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SILVER DENDRITIC ANTENNAE FOR DETECTION OF VOLATILE MOLECULES IN AIR: PART FOR "ARTIFICIAL NOSE"

MASTER'S DEGREE THESIS

supervised by Dr Ramón Álvarez and Dr Nicolás Pazos

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Abstract. The key to extracting design principles for innovative material solutions is an understanding of the materials imposed by the tradeoff of conflicting functional requirements. Most inspired systems are hierarchically organized: they have functional sub-units and final stable macrostructures. We introduce here the hierarchical organization of silver macrocrystals, silver antennae, with dendritic sub-units and study their Surface Enhanced Raman spectroscopy (SERS) spectroscopy performance. Detection of a low quantity of volatile molecules in the air is an important task in various areas of life from safety regulation to discovery of new unknown bio-pathways, which involve active volatile molecules such as pheromones. Mostly the SERS substrates are expensive due to multistep nanoparticle synthesis and the following nanoparticle organization on the surface. We, therefore, suggest changing the concept and grow in a single step hierarchically organized silver macrocrystals. We expect to detect a very small amount of molecules in the air due to its complex self-organization, millions of crystal contacts with increased SERS activity. To grow such a crystal, we used spring geometry copper (Cu) precursors resulting in geometry guided organization of silver 3D geometry dendritic porous crystals. We tested our crystals for SERS detection of benzenethiol (BT) molecule in air and proved the concept efficiency obtaining a high SERS signal from spicules of the macrocrystal. In the future, such hierarchically organized macrocrystals with functional sub-units can be the core of a design strategy of structural materials with additional integrated functionality, such as energy storage or sensing with a high potential for a diversity of engineering applications.

INTRODUCTION

Nature optimizes the object organization at different levels, from macroscale to atomic organization, to provide multifunctional structural materials, in which trade-offs are imposed by conflicting functional requirements. One such example is the hierarchical organization of crystalline structures, a biomineralization process, which incorporates functional properties of hundreds of organized active sub-units. Nevertheless, achieving a comparable level of hierarchical organization in synthetic crystalline materials is a problem especially by simple single-step rapid reactions. Surprisingly, hierarchically organized stable dendritic 3D metal macrocrystals that can be washed, dried, and scaled up are not reported. We suggest using hierarchically organized dendritic silver macrocrystals for SERS application (1), as an example strategy. The macrocrystal is potentially interesting for SERS because they have many active 'hot spots' with plasmon enhancement in one macroobject, where the 3D organization of macrocrystals can potentially give multiscattering; the porosity of the macroobject increases the chance to have contact between volatile molecule and crystal; and with a single step, easy formation of many of macrocrystals with high adhesion to any substrate after drying is possible.

The development of Surface-Enhanced Raman scattering (SERS) spectroscopy substrates with high enhancement factors remains an active area of SERS research. Gas-phase chemical detection is of critical importance for the sensing of highly toxic molecules, such as chemical warfare or toxic chemicals. Being an exciting area, which up to now was not expanded, is the possibility of using SERS to detect volatile molecules such as pheromones in the air to study different biological pathways and their regulation. SERS is perfect to be used for these kinds of molecules because it is a very sensitive and non-destructive technique.

In SERS applications, hot spots where the electromagnetic field is particularly intense, play a key role. Dendritic silver crystals organized on the surface were shown to be 'liquid' SERS active due to many 'hot spots' in their structure (2). The synthesis of Ag microflowers for use as manipulable and reusable substrates in SERS was also shown for working with ultra-low volumes of the analyte (3). Up to now, there are no data to use these systems to detect molecules in the air due to their relatively low porosity. Simultaneously, initially grown dendrites have higher porosity.

