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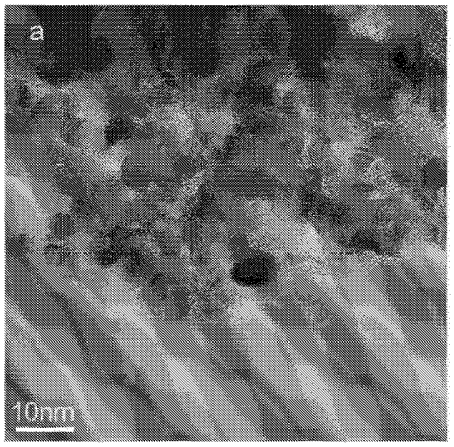
(54) **Process to prepare metal nanoparticles or metal oxide nanoparticles.**

(57) The invention is directed to a process to prepare metal nanoparticles or metal oxide nanoparticles by applyinq a cathodic potential to a solid starting metal object which solid metal object is in contact with a liquid electrolyte comprising a stabilising cation. The invention is also directed to the use of the obtained nanoparticles as a catalyst.



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PROCESS TO PREPARE METAL NANOPARTICLES OR METAL OXIDE NANOPARTICLES

The invention is directed to a process to prepare metal nanoparticles or metal oxide nanoparticles.

US-A-2010/0072434 describes a process to prepare gold nanoparticles by first preparing a polymer surfactant in an alcohol solvent and heated to its boiling point. To the boiling mixture a metal seed, i.e. chloroplatanic acid is added and subsequently HAuCl4 salt is added after which gold nano particles form around the seed.

WO-A-2007/055663 describes a process to prepare a metal nano particle wherein a metal precursor compound is contacted with a reducing agent and a capping agent to generate a reaction mixture. Exemplified metal precursor is $HAuCl_4$, exemplified reducing agent is $NaBH_4$ and the exemplified capping agent is amino acid. To this mixture sonication is applied to generate a plurality of metal colloidal particles and depositing the metal particles on a support, i.e. TiO_2, to prepare a catalyst.

US-A-2009/0325795 describes a process to prepare platinum nanoparticles wherein first a chemical compound like potassium tetrachloroplatinate is prepared. To this compound potassium iodide (KI) is added and subsequently the mixture is reduced to form the platinum nanoparticles.

At the heart of all known methods developed to make nanoparticles lies the reduction reaction of metal cations. The art is to limit the number of reduced cations per nanoparticle and keep its size as constant as possible, and that is invariably

achieved by adding extra chemical stabilizers - most methods of nanoparticles synthesis involve micelles or colloids. These contaminate the final product and adversely affect its performance, e.g. in catalysis or biological applications. In addition, the prior art processes have the problem that they involve multiple chemical synthesis steps. Furthermore these processes require additional chemicals to act as for example reducing agent, capping agent, polymer and/or a surfactant.

In a paper titled 'The Phenomenon of the Formation of Metallic Dust from Cathodes' as read by Prof. Dr. Fritz Haber at the Second Meeting of the American Electrochemical Society on September 17, 1902 an experiment was described wherein black clouds form around a lead cathode when the direct current density is increased. The same is observed for tin, bismuth, thallium, arsenic, antimony and mercury. The same paper mentions that in an acid solution a platinum wire cathode becomes black and spongy. Starting with the same platinum cathode in an alkaline solution only a slightly roughened surface was observed.

The object of the present invention is to provide a more simple process to prepare nanoparticles or metal oxide nanoparticles.

This object is achieved by the following process. Process to prepare metal nanoparticles or metal oxide nanoparticles by applying a cathodic potential to a solid starting metal object which solid metal object is in contact with a liquid electrolyte comprising a stabilising cation.

Applicants found that metal nanoparticles and metal oxide nanoparticles can be obtained in less

process steps than the prior art methods while requiring less additional chemical compounds. For example, the liquid electrolyte comprising the stabilising cation can be reused in the process according to the invention. Because less additional chemicals are used, more pure nanoparticles are obtained.

The 1902 paper as described above did not suggest that nanoparticles are formed when applying the conditions of the process according to the present invention.

