the etchant components,  $V_{\text{H}_2\text{O}}:V_{\text{HCl}}:V_{\text{H}_2\text{O}_2}$ , varied from 1:1:1 to 8:1:1. The reaction of gold dissolution proceeded with formation of the trivalent gold compound, which is readily soluble in water:



Because of the high electrode potential of gold, the above reaction proceeds slowly; long exposures of thin films to hydrochloric acid solutions do not result in any noticeable changes of their properties. To increase the gold reactivity, oxidizers such as chromic anhydride, sodium persulfate, or hydrogen peroxide are usually added to solutions. They considerably reduce the electrode potential of gold. If an oxidizer such as hydrogen peroxide is present,

then monodisperse gold sol is formed (along with process (1)) according to the Zsigmondi reaction:



The concurrent mechanism of reactions (1) and (2) still has not been studied thoroughly and requires additional analysis [23]. At the same time, one should note that the results of spectrophotometric studies show the absence of gold nanoparticles in solution absorption bands (above 520 nm) after etching the gold film.

When searching for the optimal conditions for reactions (1) and (2), we used etching time and uniformity of the obtained surface structure as the criterion. With hard compositions (1:1:1), etching off took several seconds, while it was 2 h with 5:1:1 and much longer at  $V_{\text{H}_2\text{O}} > 6$ . In keeping with reaction (2), oxygen bubbles were generated on the surface. The more concentrated (i.e., with a smaller fraction of water) the solution, the more violent and rapid the reaction. For compositions with a time of etching of longer than a minute, the films obtained were characterized macroscopically as having areas of two types: (1) more clear films (as a result of stronger etching) which formed a “background”, and (2) darker films (located where bubbles preventing film etching made contact with the film surface). As a rule, these dark films were round.

To avoid the formation of bubbles on the surface, we tested an approach with multiple (20; 30; 40 and 50 times) repeatable dips of the plate into high-concentration (1:1:1 or 1:2:2) etchant solution. In this case, however, it is rather difficult to study the dynamics of surface structure formation. In addition, the probability of getting false-negative results due to overexposure is high. Nevertheless, the use of multiple dips seems to be a sufficiently flexible approach because this enabled films of more homogeneous structure to be obtained. However, the necessity of mechanical motion and monitoring of the gas composition

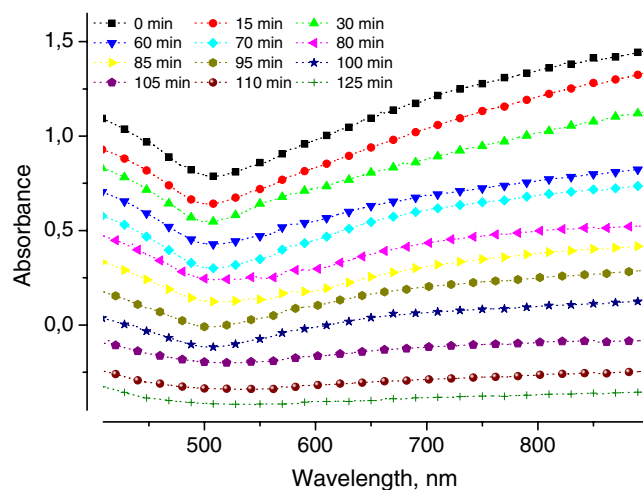
over the etchant surface reduces the technological attractiveness of the above approach. A more practical alternative mode involves continuous or repeated mixing of the etchant solution with a liquid flow directed along the plate surface. This made it possible to suppress bubble growth and obtain comparable results.

## Results

The presence of and chemical properties of an interlayer (chromium, titanium) that is applied to improve adhesion of the gold to glass usually has a profound impact on the interfacial process [24]. It is known that such a layer can influence the formation of an island film as well [25, 26]. With this in mind, we tested SPSE technology glass plates (TF1, refraction coefficient  $n=1.61$ ) with an as-sputtered gold layer (50 nm, thermally deposited in vacuum at room temperature, more details can be found in Reference [27]) three ways: (a) without an adhesion interlayer, (b) through a chromium adhesion interlayer (3 nm), and (c) through a titanium adhesion interlayer (3 nm). Monitoring of the etching reactions was performed with a two-beam spectrophotometer Unico 4802; the sample was immersed in etching composition directly in the device cell. We used the 5:1:1 etchant, with which the total etching time for samples with an adhesion layers was about 2 h. To exclude the influence of bubbles generated on the surface on the optical measurements a liquid flow directed to the plate surface was used.