In the formation of stable three-dimensional (3D) superstructures, hierarchically organized macrocrystals have attracted much attention because of the complexity of possible arrangements, such as multipods (4), snowflakes (5), hyperbranched (6), chiral structures (7), and dendrites (8), which may prove advantageous for a new generation of advanced devices such as sensors (9), batteries (10), catalyst (11) or fuel cells (12). In the same way, superstructures with high porosity at different scales are particularly attractive. Up to now, there are many successful attempts to obtain hierarchically organized silver crystals on microscale: from atomic organization and preferable orientation of crystallization to nanoblocks and final microstructure (13). At the time that we are creating a dendritic structure, the reduction of silver is necessary to create the structure (14) and, in our case, we are producing the silver reduction on a copper (Cu) displaying an array of morphologies with a rapid deposition and growth of silver nanocrystals(15). It exists an interplay of silver macroobject porosity and hierarchical organization by variation of the geometry of the precursor, copper wire, duration of reaction, and concentration of silver nitrate. We assume that silver macrocrystals organized from dendritic sub-units and geometrically optimized spicules/dendrites can be suitable for various applications, and here we focus on their SERS activity.

In our study the reaction of silver growth during reduction processes can be a model, to focus on conceptual understanding of dendritic crystal growth and the interplay between reaction and ion diffusion processes to achieve a designed organization of macroobjects at a different scale. Diffusion-Limited Aggregation (DLA) (16) is the growth process model and associated theories that help in explaining some physical form particles. An example of this are electrodeposition (17) and electroless deposition (18). DLA can be replicated through modern computer processing technology which can result into very large fractal clusters. These clusters can be grown to 10 million individual particles or more. The implementation of a selected process can vary, however, this can result in varied performance based on the implementation which affects memory usage, processing time, and the users currently available hardware (19). Mostly, DLA is used to calculate and explain the formation of metal dendrites produced electrochemically (17). An important problem in the electrochemical industry is finding and controlling the factors that not only lead to dendrite formation but also the factors which determine the morphology of the metal deposits. Simultaneously, Kuhn et al. (18) proved that in comparison with electrodeposition of dendrites, electroless deposition shows better agreement with DLA theory. This is because during the electrochemical deposition process multiple factors are influencing the overall formation of structure such as the presence of an electric field, diffusion field, and convective motion (18), which makes it difficult to obtain purely DLAs. In the case of contact metal reduction, the global electric field is substituted by a local electric field, which means that we use the potential difference of two redox couples to ensure the electron transfer.

Considering the mentioned theories, we use the reduction of silver on copper wires to find a reliable methodology for the stabilization of silver macrocrystals because the diffusion limits of contact reduction reactions determine the morphology of dendritic superstructure and may allow the formation of stable superstructures. The obtained porous hierarchically organized silver macrocrystals can be suitable for the SERS gas detection due to the following: It has many 'hot spots'; It is hierarchically organized and forms multiple light scattering microarrays; It is porous with better volatile molecule adsorption, and It is easy to deposit on various substrates. We focus on the formation of stable silver macrocrystals because they are of potential interest in different areas from optics to sensing and bio-detection, specifically, SERS in air, as our analytes are volatile compounds. The big challenge in detecting volatile analytes with SERS is to overcome the typical lack of interaction of the molecules with the substrate, which is totally necessary for the detection of a SERS signal (20). Despite all difficulty, it is interesting to use SERS for the detection of volatile molecules in comparison with classical methods due to factors such as size,

cost, sensitivity, speed, specificity, accuracy, reversibility, and reusability. In comparison with other techniques, gas chromatography-mass spectroscopy is currently the prime detection technology, however, it carries a correspondingly high price tag, offset by instrumentational complexity and lack of portability (21). On the other end, chemically doped detection papers are cheap, portable, and easy to use, but are relatively insensitive, non-specific, and prone to false positives (21). For this reason, SERS is an attractive alternative to conventional sensing modalities, especially due to recently opened prospects for SERS chips, which are even possible to integrate into phones for individual safety (20,22–25).

The necessary specifications and properties we consider that our SERS macrocrystal should have to be sensitive enough to detect volatile molecules are:

- It should be organized to have many 'hot spots' for maximum local sensitivity.
- It should be hierarchically organized to have multiple light scattering arrays.
- It should be porous to allow a high amount of volatile molecule adsorption.
- It should be easy to deposit on various substrates.
- It should allow multicycle detection.
- It should provide a quantitatively reproducible surface area and structure to enable calibration, focusing on individual sub-units.

