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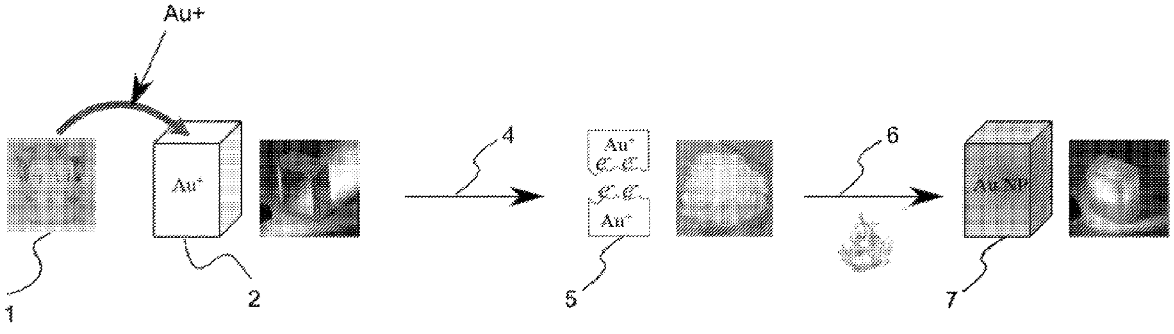


Figure 1

(57) **Abstract:** A method of forming metallic nanoparticles in glass is disclosed that creates evenly distributed metallic nanoparticles with desired size in any glass type. Formation of a source of electrons trapped on the surface of the glass particles by crushing and grinding glass material into powder followed by heat treatment of the glass powder to neutralise metal ions doped in the glass by the trapped source of electrons, followed by the aggregation and growth of the metal into nanoparticles. The present method allows the homogeneous distribution of metal nanoparticles throughout the glass volume. The size and concentration of the metallic nanoparticles is controlled by the heat treatment temperature and duration as well as the amount of metal ions.

METHOD FOR CONTROLLING THE FORMATION OF METALLIC NANOPARTICLES IN GLASS AND PRODUCTS THEREOF

Field of the invention

The present invention relates to a method of producing metallic nanoparticles in glass material.

Background

The formation of metallic nanoparticles in glass, which is referred to as striking by glass manufacturers, involves the provision of “free” electrons to neutralize metal ions present in the glass. This is typically achieved through the use of polyvalent dopants, including the known toxins PbO and As_2O_3, post-annealing in reducing atmosphere (H_2), or high-energy irradiations (x-ray, gamma- ray). However, these conventional approaches have notoriously limited the success of creating metallic nanoparticles to silicate-based glasses or localized scale (sub micrometer).

In some emerging glass manufacturing technologies such as 3D printing, which uses glass powders, post-processing of the glass powder could induce undesired coloration of the resulting products due to the formation of reduced metal species (trace metal ions reduced by fracture-induced electrons).

Summary of the invention

The method of the present invention is convenient and applicable to many different glass compositions. In particular, it is not necessarily limited to any particular oxide glass type but can also be extended to other glass materials.

For oxide glass, the size, concentration and distribution of the metal nanoparticles in the glass are able to be varied depending on specific requirements, providing the ability for the user to tune the colour and optical properties of the resulting glass.

A method of producing metallic nanoparticles in glass including the steps of:

a) preparing a glass precursor material including;

heating a combination of at least one raw glass material with a metal base material to a first temperature to form a glass precursor melt;

cooling the melt to provide the glass precursor material;

b) the glass precursor material then being ground to a predetermined particle size to form a ground glass precursor material;

c) heating the ground glass precursor material to a second temperature for a predetermined period of time to at least partially bind particles of the glass precursor material to one another.

In preference, at the second temperature the glass particles (containing metal in ionic/atomic dispersion) at least partially bind together.

In preference, the second temperature can be below, at or above the glass softening temperature defined as the temperature at which the viscosity of the glass material is approximately $10^{7.6}$ poise.

In preference, the second temperature is between about ±30% of the glass softening temperature of the ground glass precursor material.

In preference, the second temperature is between about ±20% of the glass softening temperature of the ground glass precursor material.

In preference, the second temperature is between about ±10% of the glass softening temperature of the ground glass precursor material.

In preference, the second temperature is between about ±5% of the glass softening temperature of the ground glass precursor material.

In preference, the raw glass material is at least one glass material selected from the group consisting of at least one glass network former or a combination of at least one glass network former and at least one glass network intermediate/modifier.

In preference, the glass network former is selected from at least one TeO_2, GeO_2, B_2O_3, SiO_2, P_2O_5, V_2O_5, Bi_2O_3, Sb_2O_3/Sb_2O_5, As_2O_3/As_2O_5 or combinations thereof.

In preference, the glass network intermediate/modifier is selected from at least one Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O, BeO, MgO, CaO, SrO, BaO, ZnO, PbO/PbO_2, Al_2O_3, TiO_2, ZrO_2, ThO_2, CdO, Sc_2O_3, La_2O_3, Y_2O_3, SnO/SnO_2, In_2O_3, WO_3 or combinations thereof.

