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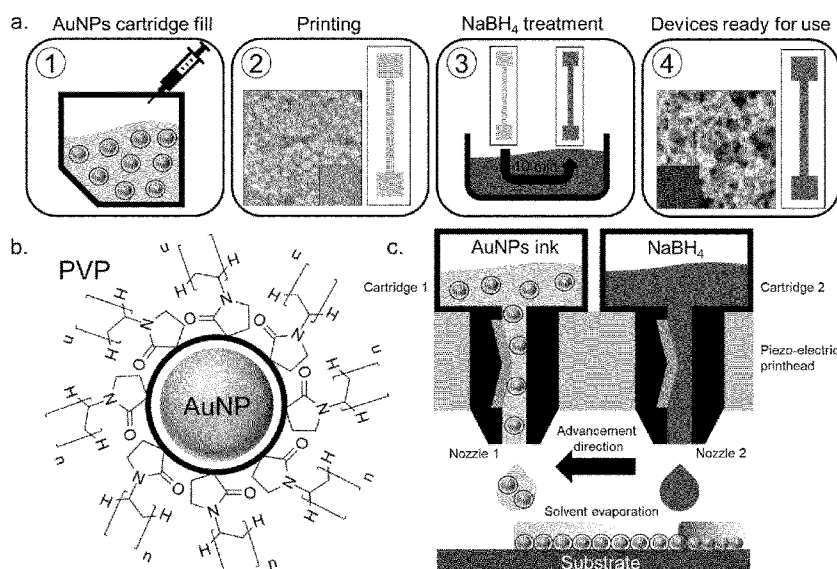
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(54) Title: A SINTERING METHOD FOR OBTAINING A NANOSTRUCTURED, POROUS AND CONDUCTIVE FILM OF NOBLE METAL NANOPARTICLES, NANOSTRUCTURED, POROUS AND CONDUCTIVE FILM OF NOBLE METAL NANOPARTICLES AND USES THEREOF

FIG 1



(57) Abstract: The present invention is directed to a novel sintering method for obtaining nanostructured, porous and conductive noble metal nanoparticle films on different substrates which is suitable for room-temperatures conditions. The sintering is a chemical sintering. The invention is also directed to a nanostructured, porous and conductive noble metal nanoparticle film obtainable by the sintering method, as well as their uses for electrochemical and/or photonic biosensing in, for example, flexible electronics.



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A SINTERING METHOD FOR OBTAINING A NANOSTRUCTURED, POROUS AND
CONDUCTIVE FILM OF NOBLE METAL NANOPARTICLES, NANOSTRUCTURED,
POROUS AND CONDUCTIVE FILM OF NOBLE METAL NANOPARTICLES AND USES
THEREOF

Field of the invention

The present invention is in the nanostructured conductive metallic materials field.

In particular, the present invention relates to a novel sintering method capable of preparing nanostructured, porous and conductive noble-metal nanoparticle films, suitable for inkjet printing nanostructured, porous and conductive metal nanoparticle films.

According to the present invention, the sintering method is a chemical sintering that chemically sinters the nanoparticles and, almost at the same time, nanostructures the film.

The present invention also relates to the nanostructured, porous and conductive noble-metal nanoparticle film as well as to a device comprising the same and uses thereof.

Background of the invention

In the last decade, inkjet printing became a popular fabrication technique in the fields of flexible electronics and biosensing, taking advantage of nanofunctional inks, typically composed of metal nanoparticles (MNPs). Despite its flexibility, high throughput and low cost, one of the unresolved issues of this technique is the need for additional post-print treatments to make the printed patterns conductive. Such post-print treatments are sintering methods.

Typically, sintering is performed by thermal annealing, plasma treatments, or photonic and microwave irradiation. The choice is typically based on the type of printing substrate, or time-related requirements, e.g., in mass fabrication lines a photonic approach is usually preferred.

However, flexible electronics and biosensing, often based on plastic or paper substrates, find obvious issues regarding thermal annealing, due to the temperatures required for that.

Alternative chemical sintering strategies have been explored. However, these alternatives often are based on the use of chemical agents, such as gases, ionic compounds, and salts to induce the metal nanoparticles de-capping/sintering, particularly used for silver nanoparticle-based inks, and not suitable for scaling at industrial scale.

In this sense, WO2022157725 discloses a silver nano-ink composition comprising plurality of mixed-phase capped nanoparticles, at least one solvent and at least one excipient. The mixed-phase capped nanoparticle comprises of 5 to 95 vol. % silver phases, and of 5 to 95 vol. % silver oxide phases. The method for obtaining the silver nano-ink composition comprises act of mixing plurality of mixed-phase capped nanoparticle with at least one solvent and at least one excipient onto a substrate for forming a conductive silver pattern through thermal curing at a temperature ranging from 40°C - 150°C. The reaction needs chemically unstable metal nanoparticles to work. In fact, the silver nanoparticle undergoes redox reaction in the media triggered by partially oxidized particles and a chemical reducing agent. Energy is needed to initiate the process and the reduction of the oxide layer takes place all over the nanoparticle surface. Unfortunately, this does not allow control over the nano-structuration of the structure.

On the other hand, 2009 Coutts *et al.* reported the use of NO₂ gas for the sintering of printed films based on thiol-stabilized AuNPs. This procedure implies the use of HNO₃ and copper for the *in-situ* formation of the gas, and its use is limited to thiol-stabilized nanoparticles. Unfortunately, the proposed method, despite making the film conductive causes a nanostructure and porosity reduction, with the consequent reduction of the surface-to-volume ratio, in turn resulting in scarce electrochemical performances.

The patent KR10-1481629 discloses a conductive metal nanoparticle ink and a method for preparing the same, in which a low temperature sintering agent is added and mixed to a dispersant-containing ink having a firing temperature of 200°C. The method reduces the typically temperatures of 250°C - 600 °C to 150°C. Several metals and alloys are listed (claims of KR). However, all the examples are performed using silver nanoparticles, which are the most desirable in this method. The sintering temperature is of 150°C for 60 minutes (Figure 2 of KR). This method uses vaporization energy of the sintering agent added to the ink. The sintering agent can be sodium borohydride. Sodium borohydride does not react directly with the materials. The system is heated to about 150°C to initiate the reaction, the temperature being a necessary condition to dissociate the hydrogen producing reagent. This being the active species inducing the destabilization of the polymeric coating of silver nanoparticles. The sintering occurs mainly thanks to the applied temperature. This method is not suitable to be scalable for several reasons, for example, it requires several steps which limits its application on an industrial scale.

The patent CN110461101 discloses a room temperature sintering method of nanocopper conductive ink. Not nanostructuring is conferred to the films. Although this method is performed

at room temperature, it is not suitable for electrochemistry because copper oxidizes easily. No other metal than copper is described, nor suggested. The method requires multiple operations [steps 1) to 5)] that limits its application at industrial scale.

The patent US2022/010160 discloses nanoparticles of a copper alloy. In particular, it is disclosed a low temperature sinterable copper nanoparticle or nanowire comprising gold, zinc, nickel, tin, or aluminum as an alloying metal and a capping agent. The method is performed decorating nanowires with nanoparticles comprising an alloy of at least 5% copper, capped with a capping agent, by a reaction solution aging and annealing procedure; printing the decorated nanowires on the porous substrate; and allowing the decorated nanowires to sinter at a temperature below 150°C, to form the conductive coating. The nanoparticles include copper that oxidizes easily and therefore having drawbacks in electrochemistry.

Therefore, methods described in the state of the art, to one degree or another, present certain disadvantages and limitations.

In view of the state of the art, there is still the need for a nanostructured, porous and conductive metallic nanoparticle film suitable for electrochemistry, whose method for obtaining it be capable of sintering the film onto substrates of low melting point such as of plastic or paper nature.

It is also still the need in the art to provide a method capable of modulate such nanostructuration, porosity and conductivity, at the film, so the film be suitable for optical, electrical and/or electrochemical applications.

Additionally, most of the methods in the art use either expensive equipment, multiple operations or high temperatures, which hinder the possibility of using most of the flexible plastic/paper substrates at room temperature, and which hinder to scale the method at industrial scale at low cost.

Therefore, it is still a need to provide a sintering method not requiring expensive equipment and be suitable for scalable at industrial level.

Thus, there is still the need to provide a method which overcomes at least one of the above-mentioned drawbacks in the art.

Moreover, it is desirable to provide a sintering method that overcomes one of the main drawbacks in the art, that is, where the typically porous, and not conductive, nanostructure defined by the deposited metal nanoparticles is sacrificed to obtain a conductive, and much

less porous, surface.

Thus, there is still the need to provide nanostructured materials, having conductivity and improved porosity, which is highly desirable in electrochemistry for applications related to, for example, healthcare, energy, and environmental and food quality monitoring.

- 5 It is also desirable to provide a sintering method suitable for inkjet printing nanostructured, porous and conductive metal nanoparticles films.

Description of the invention

The present invention was made in view of the prior art described above, and the object of the present invention is, in a first aspect, to provide a sintering method capable of preparing
10 nanostructured, porous and conductive noble metal nanoparticle films having improved porosity (nano-porosity) in a rapid and an easily scalable method at industrial level.

In particular, the first aspect of the present invention is to provide a sintering method for preparing a nanostructured noble-metal nanoparticle film, which is conductive and has improved porosity.

- 15 To solve the problem, in a first aspect, the present invention provides a sintering method, which is a chemical sintering method and is characterized in that sintering the noble-metal nanoparticles and nano-structuration of the film are carried out in a single chemical reaction, at the same time.

The method includes:

- 20 - noble metal nanoparticles capped with a capping agent,
- sodium borohydride (NaBH_4) in a determined concentration,
- preparing a noble metal nanoparticle solution, wherein the noble metal of nanoparticles is selected with the condition that it has catalytic activity with NaBH_4 ,
- preparing a sintering solution including NaBH_4 as sintering agent, optionally with a stabilizing
25 agent of NaBH_4 in solution,
- sintering of the noble metal nanoparticles and nanostructuring of the film in a single chemical reaction,
- the single chemical reaction is governed by the NaBH_4 concentration and by the fact that NaBH_4 acts simultaneously as sintering and de-capping agent,

- the chemical reaction is catalyzed by the noble metal of the nanoparticles.

As NaBH_4 acts simultaneously as sintering and de-capping agent, during the method, NaBH_4 removes the capping agent of the capped noble metal nanoparticles, allowing NaBH_4 to come into contact with the noble metal of nanoparticles to instantly initiate an intrinsic exothermic chemical reaction at the interface of the nanoparticles that creates chemical junctions between the nanoparticles, forming wells and cavities that nanostructure the film.

Unexpectedly, the authors of the present invention have found that, contrary to the state of the art, the method is capable of preparing a film of nanostructured noble metal nanoparticles, in which as the conductivity improves, the nano-porosity also improves, thus overcoming one of the main drawbacks of the state of the art.

Surprisingly, the authors of the present invention have found that the single chemical reaction is almost instantaneous and induces the sintering between the nanoparticles and at the same time the nano-structuration in the film with improved nano-porosity compared to the nanostructured films of the state of the art.

The chemical sintering is initiated using the intrinsic chemical energy generated between NaBH_4 and the capping agent during removal of the capping agent of the noble metal nanoparticles, the chemical reaction being catalyzed by the selected noble metal of the nanoparticles.

Advantageously, the chemical sintering does not require external energy sources to carry out the chemical sintering, so the method can be performed at room or ambient temperature.

Advantageously, the method is carried out in few minutes and even in real-time, which allows it to be integrated into an inkjet printing method suitable for consumer printers.

Also advantageously, the sintering method in accordance with the first aspect is of easy application, saves energy, uses standard and available chemical reagents, and inexpensive equipment.

Additionally, the sintering method in accordance with the first aspect of the present invention is also capable of changing the kinetics of the catalytic reaction of the single chemical reaction to finely module the conductivity and morphological properties of the nanostructured surfaces of the film at the desired properties for a particular application.

To that purpose, the concentrations of the reactants employed in the single chemical reaction are essential. However, the reactant that actually governs the single chemical reaction is the

NaBH₄ that simultaneously acts as sintering agent and as de-capping agent.

The authors of the present invention have been found that increasing the concentration of NaBH₄ results in a more efficient de-capping, rather than more extended nano structural changes, allowing the NaBH₄ concentration to modulate the properties of the film. The mechanism of the de-capping might explain the peculiar modes of coalescence the noble metal nanoparticles undergo in the invention.

The authors of the present invention have also been demonstrated that the concentration of the capping agent does not affect the properties of the film. In a similar way, the stabilizing agent does not contribute to the chemical reaction, but only stabilize the NaBH₄ in the solution to avoid spontaneous dissociation.

In a second aspect, the present invention is directed to a nanostructured, porous and conductive noble metal nanoparticle film obtainable by the sintering method of the first aspect of the present invention.

Surprisingly, the conductivity and porosity of the film can be modulated governed by the concentration of NaBH₄ used during the method to obtain the film.

In a third aspect, the present invention is directed to a consumer printer that uses the method according to the first aspect of the present invention.

In a fourth aspect, the present invention is directed to a device that comprises a nanostructured, porous and conductive film of noble metal nanoparticles of the second aspect defining a conductive pattern onto a substrate.

In accordance with the present invention, the substrate may be of polymeric or paper nature.

Advantageously, the substrate may be a substrate with a melting point temperature as low as room temperature.

The conductivity and morphological properties of the patterned nanostructured film can be modulated as well.