In this work, we describe the reduction of silver on copper wire in which the copper precursor, copper wire has a spring geometry to obtain a 'geometry guided' 3D shape for the formed silver macrocrystal. In the time of reaction, we observed cycles of formation of porous macrocrystals due to the interplay between reaction and diffusion processes studying the process stages for the macrocrystal orientation. The initial concentration of silver nitrate solution is shown to be important to control the reduction processes and its kinetic and resulting organization of the macrocrystal. Thus, the concentration was optimized to easily manipulate the processes to obtain macrocrystals with defined porosity, their growth on any substrate, and stability to fabricate chips based on such crystals. Finally, the macrocrystals were successfully used for the detection of Benzenethiol (BT) diluted in the air by SERS.

RESULTS AND DISCUSSION

A. Formation of stable hierarchically organized macrocrystal

In our experiment a diluted solution of $AgNO_3$, 1 wt.% $AgNO_3$ was placed in a petri dish together with a shaped, spring, copper wire. We observed that the reduction of silver on copper starts immediately and evolves in time in several stages due to, probably the interplay between reaction and diffusion processes (26) which can be important to stabilize the hierarchical organization of macrocrystals.

In our case, we were able to stabilize silver macrocrystals (**Figure 1a**), in contrast to the formation of unstable silver dendritic structures on unshaped wires. Spring copper wire geometry here allowed to guide hierarchical crystal organization, from the nanoscale to macrocrystal.

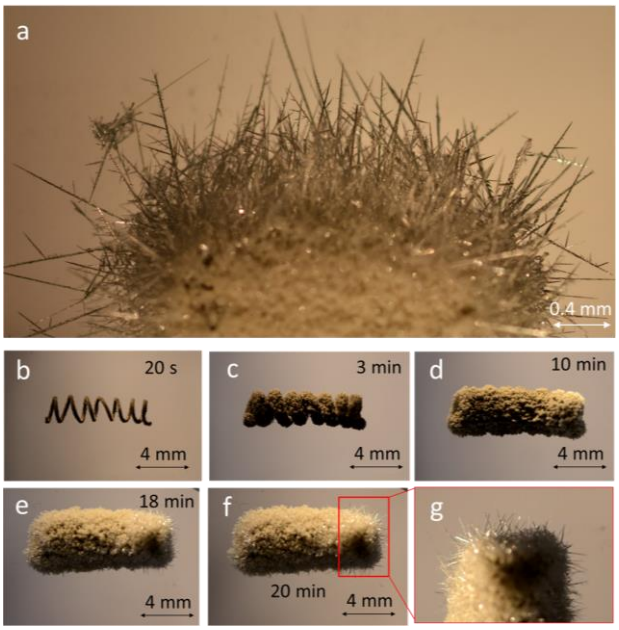

Figure 1. a) Image of silver macrocrystals formed on a copper spring in $AgNO_3$ (0.7 wt %) solution: in the centre, the finer structure is formed with well visible long dendritic spicules at the edge. (b-g) Stages of silver reduction on copper wire. The duration of silver reduction is pointed at each image: (b-d) in the first 10 min the wire is grown individually vs. (e, f) at later stages wire can be assumed as one structure independent from the initial copper geometry.

The process here was reduction of silver by copper: $2Ag^+ + Cu^0 \rightarrow Cu^{2+} + 2Ag^0$. Ag reduction on copper wire of spring geometry started immediately when the copper wire was placed into the solution (**Figure 1b**). It was seen that Ag^+ reduction on copper started with the immediate formation of very dark nucleation centres that quickly (in 1 min) turned into porous aggregates well seen as grey ones (**Figure 1 b-c**) and proven to have dendritic structure. The next

stage was the increase of crystal size. Initially, the wire grows as a 1D independent wire until the grown spring sides connect to be one unique structure (**Figure 1d**). After the system is connected to be one structure, it works cumulatively growing in many cycles with well-resolved stages of fast growth and then slowing down the visible formation of spicules (**Figure 1e-g**). At this stage silver macroobjects became white and finally, the white hierarchically organized silver macrocrystals stopped growth in 60 min and remained unchanged even after 24 hours in the case of optimized Ag concentration vs. copper (**Figure 1a**).

