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(54) **Title:** CATALYSTS, METHODS OF MAKING CATALYSTS, AND METHODS OF USE

(57) **Abstract:** Embodiments of the present disclosure provide for catalysts, methods of making catalysts, methods of using catalysts, and the like. In an embodiment, the method of making the catalysts can be performed in a single step with a metal nanoparticle precursor and a metal oxide precursor, where a separate stabilizing agent is not needed.

**CATALYSTS, METHODS OF MAKING CATALYSTS, AND METHODS OF USE**

## CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority to U.S. provisional application entitled "CATALYSTS, METHODS OF MAKING CATALYSTS, AND METHODS OF USE," having serial number 61/695,547, filed on August 31<sup>st</sup>, 2012, which is entirely incorporated herein by reference

## BACKGROUND

After polymerization, the oxidation of hydrocarbons represents the second largest contributor to the total product value in the chemical industry (18%). If the selective oxidation of hydrocarbons could be efficiently carried out without using oxidants, it would contribute to the conversion of current chemical production into a green and sustainable chemistry. Thus, there is a need for new catalysts.

## SUMMARY

Embodiments of the present disclosure provide for catalysts, methods of making catalysts, methods of using catalysts, and the like. An embodiment of the present disclosure includes a particle having a gold nanoparticle having  $\text{TiO}_x$  inorganic network disposed on the gold nanoparticle, where the gold nanoparticle is about 1 to 5 nm in diameter, and where x is about 1 to 2.

An embodiment of the present disclosure includes a particle having a metal nanoparticle having metal inorganic network or metal oxide inorganic network, disposed on the metal nanoparticle, where the metal nanoparticle is about 1 to 5 nm in diameter.

An embodiment of the present disclosure includes a process to produce a nanoparticle of a metal with a second metal or metal oxide disposed thereon comprising: reduction of a metallic salt with a single reducing agent of the second organometallic compound in a single step process, where the reducing agent acts to stabilize the nanoparticle so that a separate stabilizing agent is not used.

## BRIEF DESCRIPTION OF THE DRAWINGS

Further aspects of the present disclosure will be more readily appreciated upon review of the detailed description of its various embodiments, described below, when taken in conjunction with the accompanying drawings.

FIG. 1 illustrates a schematic of a synthesis and a HRTEM image of Au-TiO<sub>x</sub> nanocomposite, where the Au nanoparticles are about 1.5 to 2.5 μm.

FIG. 2 illustrates a graph of HRTEM image of a Au-Ti nanocomposite with Au NP size:  $2.1 \pm 0.4$  nm.

FIG. 3 illustrates solid state <sup>1</sup>H and <sup>13</sup>C NMR that were used to characterize the organic part of the composite.

FIG. 4 illustrates spectra illustrating the stabilization by titanium oxide.

## DETAILED DESCRIPTION

This disclosure is not limited to particular embodiments described, and as such may, of course, vary. The terminology used herein serves the purpose of describing particular embodiments only, and is not intended to be limiting, since the scope of the present disclosure will be limited only by the appended claims.

Where a range of values is provided, each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limit of that range and any other stated or intervening value in that stated range, is encompassed within the disclosure. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges and are also encompassed within the disclosure, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the disclosure.

Embodiments of the present disclosure will employ, unless otherwise indicated, techniques of material science, chemistry, and the like, which are within the skill of the art. Such techniques are explained fully in the literature.

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to perform the methods and use the compositions and compounds disclosed and claimed herein. Efforts have been made to

ensure accuracy with respect to numbers (*e.g.*, amounts, temperature, *etc.*), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C, and pressure is at or near atmospheric. Standard temperature and pressure are defined as 20 °C and 1 atmosphere.

Before the embodiments of the present disclosure are described in detail, it is to be understood that, unless otherwise indicated, the present disclosure is not limited to particular materials, reagents, reaction materials, manufacturing processes, dimensions, frequency ranges, applications, or the like, as such can vary. It is also to be understood that the terminology used herein is for purposes of describing particular embodiments only, and is not intended to be limiting. It is also possible in the present disclosure that steps can be executed in different sequence, where this is logically possible. It is also possible that the embodiments of the present disclosure can be applied to additional embodiments involving measurements beyond the examples described herein, which are not intended to be limiting. It is furthermore possible that the embodiments of the present disclosure can be combined or integrated with other measurement techniques beyond the examples described herein, which are not intended to be limiting.