Our spectrophotometric investigations of gold films without an adhesion layer showed that complete etching off takes several minutes. This is due to the well-known low adhesion of gold to glass [28]. Therefore, the emphasis was put on comprehensive investigations of the films with chromium and titanium adhesion layers. Figure 2 demonstrates overview of the spectrum changes during the etching for gold film with titanium adhesion layer. One can see that the spectrum becomes smoother with time (with corresponding decrease of the optical density), up to nearly complete disappearance of the minimum (while its position on the abscissa remains relatively the same). For the samples with chromium adhesion layer (Au~Cr), the process of complete etching off requires somewhat less time than in the case of a titanium layer (114 and 125 min., respectively). After, this time we did not observe absorption peaks in the region characteristic of both single gold nanoparticles (about 520–560 nm [29]) and their clusters (about 560–670 nm [30]). This indicates absence of the corresponding nanostructures on the surface and in the solution.

Shown in Fig. 3a are the plots of gold film absorption versus etching time. The data presented indicate that in the

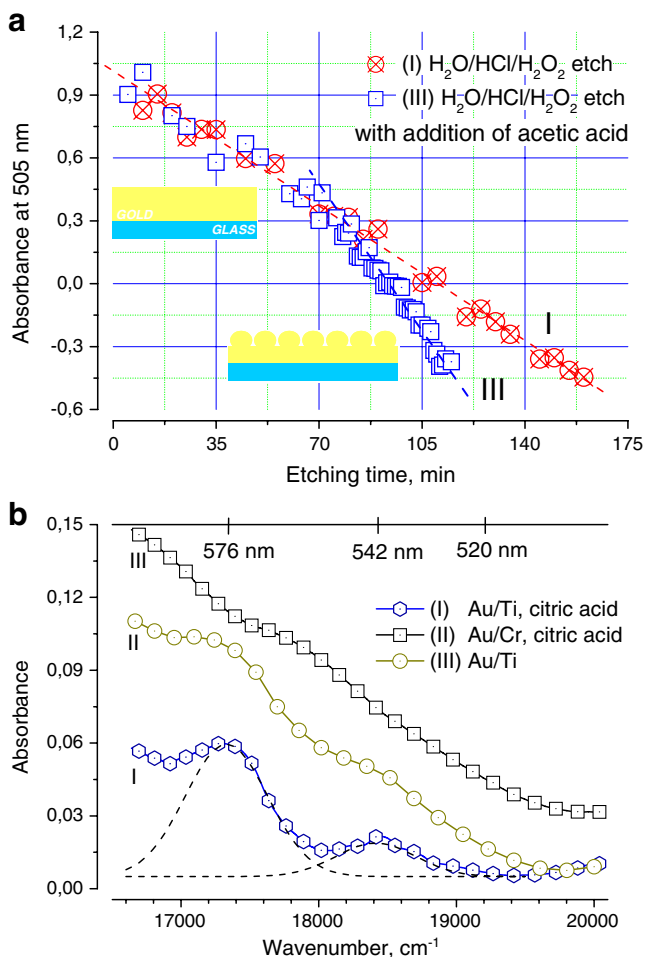


**Fig. 2** Absorption spectra of a thin gold film (50 nm) with titanium adhesion layer (3 nm) on glass surface as function of time of etching in the presence of citric acid. The etchant composition is 5:1:1