Therefore, the device can be provided with the desired electrical, electrochemical and/or photoelectrical properties for its specific use.

In still a further aspect, the present invention is directed to the use of said nanostructured, porous and conductive noble metal nanoparticle film and/or to the use of said device for electrical, electrochemical and/or photoelectrical applications.

Definitions

According to the present invention, the expression “room temperature” or “ambient temperature” means the same and encompasses any room or ambient temperature value comprised between 4°C and 45°C, preferable from 10°C to 35°C.

- 5 According to the present invention, the expression “low melting point temperature” in connection with a substrate means that the material of the substrate has a temperature melting point lower than 120°C. Therefore, the substrate may be a substrate with a melting point temperature as low as room temperature.

According to the present invention, the expression “average particle size of 15 nm”, where “15”
10 is a variable for the number of nanometers, is defined herein as the average particle size, as measured by any conventional means such as dynamic light scattering or microscopy, of a sampling of particles wherein the average is of about 15 nanometers in diameter, assuming for purposes of the calculation that the particles are approximately spherical and have an approximate diameter. Methods used to measure particle size include dynamic light scattering,
15 scanning electron microscopy or transmission electron microscopy. According to the present invention, the sampling of nanoparticles includes nanoparticles sizing between 2 nm (minimum dimension) and 50 nm (maximum dimension) measured by electron microscopy. In an embodiment, the sampling of nanoparticles includes nanoparticles sizing between 10 nm and 20 nm measured by electron microscopy. As the inventors have been demonstrated in an
20 embodiment of the present invention, gold nanoparticles are spherical and with a mean diameter size of 15 ± 5 nm.

According to the present invention, the term “polydispersity index” linked to any average particle size represents the deviation of the dimensions of the particles with respect to the average value. The greater the polydispersity index the broader the distribution of dimensions
25 of the particles. The lower the polydispersity index the more consistent the particles dimension. In other words, representing the particles dimensions in a histogram, the result is typically resembling a gaussian distribution, where the peak represents the average particle side and the standard deviation is correlated with the polydispersity index.

According to the present invention, the expression “catalytic activity” is understood in
30 connection with nanoparticles of noble metals. As it is known in the art, the catalytic activities occur at the surface, because the surface atoms have tendencies for chemisorption of gas molecules. It can be considered as a process with inputs and outputs. Electrons are a form of energy, in the case of electrocatalysis; the solid material simultaneously acts as an electrode and catalyst surface.

Brief Description of the Drawings

To better understand the description made, a set of drawings has been provided which, schematically and solely by way of non-limiting example, represents practical cases of various embodiments.

5 **Figure 1** depicts a general scheme of two embodiments of the invention, in which printing and sintering is performed by means of dipping (a: 1 to 4) using PVP capped gold nanoparticle (b) *versus* real-time integrated inkjet printing and sintering of gold nanoparticle films using a consumer printer (c).

10 **Figure 2** depicts SEM images (a-f) at different magnifications (g-l) 200 nm and (m-r) 50 nm of the sintered AuNPs-film treated with different concentrations of NaBH₄ in accordance with the examples.

Figure 3 depicts a time-concentration SEM study of the morphological effects of the NaBH₄ treatment at different NaBH₄ concentrations for times spanning from 1 to 60 minutes.

15 **Figure 4** depicts an EDX spectra of the pristine (a-b) *versus* the AuNPs film treated with 1M of NaBH₄ (c-d). All the expected elements were found in the samples, with traces of the elements present in the plastic substrate used in the study for the printing (Al).

20 **Figure 5** depicts elemental maps and XPS survey of the AuNPs films treated with the different concentrations of NaBH₄ (a); pristine refers to the film not treated with the sintering agent. Compositional information of the gold peak for the different concentrations of the NaBH₄ used (b); the ratio and the atomic% of the main Au0 4f peak remain constant, even after increasing the concentration of NaBH₄. The XPS measurements of the gold 4f_{5/2} and 4f_{7/2} peaks (c) showed a constant separation and the intensities do not appear to change proportionally with the NaBH₄ concentration.

25 **Figure 6** depicts enhanced Surface Raman Spectroscopy (SERS) using Rhodamine as a probe for the films treated with different concentrations of NaBH₄. Highlighted are the peaks characteristic of the rhodamine around 1600 cm⁻¹.

Figure 7 depicts electrochemical characterization of the films using ferro/ferricyanide 5mM at the different scan rates and methylene blue (MB) at the different concentrations of NaBH₄. The cathodic peak intensity has been made positive for graphical reasons.

30 **Figure 8** depicts substrate effect on the inkjet sintered films on Kapton for three situations: non-sintered (a), sintered with the sintering method using dipping (b), and sintered using inkjet printing with consumer printer (c).

Figure 9 depicts the sheet resistance values for the 20 mm AuNPs-ink printed squares (in red)

and resistance values of the 20 mm printed lines (in black) calculated and measured, after the 10 min treatment with different concentrations of NaBH_4 (a). The top right insets in the two plots show the layouts of the respective printed structures. Data are expressed as mean value $\pm$ standard deviation, ($n = 3$). Sheet resistance values for the 20 mm squares, after real-time inkjet sintering at increasing numbers of layers (b).

Figure 10 depicts an image of Cross-section SEM (Scanning Electron Microscopy) micrograph of the sintered gold nanoparticles (AuNPs) films. Carbon and tungsten layers have been deposited beforehand on the films in order to facilitate the process of cross-section engraving with the FIB (Focus Ion Beam lithography).

Figure 11 depicts a schematic representation of the working principle of the electrochemical sensing platform. In step 1, the viral RNA is dropped onto the electrode. In step 2, the NFC potentiostat allows to perform the electrochemical measurements via a smartphone.

Figure 12 depicts a bare IPE Characterization: (a) Image of IPE. (b) SEM image of the IPE. (c) Design of the IPE. (d) Active area and roughness of the IPEs compared to commercial screen-printed electrodes (SPEs) of comparable geometric area.

Figure 13 depicts IPEs cyclic voltammetry measurements in $[\text{Fe}(\text{CN})_6]^{3-/4-}$ 2.5 mM in PBS 10 mM, at different scan rates (a) and Randles-Sevcik plots comparing IPEs (in black) versus SPEs (in grey) (b, c, d).

Figure 14 depicts quantitative simultaneous detection of synthetic fragments of (a) ORF1ab gene and (b) N gene. (c) Kinetic of hybridization when the sensor is tested with a saturating concentration (i.e., 3 μM) of target (i.e., ORF1ab in blue, N gene in red).

Figure 15 depicts a histogram of the noble metal nanoparticles of the invention. The number-weighted average diameter was measured by direct determination using transmission electron microscopy (TEM) measuring the diameter of 163 nanoparticles ($N = 163$) from the TEM micrographs using ImageJ. The values have been plotted in Origin software using the histogram function and fitted with a Gaussian curve. The average diameter has been calculated by extracting the maximum value of the fitted Gaussian curve.

Detailed Description of the Invention

Hereinafter, the present invention is described in more detail.

The sintering method is described in the first aspect, and claimed in claim 1.

As described above, the sintering method is characterized in that sintering is a chemical sintering in which the nanoparticles are chemically sintered and the film is nanostructured, both in a single chemical reaction. The single chemical reaction can be carried out in either an

aqueous media or a solvent media.

Firstly, the fact that sintering and nano-structuring are carried out in a single chemical reaction allows the method times to be considerably reduced and makes it easier for the method to be scaled up to an industrial level.

5 Advantageously, the method does not require expensive equipment or multiple steps.

The core of the invention relies on the collection of chemical energy at the junction between the nanoparticles, taking advantage of their catalytic activity, from a specific exothermic reaction, and using this energy to chemically sinter the nanoparticles. Since the reaction strictly occurs at the nanoparticle interphase, it is rapid and effective. When all the active sites have
10 reacted, the reaction stops. This creates a unique conductive network of metal noble nanoparticles, connected in a web structure which morphological properties can be finely tuned by the concentration of the reagents, governed by the sodium borohydride concentration.

Advantageously, this happens avoiding the collapse of the pores in contrast with what normally occurs with chemical sintering methods of the state of the art.

15 Unexpectedly, during the method to obtain the film, the oxidation state of the noble metal of nanoparticles remains unchanged.

The sintering method further comprises the steps of:

- i)- depositing as a film the noble metal nanoparticle solution onto a substrate; and
- ii)- impregnating the deposited nanoparticle solution with the sintering solution.

20 Nanoparticle solution

As described above, the noble metal nanoparticle solution is prepared comprising noble metal nanoparticles in a solution media.

Also, the noble metal of nanoparticles has to be selected with the condition that it has catalytic activity with NaBH_4 .

25 The single chemical reaction depends on the catalytic activity of the noble metal of nanoparticles with the NaBH_4 . Therefore, the noble metals without specific catalytic activity such as, for example, Ag do not lead to sintering and nano-structuring via the chemical sintering method of the present invention.

Preferable noble metal nanoparticles consist of gold nanoparticles or of platinum
30 nanoparticles. The nanoparticles are of pure gold or platinum, the most used noble metals in electrochemistry as working electrodes materials.

Optionally, the nanoparticle solution can be prepared previously.

The nanoparticle solution comprises the noble metal nanoparticles in a concentration from 1% to 40% in weight. The noble metal nanoparticles concentration can be as low as 1% and up to 40% in weight in accordance with the desired properties of the film.

The noble metal nanoparticles are capped with a capping agent.

- 5 Preferable capping agent is polyvinylpyrrolidone (PVP), also commonly called polyvidone or povidone, that is a water-soluble polymer made from the monomer N-vinylpyrrolidone.

Thus, the nanoparticle solution comprises the noble metal nanoparticles with a polymeric capping layer to stabilize the colloidal dispersion against aggregation in water-based solutions. The concentration of the capping agent affects the concentration of the reactants necessary
10 for the reaction, the higher the concentration of the capping agent, the higher the concentration of the needed sintering agent (NaBH_4), but the concentration of the capping agent does not affect the electrical, electrochemical, and structural properties in the obtained film.

The noble metal nanoparticles can have a particle size from 2 nm to 50 nm, preferable from 10 nm to 20 nm. The average particle size is 15 nm measured by transmission electron
15 microscopy with a polydispersity index measured with dynamic light scattering of about 0.18.

In an embodiment, the gold nanoparticles are spherical and with a mean diameter size of 15 ± 5 nm.

Sintering solution

The sintering solution is prepared including sodium borohydride (NaBH_4), optionally with a
20 stabilizing agent of NaBH_4 in solution.

Optionally, the sintering solution can be prepared previously.

The sodium borohydride (NaBH_4) is the unique sintering agent in the solution present in a concentration from 0.001M to 1M, optionally with the stabilizing agent of NaBH_4 in solution.

It has been found that the NaBH_4 concentration has a threshold at 0.1 M from which, by
25 increasing the concentration of NaBH_4 from 0.1 M to 1M, the film also increases conductivity and surface-to-volume ratio, and *vice versa* by decreasing the concentration of NaBH_4 from 0.1M to 0.001M (Table 1).

The nanoparticle solution and/or the sintering solution may further include solvents such as ethylene glycol (EG), ethanol and isopropyl alcohol. Ethylene glycol (EG) can be added to the
30 solution to increase the viscosity and ethanol and isopropanol act on the surface tension.

The reaction is suitable in a media including water, ethanol, methanol, isopropanol alcohol, ethylene glycol, pure or mixed or other solvents.

On the other hand, the authors of the present invention have found that the single chemical reaction is not particularly sensitive to temperature because it relies on the nano-chemical environment at junction between the nanoparticles.

Advantageously, the sintering method can be carried out at ambient/room temperatures, in which the single chemical reaction allows a simple and rapid fabrication of nanostructured, porous and conductive noble metals nanoparticles films on different substrates, so various types of substrates are suitable for use in the method.

Therefore, the sintering method is suitable for any type of substrate, even substrates of low melting point temperature, such as those of a polymeric or paper nature, in particular PET, PEN, Kapton, normal paper, as long as they do not react with the sodium borohydride as sintering agent.

Thus, the method according to the first aspect of the present invention can be carried out at room temperature, which includes a temperature between 4°C and 45°C, preferable between 10°C and 35°C. Temperatures higher than 45°C and up to 80°C can be work as well. However, at temperatures of 80°C and higher, the reaction is violent and damages the printed structures.

The fact that the sintering method can be performed at ambient/room temperature allows the noble metal nanoparticle film to be impregnated with the sintering solution using several techniques known in the art that include, but are not limited to, immersion (dipping), inkjet printing, drop casting, aerosol spraying, which are easily scalable and can be automated.

In one embodiment, the noble metal nanoparticles films deposited in the first step are immersed into the sintering solution for 10 min for impregnating the deposited films, which resulted the time after which no relevant changes in the properties of the obtained nanostructured, porous and conductive noble metal nanoparticle films have been recorded. In fact, the reaction is almost instantaneous and up to 80% of the final film conductivity can be obtained simply impregnating by immersing and removing the film in the sintering solution. Preferably, immersing includes water washing the film after the removal from the sintering solution.

The sintering method according to the first aspect can be implemented to print patterns of the films using consumer printers.

Thus, it is a further aspect of the present invention to provide a consumer printer using the method according to the first aspect of the present invention.

In this aspect, the consumer printer is provided with at least two cartridges connected to a single printhead, wherein the first cartridge is loaded with a noble metal nanoparticle solution as a first ink, and the second cartridge is loaded with a sintering solution, optionally with a

stabilizing agent of NaBH_4 in solution, as a second ink, that in use, on a suitable substrate for printing a designed pattern, comprises printing the first ink in accordance with the designed pattern on the substrate, and overprinting the first ink with the second ink, thereby the pattern forms a film that sinters and nanostructures in a single chemical reaction.