In preference, the raw glass material is at least one glass material selected from the group consisting of tellurite (TeO_2-ZnO-Na_2O [TZN]), germanate (GeO_2-Na_2O [GN]), borate (B_2O_3-Na_2O [BN]) phosphate (P_2O_5-Ag_2) [PAg]), borosilicate (commercial BK7) and silicate (SiO_2-Na_2O [SN], SiO_2-CaO-Na_2O [SCN], and commercial Gaffer Batch, K100 and F2).

In preference, the metal base material is a noble metal material.

In preference, the method step a) includes addition of at least one dopant material.

In preference, the metal base material is selected from at least one noble metal, metal alloy, metal compound (metal oxide, metal salt: metal chloride/sulfide/nitrite) or combinations thereof.

In preference, the at least one dopant material is selected from at least one noble metal, metal alloy, metal compound (metal oxide, metal salt: metal chloride/sulfide/nitrite) or combinations thereof.

In preference, the at least one noble metal is selected from the group consisting of copper, ruthenium, rhodium, palladium, silver, osmium, iridium, platinum and gold.

In preference, the noble metal is in a concentration of between 1 ppm and 2000 ppm.

In preference, the noble metal is in a concentration of between 5 ppm and 20 ppm.

In preference, the noble metal is in a concentration of between 8 ppm and 15 ppm.

In preference, the noble metal is in a concentration of 10 ppm.

In preference, the glass precursor material is ground to a predetermined particle size of between 0.01 – 1000 micrometre.

In preference, the glass precursor material is ground to a predetermined particle size of between 0.01 – 10 micrometre.

In preference, the predetermined period of time of heating the ground glass precursor material to the second temperature is between about 5 min and about 24 h.

In preference, the predetermined period of time is between about 10 min and about 6 hr.

In preference, the predetermined period of time is between about 10 min and about 2 hr.

In preference, the second temperature is the temperature at which the viscosity of the glass material is approximately $10^{7.6}$ poise.

In preference, the glass material TeO_2-ZnO-Na_2O (TZN) is in the ratio of 75:15:10 mol%.

In preference, the glass material GeO_2-Na_2O (GN) is in the ratio of 70:30 mol%.

In preference, the glass material B_2O_3-Na_2O (BN) is in the ratio of 70:30 mol%.

In preference, the glass material P_2O_5-Ag_2O (PAg) is in the ratio of 50:50 mol%.

In preference, the glass material SiO_2-CaO-Na_2O (SCN) is in the ratio of 70:10:20 mol%.

A glass article formed by the method of:

a) preparing a glass precursor material including;

heating a combination of a metal base material with at least one raw glass material to a first temperature to form a glass precursor melt;

cooling the glass precursor melt to provide the glass precursor material;

b) the glass precursor material then being ground to a predetermined particle size to form a ground glass precursor material;

c) heating the ground glass precursor material to a second temperature for a predetermined period of time to at least partially bind particles of the glass precursor material to one another.

A further embodiment of the invention resides in a method for controlling the formation of metallic nanoparticles in an oxide glass containing a metal compound where said method includes:

a. crushing the glass containing a noble metal base material or at least one dopant to a powder to produce a source of electrons on the glass powder surface;

b. reheating the glass powder at a temperature for a certain duration to at least partially bind particles of the glass precursor material to one another to allow the metal ions in the glass to be reduced by the source of electrons to form a metallic nanoparticle, or optionally adding an oxidant to remove at least some of the electrons to control or eliminate the formation of the metallic nanoparticle.

Yet a further embodiment of the present invention resides in a method for controlling the formation of metallic nanoparticles in an oxide glass where said method includes

a. forming a metal ion-doped precursor glass melt by incorporating a metal compound into the glass batch and melting at an elevated temperature;

b. Cooling the precursor glass melt to solidify the precursor glass

c. Crushing the solidified precursor glass in to a powder to produce a source of electrons on the glass powder surface;

d. Reheating the glass powder to a second temperature for a certain duration to at least partially bind particles of the glass precursor material to one another to allow the metal ions in the glass to be reduced by the source of electrons to form a metallic nanoparticle, or optionally adding an oxidant to remove at least some of the electrons to control or eliminate the formation of the metallic nanoparticle.

Brief description of the drawings

Figure 1 is a schematic flow chart of the method of the present invention, showing Au doped TZN glass as an example;

Figure 2 shows photographs and extinction spectra of (a) TZNAu1-4; (b) GNAg, GNAu, BNAu, PAg and SCNAu glasses; (c) Gaffer-BatchAu, Gaffer-BatchAuAg, K100Au, BK7Au and F2Au glasses;

Figure 3(a) shows scanning electron microscope image of Au nanoparticles in TZNAu1 and 3(b) elemental analysis data;

Figure 4 is a schematic diagram showing the two main methods associated with the invention;

Figure 5(a) shows extinction spectra of reheated samples using glass powders of small grain size, medium grain size, and large grain size;

Figure 5(b) shows optical microscope images of glass powder of small grain size, middle grain size and large grain size.