It should be noted that, as used in the specification and the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a support” includes a plurality of supports. In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings unless a contrary intention is apparent.

Each of the applications and patents cited in this text, as well as each document or reference cited in each of the applications and patents (including during the prosecution of each issued patent; “application cited documents”), and each of the PCT and foreign applications or patents corresponding to and/or claiming priority from any of these applications and patents, and each of the documents cited or referenced in each of the application cited documents, are hereby expressly incorporated herein by reference. Further, documents or references cited in this text, in a Reference List before the claims, or in the text itself; and each of these documents or references (“herein cited references”), as well as each document or reference cited in each of the herein-cited references (including

any manufacturer's specifications, instructions, etc.) are hereby expressly incorporated herein by reference.

Prior to describing the various embodiments, the following definitions are provided and should be used unless otherwise indicated.

### *Discussion*

Embodiments of the present disclosure provide for catalysts, methods of making catalysts, methods of using catalysts, and the like. Catalysts of the present disclosure can be useful in various catalytic transformations. In an embodiment, catalysts of the present disclosure can be used for the direct propylene epoxidation with molecular oxygen in the presence of a sacrificial reductant based on such bifunctional systems (catalyst).

In an embodiment, the method of making the catalysts can be performed in a single step with a metal nanoparticle precursor and a metal oxide precursor, where a separate stabilizing agent is not needed. In an embodiment, using methods of the present disclosure allows stabilization of the catalyst so that very small metal nanoparticles (*e.g.*, 1 to 3 nm) can be formed, which is advantageous.

In an embodiment, the catalyst (also referred to as a "bifunctional catalyst") is a metal nanoparticle having a metal or metal oxide inorganic network disposed (*e.g.*, 0.1 to 99% coverage, about 1 to 50% coverage, or about 10 to 30% coverage, of the surface of the metal nanoparticle) on the metal nanoparticle. In an embodiment, the metal nanoparticle is exposed so that it can be involved in catalytic reactions. In an embodiment, the metal nanoparticle is about 1 to 5 nm, about 1 to 3 nm, or about 1.5 to 2.5 nm, in diameter. In an embodiment, the metal nanoparticle can be a late transition metal, Au, or Ag. In an embodiment, the metal nanoparticle can be Au and can have a diameter of about 1 to 5 nm, about 1 to 3 nm, or about 1.5 to 2.5 nm. In an embodiment, the metal of the metal organic network can be Ti, Zr, Hf, Al, or Si. In an embodiment, the metal oxide of the metal oxide organic network can be represented by  $M_yO_x$  in which M is Ti, Zr, Hf, Al, or Si, and x and y are appropriate for the oxide formed (*e.g.*, x can be 1 to 3 and y can be 1 or 2). In an embodiment, the metal organic network or the metal oxide organic network can be about 1 nm or less to 5 nm, about 1 or less to 3 nm, or about 1 or less to 2.5 nm, in diameter. In a particular embodiment, the catalyst can be a gold nanoparticle having a  $TiO_x$  inorganic

network disposed on the gold nanoparticle, where the gold nanoparticle is about 1 to 5 nm in diameter, wherein x is about 1 to 2.

As described in more detail herein, embodiments of the present disclosure can include a process to produce a nanoparticle of a metal with a second metal or metal oxide (reducing agent) disposed thereon in a single step. In an embodiment, the method includes the reduction of a metallic salt with a single reducing agent (second organometallic compound) in a single step process. This is opposed to other methods that include multiple steps and also includes a reducing agent and a stabilizing agent. In an embodiment, the reducing agent acts to stabilize the nanoparticle so that a separate stabilizing agent is not used in the process for making the catalyst.

In an embodiment, the metallic salt is a metal nanoparticle precursor and the second organometallic compound is a metal oxide precursor (or metal precursor if the catalyst includes a metal inorganic network). In an embodiment, the metal oxide precursor can be derived from a family of ligands having amido ligands (*e.g.*, titanium metal precursor can include  $Ti(NR_2)_4$ , where R is an alkyl organic ligand, R=Me, Et, propyl, etc.). Additional details are provided below.

It is known, that many functional properties of materials depend on the size of nanoparticles. For Au particles, catalytic properties are known to vary with the size of the crystallite and depend also of the effect of the support. Presently, two agents, a reducing agent and a stabilizing agent, are needed to produce gold nanoparticles. Here the reduction of the metal, gold, and the formation of the support, metal oxide inorganic network, can be done both at the same time without any use of organic compound. Thus, the synthesis of embodiments of the present disclosure can be performed faster and use less chemicals.