Also, submitting our structure under vigorous shaking, we observed that it is easy to form stable silver macrocrystals on different substrates with good adhesion such as silicon due to the porous structure of macrocrystals (**Figure 2**).

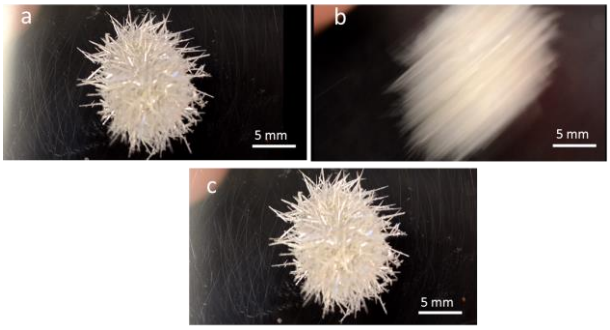

Figure 2. Images of macrocrystal in the dried state on silicon (a) before, (b) during, and (c) after vigorous shaking prove the stability of macrocrystal and its good adhesion to a substrate.

B. Key parameters for optimization of hierarchically organized macrocrystal stability

The duration of reaction and reagent concentration play key roles in the synthesis process. The chemical reaction of contact metal reduction is a heterogeneous process with two different stages: a stage of reaction that is kinetically driven and a stage of diffusion when diffusion is a limited process. The more copper ions formed during the reaction, the higher their concentration will be in the vicinity of the copper plate, which results in a more positive redox potential of copper. This can be considered as a decrease in the available electrons in the reaction zone. The concentration of Ag+ ions decreases in the reaction zone because the silver deposit takes the electrons of copper. When the concentration gradient no longer increases and the distance between formed dendritic branches is stabilized one might have a stable 3D macrostructure.

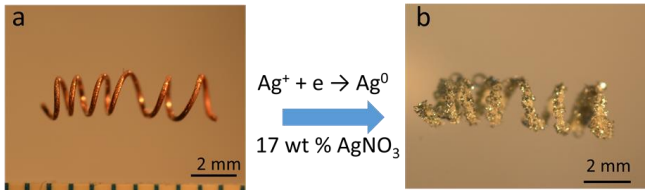

Figure 3. Images of a copper spring (a) before and (b) after 5min of silver reduction on it from concentrated, 17 wt %, $AgNO_3$ solution.

Here we follow 3D structure stabilization vs. used silver ion concentration on copper wire of spring geometry. It was found that during the reaction, the reagent concentration plays a key role in the structure growth. With the increase of the concentration of $AgNO_3$, the excess of silver ions can accelerate the reaction, resulting in more nucleation sites and a higher growth speed. For example, when the concentration of $AgNO_3$ was 17 wt %, the copper wire was covered with a dense Ag layer after 5 min with no further growth (**Figure 3**). But, when the concentration of $AgNO_3$ was decreased to 1 wt %, a stable hierarchically organized macrocrystal (**Figure 4a,b**) was obtained.

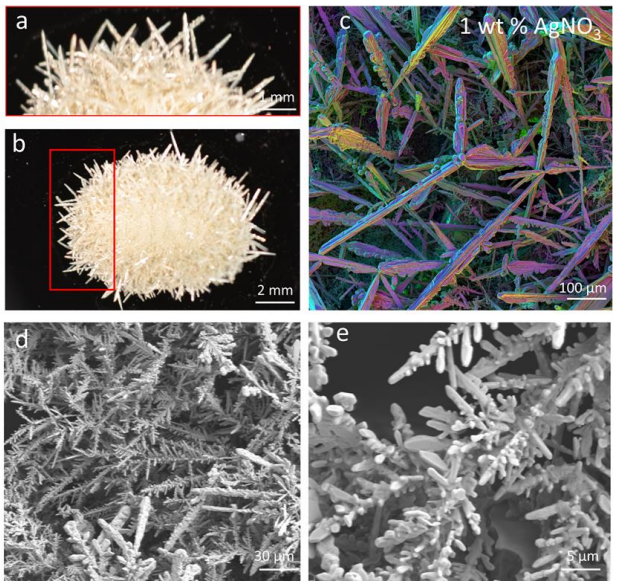

Figure 4. Hierarchical dendritic organization of silver macrocrystals formed in 1 wt % solution of $AgNO_3$ on a copper spring. (a, b) microphotographs; (c-e) scanning electron microscopy (SEM) images of dendritic silver crystals formed at different scales and resulting in complex geometry and hierarchical organization of final macrocrystal.