For the present invention the term nanoparticles will have the meaning of any particle having a smallest dimension of less than 1000 nm, preferably less than 200 nm, and more preferably less than 100 nm. The smallest dimension will be the smallest diameter of the particle. The nanoparticles as obtained by the process may be attached to a solid surface or be present in a liquid as a solid/liquid suspension. The process includes processes which make particles of which more than 50 wt% are nanoparticles, more preferably of which more than 80 wt% are nanoparticles and even more specific wherein more than 95 wt% of the particles are nanoparticles as defined above.

The liquid electrolyte may be any liquid which has the ability to oxidise the above described anionic metal to its metallic state. Another feature of the electrolyte is that it has so-called mobile charges, i.e. it must have the ability to transfer a current from a cathode to an anode. Such mobile charges are suitably cations and anions. An example of an electrolyte is a molten salt of NaOH or an

aqueous solution of NaCl. Preferably the electrolyte comprises water.

The electrolyte will comprise a stabilising cation. Suitable stabilising cations are those which do not or only very slightly reduce on the surface of the cathode under the conditions of the process according to the present invention. Such reduction would result in that a layer of this compound would form on the surface of the metal object resulting in effectively terminating the formation of the metal nanoparticles. Applicants found that the stabilising cation is preferably an alkali or an alkaline earth cation. Examples of suitable cations of this type are Na^+, Li^+, K^+, Cs^+, Mg^{2+}, Ca^{2+} and Ba^{2+}. Applicants further found that ammonium cation or a n-alkylammonium cation can be used as the stabilising cation (with n ranging between 1 and 4) and wherein the alkyl groups can be any alkyl group having 1 to 10 carbon atoms, more preferably wherein the alkyl group is a methyl, ethyl, n-propyl, iso-propyl, n-butyl or tert-butyl group. A suitable n-alkylammonium cation is tetra-tert-butylammonium. Applicants found that the choice for the accompanying anion is not critical. Examples of suitable anions are Cl^-, SO_4^{2-}, HSO_4^-, ClO_4^-, F^-, NO_3^-, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, BO_3^{3-}, HBO_3^{2-}, $H_2BO_3^-$, and OH^-.

Preferred liquid electrolyte comprises a stabilising cation, water and an anion. It is found that the pH of the liquid electrolyte at the start of the process is not critical. Increasing the concentration of the stabilising cation in the electrolyte has resulted in a faster formation of

the nanoparticles. A preferred electrolyte is an aqueous solution comprising an alkali or alkaline cation as the stabilising cation in a concentration between 0.1 mol/l and saturation.

The metal or metals are preferably chosen from the groups of the Periodic Table of Elements starting at 3 to and including group 15 and more preferably Groups 3 to and including group 13, wherein the groups are numbered according to the system adopted by IUPAC. Suitable metals of these groups are Y, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Rh, Ag, Ta, W, Re, Os, Ir, Pt, Au, Al, Si, Ga, Ge, As, In, Sn, Sb, Te, Tl, Pb and/or Bi and more suitably the metals as illustrated in the examples.

The starting metal object may be an alloy of two or more metals or may consists substantially of one metal. By substantially pure metal is meant that the composition comprises more than 98 wt% of the metal or especially even more than 99.5 wt% of the metal. Examples of possible alloys are PtNi, PtIr, PtRh, PtRu, PtCo, PtMo,PtAu,PtAg, PtRuMo, PtFe, AuCu, PtCu, PtOs, PtSn, PtBi, CuNi, CoNi, AgCu, AgAu and NiSn, and more suitably the alloy combinations as illustrated in the examples. It has been found possible to prepare nanoparticles starting from an alloy.

Applicants have found that when the cathodic potential is applied as a direct current (dc) voltage nanoparticles form on the surface of the metal object. In this manner a metal object coated with nanoparticles is obtained. The metal or metal alloy is or comprises preferably of a metal chosen from the groups of the Periodic Table of Elements

starting at 3 to and including group 13 wherein the groups are numbered according to the system adopted by IUPAC a more suitably the metals as illustrated in the examples. The starting metal object may also be a metal object coated with a different metal. In this manner a metal object coated with nanoparticles of a different metal may be obtained. This could be a method to minimise the use of the, e.g. more expensive, metal of the nanoparticles. The presence of the nanoparticles on the surface of the object significantly increases the surface area and thus, for example the catalytic properties of the metal object. The invention is also directed to a process to prepare such a coated metal object, wherein first a direct current is applied as described above and subsequently the liquid electrolyte solution is removed from the object by washing with water, preferably deionised water or ultrapure water.