In an embodiment, the catalysts can be metal nanoparticles having a metal or metal oxide (or a different type of metal) disposed on the surface of the metal nanoparticle. In an embodiment, the metal nanoparticle can be gold and the metal oxide can be  $TiO_x$ , where the titanium complex is directly graphed onto the gold nanoparticle. These inorganic-organometallic hybrids could then be oxidized under mild conditions in order to transform the well-defined and tunable Ti organo-shell into a Au- $TiO_x$  nanocomposite (or Au-Ti nanohybrid in case of only partial oxidation of the organometallic shell) with privileged interaction via *e.g.*, an oxygen atom between Au and Ti centers.

In an embodiment, the bifunctional Au-Ti (catalysts of the present disclosure) of the present disclosure includes small Au nanoparticles (*e.g.*, about 1 and 5 nm) that are active for catalysis. Traditional reducing agents and stabilizing agents are not necessary to reduce the gold precursor. Indeed, the titanium metal oxide precursor chemical, titanium amide complex, plays the role of both reducing and stabilizing agent. This complex reduces the gold(III) to gold(0) and creates the inorganic network  $\text{TiO}_x$  which stabilizes the gold nanoparticles. As a result, very small gold nanoparticles (*e.g.*, about 1 nm) can be produced without addition of any extra stabilizing agents. It is known that it is very difficult to stabilize such small particles, but embodiments of the present disclosure can accomplish this goal.

As described above, embodiments of the present disclosure include a one-pot synthesis to produce a bifunctional catalytic system, such as a gold (Au) (metal nanoparticle) and titanium (Ti) (metal oxide) metal based bifunctional catalytic system.

In an embodiment, the synthesis involves a metal nanoparticle precursor (*e.g.*, gold precursor) and a metal oxide precursor (*e.g.*, a titanium amide complex), which is moisture sensitive and water soluble.

In an embodiment, the gold precursor can include gold(III) chloride trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) and the dimethyl(acetylacetonate) gold(III) ( $\text{Au}(\text{acac})\text{Me}_2$ ). In an embodiment, the titanium metal precursor can include  $\text{Ti}(\text{NR}_2)_4$  contains amide groups, where R is an alkyl organic ligand, R=Me, Et. In an embodiment, the reaction solvent is anhydrous tetrahydrofuran (THF). In an embodiment, the reaction includes water.

In an embodiment, the synthesis is carried out under a gas (*e.g.*, argon) atmosphere. In an embodiment, gold precursors  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{Au}(\text{acac})\text{Me}_2$  are bought from Sigma Aldrich and Strem Chemical respectively. The titanium amide complexes are also commercial but they are synthesized according to the literature (Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* 1960, 3857).

The following describes an embodiment of a method for producing a catalyst of the present disclosure. In particular, a typical experiment using  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  is described below. A mixture of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (100 mg, 0.254 mmol, 1 eq) and water (45.7  $\mu\text{L}$ , 2.54 mmol, 10 eq) in THF (106 mL) was added drop wise via a cannula to a solution of  $\text{Ti}(\text{NMe}_2)_4$  (142 mg, 0.635 mmol, 2.5 eq) in 15 mL of THF. After 15 min, the yellow

reaction mixture turns into purple. At the end of the addition the gold concentration is  $2.1 \times 10^{-3} \text{ mol. L}^{-1}$ , the reaction mixture is heated at  $70 \text{ }^\circ\text{C}$  under argon atmosphere during 1 hour. Then the material is centrifuged (8 000 rpm, 5 min) to remove the solvent, washed with deionized water, ethanol and dried at  $80 \text{ }^\circ\text{C}$  in an oven during 1 hour followed by 4 hours under vacuum at room temperature.

The following describes another embodiment of a method for producing a catalyst of the present disclosure. In particular, a typical experiment using  $\text{Au}(\text{acac})\text{Me}_2$ . A solution of  $\text{Au}(\text{acac})\text{Me}_2$  (100 mg, 0.306 mmol, 1 eq) in THF (130 mL) was added drop wise via a cannula to a solution of  $\text{Ti}(\text{NMe}_2)_4$  (171 mg, 0.765 mmol, 2.5 eq) in 16 mL of THF. At the end of the addition 55  $\mu\text{L}$  of water (3.06 mmol, 10 eq) was added into the yellow reaction mixture, which turns into a white color. The reaction mixture is heated at  $85 \text{ }^\circ\text{C}$  during 2 hours, the reaction mixture turns into pink/purple. The same work up was used to treat this material.