Detailed description of the invention

All glasses in the following examples were fabricated using tellurite (TZN), germanate (GN), borate (BN), phosphate (PAg) and silicate (SN, SCN, and commercial Gaffer Batch, K100, BK7 and F2) glass with composition (in mol%) 75TeO_2-15ZnO-10Na_2O (TZN), 70GeO_2-30Na_2O (GN), 70B_2O_3-30Na_2O (BN) 50P_2O_5-50Ag_2O (PAg), 70SiO_2-30Na_2O (SN), 70SiO_2-10CaO-20Na_2O (SCN), and commercial glass products from Gaffer Glass (Gaffer-Batch), Kugler glass (K100), Schott (BK7 and F2). Commercially sourced raw materials were used, including TeO_2, GeO_2, B_2O_3, $(NH_4)HPO_4$, SiO_2, ZnO, Na_2CO_3, $AgNO_3$ and commercial Gaffer-Batch, K100, BK7 and F2 powder. Recycled glass material may also be used in combination with other raw glass material.

Gaffer Batch material was commercial sourced from JM & KE van Domburgh trading as Artisand and has the following composition:

Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS

NAME	CAS RN	%
silica crystalline - quartz	14808-60-7	30-60
sodium carbonate	497-19-8	10-30
calcium carbonate	471-34-1	1-10
sodium borate anhydrous	1330-43-4	1-10
spodumene	1302-37-0	1-10
potassium carbonate	584-08-7	1-10
sodium nitrate	7631-99-4	1-10
zinc oxide	1314-13-2	1-10
antimony trioxide	1309-64-4	<1

K100 was commercially sourced from SPEZIALGLASHÜTTE KUGLER COLORS GmbH Reifträgerweg 29, 87600 Kaufbeuren-Neugablonz, Germany

BK7 and F2 were sourced from Schott Australia Pty Ltd.

The method of the present invention is based on a three step process:

Figure 1 shows a general overview of the process where glass precursor material 1 is heated with a metal doping material (Au in this example) to form a precursor glass material 2, which in this example is Au doped TZN glass. The Au doped TZN glass is subsequently ground 4 in a mortar to provide a fine glass powder 5 in which electrons are formed on the surface of the fine glass powder. The fine glass powder 5 is then heated again 6 to provide the Au nanoparticles in the glass material 7.

1. Preparation of glass precursor material.

The glass material 10 is melted together with predetermined amount of $HAuCl_4$ or $AgNO_3$ or other metal compounds 15 in an alumina crucible 20 at high temperature T1 (first temperature), to form a glass melt 25, which applies for Au/Ag doped GN, BN and SCN, PAg and commercial Gaffer-Batch, K100, BK7 and F2 glass. Colourless noble metal ions doped precursor glass (colourless) was then obtained by quenching or cooling the high temperature glass melt 25 into a mould to provide the cooled glass precursor material 30. Alternatively, the metal ions, such as for example noble metal ions 55 from a gold crucible (the source of noble metal material), are introduced into the glass 50 by firstly melting the glass raw materials 50 in a gold crucible 60, at high temperature T1 (first temperature), to form a glass melt 65 which applies for Au doped TZN glass with the Au concentration controlled by the melting temperature/time. Colourless noble metal ions doped precursor glass (colourless) was then obtained by quenching or cooling the high temperature glass melt 65 into a mould to provide the cooled glass precursor material 70.

2. Introducing a source of electrons (reducing agent) for the reduction of noble metal ions

The glass precursor material 30 or 70 is then ground by mechanical action, which can be carried out with a mortar and pestle to provide a substantially uniform fine glass powder (micron size particles 81) to provide a ground glass precursor material 80. The size of the particles 81 in the fine glass precursor material powder 80 is predetermined by the user, smaller sized particles have shown to yield more consistent results than larger particles.

The action of the grinding action on the precursor glass material in a mortar made from agate creates electrons 82 on the surface or near surface of the particles 81 of the ground glass precursor material 80. In this process, the chemical bonds that connect the elements which build up the precursor glass material are broken and results in the formation of electrons 83 and metal ions/atoms 83 trapped at surface or near surface defects on the ground precursor glass material 80.

3. Reduction of noble metal ions and formation of noble metal nanoparticles

The ground precursor glass powder material 80 is then heated to a second temperature T2 to at least partially bind the particles 81 of the glass precursor material to one another to form the glass material 90 with the glass particles 91 having metal nanoparticles 92 .

During this T2 heating step the trapped electrons in the glass material 80 reduce the noble metal ions to atoms that then nucleate and grow into noble metal nanoparticles. The metal nanoparticles give the glass certain colours originating from the surface plasmon resonance (SPR) of the noble metal nanoparticles (absorption and scattering of light at certain wavelengths), which depends on the type, concentration and size of the nanoparticles as well as the refractive index of the glass (type of glass).

The concentration and size of the metal nanoparticles 92 in the glass depends on the concentration of the introduced noble metal ions as well as the reheating temperature and time.

If the formation of metallic nanoparticles is undesired upon heat-treatment of the powder, the neutralization and growth of nanoparticles can be prevented by eliminating the electrons on the surface of the glass particles by using oxidants.

In the examples below TZN glass is shown as the major illustration system, with further examples of GN, BN, SN, SCN, PAg and commercial Gaffer-Batch, K100, BK7 and F2 glass. The concentration of introduced noble metal ions, glass melting temperature/time, and reheating temperature/time are given in the table blow. Extinction spectra of the formed colored glasses as well as their corresponding colour are shown in Figure 2.