- 5 In an embodiment, the sintering method is carried out using a consumer printer. The consumer printer has multi-ink (color) cartridges connected to a single printhead with separated nozzle arrays can be used. The loading of the ink solution (nanoparticle solution) in a color channel, for example cyan, and of the sintering solution in a second one, for example yellow, allows for the implementation of sintering of the printed film in mixed color, for example, green. The film
10 is impregnated with the desired amount of sintering solution to initiate the chemical reaction. The desired amount can be more than one layer of the sintering solution. In this embodiment, the preferable sodium borohydride concentration is >0.1 and up to 1M .

A conductive pattern is then obtained by means of the consumer printer.

- Advantageously, a real-time sintering via inkjet printing can be performed with the sintering
15 method defined in the first aspect of the present invention.

The authors of the present invention have found that the selection of an appropriate concentration subrange of the sintering agent NaBH_4 results in films that share surface morphology and conductivity properties.

- Advantageously, the films reveal similar optical, electrical, and electrochemical properties in
20 said concentration subranges, which allows finely tuning the surface morphology and conductivity properties of the films. Table 1 below describes the concentration subranges as well as their effects on the optical, electrical, and electrochemical properties and how such concentration range influence on the film structure.

Table 1

Concentration of NaBH_4	Effect on the properties	Effect on the structure
0.001 – 0.01 M	High SERS effect, low conductivity, low electrochemical properties	Low porosity, constant nanoparticle size
>0.01 – 0.1 M	Enhanced SERS effect, medium-high conductivity, medium-high electrochemical properties	Medium – high porosity, creation of the network of particles
>0.1 – 1 M	Low SERS effect, high conductivity, high electrochemical properties	High porosity, extended network of particles

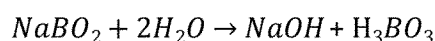
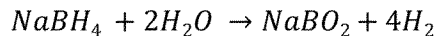
Therefore, the method is capable of modulate the conductivity, porosity and light absorbance of the film by varying the concentration of NaBH₄.

Advantageously, the time treatment of the NaBH₄ does not modify substantially the morphology properties of the nanostructured, porous and conductive noble metal nanoparticle film obtainable by the sintering method of the first aspect of the invention. This proves the suitability of the sintering method for on-line noble metal nanoparticle film inkjet printing using consumer printers.

For consumer printers, it is preferable the presence of the stabilizing agent.

In an embodiment, the sintering solution includes sodium borohydride (NaBH₄) and a stabilizing agent of the sodium borohydride in solution. The stabilizing agent does not contribute to the chemical reaction but only stabilize the NaBH₄ in the solution to avoid spontaneous dissociation.

Preferable stabilizing agent is sodium hydroxide (NaOH). The sodium hydroxide can be present in a concentration from > 0 to 1M. The high NaOH concentration can be used to further stabilize the NaBH₄, thereby modifying the equilibrium of the dissociation reaction at high pH values.



A low concentration of NaOH, for example, just 0.2% of NaOH in water solution, is enough to stabilize the NaBH₄ solution for several weeks without losing the significative amounts of NaBH₄ by spontaneous dissociation.

As described above, in a second aspect, the present invention is directed to a nanostructured, porous and conductive noble metal nanoparticle film obtainable by the sintering method of the first aspect of the present invention.

The nanostructured, porous and conductive film of noble metal nanoparticles has modulable conductivity and porosity.

Advantageously, the nanostructured, porous and conductive nanoparticle film of the second aspect is conductive and porous, and such properties can be finely modulated to the desired values.

The nanostructured, porous and conductive film of noble metal nanoparticles has a network structure with extended nano-structuration inside the film, in which the noble metal nanoparticles are organized governed by the concentration of NaBH₄ used during the method

to obtain the film.

As it can be seen in Figure 10, the feature's characteristics of the nanostructure are present deep inside a gold nanoparticle film after sintering on a Mitsubishi substrate. The carbon and tungsten layers have been deposited beforehand on the films in order to facilitate the process of cross-section engraving with the FIB (Focus Ion Beam lithography), and to ensure no damages to the film are introduced during the cutting. The gold nanoparticle (AuNPs) films were prepared by inkjet printing using gold nanoparticles with average size of 15 nm, and with a concentration of 15% wt. in a nanoparticle solution comprising water, ethylene glycol, ethanol, and isopropanol. The films were impregnated with the sintering solution comprising 1M NaBH₄ and 0.05 M NaOH, at room temperature for 10 min, to produce the nanostructure with the larger pores.

The printed nanostructured, porous and conductive noble metal nanoparticle films revealed a compact layer of nanoparticles sintered on the bottom, which gives the electrical macroscopic proprieties, and a disordered net-like structure on the top, giving the peculiar electrochemical proprieties at high sintering concentrations of NaBH₄.

The concept of creating a noble metal nanoparticle network which is both nanostructured and conductive with improved nano-porosity is described herein for the first time, since the drawback for obtaining conductive films with the sintering methods in the art is the loss of the nanostructure and relying on to post treatments to the sintering eventually to then reobtain it. In the state of the art, the typically porous and not conductive nanostructures defined by the deposited nanoparticles is sacrificed to obtain a conductive and much less porous surface.

Conductivity and Porosity

Herein, the increase of the conductivity has been evaluated by means of a decrease of the sheet resistance and *vice versa*. To measure the conductivity of the obtained films, the four-point probe method (44P) has been used, which is widely known for the measurement of sheet resistivity, also known as surface resistivity.

Table 2 below includes the values of the sheet resistance for the films at the different porosities and coefficient k₀ for the electron transfer using a standard probe (ferro/ferricyanite redox couple) which is correlated to the efficiency of the redox reaction on the film surface, and in this case the porosity of the film, see Figure 7.

Table 2

	Sheet resistance (Ω) (Conductivity property)	k^0 (cm s^{-1}) (Porosity-related property)
Low porosity-low conductivity	22.1 ± 1.4	0.0014
Medium porosity-medium conductivity	8.5 ± 0.7	0.004
High porosity-high conductivity	1.5 ± 0.4	0.0076

The more porous the film the higher would be the efficiency of the reaction due to proximity effects and higher area of the film.

The electrical characterization of the nanostructured, porous and conductive nanoparticle film revealed a proportional decrease of the resistance with increasing concentrations of sodium borohydride within the range from 0.001M to 1M.

Furthermore, the nanostructure of the film varies with the concentration of sodium borohydride.

It is theorized that this effect could be due to the necking process related to the sintering after the removal of the capping agent. The sintering method not only creates junctions between nanoparticles making the film conductive but also increases the porosity of the film in favor of a greater nano-structuration consequently increasing the surface-to-volume ratio.

As it will be demonstrated in the assays included in the example section and figures, the morphological change of the surface with the NaBH_4 treatment at different concentrations is not attributable to the "oxidative variation" of the film but are attributable to changes in the nanostructure, mainly to the organization and nanoparticle shape changes.

Advantageously, the nano-structural change onto metal nanoparticles film can be finely tuned.

The nanostructured, porous and conductive nanoparticle film has a homogenous net-like structure. The reason lays in the nature of the processes: on the one hand, the solid-state of the film and, on the other hand, the colloidal model. The modes of coalescence of the metal nanoparticles are able to change in accordance with the NaBH_4 concentration, and thereby it is assumed that this phenomenon is governed by two main driving forces: (i) spatial confinement and (ii) de-capping rate.

For high concentrations of sodium borohydride equal or higher than 0.1 M, the capping agent (PVP) destabilization rate is also high, the removal of the capping agent almost instantaneous, or in the range of seconds. The disposition of the noble metal nanoparticles in the film is governed by the printing and drying process, while during the sintering the noble metal

nanoparticles start necking in all directions, toward the closest metal nanoparticles, creating a 3D porous network, given a large degree of freedom on the surface when the capping agent (PVP) is removed, and given a large amount of sintering agent and solution available. The situation is similar in the case of the sintering using a consumer inkjet printer, where the nanostructure changes after reaching a threshold value of layers ($n=3$) of sintering agent.

For low concentrations, or volumes (for sintering using a consumer inkjet printer), of sodium borohydride, lower than 0.1M, a slower destabilization of the capping agent layer is induced, resulting in no apparent change in the superficial nanostructure.

Chemical sintering

There are no external sources of energy. The reaction is limited by the intrinsic chemical energy created during the sintering method, between sodium borohydride and capping agent, thus the network forming process stops when the thermodynamic equilibrium is reached. In other words, the process stops when the desorption/reabsorption of capping agent and the stability of the sintered noble metal nanoparticles reach balance. Dynamic equilibrium could explain why in the sintering method according to the first aspect, the noble metal nanoparticles do not drastically change their dimensions, neither form grains nor collapse.

The mechanism of the de-capping might explain the peculiar modes of coalescence the noble metal nanoparticles undergo in this invention. It has been reported that PVP, as capping agent, has different binding modes on noble metal nanoparticles, depending on the size, length of the chain, and branching. Observing the broad size distribution of the noble metal nanoparticles used in the sintering method, it is reasonable to expect a contribution coming from the different binding modes of the capping agent.

The present inventors have been demonstrated in the performed assays (Figure 5) that using gold nanoparticles and different concentration of NaBH_4 , the sintering method revealed the absence of variation in the gold peak (Figure 5a) that suggests that no relevant interaction between the nanoparticle's gold and the sodium borohydride takes place, with no change in the formal oxidative state of the gold coming from the treatment. In fact, the ratio between the components related to the Au (0) and the Au (+1) does not change during the different concentrations of NaBH_4 , and remains constant even after changes in concentration of several orders of magnitude (Figure 5b). To understand this phenomena, different interpretations have been theorized by the authors of the present invention: i) according to the already proposed mechanism from *Ansar et al*, it has been found that the substitution of the PVP as capping agent with hydride does not affect the gold oxidation state, and no change in the electronic shell of the Au can be detected; ii) the formal hydride species interacts directly with the polymer PVP, guided by the coordination of the polymer PVP to the nanoparticle

putting strains on the chemical amide bonds of the PVP. It is assumed that the mechanisms of de-capping take place at the same time. In both cases, the hydride formal species can react with water or the PVP creating hydrogen (bubbles form on the films when in contact with the NaBH₄), in an exothermic reaction which may be the source of energy inducing the coalescence. This energy, coming directly from the reaction, promotes the sintering. At the higher concentrations of NaBH₄ also modulates the nano-structuration, with distinctive electrochemical and optical proprieties, such as the color change caused by the change in the scattering properties of the material due to the neo-formed nanostructure.

In conclusion, it is provided an easy, implementable sintering method for noble metal nanoparticle solution capable of tuning nanostructure, porosity and conductivity of the films.

By the sintering method described herein it is then possible to fabricate and modulate nano-functional structures in a direct and straightforward way.

In the fourth aspect, the present invention is directed to a device comprising a nanostructured, porous and conductive film of noble metal nanoparticles on a substrate, which is characterized in that the nanostructured, porous and conductive film of noble metal nanoparticles defines a conductive pattern on the substrate.

The substrate can be of any type of material as long as does not react with the sodium borohydride. The substrate may be of polymeric or paper nature.

Advantageously, a substrate of polymer or paper materials is suitable for using in the method of the present invention due to that it is not hindered by the temperatures employed in the method for the reasons explained above.

In an embodiment, the device is an electrode.

In another embodiment, the device is a sensor. A sensor includes a biosensor or a photonic biosensor.

The tuning of the nanostructure can be exploited for the waste-free, easy, and rapid fabrication of efficient electrochemical transducers or interfaces, fundamental in the fields of biosensing.

Particularly interesting are nanostructured, porous, AuNP or PtNP films, which can be used for highly efficient and robust detection of organic and inorganic molecules like as heavy metals, small molecules, proteins, oligonucleotides, and even whole organisms such as virus and bacteria. Noble metals nanoparticles of Au and Pt are expensive compared to other metal nanoparticles, so cutting the expenses/materials waste related to all the fabrication steps of nanostructured devices represent a great economical advantage.

The tuning of the nanostructure can potentially be used to prevent the access to the interior

of the material to the biggest molecules and interferents, or to increase the efficiency of the detection of a specific molecule by using aptamers as bioreceptors. Furthermore, the nanostructure is suitable for efficient gas sensing devices and sequestration/removal applications.

5 In this sense, the authors of the present invention have been demonstrated in Example 4 and Figures 11 to 14 a practical application of a sensor or biosensor device comprising the nanostructured, porous and conductive film of noble metal nanoparticles according to the fourth aspect of the present invention on a substrate.

Figure 11 depicts a schematic representation of the sensor or biosensor device. The working
10 principle of the electrochemical sensing platform includes two steps. In step 1, the viral RNA is dropped onto the electrode. In step 2, the NFC potentiostat allows to perform the electrochemical measurements via a smartphone. The digital electrochemical output is transmitted wirelessly via NFC. In the inset, the DNA-based detection strategy: ORF1ab and N gene capture probes are immobilized on the gold electrode. The ORF1ab and N gene
15 labelling probes, which are labelled with methylene blue (MB) and ferrocene (Fc), respectively, are free in the solution. In the presence of the targets (ORF1ab and N gene), the formation of RNA-DNA duplexes brings the redox tags close to the electrode surface. This proximity enables electron transfer, which leads to the appearance of two different peaks, and thus provides a result of the performed test, see detailed Example 4, and Figures 12 to 14.