Typical stable macrocrystals consist of a centre skeleton of dendritic units formed at the initial stages of silver reduction on copper wire (**Figure 4 c-e**) and microspicules formed at the later stages.

The SEM images of entire crystals at different stages of growth are shown in **Figure 5a-b** after 20 min and 60 min respectively. After 20 min of growth, Cu wire

still can be seen in the centre, as well as a densely packed layer, which consists of dendritic sub-units and short microspicules. After 60 min, the microspicules become longer and stabilize the macrocrystal both in solution and in dried states.

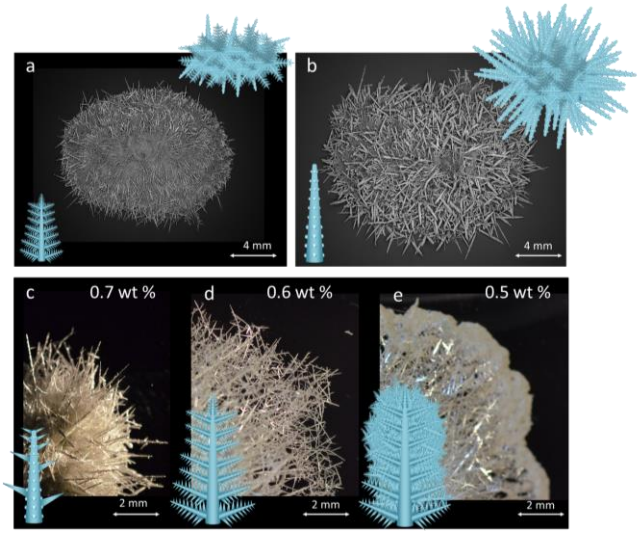

Figure 5. (a-b) Hierarchical dendritic organization, SEM, of silver macrocrystals formed in 1 wt % solution of $AgNO_3$ on copper spring (a) in 20 min; (b) in 60 min. (c-e) optical image of edge of macrocrystal vs. concentration of $AgNO_3$: (c) in 0.7 wt %; (d) in 0.6 wt %; (e) in 0.5 wt % solution of $AgNO_3$. Insets show (a,b right) schematic of organization of macrocrystal at different stages such as (a) densely packed dendrites with short spicules at the beginning stages of growth, and (b) microspicules as the main unit of macrocrystal at one hierarchy level of organization to dendrites at another higher resolution level; (a-e left) schematic of the most pronounced unit in the complex unit organization.

Further decreasing the concentration (**Figure 5c-e**) of $AgNO_3$ from 0.7 wt% to 0.5 wt% generates macrocrystals with secondary dendritic structures, not in the centre of the macrocrystal microspicules, but grown on microspicules at the edge of the macrocrystal, microcrystal edge termination. Simultaneously, the collapsed, terminated, macrocrystal edge (**Figure 5e**) can be explained by a closed cycle of sub-dendrites growth. Thus, units of dendrites are grown from spicule to dendrite, longer spicule – dendrite, until the critical concentration of silver does not allow the formation of defected-free crystals. The concentration of Ag^+ of 1wt% was optimal for the formation of a stabilized structure with open spicules without edge termination. One that is possible to dry easily, wash, and scale up. Simultaneously lower concentrations result in an edge termination that is characterized by various silver dendrites and spicules geometers.

The common feature of stable geometry is the formation of well-defined silver grains (seen in **Figure 6(I)**) vs. silver atoms missing various collapsed edge structures (seen in **Figure 6(II)**).