These can produce  $\text{Au-TiO}_x$  nanocomposites, where the features include: pink colloidal solutions are obtained; small gold nanoparticles are formed, the particle size is about 1 (first process described directly above) to 5 nm (the second process described directly above), the  $\text{TiO}_x$  matrix is amorphous, and the  $\text{TiO}_x$  stabilized the gold nanoparticles.

## EXAMPLES

### Example 1

#### A)

A mixture of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (50 mg, 0.127 mmol, 1 eq) in THF (53 mL) was added drop wise via a cannula to a solution of  $\text{TiCl}_4$  (60 mg, 0.317 mmol, 2.5 eq) in 7.5 mL of THF. At the end of the addition, the reaction mixture is heated at  $70 \text{ }^\circ\text{C}$  under argon atmosphere during 1 hour. No color change occurred.

Example 1A) shows that the mixture of a metallic salt of Au is not reduced by a titanium complex with any ligand.



B)

A Au salt was mixed with a titanium complex containing amido ligand to produce a gold nanoparticle covered with TiO<sub>2</sub> amorphous layer.

In particular, a mixture of H<sub>2</sub>AuCl<sub>4</sub>·3H<sub>2</sub>O (100 mg, 0.254 mmol, 1 eq) in THF (106 mL) was added drop wise via a cannula to a solution of Ti(NMe<sub>2</sub>)<sub>4</sub> (142 mg, 0.635 mmol, 2.5 eq) in 15 mL of THF. After 15 min, the yellow reaction mixture turns into purple. At the end of the addition, the reaction mixture is heated at 70 °C under argon atmosphere during 1 hour. Then the material is centrifuged (8 000 rpm, 5 min) to remove the solvent, washed with deionized water, ethanol and dried at 80 °C in an oven during 1 hour followed by 4 hours under vacuum at room temperature.

STEM images were done after the end of the addition. It underlined the stabilization of the Au core by a matrix of titanium oxide. FIG. 4 illustrates spectra illustrating the stabilization by titanium oxide.

C)

A Au salt was mixed with a titanium complex containing amido ligand to produce small gold nanoparticles.

A mixture of H<sub>2</sub>AuCl<sub>4</sub>·3H<sub>2</sub>O (100 mg, 0.254 mmol, 1 eq) in THF (106 mL) was added drop wise via a cannula to a solution of Ti(NEt<sub>2</sub>)<sub>4</sub> (214 mg, 0.635 mmol, 2.5 eq) in 15 mL of THF. At the end of the addition, the yellow reaction mixture turns into light purple, then the reaction mixture is heated at 70 °C under argon atmosphere during 1 hour. HRTEM images were done at the end of the addition and shown small 2.1 Au NPs.

**Example 2**

After polymerization, the oxidation of hydrocarbons represents the second largest contributor to the total product value in the chemical industry (18%). If the selective oxidation of hydrocarbons could be efficiently carried out by dioxygen or air alone instead of using oxidants, it would contribute to the conversion of current chemical production into a green and sustainable chemistry. Selective epoxidation is carried out by using oxidizing agent associated with catalytic transition metal complexes. It can be based on gold/titania catalysts using a mixture of hydrogen and oxygen under mild conditions. To

design new catalysts, the key challenge is to control the fabrication of well-defined nanoparticulate materials to increase the catalytic activity.

The strategy presented here to prepare new catalysts containing gold and titanium consists in a one pot synthesis using exclusively gold and titanium precursors in solution (no reducing or stabilizing agent is present). This new way leads to the formation of Au-TiO<sub>x</sub> nanocomposite containing small gold nanoparticles within a hybrid TiO<sub>x</sub> matrix. FIG. 1 illustrates a schematic of a synthesis and a HRTEM image of Au-TiO<sub>x</sub> nanocomposite, where the Au nanoparticles are about 1.5 to 2.5 μm.

The titanium complexes play a role because they contain organic ligands which act as reducing agents and subsequently stabilizing agents for the Au particle formed. Compared to the metal surface organometallic approach which has led to Au@SiC<sub>8</sub>, no addition of strong reducing agent such as NaBH<sub>4</sub> is needed to carry out reduction of the gold precursor in the presence of an organometallic compound of the second element.