Extinction spectra of (a) TZNAu1-4; (b-c) GNAg, GNAu, BNAu, PAg, SCNAu, Gaffer-BatchAu, Gaffer-BatchAuAg, K100Au, BK7Au and F2Au glasses are shown in Figure 2(a)-(c). We observed that TZNAu1-4 illuminated under tungsten light (white) shows dichroic effect (transmission of blue colour at the back of glasses while reflection of orange colour at the front surface of glasses). Dichroic effect of TZN Au glass results from Au nanoparticles larger than 50nm (the average sizes of Au nanoparticles in TZNAu1-4 glasses all exceed 60nm) so that light absorption and scattering are both prominent. The observed colour produced in GNAg, GNAu, BNAu, PAg, , SCN, Au Gaffer-BatchAu, Gaffer-BatchAuAg, K100Au, BK7Au and F2Au glasses are mainly due to light absorption by Ag/Au/AuAg nanoparticles of sizes smaller than 50nm.

Glass name	Glass type	Melting temperature and time T1	Metal ions / concentration (ppm weight ratio)	Reheating temperature and time T2	Glass color
TZNAu1	TZN	750°C, 1h	Au (Au crucible), 10 ppm_w	540°C, 10 min	Dichroic (blue in transmission and orange in reflection)
TZNAu2	TZN	750°C, 1h	Au (Au crucible), 10 ppm_w	560°C, 10 min	Dichroic (blue in transmission and orange in reflection)
TZNAu3	TZN	750°C, 1h	Au (Au crucible), 10 ppm_w	540°C, 30 min	Dichroic (blue in transmission and orange in reflection)
TZNAu4	TZN	800°C, 1h	Au (Au crucible), 30 ppm_w	540°C, 20 min	Dichroic (blue in transmission and orange in reflection)
GNAg	GN	1250°C, 3h	Ag ($AgNO_3$), 1000 ppm_w	600°C, 2 h	Caramel
BNAu	BN	1100°C, 3h	Au ($HAuCl_4$), 5 ppm_w	550°C, 2 h	Pink
GNAu	GN	1250°C, 3h	Au ($HAuCl_4$), 50 ppm_w	600°C, 2 h	Maroon
BNAu	BN	1100°C, 3h	Au ($HAuCl_4$), 5 ppm_w	550°C, 2 h	Pink
PAg	PAg	600°C, 0.5h	Ag (AgNO3), 50 mol%	300°C, 2 h	Yellow
SCNAu	SCN	1400 °C, 2h	Au ($HAuCl_4$), 200 ppm_w	750 °C, 10 h	Purple
Gaffer-BatchAu	Gaffer-Batch	1400 °C, 2h	Au ($HAuCl_4$), 50 ppm_w	750 °C, 2 h	Tomato
Gaffer-BatchAuAg	Gaffer-Batch	1400 °C, 2h	Au ($HAuCl_4$), 50 ppm_w Ag ($AgNO_3$), 400 ppm_w	900 °C, 10 h	Pumpkin
K100Au	K100	1400 °C, 2h	Au ($HAuCl_4$), 400 ppm_w	650 °C, 2 h	Rose

BK7Au	BK7	1400 °C, 2h	Au ($HAuCl_4$), 200 ppm_w	800 °C, 2 h	Wine
F2Au	F2	1400 °C, 2h	Au ($HAuCl_4$), 200 ppm_w	750 °C, 2 h	Ruby
BNAu	BN	1100°C, 3h	Au ($HAuCl_4$), 5 ppm_w	550°C, 2 h	Pink

As shown in figure 3 (a) scanning electron microscope (SEM) image of Au nanoparticles (Au NP) in TZNAu1 with size determined to be 61nm; 3(b) elemental analysis of the grey background (glass matrix) showing mainly Te, Zn and Na and O signals, and white Au NP showing intense Au signal

As shown in figure 5(a) various extinction spectra of reheated samples using glass powders of small grain size 100 (solid lines), medium grain size 110 (dashed lines), and large grain size 120 (dash dot lines). Extinction spectra at six different location on each sample are provided to show the homogeneity of each sample. Figure 5(b) are optical microscope images of glass powder of small grain size 101 (top), middle grain size 111 (middle) and large grain size 121 (large). The sample made using glass powder of small grain size is homogeneous via naked eye and extinction spectra, while the homogeneity of color and extinction spectra become increasingly worse with increasing the grain size of glass powder. Also, a decrease and redshift of the SPR peak intensity and position is observed with the increase of the glass particle grain size, which indicates the formation of less Au NPs with larger in size

This method of the present invention provides an environmentally friendly way in which to introduce or form metal nanoparticles in glass material without the need to use toxic dopants such as PbO, As_2O_3, etc. It is safe, energy efficient and cost efficient, without the need to use reducing gas and relevant equipment, or high energy irradiation devices. The preparation method is scalable and easy to be implemented for mass production.

This method also provides a way of preventing the undesired coloration of the glass produced via glass powder based manufacturing techniques.