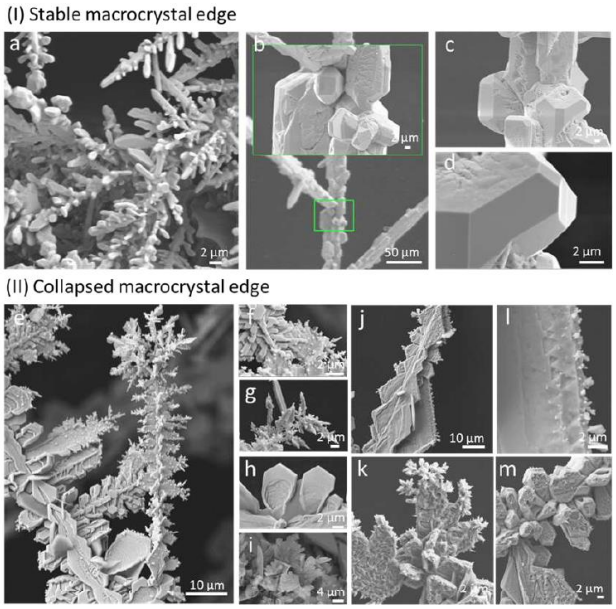

Figure 6. Overview of structures of "open"—stable macrocrystal—edge features and "closed", terminated—collapsed one. SEM image of **(I)** not identical, but similarly organized and reproducible (a) dendritic structures, (b-d) spicule's features pointing to individual microcrystals, and perfect individual crystal planes; **(II)** Various morphologies with one common feature—channels and defects in crystal planes—absence of silver atoms to build up ideal crystal grains (e) two microspicules of different organization, (f) networking in structure, (g) submicron dendritic organization, (h) hexagonal planes with cycle defects in the middle, (i) thin one dimensional sheets, (j) one more specular type, (l) higher resolution of the grain from (j) with visible steps in growth and triangle defects at the edge, (k) crystals with submicron channels and terminated with nanosized dendrites, (m) individual microcrystals common with microcrystals pointed in (**I**, b inset) also have not enough atoms to build up not defected microcrystal, with channels defects.

All the structures shown in **Figure 6(II)** had channels or defects in crystals due to lack of building material, ions. The fact can be explained by a termination of ion diffusion, which was drastically slowed down at the stage of fast crystal growth. When the crystal is growing too fast into one orientation, the lack of ions for the redox reaction occurs quickly and the structure itself "freezes" until the needed quantity of ions would be again near the edge to have a next reaction step.

The results of the research reflect the unusual processes of self-organization with the subsequent formation of hierarchically organized silver macrocrystals. Contrary to the processes of equilibrium crystal growth, when the formation of new crystal grains is attributed to nucleation processes, in our considered cases, the hierarchical organization of macrocrystals proceeds with much

more difficulties. Stages of nucleation that increase in their quantity, merging with each other, and periodic growth alternate simultaneously with a continuous change of the composition of the solution. During the precipitation of silver on copper and crystal organization, the processes of ion diffusion vs. reaction and crystallization of silver are the most important.

One of the possible reasons for a periodic growth of silver dendrites and their organization can be the following: if the kinetics of silver reduction is dependent on the ratio between Cu^0:Ag^0:Cu^+:Cu^{2+}:Ag^+ in solution during the anodic dissolution of copper and cathodic silver reduction vs. diffusion of ions, at a certain point, one of the stages becomes limiting. Considering fast release kinetics, one can assume, that diffusion is limiting. At the moment of exothermic recrystallization terminating the copper surface, the copper dissolution speeds up. The interplay between the processes determines a periodic character of silver macrocrystal organization. The tendency of silver recrystallization can be attributed to non-equilibrium conditions known, for example, also to occur during the formation of silver on electrodes during discharge (27,28).