20 Moreover, other fields of interest can be fabrication of devices with improved optical properties for Surface Enhanced Raman Spectroscopy (SERS), a fundamental technique used for photonic biosensors. In these applications, it is preferable tuning the nanostructure using lower concentrations of sodium borohydride and producing more ordered arrangement of the metal nanoparticles, which is known to cause an enhancement of this effect.

25 Finally, the integration of the sintering method in inkjet printers adding the reagent sodium borohydride in one or more of the available cartridges and the noble metal nanoparticle solution in the other ones, allows controlling and speeding up all the protocol, scaling-up and automating the sintering method of the present invention.

Therefore, the sintering method of the present invention can be provided as an all-in-one
30 production system to fabricate the desired layout in the device and sinter it in real-time without any waste of time or materials.

The present invention is also directed to the use of a nanostructured, porous and conductive noble metal nanoparticle film according to the second aspect and to the use of a device according to the fourth aspect in electrical, electrochemical and/or photoelectrical

applications.

According to the present invention, the sintering method or the nanostructured, porous and conductive noble metal nanoparticle film have at least one of the following advantages:

- the sintering method relies on a unique chemical reaction on the noble metal nanoparticle interphase, which has the effect of inducing chemical sintering between the nanoparticles and at the same time the nano-structuration of the film;
- the sintering method can be carried out in few minutes and even in real-time, which allows it to be integrated into an inkjet printing method suitable for consumer printers;
- the sintering method provides a fast, easy, and scalable way to sinter and nano-structure noble metal nanoparticles films independently from the temperature, just by using the unique nature of the proposed chemical reaction and starting materials;
- the sintering method can be performed at ambient/room temperature;
- the sintering method can be performed on low melting point substrates like as paper, plastic, etc., by using only standard and accessible chemical reagents.

Examples

Hereinafter, the present invention is described in more detail and specifically with reference to the Examples and Figures, which however are not intended to limit the present invention.

Example 1

The synthesis of nanoparticles can be carried out by any method known in the state of the art. The following is just one way to do it.

Ultrapure, water-based gold nanoparticles were synthesized via pulsed laser ablation in liquids by RHP-Technology in a single-step approach enabling the synthesis of size-controlled and highly stable colloids at room temperature and atmospheric pressure. The laser system included an InnoSLab, nanosecond pulsed laser (IS400, Edgewave) delivering 7 ns full-half width maximum (FWHM) pulses at 1064 nm, at a repetition rate of maximum 10 kHz and pulse energy of 40 mJ. The laser beam was focused by a high-speed galvo scanner (intelliSCAN III-10, Scanlab) through a telecentric 65 mm focal length F- θ quartz lens (S4LFT4065/328, Sill Optics). Spherical shaped gold nanoparticles with a mean diameter size of 15 ± 5 nm were generated from a 99.99% pure gold target (Agosi AG) in a closed flow chamber whereas the laser beam was coupled horizontally into the process chamber. As liquid media, 1 L Type I. water (>18 M Ω cm, Milli-Q, Merck-Millipore) containing 0.01 mM Polyvinylpyrrolidone (PVP10, Sigma Aldrich) was used while a controlled liquid flow of 500 mL/min was generated by a non-contact tube pump (Heidolph, Hei-FLOW Precision 06) circulating the liquid between a liquid

reservoir and the ablation chamber. Upconcentration of the gold colloid into a high-stable nanoink was achieved by rotary evaporation (Hei-VAP Precision, Heidolph) (35°C, 35 mBar, 140 rpm) to remove the excess water and to adjust the NP concentration.

Nanoparticle ink - Nanoparticle solution

5 A water-based gold-ink with 26.5 w% solid particle content was thus obtained, that showed excellent long-term stability.

The nanoparticle ink formulation or nanoparticle solution was then adjusted to 15 w% AuNP concentration including 1.6 mM PVP capping agent in a printing solution composed of water (72%), ethylene glycol (25%), ethanol (2%) and isopropyl alcohol (1%).

10 In this example, the AuNPs had an average particle size of 15 nm with an index of polydispersity of 0.18.

Example 2 *Sintering method by immersing*

The nanoparticle solution was as prepared in Example 1.

15 The printed patterns using the nanoparticle solution were designed in Autodesk AutoCAD 2020 and were composed of 2 connection pads (3 mm x 3 mm) and a 2 cm long 600 µm wide line connecting them.

Sintering solution

20 Several sintering solutions were prepared dissolving sodium borohydride to 0.001, 0.01, 0.1, 0.5 and 1M in 0.2% sodium hydroxide to stabilize the sintering agent and slow down the decomposition reaction.

Sodium borohydride powder (purity 98% and MW of 37.83 g/mol) and sodium hydroxide pellet (purity>98%, MW of 40.05 g/mol) were purchased from Sigma Aldrich. Ultrapure MilliQ Millipore deionized water (18.2 MΩ/cm) was used for the preparation of the solutions.

25 The substrates used for printing were transparent polyethylene terephthalate (PET) A4 sheets with a porous coating to allow the immediate drying of the AuNPs water-based ink and optimal adhesion (Mitsubishi Paper Mills NB-TP-3GU100).

30 The printed devices were immersed in each several sintering solutions in glass Petri dishes, right after the preparation. The sintering solution was left reacting under agitation for 10 min at room temperature. After that, the devices were removed and placed in a Milli-Q water bath twice, to stop the reaction and remove eventual side products. The washed devices are gently dried with a towel to remove the water excess and with nitrogen until completely dried (Figure 1a).

Example 3 *Inkjet Real-time Sintering method*

Implementation of the sintering method directly inside the inkjet printer was performed. Gold inkjet-printed lines were fabricated using an Epson XP15000 consumer printer.

In this example, all was implemented inside a small desktop inkjet printer to have compact equipment technically able to perform the fabrication of films and the sintering of the gold nanoparticles, inducing the nanostructure (Figure 1 c).

The sintering solution composition was modified to ensure the correct parameters for printability. The sintering solution was prepared by dissolving sodium borohydride in a solution containing 72% NaOH solution 0.5 M, ethylene glycol 21%, Ethanol 2%, and isopropyl alcohol 1%, to reach a final concentration of 0.5 M.

Kapton substrate was used since it does not have the permeable coating typical of the commercial Mitsubishi sheets, the solution can stain over the film more time reacting with the gold nanoparticles. Kapton sheets were purchased from DuPont. The printing was performed on A5 sheets treated with NaOH 4M increase the surface wettability.

Consumer printers have multi-ink (color) cartridges connected to a single printhead with separated nozzle arrays.

6 ml of the ink solution prepared in Example 1 was poured into an empty cartridge (supplier) already installed on the printer printhead (cyan channel). The loading of the AuNPs solution in a color channel (e.g. cyan) and of the sintering agent in a second one (e.g. yellow) allows for the implementation of sintering of the printed AuNPs by printing the desired designs in mixed colors (e.g. green).

The sintering solution was loaded inside the cartridge and placed in the yellow channel performing multiple prints on the gold films, drying after the printing, and performing the washing only at the end of the desired amount of deposition. This is been done for two reasons: first to increase the local concentration of the agent before, and second to mimic the situation of a real-time printing and sintering where the sheets undergo multiple passes before being washed or used. The gold films, for sake of simplicity, were cut and attached to a paper sheet to be placed inside the printer.

The morphology was investigated using HR-SEM showing an evident change in the nanostructure after printing 3 layers of sintering solution, see Figure 8 and Figure 9.

The nanoparticles form the network of connection once the threshold concentration is reached. There is a critical value to reach and start to have a clear change in the electrical and morphological proprieties, previously the concentration, in this case, the number of prints,

which is related to the volume of solution deposited.

Surface characterizations

Pictures of the printed lines were acquired by an Andostar ADSM302 optical microscope, keeping the same focus and brightness during the whole study.

5 SEM analysis was performed by an XHRSEM Magellan 400L Thermo Fisher Scientific microscope. The images were collected operating in a high vacuum with an electron beam energy of 2 kV and secondary electrons in-lens detector. See Figures 2 and 3.

Figure 2 as well as Figure 3 both reveal that 0.1 M is the threshold NaBH_4 concentration for triggering an extended nanostructure change. Conversely, time in this timeframe does not
10 appear to have an evident effect on the morphology.

From a macroscopic point of view, the treatment produced an unexpected change in the color of the gold nanoparticle film, with a variation from a gold color to deep brown, proportionally to the NaBH_4 concentration, see Figure 2 (a-f). Therefore, the pristine, untreated and non-conductive, and the sintered conductive AuNPs-films obtained by the treatment performed
15 with different NaBH_4 concentrations have been subjected to physicochemical characterization, to determine the nature of this change. The morphological change of the surface with the treatment could explain the color variation of the films, because of different light absorbance. To verify this hypothesis, compositional alterations of the surface were analyzed with EDX (Figure 4) and XPS (Figure 5).

20 The chemical and compositional analysis was performed using standard methods like XPS and EDX, to have information about the surface level and the more depth levels of the films. Boron, was not detected, even when high concentrations of NaBH_4 were used. The accumulation of the by-product of the reaction appears to not occur. The metaborate is soluble and can be eliminated during the reaction time, done agitating and the sequent washing steps.
25 It is also worth considering that these nanoparticles are negatively charged on the surface (Zeta Potential measurements) with a formal ZP of -42 eV in water solution so electrostatic repulsion is likely to contribute.

An energy-dispersive X-ray spectroscopy (EDX mapping) was performed right after taking the pictures increasing the energy to 6 kV and looking for gold, carbon, oxygen, nitrogen, and
30 sodium elements, see Figure 4.

An X-ray photoelectron spectroscopy (XPS) analysis was performed at room temperature by a SPECS PHOIBOS 150 hemispherical analyzer (SPECS GmbH, Berlin, Germany) with a base pressure of 5×10^{-10} mbar using monochromatic Al K alpha radiation (1,486.74 eV) as excitation source, with a power of 300 W. The energy resolution was 0.62 eV, as measured

by the full width at half maximum (FWHM) of the Ag 3d_{5/2} peak for sputtered silver foil. The spectra were calibrated using C 1s at 284.8 eV as reference. The data analysis and fitting were performed using CasaXPS software. The constructed peak model was defined by using a Voigt function, with a Shirley background for the Au 4f. The ratio between the areas of the two 4f orbitals in the gold was fixed as a constraint considering the degeneration of the two orbitals, see Figure 5 (a-b). No other additional constraints were used to allow the model to fit the data realistically and in a meaningful fashion.

The high-resolution XPS spectra of the Au 4f, see Figure 5 (d), show the doublets corresponding to the photoemission peaks of the 4f_{5/2} and 4f_{7/2} orbitals, at binding energies of 87.79 eV and 84.12 eV, respectively with a peak-to-peak distance of 3.67 eV. The data is coherent with the nanoparticles being in the metallic form with formal oxidation state Au(0). Both the distance and the position of the peaks remain constant with the treatment. The peak intensities change accordingly to the extent of the removal when the concentration of NaBH₄ is increased. These data prove that the color changes of the films are not attributable to the 'oxidative variation' of the film, but are attributable to changes in the nanostructure.

To shed further light on the differences in nanostructure Enhanced Scattering Raman Spectroscopy (SERS) was used to characterize the morphological differences of the films subjected to different sintering treatments; Rhodamine was used as a probe, and the intensity of its characteristic peak (1626 cm⁻¹) taken as signal. The Rhodamine signal increased until a maximum value for the films treated with 0.01M NaBH₄, then decreases further increasing the sintering agent concentration. Numerous factors influence the SERS phenomena, such as the nature and the morphology of the metal on the substrate; among others, particularly significant is the organization and nanoparticles shape, see Figure 6. As observable in the SEM images (Figure 2), the 0.01M treated substrate same to have the more favorable compromise between AuNPs morphology and distance.

Electrochemical characterizations

For all the electrochemical measurements, one connection pad has served as contact and the other as a working electrode. A reproducible working electrode area has been obtained insulating the AuNPs connection line (between the two pads) with screen printing insulating paste. The three-electrode electrochemical cell was completed with an external standard reference (Ag/AgCl 3M KCl) and counter (platinum wire) electrodes. The electrochemical characterizations have been performed using a PalmSens4 potentiostat. CVs were performed in 5 mM ferro/ferricyanide in PBS, scanning the potential from -0.35 to 0.65 V with scan rates of 25, 49, 64, 81, 100, 144, 196, 289, 400, 484 mV/s. The recorded spectra in H₂SO₄ 0.5 M were done with a scan rate of 100 mV/s using a scanning potential from -0.35 to 1.55 V. The

cleaning in sulfuric acid has been performed using a scanning potential from -0.35 to 1.55 V, with a scan rate of 200 mV/s, performing 15 complete scans.

Square wave voltammetry (SWV) was used to obtain the MB calibration curve for the treated devices. SWV parameters used: equilibration time 10 s at 0.1 V, frequency 25 Hz, amplitude 25 mV, potential ranging from 0.1 to -0.5 V vs Ag/AgCl (reduction peak of the methylene blue), E step of 0.003 mV. The concentration of methylene blue (MB) ranged from 100 nM to 1 mM.