Claims

1. A method of producing nanoparticles in glass including the steps of:

a) preparing a glass precursor material including;

heating a combination of at least one raw glass material with a metal base material to a first temperature to form a glass precursor melt;

cooling the melt to provide the glass precursor material;

b) the glass precursor material then being ground to a predetermined particle size to form a ground glass precursor material;

c) heating the ground glass precursor material to a second temperature for a predetermined period of time to at least partially bind particles of the glass precursor material to one.

2. The method of claim 1, wherein the at least one raw glass material is at least one glass material selected from the group consisting of tellurite (TZN), germanate (GN), borate (BN), phosphate (PAg), borosilicate (commercial BK7) and silicate (SN, SCN, and commercial Gaffer Batch, K100 and F2) glass.

3. The method of claim 2, wherein the at least one raw glass material is at least one raw glass material selected from the group consisting of TeO_2-ZnO-Na_2O (TZN), GeO_2-Na_2O (GN), B_2O_3-Na_2O (BN), P_2O_5-Ag_2O (PAg), SiO_2-Na_2O (SN), SCN (SiO_2-CaO-Na_2O) and of commercial glass products from Gaffer Glass (Gaffer), Kugler glass (K100), Schott (BK7 and F2).

4. The method of any one of the above claims, wherein the glass material is a combination of at least two glass materials.

5. The method of any one of the above claims, wherein the nanoparticles are metallic nanoparticles.

6. The method of any one of the above claims, wherein the metal base material is selected from at least one noble metal, metal alloy, metal compound (metal oxide, metal salt: metal chloride/sulfide/nitrite) or combinations thereof.

7. The method of any one of claims 6 or 7, wherein the at least one noble metal is selected from the group consisting of ruthenium, rhodium, palladium, silver, osmium, iridium, platinum and gold.

8. The method of any one of the above claims, wherein the second temperature is a temperature at which the viscosity of the glass material is approximately $10^{7.6}$ poise.

9. The method of one of claims 6 - 8, wherein the noble metal is in a concentration of between 1 ppm and 2000 ppm.

10. The method of claim 9, wherein the noble metal is in a concentration of between 5 ppm and 20 ppm.

11. The method of claim 10, wherein the noble metal is in a concentration of between 5 ppm and 20 ppm.

12. The method of claim 11, wherein the noble metal is in a concentration of between 5 ppm and 20 ppm.

13. The method of claim 12, wherein the noble metal is in a concentration of between 8 ppm and 15 ppm.

14. The method of claim 13, wherein the noble metal is in a concentration of 10 ppm.

15. The method of any one of claims 1 -15, wherein the glass precursor material is ground to a predetermined particle size of between 0.01 – 1000 micrometre.

16. The method of claim 15, wherein the glass precursor material is ground to a predetermined particle size of between 0.01 – 10 micrometre.

17. The method of any one of claims 1 - 16, wherein the predetermined period of time of heating the ground glass precursor material to the second temperature is between about 5 min and about 24 h.

18. The method of any one of claims 1 - 17, wherein the predetermined period of time is between about 10 min and about 6 hr.

19. The method of any one of claims 1 - 18, wherein the predetermined period of time is between about 10 min and about 2 hr.

20. The method of any one of the above claims where the glass precursor material is ground in a mortar made from agate.

21. The method of the above claims, wherein the crucible is a gold crucible (for TZN) or a alumina crucible for (BN, GN, SCN, PAg, and commercial Gaffer Batch, K100, BK7 and F2).