case of pure etchant the thickness of the film linearly decreases with the time in keeping with the classical Beer–Lambert–Bouguer law [31]. In the presence of additive (citric acid), the etching process seems very similar to pure etchant during above 70 min (above half of the film thickness); whereas after that, the curve slope increases in half. In-depth analysis of the spectra shows that at the same time interval, new absorption bands occur in the spectrum depending on the type of adhesion layer and the presence of additive in the etching composition. In Fig. 3b are the typical absorption spectra of gold films observed at etching times above 85 min. For the gold film deposited through the titanium adhesion layer in the 5:1:1 etchant, two absorption peaks appear within the 65–120 min. time interval. They lie near 542 and 576 nm and are characteristic of gold nanostructures. Further exposure led to the disappearance of those peaks. This indicates structural breakdown due to complete etching off of the surface. Addition of 2 g of citric acid to the 5:1:1 etchant solution (total volume of 7 ml, citric acid concentration 1.4 M/L) resulted in increase of both the contrast of the above absorption bands (the peaks were at the same wavelengths as they were in the absence of citric acid) and the time interval of their appearance. The observed effects were markedly clearer for the peak near 542 nm that corresponded to single nanoparticles. Further etching led to complete breakdown of the surface structure. Interpretation of the dependencies obtained requires a literature study of the chemical properties of the metals used in the adhesion layers, in particular, as pertaining to the different characteristics of their interaction with the etchant solution.

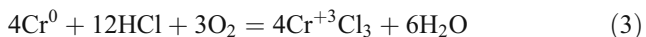
In addition to its high adhesion to both glass and gold, chromium dissolves well in both acids and alkalis. To illustrate, when chromium is dissolved in hydrochloric acid,





**Fig. 3** Change of the optical density at 505 nm (a) and absorption spectra (b) of gold films (50 nm) against the same substrate during the etching procedure. (I) sputtered through a titanium adhesion layer (3 nm) and exposed to etching in the presence of citric acid; (II) sputtered through a chromium adhesion layer (3 nm) and exposed to etching in the presence of citric acid; (III) sputtered through a titanium layer and exposed to etching without citric acid. The etchant composition is 5:1:1, concentration of citric acid is 1.4 M/L, etching time is 85 min

chromium (II) chloride (CrCl<sub>2</sub>) is generated. The latter is rapidly oxidized by atmospheric oxygen to chromium (III) chloride (CrCl<sub>3</sub>) in which the oxidation number of chromium is +3 [32]:



If one would also take into account that thin chromium films on glass are usually needle-shaped, then the observed features of etching of gold on the chromium sublayer would look as expected. When the etchant solution comes to the chromium interlayer (e.g., via the crystallite boundaries), the rate of chromium interaction with it is much higher than the rate of gold dissolution. Dissolution of chromium in the reaction medium due to process (3) leads to gold flaking

and considerable acceleration of gold dissolution because of an increase in the total area accessible to the etchant.

Contrary to chromium, titanium is resistant to diluted solutions of inorganic acids (except for hydrofluoric acid due to a complexation reaction). In particular, at room temperature titanium is extremely resistant to hydrochloric acid, to wet chlorine, and to the extreme, aqua regis [33] (even when ground). As a result, in the case of titanium interlayer, the titanium does not take part in the reaction and gold is being etched off gradually.

### Discussion

The effect of additives on the growth of nanoparticles may also be considered for directed patterning of the surface. In metal nanoparticles that have been grown in the presence of growth-inhibiting additives, a connection between the particle size and the stable spatial arrangement of additive molecules is realized under defined conditions. Analogous to crystal growth, the reverse process, i.e., the dissolution of the metals in the presence of additives, also can produce etching structures of specific size and orientation [34]. The drastic changes produced by the presence of the additives described above reveal a great deal of specific interaction between the additive and the surface structures of the film. The optical and hence morphological changes are thereof in direct relation to the adsorption/inhibition processes occurring on a supramolecular level.

The dissolution of a given surface, as is well known, begins at the exit point of a fault. In the case of polycrystalline films, this is normally at the inter-crystallite boundaries. Dissolution begins at this center, radiating in various directions at the same relative rates one would see during crystal growth. Under such conditions, the crystal's structure is retained overall. However, if the solution contains an additive which selectively binds to a given part of the surface, the rates of dissolution in the various directions will be different from that in the pure etching solution. The rate of dissolution will, therefore, decrease perpendicularly to the affected part, as opposed to an unaffected one, and in the last case, etched pits will appear at the faults.

### Oriented Adsorption of Tailored Etching Additives on the Gold Surface

An accumulation of additive molecules at the interface only occurs in places where some gradient of physical or chemical properties are present. Therefore, the surface properties of a substrate will determine the behavior of possible additives. Among a rather rich arsenal of approaches to formation of a stable organic coat for gold

nanoparticles such as the use of micellar structures [35, 36], self-assembled thiocompounds [37], and so on, those approaches using polytopic chelates are of particular interest. For instance, the use of citric acid makes it possible to form a spatially stable organic architecture that envelopes a gold particle due to the formation of coordination bonds between the carboxyl groups of citric acid and gold atoms [38].