Figure 7 shows the results for the CVs and SWV at the different concentrations of the NaBH_4 . The response varies linearly with the concentration, and this is reflected by observing the slope of the curve in the central column: the higher the concentration, the higher the slope of the linear fit. For the SWV instead, the peak height is the reference value to evaluate, related to the response that the film has to a specific concentration of an electroactive species. The results of the two-technique are coherent, even though they were performed on different batches of printed gold, showing reproducibility and reliability of the morphological effect on the electrochemical proprieties. From the CVs, specifically, the peak maximum and square root of the scan rate is possible to calculate, using the Randall-Sevick equation, a value of the electroactive area of the gold film. Important to understand that this is not a value of porosity, nor should be taken as such: is a value of the amount of material on the surface involved during the redox process. Nonetheless is a useful index of the effectiveness of the treatment and measures the electron transfer constant k_0 , a value of the efficiency of the redox process.

Table 2 above includes the values of the sheet resistance for the films at the different porosities and coefficient k_0 for the electron transfer, see also Figure 7.

As shown Table 2, the values of the area increase with the concentration of NaBH_4 as well as the electron transfer constant k_0 . The increase of the electron transfer constant is coherent with what was expected. The porosity and morphology change induced by the treatment, creating the net-like structure, creates wells and cavities, where the redox reaction happens at a faster rate, due to a sum of different phenomena.

Electrical resistance and Conductivity

The electrical resistance of the AuNPs films printed lines was measured by a Keithley DMM6500 multimeter with standard probes, simply touching the pads at the two extremes of each line.

The four-point probe method (44P) is widely known for the measurement of sheet resistivity, also known as surface resistivity. The general method consists of performing a 4-wire measurement in some conditions. A requirement is that the 4 probes must be equidistant. Another requirement is that the thickness of the film is less than 0.4 of the separation between

the probes. Finally, the probes must be centered in the area to be measured. A geometric correction C is necessary to apply when the ratio between the side of the square (W) and the separation between probes (S) is less than 40. Haldor Topsøe, in *Geometric Factors in Four Point Resistivity Measurement (1966)*, provides a table where the correction factor is indicated, with which it is possible to interpolate.

The sheet resistivity R_{sq} can be calculated by the following equation:

$$R_{sq} = \frac{\pi}{\ln(2)} \cdot C \cdot \left(\frac{\Delta V}{I} \right) = 4 \left(\frac{\Delta V}{I} \right)$$

wherein $(\Delta V/I)$ is the value reported by a multimeter and C is the correction factor.

Likewise, there is an excellent correlation between the sheet resistance measurements and the 2-wire measurements made on the simple traces as seen in Figure 9 (a). The central bar is the sheet resistance multiplied by the aspect ratio of the trace, that is, 33.33 squares, which corresponds to dividing the length of the trace by its width. Finally, the bar on the left is the resistance measured with the 2-wire method. It can be seen that when the area is smaller, particularly for fine traces, chemical sintering is more effective, this result in a lower resistance value, especially in high NaBH_4 concentrations. Additionally, the traces sintered at a high concentration of NaBH_4 , show less standard deviation.

Regardless of the type of measurement, a decrease in resistance to increasing concentration of NaBH_4 is evidenced up to 0.1 M. Figure 9 (b) shows the resistivity obtained for the real-time sintering, performed by placing the NaBH_4 solution in a dedicated cartridge of the printer. In this case, 0.5 M NaBH_4 was used and different passages (named layers) with the printer have been performed onto the ink-jet printed gold film. Since the two methods to measure the sheet resistance returned complementary results, for this test only four-point probe measures were performed. There is a minimum amount of NaBH_4 layers required to obtain the sintering. Up to two NaBH_4 layers, the sintering is scarce and not reproducible, indicating a not complete and heterogeneous treatment. Starting from 3 layers of NaBH_4 , a complete and reproducible sintering was obtained; this is evidenced by the sharp decrease in resistivity and the low standard deviation. Noteworthy, the resistivity obtained with the real-time treatment result like the ones obtained off-line.

Example 4 Biosensing device

A multiplexed DNA-based sensing platform prepared using the sintering method according to the present invention was fabricated for SARS-CoV-2 diagnostic.

The multiplexed DNA-based sensing platform utilizes inkjet-printed nanostructured gold electrodes and an inkjet-printed battery-free near-field communication (NFC) potentiostat for

the simultaneous quantitative detection of two SARS-CoV-2 genes, the ORF1ab and the N gene. The detection strategy based on the formation of an RNA-DNA sandwich structure leads to a highly specific electrochemical output. The inkjet-printed nanostructured gold electrodes providing a large surface area enable efficient binding and increase the sensitivity. The inkjet-printed battery-free NFC potentiostat enables rapid measurements and real-time data analysis via a smartphone application, making the platform accessible and portable. With the advantages of speed (5 min), simplicity, sensitivity (low pM range, ~450% signal gain) and cost-effectiveness, the proposed platform is a promising alternative for point-of-care diagnostics and high-throughput analysis that complements the COVID-19 diagnostic toolkit.

Nanostructured inkjet-printed electrodes (IPEs) were fabricated following the method of the invention, which allows precise control of size and surface morphology (Figure 12a–c). The active surface area of these printed electrodes calculated from the gold oxide reduction peak area of cyclic voltammograms under acidic conditions (i.e., H_2SO_4 0.05 M) (Xiao *et al.*, 2007) is $3.2 \pm 0.2 \text{ cm}^2$, with a roughness factor (calculated as the ratio of real to geometric area) of 28 ± 2 , which is more than 10 times higher than that of smooth electrodes (i.e., screen-printed electrodes) (Figure 12d).

The heterogeneous electron transfer constant k^0 extrapolated from cyclic voltammetry measurements in $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (2.5 mM in PBS 10 mM), at different scan rates, using the Nicholson method (Nicholson, 1965; Nicholson and Shain, 1964), shows that IPEs outperform classic smooth screen-printed electrodes (SPE) by more than a factor of two, with a k^0 of 0.0261 cm s^{-1} and 0.098 cm s^{-1} , respectively, and a peak-to-peak distance of 77 versus 91 mV at a scan rate of 0.025 V s^{-1} . These results indicate that porosity and nanostructuration are an important factor in improving electroanalytical performance, even for low-cost disposable platforms (Figure 13).

Here it was designed and developed a highly versatile and cost-effective DNA-based sensor platform to detect RNA fragments in rapid time and without washing steps. It was developed capture and signalling probes that respond simultaneously to two different genes without interfering with each other (Figure 14). It was printed nanostructured electrodes with increased surface area that provide a larger number of sites for the capture probes and also improve accessibility during hybridization, resulting in fast and efficient binding. The inkjet-printed electrodes were integrated with an NFC potentiostat that allows measurements to be performed and data to be collected in real time using a smartphone. The direct printing of the antenna together with the electrode increases the cost-effectiveness of the device with a production cost of about €2 (see Table 3 below) and a production time in the order of minutes.

Table 3: IPE devices cost analysis.

Type	Item	Amount/ package	Cost (€)	Pages per unit amount	Cost/page (€)
Materials	AuNP ink	6 ml	1200	≈ 8	25
	AgNP ink	100 ml	230.82	≈ 7	0.33
	Substrate	100 sheets	146.19	1	1.46
	Wax tablet	1	30.25	≈ 300	0.1
	Lamination sheets	20 sheets	<20	1	<1
	Additional items (per each biosensor)			Page cost+	26.89 € (104 sensors)
	SIC4341 chip	1	1.5*	/	1.5*
				Total Cost per sensor+	1.76 €
Equipment	EPSON XP15000	/	314.99		
	Epson empty cartridge		<30		
	ColorQube 8850	/	<300		
	Lamigator	/	<150		
	Oven	/	<100		
Fixed costs			<900 €		

+Calculations based on a layout containing 104 sensors per each printed page

* Cost of the single chip can be reduced purchasing larger quantities.

It is emphasized that the total cost of the single device can be significantly reduced by bulk purchases. This economic perspective not only improves the practicality of the device, but also opens up opportunities for scalable production, enhancing the potential impact of this invention in real-world applications. It is worth noting that the herein multiplexing single-step direct sensing method does not rely on an amplification step and therefore does not achieve the sensitivity of the gold standard real-time reverse transcription polymerase chain reaction (RT-PCR) (*Kubina and Dziedzic, 2020*). However, this platform is promising as it enables a fast response (5 min) without multi-step, wash and reagent-intensive processes. In addition, the cost of our platform is much lower than the cost of RT-PCR, because unlike RT-PCR, which is not only reagent-intensive but also requires well-trained technicians, this platform does not require specialized technicians and the measurements are performed with a low-cost, portable potentiostat using a standard smartphone. Further validation is required, especially for high viral load samples, such as saliva, which could potentially be detected without an amplification step (*Herrera et al., 2021*). In the upcoming studies, the inventors aim to validate the effectiveness of the herein sensing platform by testing it with real samples. The specificity of the sensor, which targets 30 bases within the SARS-CoV-2 genes, makes us confident that we will be able to detect ORF1ab and the N gene in real samples. It is believed that the proposed platform, which enables rapid, accessible and cost-effective detection of SARS-CoV-2, is a valuable addition to the COVID-19 diagnostic toolkit. Although different detection kits are available on the market, the herein platform is characterized by the simultaneous detection of two different genes, which enables a higher accuracy in COVID diagnosis. Finally, it is emphasized that this platform can be easily adapted for the detection of other viruses as well

as long non-coding RNAs by simply changing the sequences of the capture and signalling probes. This requires designing probes with bases that are complementary to specific regions of the target virus, thus expanding the platform's applications. In summary, the herein multiplexed, single-step, signal-ON platform is a promising solution for point-of-care

5 diagnostics and high-throughput analysis.

CLAIMS

1. A sintering method for obtaining a nanostructured, porous and conductive film of noble metal nanoparticles, the method comprising noble metal nanoparticles capped with a capping agent, and NaBH₄ in a determined concentration, **characterized in that** the method comprises:

- 5 - preparing a noble metal nanoparticle solution, wherein the noble metal of nanoparticles is selected with the condition that it has catalytic activity with NaBH₄, and
- preparing a sintering solution including NaBH₄ as sintering agent, optionally with a stabilizing agent of NaBH₄ in solution,

and in that the method comprises sintering of the noble metal nanoparticles and
10 nanostructuring of the film, both in a single chemical reaction,

 wherein the single chemical reaction is governed by the NaBH₄ concentration and by the fact that NaBH₄ acts simultaneously as sintering and de-capping agent, so the NaBH₄ removes the capping agent of the capped noble metal nanoparticles, allowing NaBH₄ to come into contact with the noble metal of nanoparticles to instantly initiate an intrinsic exothermic chemical
15 reaction at the interface of the nanoparticles, thereby creating chemical junctions between the nanoparticles and forming wells and cavities that nanostructure the film, the chemical reaction being catalyzed by the noble metal of the nanoparticles.

2. The method of claim 1, wherein the capping agent of the capped noble metal nanoparticles is polyvinylpyrrolidone.

20 3. The method of claim 1, wherein the noble metal with the condition that has catalytic activity with NaBH₄ is selected from gold or platinum.

4. The method of any one of claims 1-3, wherein the noble metal nanoparticles consist of gold nanoparticles or of platinum nanoparticles.

5. The method of any one of claims 1-4, which is performed at room temperature.

25 6. The method of claim 1, wherein the noble metal nanoparticle solution includes capped noble metal nanoparticles in a concentration from 1% to 40% by weight.

7. The method of any one of previous claims, wherein the noble metal nanoparticles have an average particle size of 15 nm measured with transmission electron microscopy and with an index of polydispersity of 0.18 measured by dynamic light scattering.

30 8. The method of claim 1, wherein the sintering solution includes NaBH₄ as sintering agent and a stabilizing agent of NaBH₄ in solution.

9. The method of claim 8, wherein the stabilizing agent of NaBH_4 in solution is NaOH in a concentration >0 to 1M .

10. The method of any one of previous claims, wherein the NaBH_4 concentration is between 0.001M and 1M .

5 11. The method of any one of previous claims, wherein the NaBH_4 concentration has a threshold at 0.1 M from which, by increasing the concentration of NaBH_4 from 0.1 M to 1M , the film also increases conductivity and surface-to-volume ratio, and *vice versa* by decreasing the concentration of NaBH_4 from 0.1M to 0.001M .

10 12. The method of any one of previous claims, wherein the noble metal of nanoparticles has an oxidation state that remains unchanged during the method to obtain the film.

13. The method of any one of previous claims, wherein the film has conductivity and porosity that are tunable by varying the concentration of NaBH_4 .

14. The method of any one of previous claims further comprising the steps of:

i)- depositing as a film the noble metal nanoparticle solution onto a substrate; and

15 ii)- impregnating the deposited nanoparticle solution with the sintering solution.

15. The method of any one of previous claims, which is implemented in a consumer printer.

16. A consumer printer using the method defined in claims 1 to 15, wherein the consumer printer is provided with at least two cartridges connected to a single printhead,

20 wherein the first cartridge is loaded with a noble metal nanoparticle solution as a first ink, and the second cartridge is loaded with a sintering solution, optionally with a stabilizing agent of NaBH_4 in solution, as a second ink, that in use, on a suitable substrate for printing a designed pattern, comprises printing the first ink in accordance with the designed pattern on the substrate, and overprinting the first ink with the second ink, thereby the pattern forms a film that sinters and nanostructures in a single chemical reaction.

25 17. A nanostructured, porous and conductive film of noble metal nanoparticles obtainable by the method defined in claims 1 to 15.

18. The nanostructured, porous and conductive film of claim 17, having modifiable conductivity and porosity governed by the concentration of NaBH_4 used during the method to obtain the film.