#### PARTICLES SIZE WITH LIGAND R<sub>2</sub>

HRTEM was used to study the effect of the synthesis parameters on the size, size distribution and morphology of the Au-TiO<sub>x</sub> composite. By selecting an appropriate ligand of the titanium complex, small Au NPs with a spherical shape and a homogeneous distribution could be obtained. The TiO<sub>x</sub> matrix appears amorphous on the HRTEM image. FIG. 2 illustrates a graph of HRTEM image of a Au-Ti nanocomposite with Au NP size:  $2.1 \pm 0.4$  nm.

#### CHARACTERIZATION OF THE INORGANIC NETWORK BY NMR

FIG. 3 illustrates solid state <sup>1</sup>H and <sup>13</sup>C NMR that were used to characterize the organic part of the composite. The inorganic network is made of Ti-O-Ti bonds. The protons of the hydroxyl groups born by Ti are clearly seen on the solid NMR spectrum. Also, due to incomplete condensation during the synthesis, some R ligands are retained in the pseudo-titania network. Furthermore, the hybrid nanocomposite also contains tetrahydrofuran solvent molecules.

#### CONCLUSION

The new bifunctional systems Au-Ti contain small Au nanoparticles (between 1 and 5 nm) that can potentially be active for catalysis and for the epoxidation reaction with molecular oxygen in particular. Reduction of gold(III) to gold(0) and formation of the TiO<sub>x</sub>

inorganic network with residual organic functions, which stabilizes the Au NPs, rely on the Ti precursor and on the synthesis conditions. Strong interaction between gold and TiO<sub>x</sub> is expected.

It should be noted that ratios, concentrations, amounts, and other numerical data may be expressed herein in a range format. It is to be understood that such a range format is used for convenience and brevity, and thus, should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. To illustrate, a concentration range of “about 0.1% to about 5%” should be interpreted to include not only the explicitly recited concentration of about 0.1 wt% to about 5 wt%, but also include individual concentrations (*e.g.*, 1%, 2%, 3%, and 4%) and the sub-ranges (*e.g.*, 0.5%, 1.1%, 2.2%, 3.3%, and 4.4%) within the indicated range. In an embodiment, the term “about” can include traditional rounding according to the measuring technique and the numerical value. In addition, the phrase “about ‘x’ to ‘y’” includes “about ‘x’ to about ‘y’”.

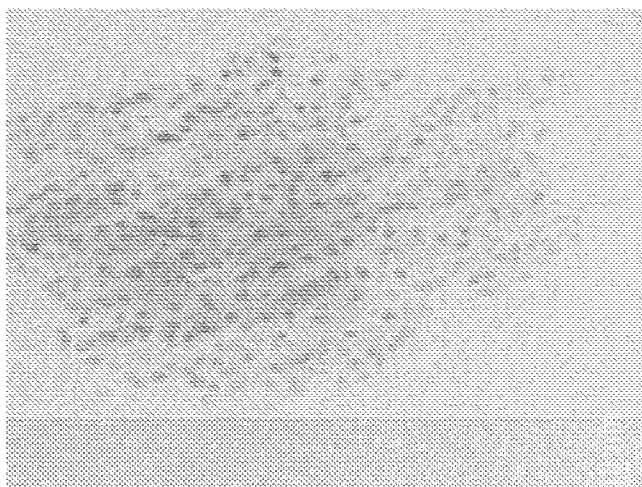
While only a few embodiments of the present disclosure have been shown and described herein, it will become apparent to those skilled in the art that various modifications and changes can be made in the present disclosure without departing from the spirit and scope of the present disclosure. All such modification and changes coming within the scope of the appended claims are intended to be carried out thereby.

## CLAIMS

We claim at least the following:

1. A particle comprising: a gold nanoparticle having  $\text{TiO}_x$  inorganic network disposed on the gold nanoparticle, wherein the gold nanoparticle is about 1 to 5 nm in diameter, wherein x is about 1 to 2.
2. A particle comprising: a metal nanoparticle having metal inorganic network or metal oxide inorganic network, disposed on the metal nanoparticle, wherein the metal nanoparticle is about 1 to 5 nm in diameter.
3. The particle of claim 2, wherein the particle is composed of a late transition metal, Au, or Ag.
4. The particle of claim 2, wherein the metal is Au.
5. The particle of claim 2, wherein the metal oxide inorganic network is  $\text{M}_y\text{O}_x$  in which M is Ti, Zr, Hf, Al, Si, and x is 1 to 3 and y is 1 or 2.
6. The particle of claim 2, wherein the metal oxide inorganic network is a  $\text{TiO}_x$  inorganic network, wherein x is about 1 to 2.
7. The particle of claim 2, wherein the metal nanoparticle has a diameter of about 1.5 to 2.5.
8. A process to produce a nanoparticle of a metal with a second metal or metal oxide disposed thereon comprising: reduction of a metallic salt with a single reducing agent of the second organometallic compound in a single step process, wherein the reducing agent acts to stabilize the nanoparticle so that a separate stabilizing agent is not used.
9. The process of claim 8, wherein the reducing agent of the second organometallic compound is  $\text{Ti}(\text{NR}_2)_4$ , where R is an alkyl organic ligand.