Suitably the coated object as described above is used as a catalyst, for example in the case of platinum, copper, gold, rhodium or a platinum alloy; as a photocatalyst, for example for titanium oxide; as a capacitor, for example when a ruthenium oxide covered object is used; as a storage means of chemical substances for example as a storage means of hydrogen in the form of metal hydrides such as nickel hydrides, titanium hydrides or aluminium alloy hydrides. This type of high-area substrates may also be used for the enhancement of surface-related signals in, for example, SERS (Surface Enhancement Raman Spectroscopy). The preferred metals for this application are Au, Cu and Ag.

The liquid electrolyte is suitable separated from the coated metal object and advantageously reused in

the process according to the invention. When applying the cathodic potential as a direct current (dc) voltage it is preferred to use an inert anode, for example a graphite anode. The anode will also be in contact with the liquid electrolyte. The required voltage is more cathodic than the so-called potentials of zero charge. In order to proceed with an acceptable speed of formation of nanoparticles, the applied voltage is more cathodic than the onset of the hydrogen evolution reaction. The optimum voltage will for example depend on the metal, the liquid electrolyte and the stabilising cation and the desired size of the nanoparticle. A suitable voltage is between 0.1 V and 30 V more cathodic than the onset of the hydrogen evolution reaction. Applicants found that the process proceeds well in this range. Higher voltages may be applied but will not substantially improve the speed of the reaction. Illustrative conditions will be provided in the examples.

Applicants further found that when the potential is applied as an alternating current (ac) voltage a suspension of nanoparticles in the liquid electrolyte is obtained. In a situation of alternating current the movement of the electric charge periodically reverses direction. It is believed that the alternating current enables the nanoparticles as formed when the metal object is in the cathodic state to leave the metal object when said object is in its anodic state. Preferred frequencies range from 1 to 10000 Hz. The preferred voltage amplitude is between 1 V and 30 V. Applicants found that the process proceeds well in this range. Higher voltages may be applied but will

not substantially improve the speed of the reaction. The form of the alternating current may be any form, for example square, sinusoidal or triangular. The application of the alternating current (ac) voltage can be made between two metal objects with the same composition, in contact with the liquid electrolyte. This will result in that nanoparticles will be formed at both objects and eventually totally dissolve into the liquid electrolyte. Alternatively, the ac voltage can be applied between two electrodes of different composition. If both electrodes are active for the formation of nanoparticles, a mixture of two types of nanoparticles can be obtained. Alternatively, one of the electrodes may be of an inert material, like graphite, and therefore, nanoparticles will only be formed on the other electrode.

The nanoparticles as present in the liquid electrolyte are suitably separated from the liquid electrolyte to obtain an end or an intermediate product. Separation can be achieved by many different methods, like precipitation or filtration. Preferably said separation is performed by means of centrifugal force to obtain a phase rich in nanoparticles and a phase of electrolyte. Possible separation processes which use a centrifugal force are a hydrocyclone or a centrifuge. Preferably a centrifuge is used. Suitably the electrolyte is re-used in the process according to the invention as described above. The phase rich in nanoparticles is subsequently diluted with water, preferably deionised water or ultrapure water. In order to redisperse the nanoparticles in the added water it is preferred to apply sonication. Sonification may

be performed at conditions known to the skilled person. In order to effectively remove any remaining liquid electrolyte, the steps of centrifugation, dilution with water and sonication can be repeated several times, preferably between 3 and 10 times.

The nanoparticles as obtained may be dissolved to form a suspension in any suitable liquid, suitably water. Surfactants or polymers may be added to achieve a more stable suspension. Examples of suitable surfactants or polymers are Cetyl Trimethyl Ammonium Bromide (CTAB), Tetradecyl Trimethyl Ammonium Bromide (TTAB), surfactants of the Brij® type as obtainable from Sigma-Aldrich and Polyvinylpyrrolidone (PVP). The suspended nanoparticles may be used as an intermediate product suited to transport the nanoparticles from the manufacturer to its end user or as a means to affix the nanoparticle to said support.