30 19. The nanostructured, porous and conductive film of any one of claims 17-18, wherein the film has a network structure with extended nano-structuration inside the film, in which the noble

metal nanoparticles are organized governed by the concentration of NaBH_4 used during the method to obtain the film.

20. A device comprising a nanostructured, porous and conductive film of noble metal nanoparticles defined in claims 17 to 19 on a substrate, **characterized in that** the
5 nanostructured, porous and conductive film defines a conductive pattern on the substrate.

21. The device of claim 20, wherein the substrate is of polymeric or paper nature.

22. The device of any one of claims 20-21, wherein the device is an electrode.

23. The device of any one of claims 20-21, wherein the device is a sensor.

24. Use of a nanostructured, porous and conductive film of noble metal nanoparticles defined
10 in claims 17 to 19 for electrical, electrochemical and/or photonic applications.

- . -

FIG 1

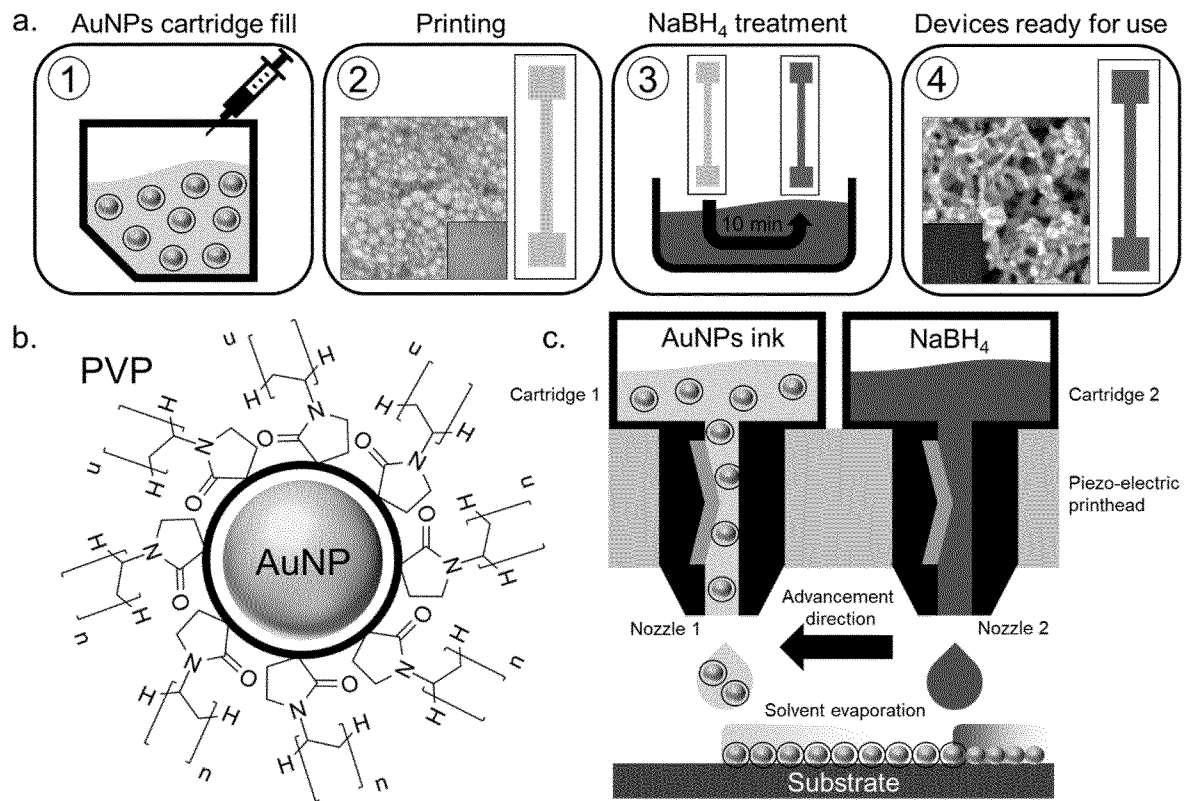


FIG 2

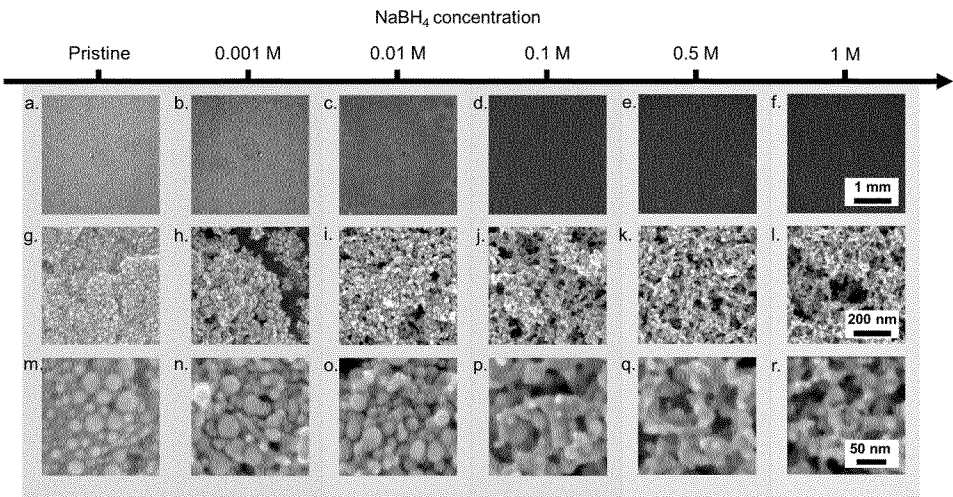


FIG 3

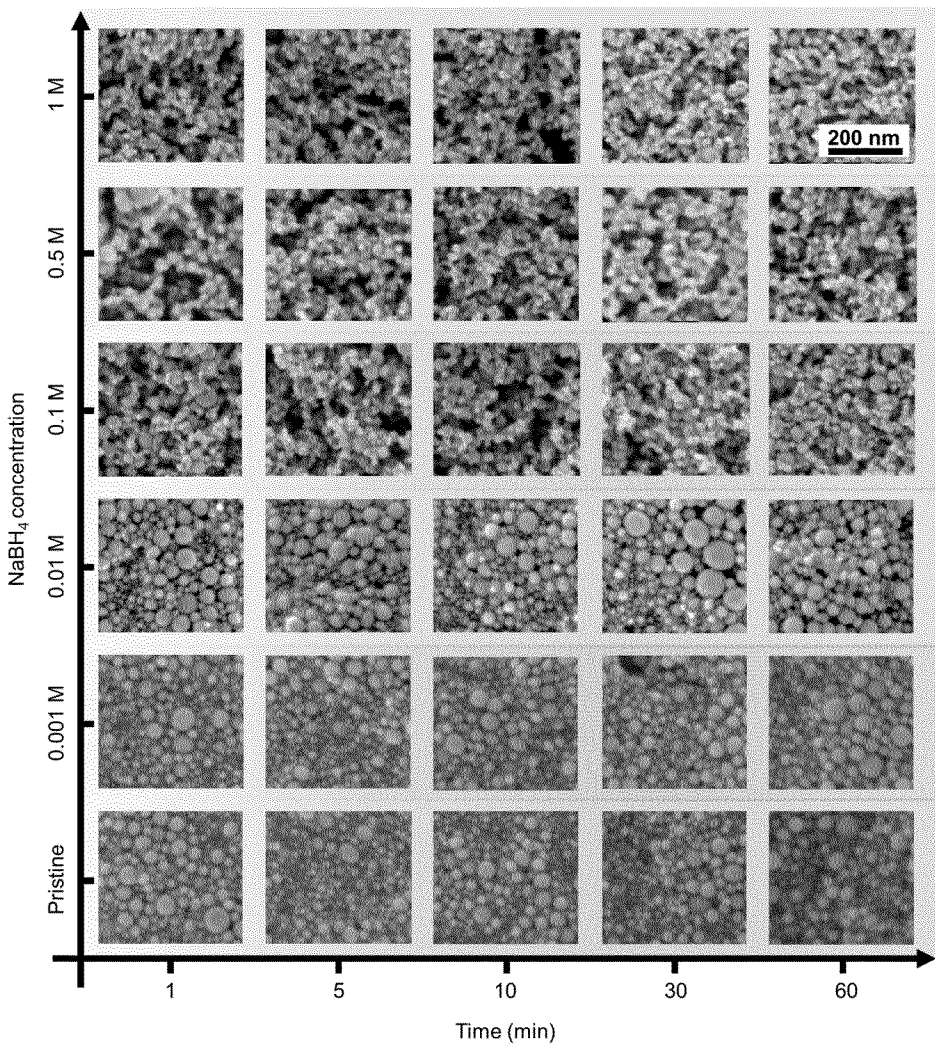


FIG 4

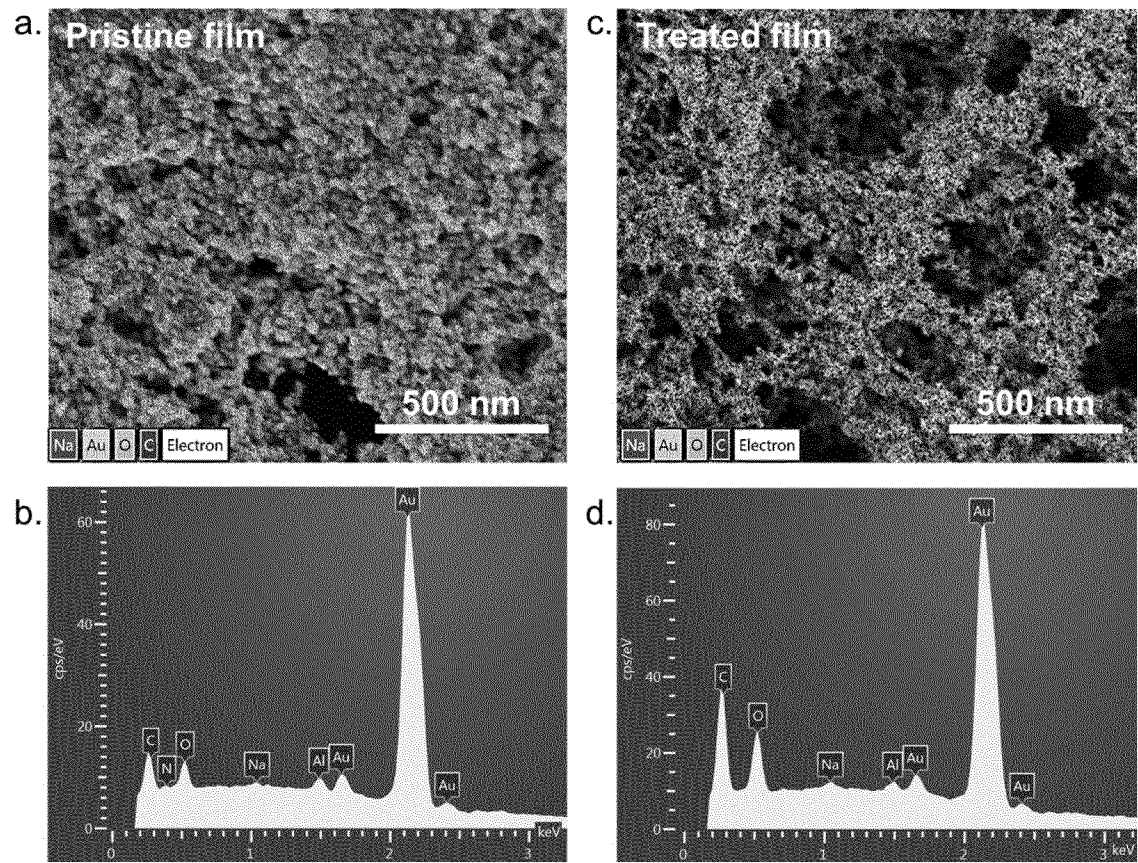


FIG 5

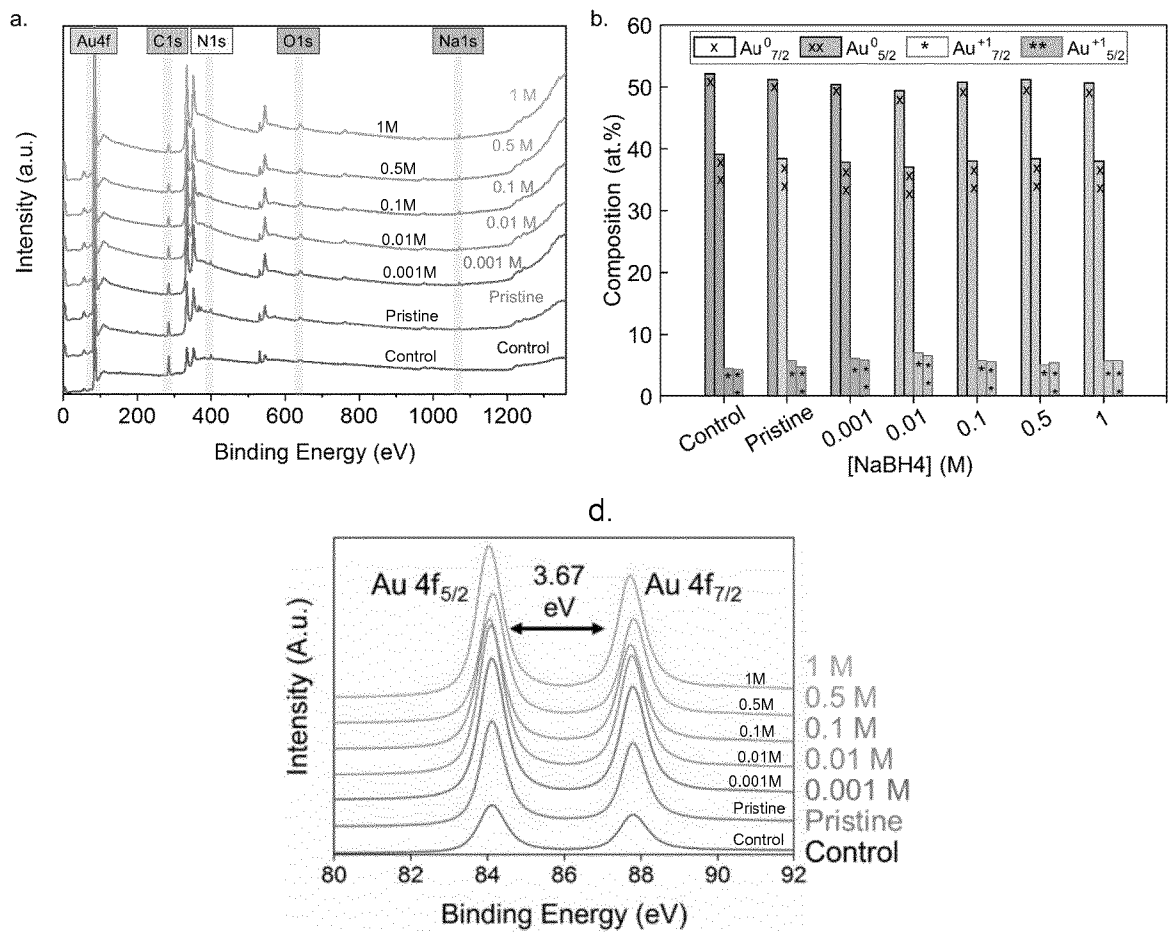


FIG 6

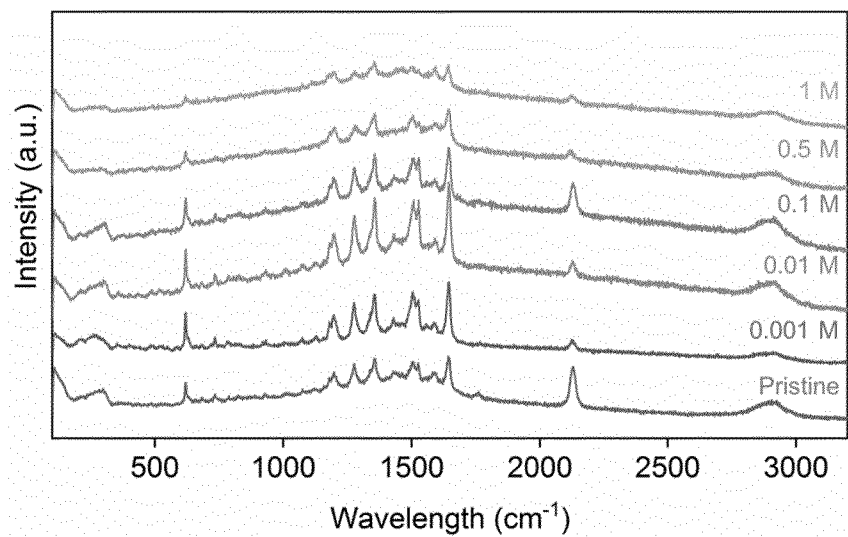


FIG 7

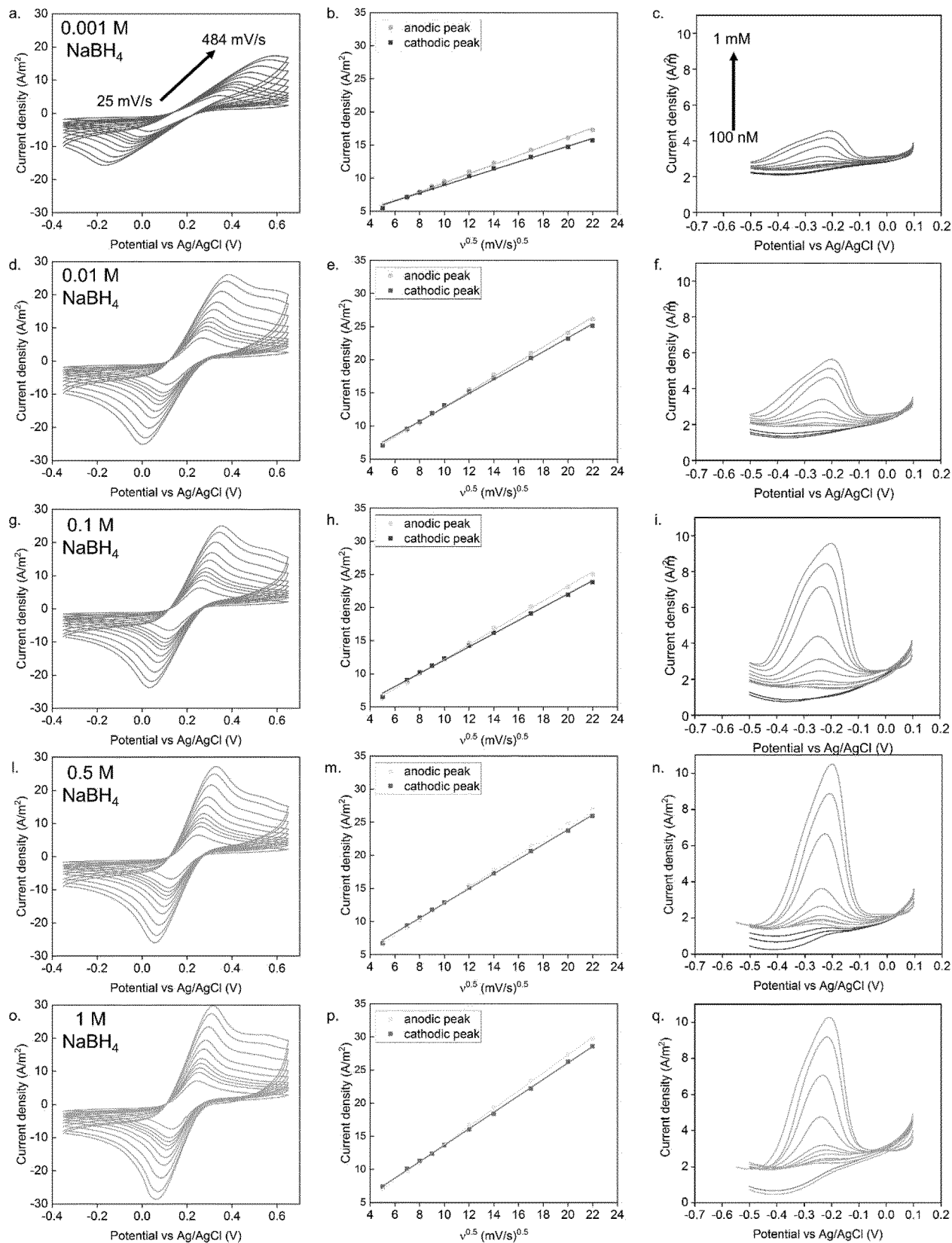


FIG 8

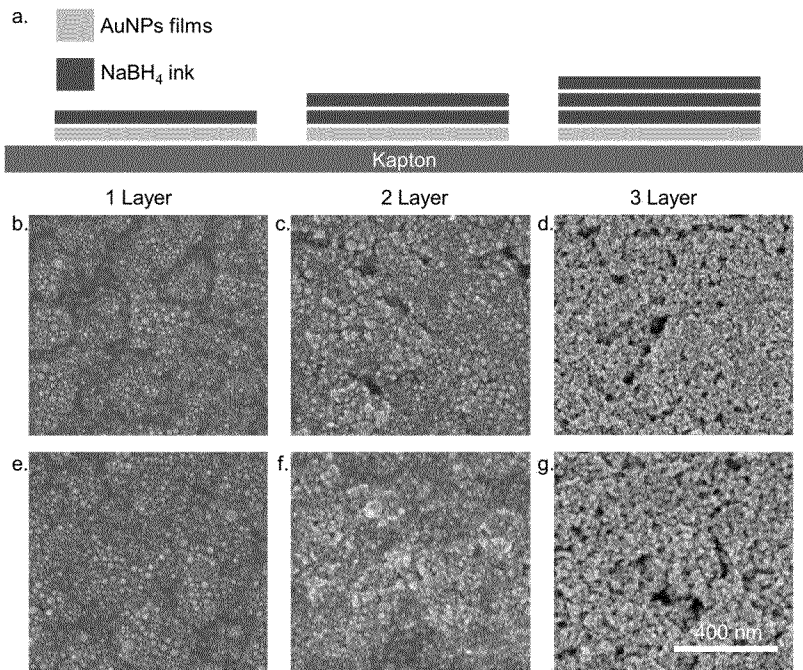


FIG 9

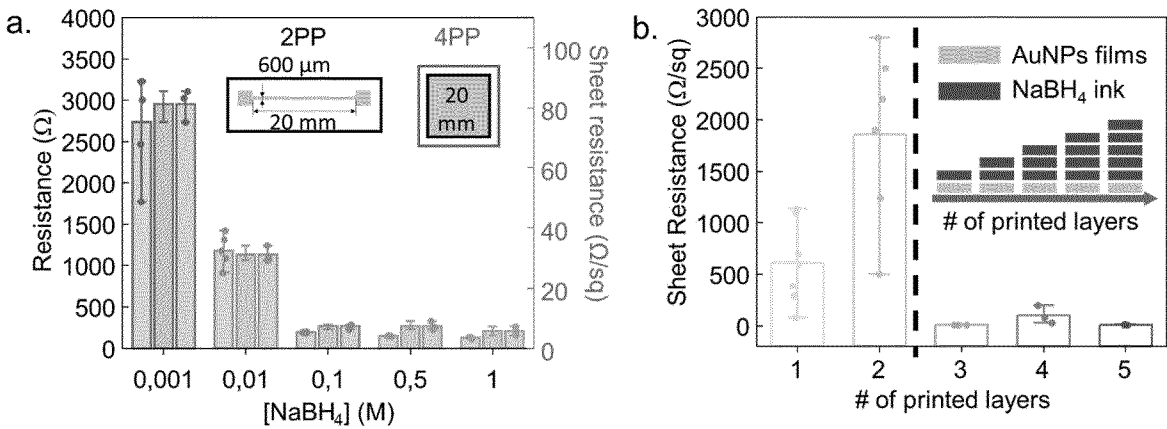


FIG 10

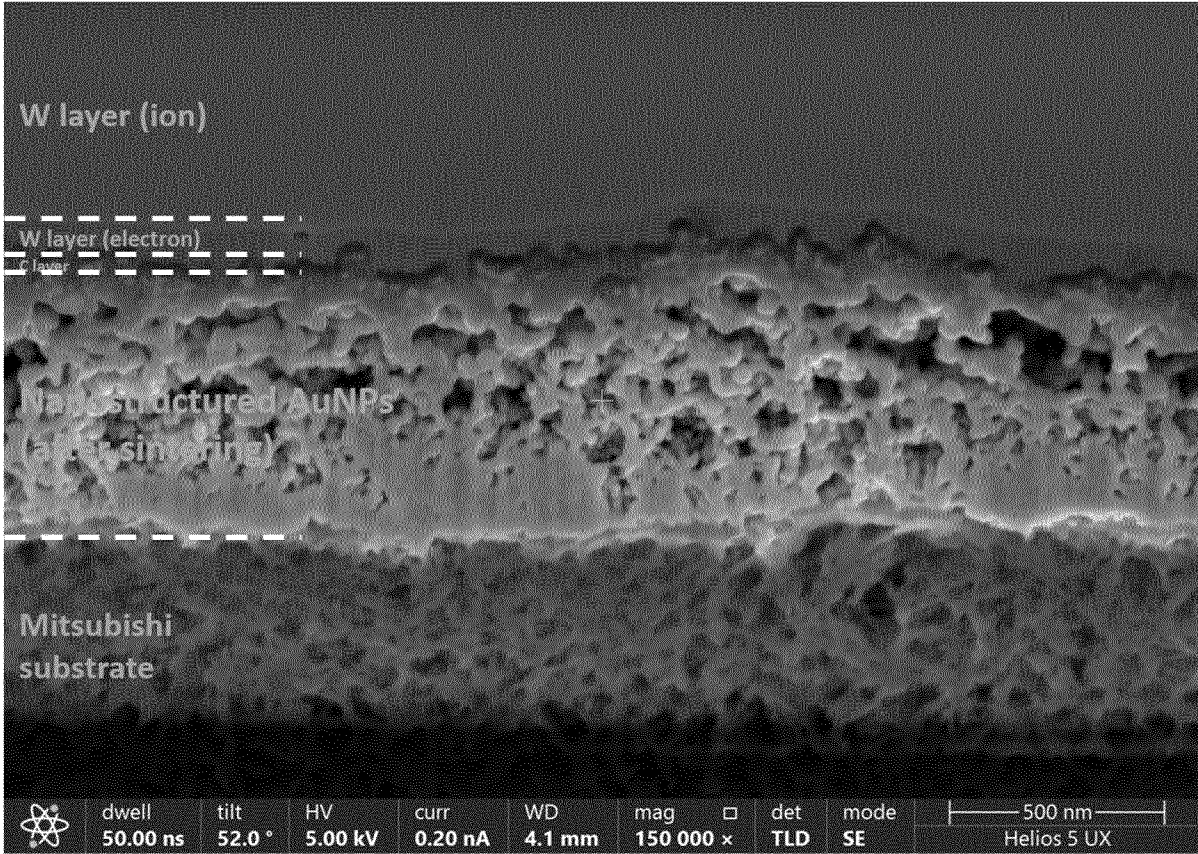


FIG 11

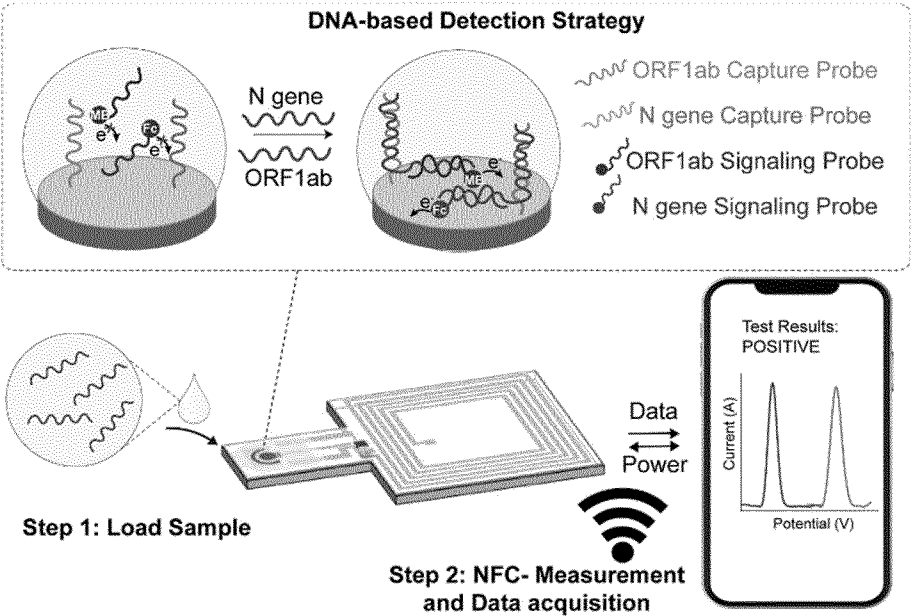


FIG 12

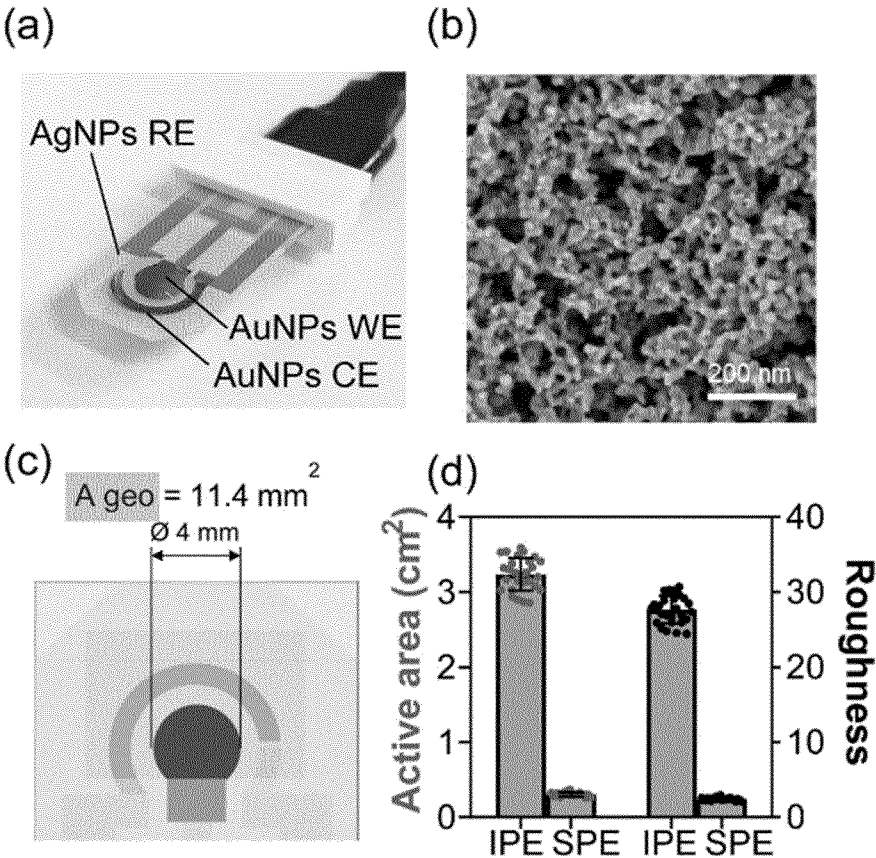


FIG 13

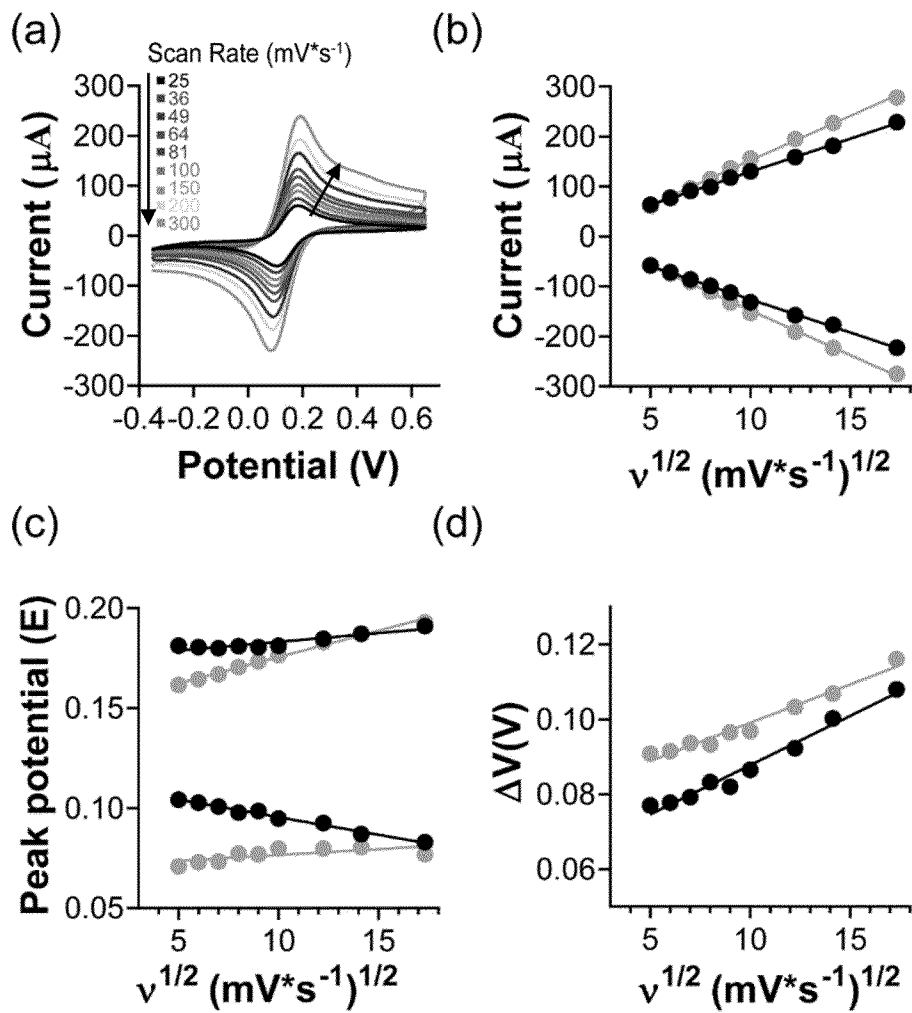


FIG 14

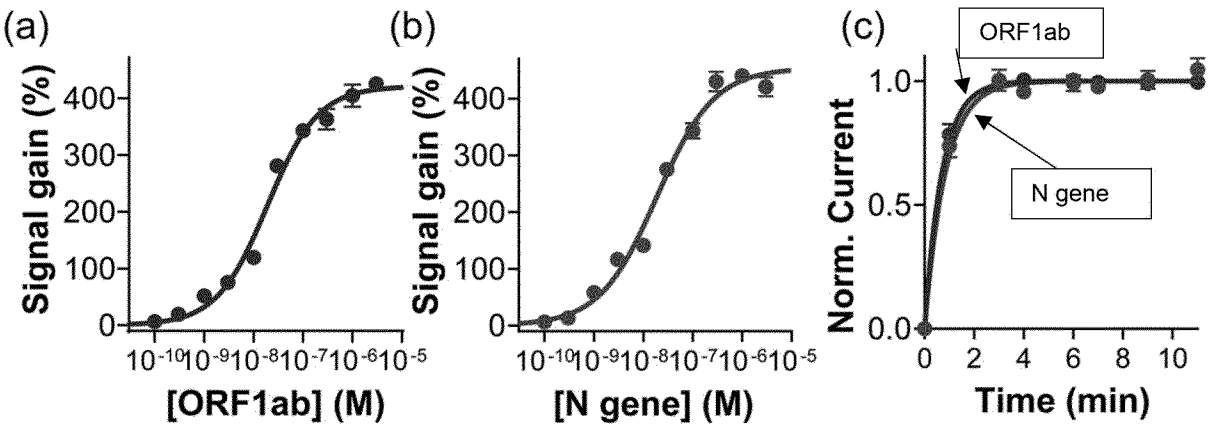