10. The process of claim 8, wherein metallic salt is selected from: gold(III) chloride trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) or dimethyl(acetylacetonate) gold(III) ( $\text{Au}(\text{acac})\text{Me}_2$ ).
11. The process of claim 8, wherein the reducing agent of the second organometallic compound is  $\text{Ti}(\text{NR}_2)_4$ , where R is an alkyl organic ligand and the metallic salt is selected from: gold(III) chloride trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) or dimethyl(acetylacetonate) gold(III) ( $\text{Au}(\text{acac})\text{Me}_2$ ).
12. The process of claim 8, wherein the nanoparticle is composed of a late transition metal, Au, or Ag.
13. The process of claim 8, wherein the metal oxide is  $\text{M}_y\text{O}_x$  in which M is Ti, Zr, Hf, Al, Si, and x is 1 to 3 and y is 1 or 2.
14. The process of claim 8, wherein the metal is Au and the oxide is derived from an organometallic compound derived from a family of ligands with amido ligands.
15. The particle of claim 8, wherein the metal nanoparticle has a diameter of about 1.5 to 2.5.



HRTEM image of a Au-TiO<sub>x</sub> nanocomposite containing 1.5-2.5 nm Au

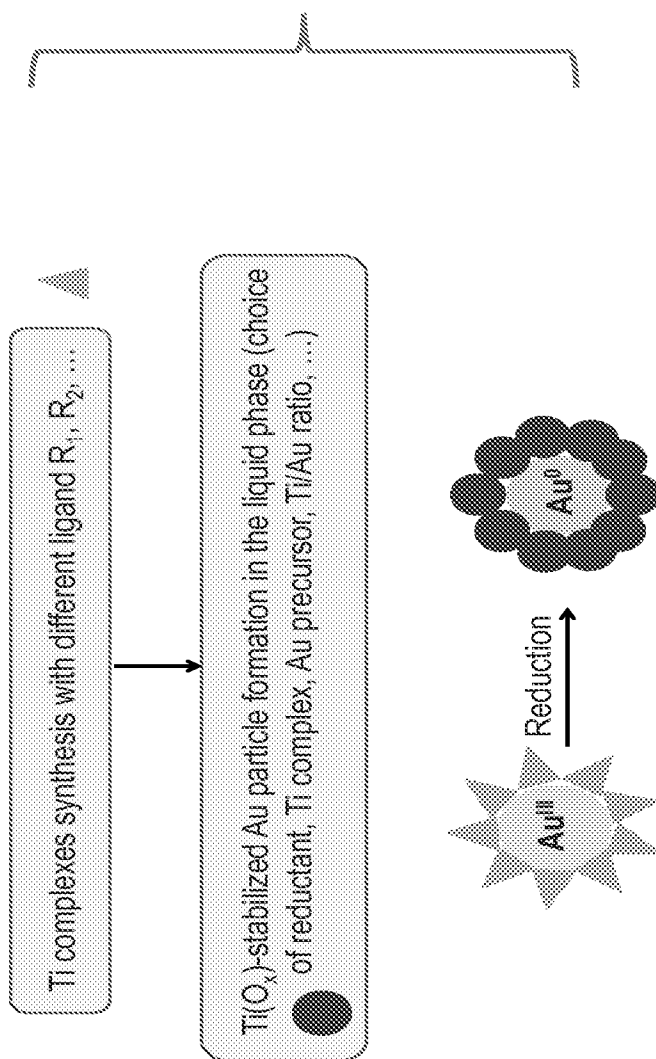
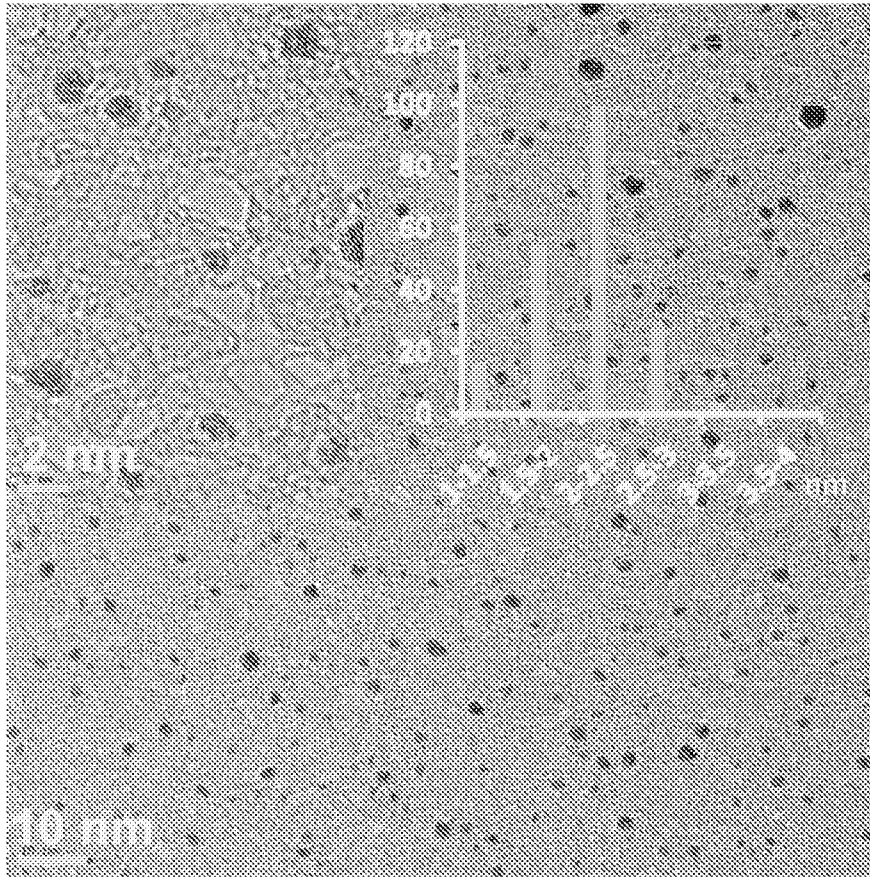