For some catalytic end uses of the nanoparticles it is preferred to affix the nanoparticles to the surface of a suitable support. Generally, any support capable of supporting and providing adequate dispersion for the nanoparticles can be used. Preferably, the support is stable in the local environment where the catalyst is to be used. The support has a surface area and/or porosity sufficient to provide dispersion of the nanoparticles. However, a support with increased porosity provides more intimate contact between reactants and catalytic material. Examples of suitable solid supports are silica gels, derivatized plastic films, glass beads, cotton, plastic beads, alumina gels, polymer resins, a zeolite, a molecular sieve, a carbon, an inorganic oxide, an inorganic

hydroxide, a mixed inorganic hydroxides or mixed inorganic oxides. Specific examples of these supports are further described in WO-A-2007/055663, which publication is hereby incorporated by reference.

The nanoparticles are preferably fixed to the support by mixing the support with the suspension followed by washing with a solvent to remove the excess of the surfactant. The catalyst may optionally be calcined. Alternatively the nanoparticles can be loaded on a support by first preparing a reverse microemulsion of the nanoparticle as described in WO-A-2008/101602. This publication also describes an alternative support suited for the nanoparticles prepared according to the present invention. The alternative support are fabrics from activated carbon fibers, acrylonitril fibers, glass fibers, ceramic fibers, metal fibers or fleece composite oxides of activated carbon fibers.

The catalyst comprising the nanoparticles as obtained by the present process may be used in various reactions, such as hydrogenation, hydrotreating, hydrocracking, hydroisomerisation, hydrofinishing, reforming, Fischer-Tropsch reactions and methanol to olefin reactions. Suitably the metal or metal alloy comprises a Group VIII metal. The nanoparticles are also suited as catalyst in a fuel cell to catalyse the oxidation of methanol. It has been found that the platinum nanoparticles as prepared by the process according to the present invention have improved catalytic activity for the oxidation reaction of methanol. It has been also shown that these nanoparticles have improved

catalytic activity for the oxidation reaction of CO, which is a typical poison intermediate in the oxidation of small oxygenated organic compounds.

The nanoparticles are also suited as catalyst in a fuel cell to catalyse the oxidation of hydrogen, ethanol, formic acid, ammonia, borohydride and other organic compounds and the reduction of oxygen. Suitably the metal or metal alloy is platinum, copper, gold, rhodium, nickel or a platinum alloy. The nanoparticles are also suited as catalyst for neutralization of exhaust gases from, for example, an automobile engine or industry. Suitably the metal or metal alloy is gold or a platinum alloy. The nanoparticles are also suited as catalyst for waste water treatment for, for example, reduction of nitrates and nitrites. Suitably the metal or metal alloy is gold, platinum, rhodium or a platinum alloy. The nanoparticles can also be used as electrodes in electrochemical sensors in, for example, HPLC. The nanoparticles can also be used in photovoltaics or photocatalysis. Suitably nanoparticles of titanium oxide are used for this application. The nanoparticles may also find use as part of a conductive nano ink. Suitably gold, silver or copper nanoparticles are used for this application.

Nanoparticles comprising silver as prepared according to the present invention may advantageously find use as part of an anti-microbial device or composition, for example as part of wound dressing, clothing, filters, cloth, ointment or paint.

The invention will be illustrated with the following non-limiting examples

Example 1

A 100 µm diameter platinum wire having a purity of 99.99 wt% was submerged by 1 mm in an aqueous solution containing 10 M NaOH. Said solution was prepared with ultrapure water (Millipore MilliQ gradient A10 system, 18.2 MΩ cm, 3 ppb total organic carbon) and NaOH (99.9% from Sigma-Aldrich). For 1000 seconds a cathodic potential of -10 V dc (direct current) was maintained. Vitreous carbon is used as anode to rule out the possibility of formation of interfering species by anode dissolution. The platinum wire was rinsed with ultrapure water and observed using SEM (scanning electron microscope). The SEM images as shown in Figures 1 and 2 showed the formation of nanoparticles having a size of <50 nm which were coated on the surface of the platinum wire. It was observed that even the vigorous H_2 gas evolution during the cathodic treatment was not able to dislodge the particles from the surface.