In spite of more than fifty years of stabilizing gold nanoparticles by citric acid, the mechanism of that process is still not properly understood. The results of quantum mechanical calculations of organic structures on the metal surface [33, 39] are traditionally used to rationalize this stabilization. For instance, it is believed that because gold atoms have unfilled d-orbitals, the surface interacts more readily with systems containing negative electron density (a negatively charged center). Adopting such a standpoint as pertaining to surface processes has a number of drawbacks. Among these drawbacks are two of concerns in particular: (1) neglect of the effects of surface topography (and, consequently, the accessibility to unfilled d-orbitals in the reaction centers of many organic molecules) and (2) the neutrality of atoms located in the near-surface region of metal. The latter drawback is not self-evident, especially for extremely small objects (when the contribution from surface atoms is big). Yet, when in a solvent that can stabilize the ions of a given metal; it has no clear experimental verification either.

A solid, being in the equilibrium state, coexists with its vapor at any finite temperature and pressure [40]. Formation of a near-surface double layer in such cases (as is well known in electrochemistry and colloid chemistry) does not seem impossible [41]. Owing to the equilibrium dissociation of gold atoms occurring at the interface between phases, the cations of the same material can form the potential of the double layer. Stabilization of metal cations in the polar environment of the solvent occurs due to solvation effects. In this case, of principal importance is the fact that the process in the near-surface region is determined predominantly by the readsorption effect [42, 43] rather than actual metal dissolution. The rather low surface tension of gold [44] and the high mobility of thiols at the gold surface are in good agreement with these assumptions and illustrate the high mobility of metal atoms in the near-surface region. This process may be presented as it shown at the scheme on Fig. 1. If there are strong complexing agents and corresponding experimental conditions (temperature, solvent polarity, etc.), then a metal ion in the readsorption layer may break away from the surface (because of its higher stabilization in the solvate–chelate surrounding) and go into solution. To illustrate, it was shown in [45] that copper sol nanoparticles in hexane contained copper (II) ions. As the oxidation of Cu (0) to Cu (II) by oleic acid and oleic amine seems unlikely because of

the low oxidation potential of those compounds, they can undoubtedly stabilize the present metal ions with formation of complex compounds.

The above-mentioned model of double layer formation at the metal/liquid interface explains the generation of metal ions by the processes occurring at the metal surface itself. Such a model also makes it possible to explain the formation of both gold thiolates bound predominantly by electrostatic forces and the citric acid coat that was discussed above. Because of the presence of anion centers in a citric acid molecule, orientation of that center at the nanoparticle occurs. This orientation is stabilized by the formation of a close-packed structure similar to that observed for its crystals (top right, Fig. 1) [46]. Further discussion of this point follows below.

### Formation of 3D Inhibiting Surface Architectures

The effect of tailored additives is not restricted to direct interaction with a definite surface pattern, but also extends to the aggregation of molecules to form higher supra-molecular structures. Therefore, the inhibiting activity of additives also depends on the form and size of surface elements. There is a stereochemical relationship between the structure of the affected surface fragments and the supramolecular structures of the inhibiting architecture.

The different adsorbed phases are based on a two-dimensional arrangement as the result of surface diffusion (transfer) and relaxation (packaging into more stable structures). The molecules are arranged into domains, which are roughly as thick as the molecules are long, and whose boundaries are not rigid but constantly fluctuate. The surface and intermolecular interactions inside the adsorbed superstructure reflect their degree of order and stability. Stable shells of citric acid molecules are formed owing to formation of hydrogen bonds between the adjacent molecules via a hydroxyl and/or carboxyl group. The stability and structure of such molecular architectures are dictated by a number of factors, such as temperature, additive concentration, size, and form of the surface elements. Rearrangement in the citric acid layer proceeds by formation and/or breakdown of a fluctuating network of intermolecular bonds within the definite surface fragments.