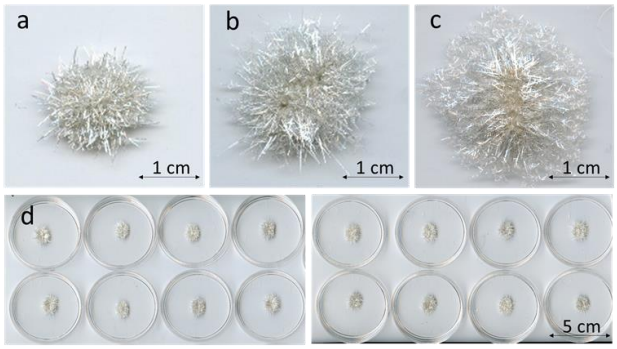

Figure 7. Silver macrocrystals grown on copper wire with 3D spring initial geometry in 1 wt.% $AgNO_3$ solution. (a-c) Images of various macrocrystals (dry state, adhered to Petri dishes) formed on copper wire of different lengths: (a) 0.6 cm; (b) 1 cm; (c) 1.2 cm. (d) It is easy to form many crystals not identical, but having similar properties and periodicity of hierarchical organization.

We also varied the copper initial length, concentration, available surface for reaction (**Figure 7 a-c**) and find, that we may, together with silver concentration, use copper to guide the formation of stable microcrystals. Thus, after the silver to copper concentration ratio was optimized, we were able to form reproducible macrocrystals, having the same organization units at a different scale. In the end, reproducible macrocrystals were formed, if the parameters were constant—not identical, but having the same hierarchical organization of dendrites and spicules at different sizes from nano- to micro-scales (**Figure 7d**). These parameters were found for copper in the geometry of spring for 5.4 cm diameter of the petri dish, 1wt% of $AgNO_3$, and 10 mL of solution.

Figure 8. The blue color of the solution from the crystal is due to Cu^{2+} that is released to the solution during silver reduction and redox reactions between Cu^0 and Ag^+.

After the formation of macrocrystals, the solution can be taken out and its blue color (**Figure 8**) indicates the presence of Cu^{2+}. The finished dried macrocrystals had very good adhesion to any substrate where they were grown on.

C. A macrocrystal active for SERS detection of gas molecules

The SERS sensitivity of the prepared silver macrocrystal was investigated by using benzenethiol as a volatile probe molecule. The samples were incubated overnight with BT (10 µL, 10^{-3}M) in a closed Petri dish. Later, the material was studied with three different laser lines (514, 633, and 785 nm) with either a confocal microscope objective (50x) or a non-confocal macrosampling lens. **Figure 9a** shows the three different positions (top, medium, and bottom) where SERS was acquired with the 50x objective, and the volume cylinder acquired with the lens. All the excitation lines produce the characteristic SERS spectra of BT (**Figure 9b**) with bands typically at 998 cm^{-1}(ring stretching band), 1022 cm^{-1}, and 1072 cm^{-1} (29). However, signal intensity differs both with the excitation laser line and with the objective/lens and position (**Figure 9c**).

For the laser light, it becomes obvious that the signal remarkedly increases as the light redshifts. This is

consistent with the typical localization in effects in spiked particles as a consequence of the electromagnetic localization in the apex of those tips (30). On the other hand, intensity not only also increases when using the lens rather than the objective but its standard deviation decreases. This fact can be explained considering, first, the excitation volume of the objective/lens (1 μm^2 x ~1 μm for the objective Vs. 1 mm^2 x ~2 mm for the lens) and, second, the three-dimensional nature of the material with the subsequent generation of three-dimensional hot spots (31).