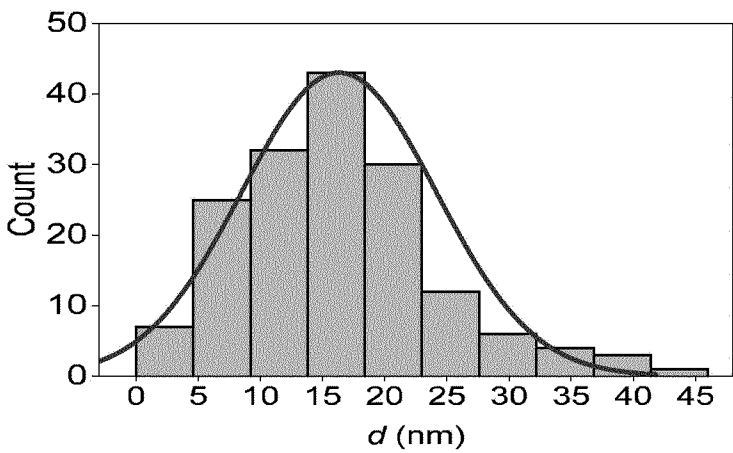


FIG 15



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/068272

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	B22F1/0545	B22F1/102	B22F3/23	C22C1/04	C09D11/52
	C09D11/54	H05K1/09	H05K3/12	B22F7/04	C09D11/322
ADD.					
According to International Patent Classification (IPC) or to both national classification and IPC					
B. FIELDS SEARCHED					
Minimum documentation searched (classification system followed by classification symbols)					
B22F C22C C09D H05K					
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched					
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)					
EPO-Internal, WPI Data					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the relevant passages				Relevant to claim No.
X	KR 101 481 629 B1 (AMOGREENTECH CO LTD [KR]) 16 January 2015 (2015-01-16)				1-14, 17-20, 22,24
Y	claims 1, 8				15
A	paragraphs [0039], [0061]				16,21,23

X	US 2022/010160 A1 (ZHONG CHUAN-JIAN [US] ET AL) 13 January 2022 (2022-01-13)				16-24
Y	example 3				15
A	paragraphs [0392], [0500]				1-14

X	US 2012/168684 A1 (MAGDASSI SHLOMO [IL] ET AL) 5 July 2012 (2012-07-05)				17-22,24
A	paragraph [0056] - paragraph [0058] paragraphs [0061], [0066], [0072] paragraph [0094] example 1				1-15,23

	-/-				
☒ Further documents are listed in the continuation of Box C.					
☒ See patent family annex.					
* Special categories of cited documents :					
"A" document defining the general state of the art which is not considered to be of particular relevance			"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention		
"E" earlier application or patent but published on or after the international filing date			"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone		