22. A glass product containing metallic nanoparticles produced by the method of any one of claims 1-21.

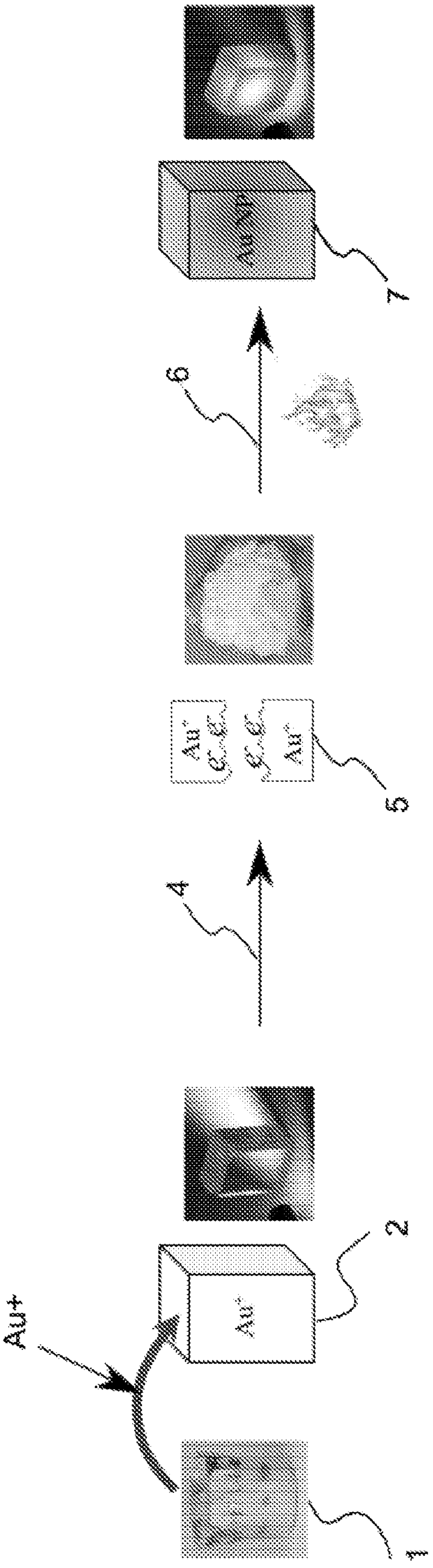


Figure 1

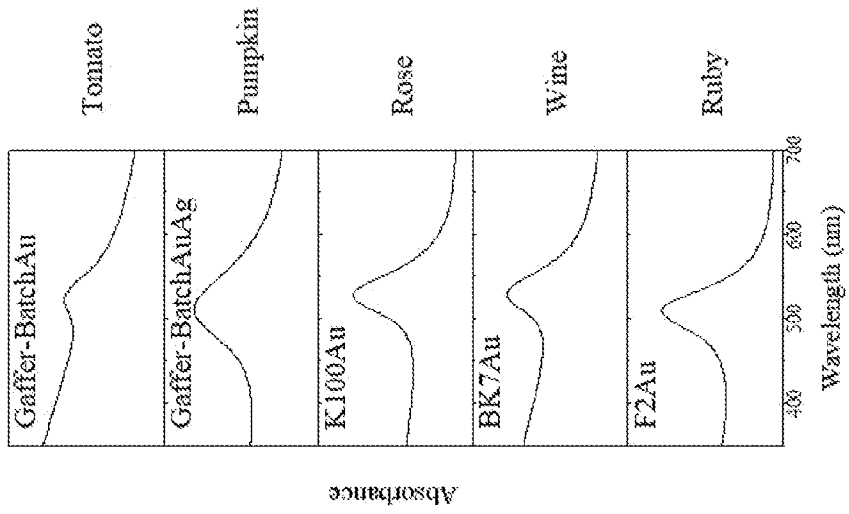


Figure 2(c)

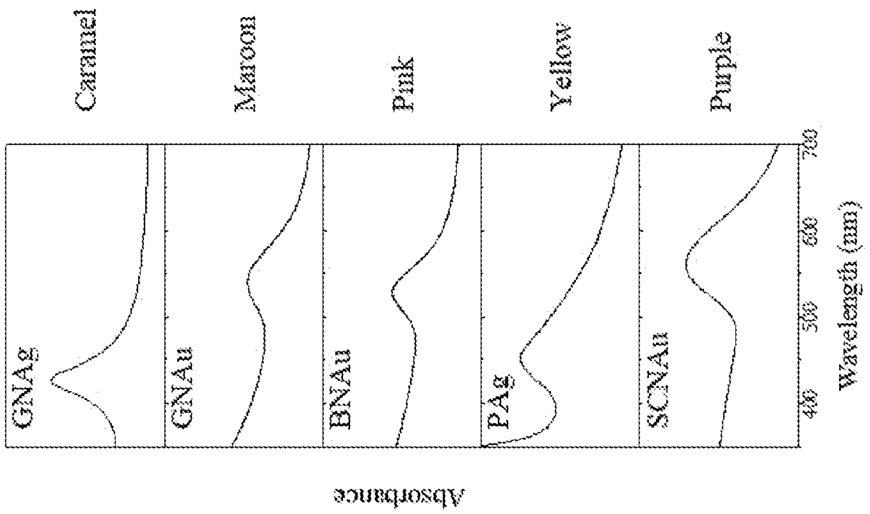


Figure 2(b)

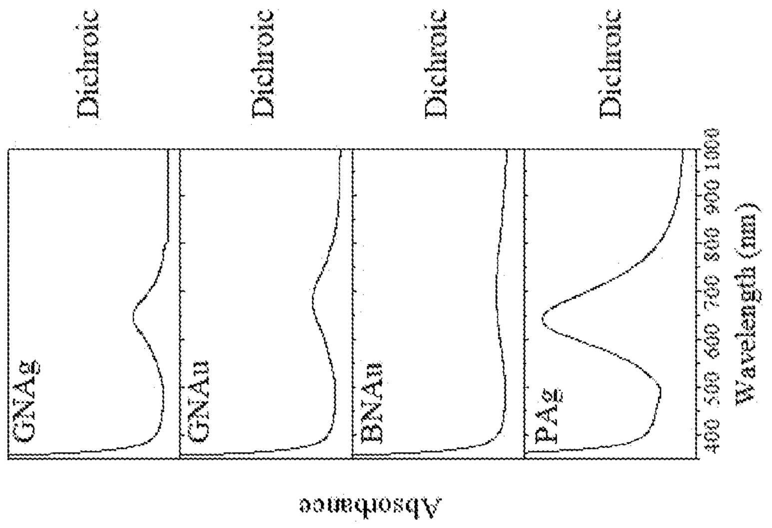


Figure 2(a)