It is well known that the higher the complexity and diversity of bonds in the system, the more stable the structure formed will be. The character of the functional sites of the citric acid network, as well as their number, depends on the object shape and size, which, in turn, are determined by the etching process itself. It is necessary to stress that since citric acid retains its physical–chemical properties under the conditions used, a possible change of reactivity during the etching process can be neglected. However, one should note that the variation of chemical

functionality of a nano-object itself as related to its size could play certain role in the formation of the organic stabilizer network. Unfortunately, this area has not yet been studied thoroughly, and it is too early to draw conclusions concerning the role of such effects.

The macroscopic solids, due to stochastic uniformity of surface roughness, usually demonstrate weakly bound surface layers of such compounds as citric acid; formation of continuous films is restricted by topographic randomization of directions in space. However, during the etching, formation of stable organic structures spanned on the surface of 3D interfacial objects becomes possible. For instance, a fluctuation network is formed spontaneously during the etching process as the surface structure reaches a size that corresponds to the most thermodynamically stable state of the surface-bound citric acid spatial networks. This stabilizes the structure considerably due to the slowing down of its dissolution according to process (1). As the typical particle size decreases below a critical value  $d_{cr}$  (that is characteristic of a network with a certain number of sites, number and orientation of bonds on each site, etc.), a fluctuational breakdown of the associated salt network (that is characteristic for  ${}^{(i-1)}d_{cr} < d < {}^i d_{cr}$  where  $i$  is the network type) occurs. Then the process continues in a similar way until the object reaches such sizes at which formation of a stable adsorption network becomes impossible.

### Concluding Remarks and Outlook

Using specific additives, it has been shown to be possible to control not only the growth but also the dissolution of crystals. The size-controlled chemical dissolution of gold is driven by a competition between self-organized passivation of surface nanofragments by citric acid shells and soft etching by a nonoxidative composition containing a solution of hydrochloric acid and hydrogen peroxide. Continuous monomolecular coatings with fluctuating edges and stable structures for a definitive form and size of the surface fragments are the result of both the ability of additives to adsorb on the surface and the ability of adsorbed components to migrate at the interface and rearrange the supramolecular structure of the inhibiting shell [39]. The feature of such an inhibiting coat is the presence of an effective negative charge on originating from the outermost carboxyl groups of a shell. The advantage of such structures is the possibility of a further displacement reaction of particular citric acid molecules with ligands (e.g., thiols, etc.) that have a much more favorable coordination bond with the nanoparticle material. The wasteless process with further ex-solution of gold or gold nanoparticles instills an ecological nature to this technology.

The proposed SPSE technology is related, in a sense, to the well-known Rehbinder effect—spontaneous dispersion of continuous media that leads to the formation of lipophilic colloidal systems [47, 48]. A condensative mode of spontaneous dispersion via the mechanism of dissolution–condensation is similar to the present work. In the classical version, the fluctuational association of molecules in equilibrium with particles of a dispersed phase according to a particular process (e.g., such as (1)) is considered. Of key interest to us in this work, however, were the processes of formation and stabilization of surface nanostructures that remain after such dissolution process (i.e., a fingerprint of the etching process per se on the initially continuous gold film). At the same time, it seems that the mathematical approaches usually applied to describe the Rehbinder effect might be efficiently used for self-terminated dissolution as well. This in particular describes an intimate relationship between the Rehbinder effect and the problems of formation and stability of nanodisperse systems.

We hope, that this work open the way for simple chemical procedures for the fabrication of substrates supporting both p- and I-SPR for both academic research as well for the development of various bioanalytical methods [49]. The defining factor of the success will depend on the variety of additives that passivate the surface of nanofragments and prevent its further dissolution. Consequently, a systematic variation of the metal films' habit in a predictable manner with specific additives ought to be possible. It can be the basis for modern plasmonic materials that are composite systems with spatially-distributed modulation of the dielectric constant and with local “bonding” areas of a propagative electromagnetic wave. The propagation of electromagnetic excitations in such structures is not entirely limited by diffraction limit and this wave can propagate along surface nanostructures with speed exceeding the carrier mobility in metals. These properties of the plasmon–polariton state define its prospects for quantum information processing in high-speed optoelectronics. It is expected that the use of SPP instead of conventional electronic circuits will achieve revolutionary changes in optoelectronics, in particular as a basis for high-efficient light emitters and lasers, optical switchers and filters, advanced waveguides and systems for ultrafast optical computing.

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