FIG. 1



*HRTEM image of a Au-Ti  
nanocomposite with Au  
NP size:  $2.1 \pm 0.4$  nm*

**FIG. 2**

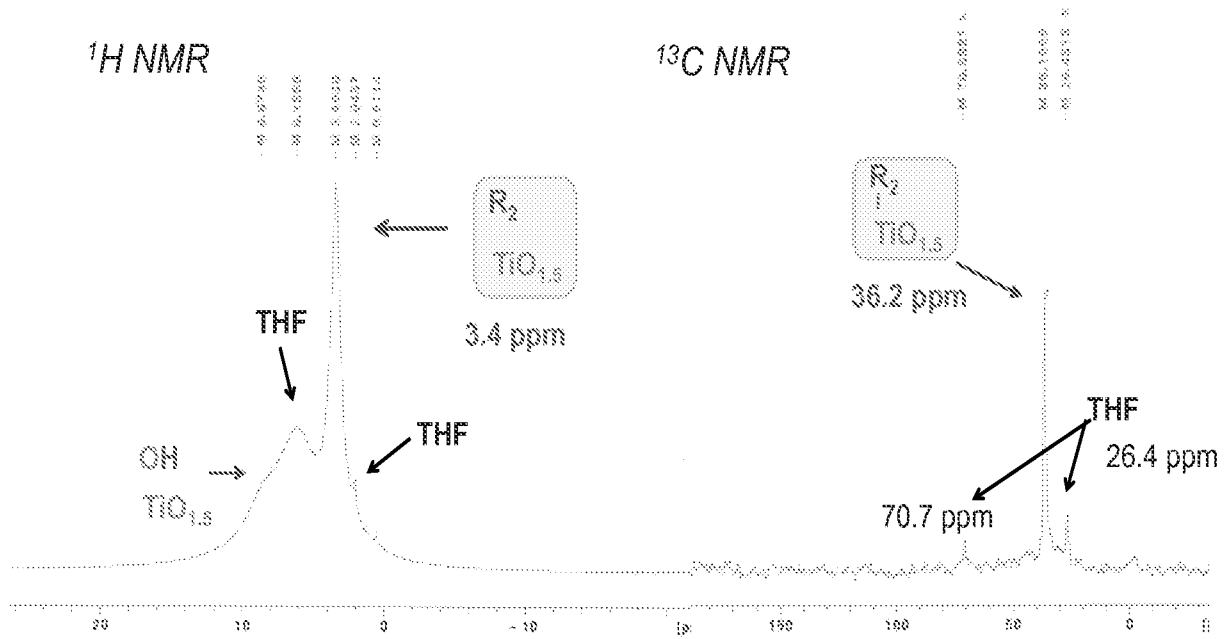


FIG. 3



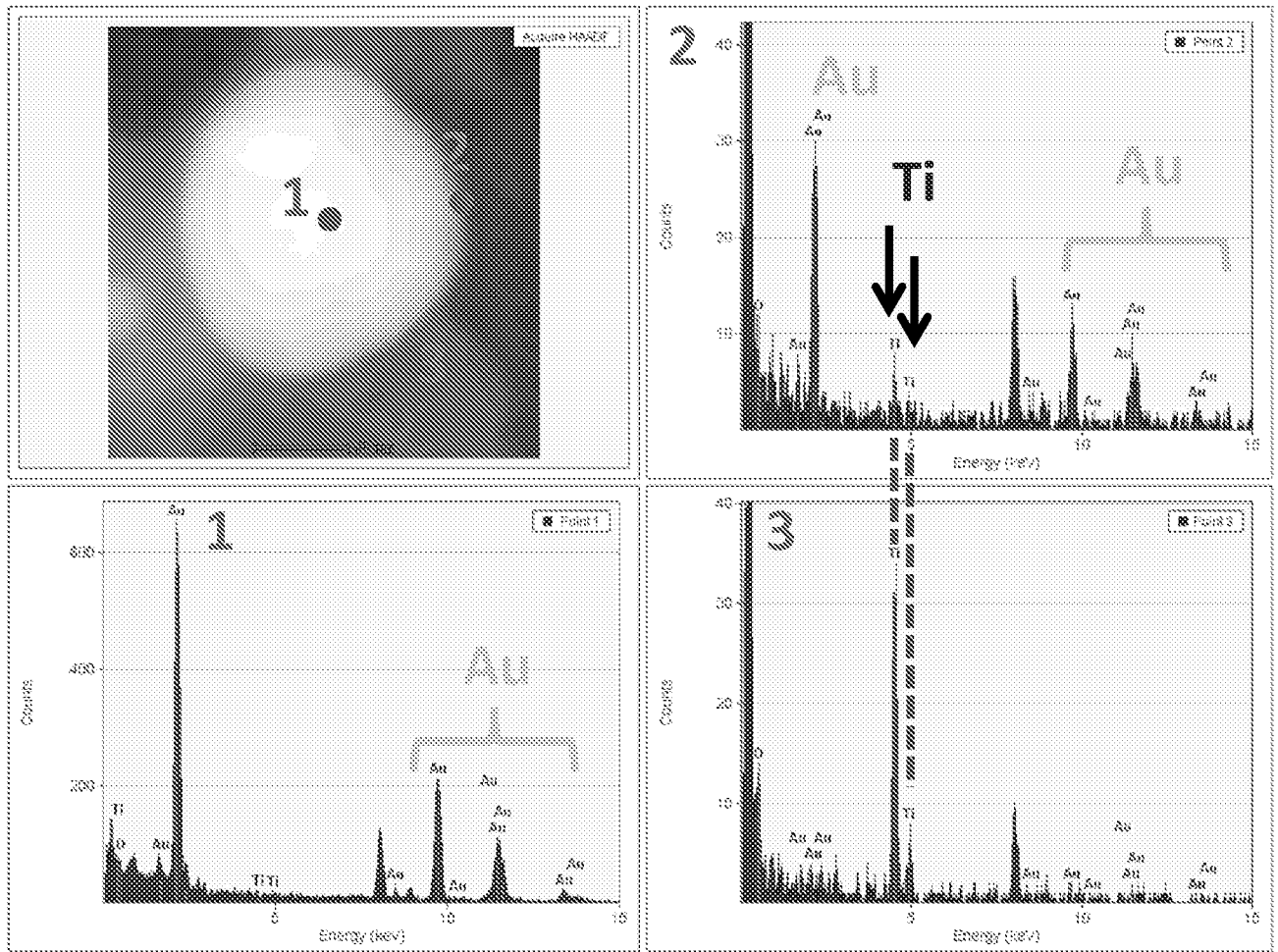


FIG. 4