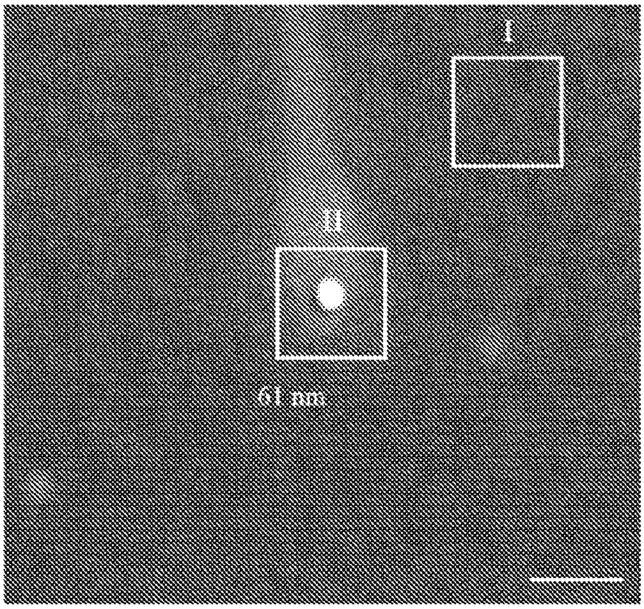


Figure 3(a)

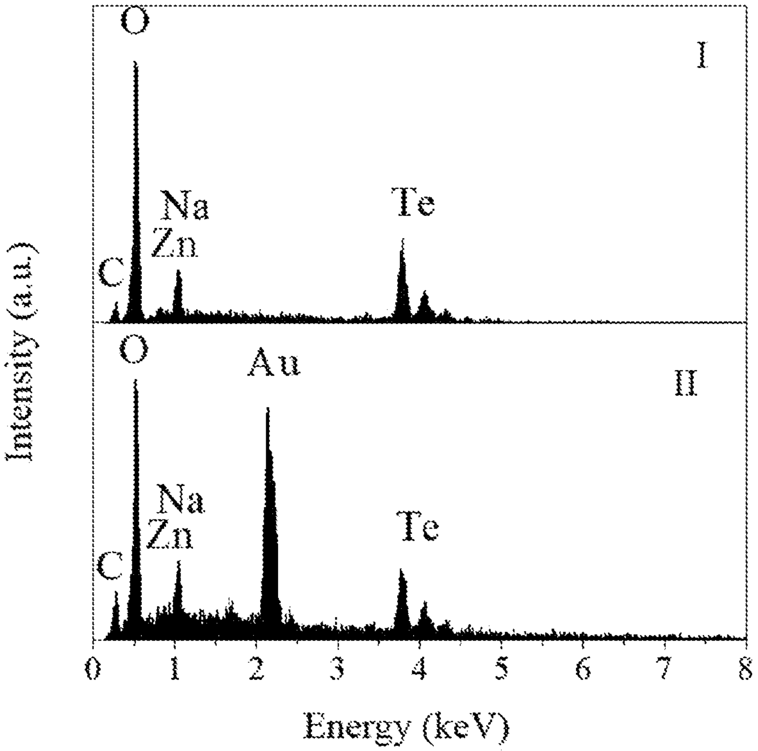
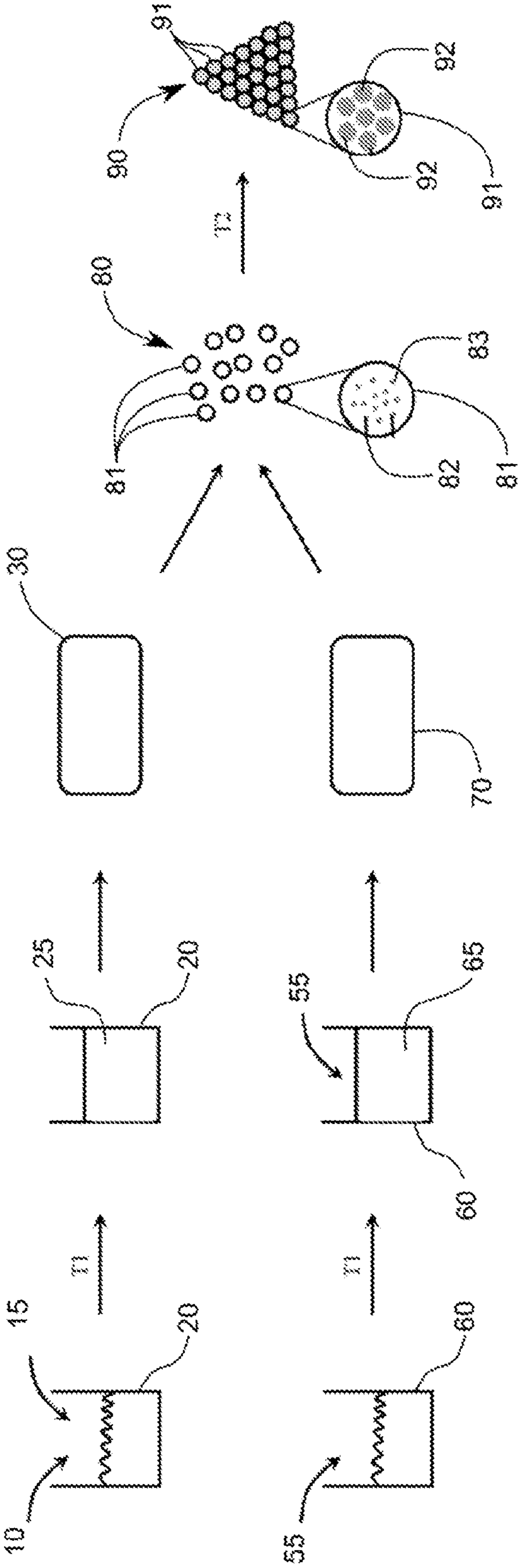