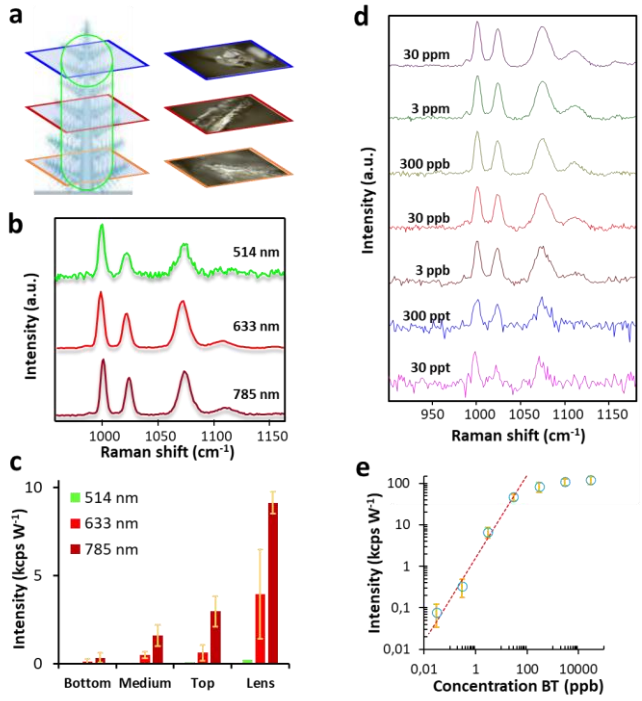

Figure 9. (a-c) SERS characterization of the sample with benzenethiol and three laser lines. (a) Representation of the 3 planes used to do the characterization of the spicules. (b) SERS spectra obtained with the 3 different lasers. (c) Graph representing the amount of SERS intensity by using a confocal 50x objective focused in three different planes or using a macrolens. (d) SERS ultradetection of benzenethiol in the gas phase. Each spectrum represents the different concentrations of BT in the air used to incubate the sample. (e) Graph representing the tendency of the SERS intensity depending on the concentration of BT used to incubate the macrocrystal.

Thus, to study the potential use of these materials for gas sensing we chose the infrared illumination with the lens. For detection in the gas phase, the samples were enclosed in a Petri dish with a drop in the side of diluted BT (10 µL), with concentrations ranging from 10^{-3} M (30 ppm) to 10^{-11} M (0.3 ppt). Notably, the characteristic SERS spectra of BT can be unambiguously recognized down to the ppt regime (**Figure 9d**). The representation of the concentration with the intensity (**Figure 9e**) shows a linear dependence at low concentrations (from 30 ppt to 3o ppb) with a plateau for higher concentrations, signal of the saturation of the most optical efficient regions (tips) which also are the most reactive (32).

EXPERIMENTAL SECTION

A. Synthesis of silver macrocrystal.

A diluted solution of $AgNO_3$, 1 wt.% $AgNO_3$ was placed in a petri dish together with a shaped, spring, copper wire. The $AgNO_3$ concentration was accurately controlled, as well as the morphology, sizes, and reproducibility. The reaction was at room temperature without stirring. After the formation of stable macrocrystal, the solution was removed (solution had blue color due to Cu^{2+} ions). Then, the macrocrystals were washed two times gently using deionized water and then dried in air at room temperature overnight.

B. Macrocrystal codification with BT

The Ag macrocrystals samples were incubated overnight in big Petry dishes with different concentrations of BT, from 10^{-3} M to 10^{-11} M in ethanol. One drop of BT (10 µL) of different concentrations is deposited in Petry dishes to produce a vapor codification of the structure because of the volatile property of BT.

C. Characterization

The different pictures are obtained with an environmental scanning electron microscope (JEOL 6400 or a field emission scanning electron microscope (Themo Fisher Scios 2). SERS spectra were collected in backscattering geometry with a Renishaw Invia Reflex system equipped with a 2D-CCD detector and a Leica confocal microscope. Excitation of the sample was carried out with either a 514, 633, and 785 nm laser line with the acquisition time ranging from 1 to 10 s and the power at the sample of about 0.15 and 3 mW. The laser was focused on the sample in three different planes with a ×50 objective or using a macrolens.

CONCLUSIONS

We were able to form stable hierarchical silver macrocrystals with dendritic silver as a sub-unit with a fast, easy model reaction. The concept of such crystal organization can be expanded onto crystallization, where the interplay between

reaction and diffusion occurs, so the chemistry in solution allows to optimize the process and to generate a library of achievable macrocrystals by variation of precursor size, shape, metal ion concentration and duration of the process. These macrocrystals can be formed on various substrates: glass, plastic, silicon, papers, cellophane, and chips for integration into portable devices with potential application in different areas. Here we demonstrated that the system is active for SERS detection of gas molecules in the air. In the end, macrocrystals were sensitive to detect gas molecules because of their organization into a dense pack of 3D 'hot spots'; to have multiple light scattering through hierarchically organized macroarray, and a high amount of molecule adsorption. For this reason, they provide a quantitatively reproducible surface area and structure to enable calibration focusing on individual sub-unit spicules.

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