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)			"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art		
"O" document referring to an oral disclosure, use, exhibition or other means			"&" document member of the same patent family		
"P" document published prior to the international filing date but later than the priority date claimed					
Date of the actual completion of the international search			Date of mailing of the international search report		
27 September 2024			16/10/2024		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016			Authorized officer Fodor, Anna		

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/068272

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 110 461 101 A (UNIV TSINGHUA) 15 November 2019 (2019-11-15) abstract example 2 -----	1 - 24
A	ZHUANG HUI ET AL: "Chemical sintering of direct-written silver nanowire flexible electrodes under room temperature", NANOTECHNOLOGY, INSTITUTE OF PHYSICS PUBLISHING, BRISTOL, GB, vol. 28, no. 28, 23 June 2017 (2017-06-23) , page 285703, XP020317724, ISSN: 0957-4484, DOI: 10.1088/1361-6528/AA76CE [retrieved on 2017-06-23] 2.3 Direct-writing of Ag NW electrodes and low temperature sintering -----	1 - 24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/068272

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
KR 101481629	B1	16-01-2015	NONE
US 2022010160	A1	13-01-2022	NONE
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		EP 2411560 A1 01-02-2012	
		JP 2012521493 A 13-09-2012	
		KR 20130010101 A 25-01-2013	
		US 2012168684 A1 05-07-2012	
		WO 2010109465 A1 30-09-2010	
CN 110461101	A	15-11-2019	NONE