Figure 3(b)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91

Figure 4

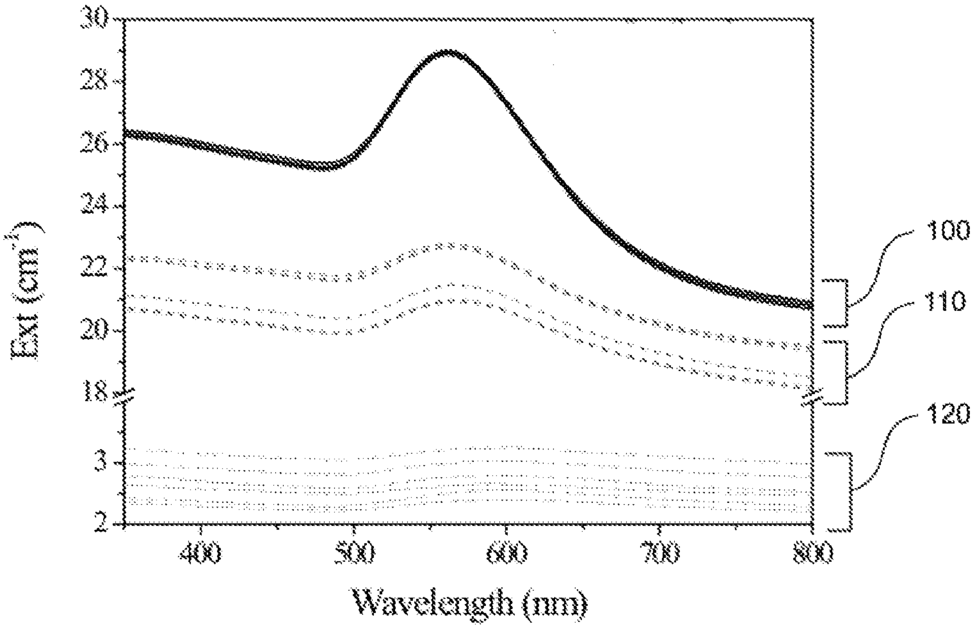

Figure 5(a)

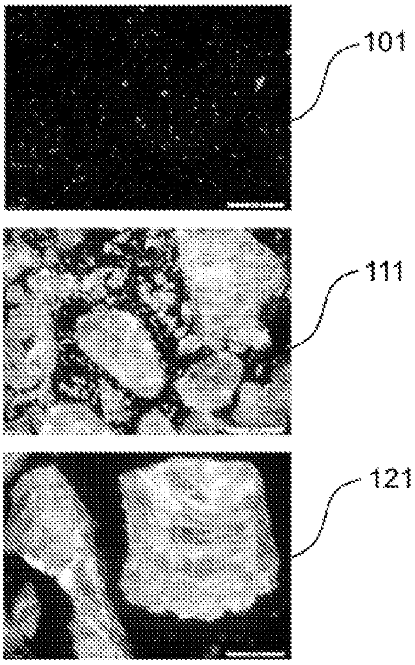

Figure 5(b)

INTERNATIONAL SEARCH REPORT	International application No. **PCT/AU2018/051115**

A. CLASSIFICATION OF SUBJECT MATTER

C03C 14/00 (2006.01) B82Y 30/00 (2011.01) C03C 4/02 (2006.01)

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)

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)

PATENW, CAPLUS, REGISTRY, GOOGLE, GOOGLE SCHOLAR, ESPACENET: CPC/IPC marks C03C, C03C14/004 and C03C14/006 (in applicable databases); with keywords (glass, metal, nanoparticle, tellurite, germanate, borate, silicate, ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, gold, grinding) and like terms

ESPACENET, GOOGLE SCHOLAR, CAPLUS, IP AUSTRALIA INTERNAL DATABASES: Applicant/inventor name search

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

☒ 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 23 November 2018	Date of mailing of the international search report 23 November 2018
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	**Authorised officer** Alan Criddle AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262832846

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/0116106 A1 (SERVIN et al) 09 May 2013 Abstract; [0016], [0017], [0030]–[0032]; Examples	1–22
X	US 2009/0325775 A1 (YEH) 31 December 2009 Abstract; [0041]–[0044]	1, 6, 7, 9–18, 22
X	US 2008/0191834 A1 (LIEN et al) 14 August 2008 Abstract; [0021]	22
X	WO 2016/040480 A1 (THE CURATORS OF THE UNIVERSITY OF MISSOURI) 17 March 2016 Abstract	22
X	CN 105753315 A (NINGBO UNIVERSITY) 13 July 2016 Abstract	22

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2018/051115**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
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		US 2018177920 A1	28 Jun 2018
		WO 2016040481 A1	17 Mar 2016
CN 105753315 A	13 July 2016	CN 105753315 A	13 Jul 2016
		CN 105753315 B	09 Nov 2018

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.