Example 1a and 1b

Example 1 was repeated except that the metal was Ir or Re. The cathodic potential was -30 V (dc) and the electrolyte was an aqueous solution of 1 M $NaClO_4$. The solution of $NaClO_4$ was prepared from $NaClO_4$ 99.9% from Sigma-Aldrich. The experiment was continued for 30 minutes. Inspection of the cathodes, after that the electrolyte was removed by washing with deionised water, showed that the surface of the Ir and Re cathode was coated with nanoparticles of Ir and Re respectively.

Example 2

Example 1 was repeated except that an alternating current at 100 Hz and 20 V peak to peak (p-p) square

wave ac was applied in 10 M NaOH. After around 100 seconds the platinum wire part as submerged in the liquid electrolyte was totally 'dissolved'. The aqueous solution had turned black, and consists of a suspension of nanoparticles. The electrolyte in the nanoparticles solution was subsequently removed by successive steps of centrifugation at 3000 rpm using a Hettich EBA 20 Centrifuge), dilution with ultrapure water and sonication in an ultrasonic bath at 40 kHz using a Branson ultrasonic cleaner Model 2510. The cleaned suspension of nanoparticles was deposited on a grid for further investigation using a transmission electron microscope (TEM). It was found that platinum nanoparticles had formed having a size ranging from 4 to 30 nm. Lattice spacing as well as Energy Dispersive X-ray (EDX) spectrum measured correspond exactly to platinum. Figure 3 shows the TEM image. Figure 4 shows the EDX spectrum.

Comparative Experiment A

Example 1 and 2 was repeated, except that instead of an aqueous solution containing NaOH, an aqueous acid solution of H_2SO_4, $HClO_4$ or HCl was used, with concentration between 1 M and 10 M. Under the remaining conditions of Example 1 and 2 no formation of metal nanoparticles was observed.

Example 3

Example 2 was repeated using a gold wire instead of the platinum wire. In this way, a solution with gold nanoparticles is obtained, which was cleaned as described in example 2. After further investigation of said solution using a transmission electron microscope (TEM) it was found that gold nanoparticles had formed having a size ranging from

4 to 30 nm. Lattice spacing as well as EDX spectrum measured correspond exactly to gold. Figure 5 shows the TEM image. Figure 6 shows the EDX spectrum.

Examples 4

Example 2 was repeated wherein the following aqueous electrolyte compositions were used: 10 M NaOH, 1 M NaOH, 1 M tetra-tert-butylammonium hydroxide, 1 M LiOH, 1 M CsOH,1 M KOH, 1 M NH_4Cl, 1 M NaCl, 1 M $NaClO_4$, 0.5 M K_3PO_4, 0.5 M $BaCl_2$, 1 M NH_4F, 1 M Na_2SO_4, 1 M $NaNO_3$, 1 M H_3BO_3 +1 M NaH_2BO_3 and 1 M NaF. In all examples the formation of platinum nanoparticles in the solution was observed.

Example 5

Example 2 was repeated wherein the following aqueous electrolyte composition was used: 10 M NaOH. The voltage was varied according to the following list: 28 V p-p, 24 V p-p, 16 V p-p, 12 V p-p, 8 V p-p, 4 V p-p. For all voltages the formation of platinum nanoparticles in solution was observed.

Examples 6

Example 2 was repeated wherein the following electrolyte composition was used: 10 M NaOH and wherein the metal was varied: Ni, Rh, Ag, Nb, Al, Co, Mo, Y, V, and Ru. The formation of nanoparticles in the solution was observed for all metals. In case of ruthenium a ruthenium oxide nanoparticle was isolated from the solution.

Examples 7

Example 2 was repeated wherein the following electrolyte composition was used: 1 M NaOH and wherein the metal was Cu, V, In, Rh and Mn. The formation of nanoparticles of said metals in the solution was observed.

Example 8

Example 6 was repeated except that the metal was Au and the voltage was 30 V p-p. The formation of gold nanoparticles in the solution was observed.

Example 9

Example 2 was repeated except that the electrolyte was molten NaOH. The formation of platinum nanoparticles was observed.

Example 10

Example 9 was repeated at 10 V p-p alternating current. The formation of platinum nanoparticles was observed.

Examples 11

Example 7 was repeated wherein the following metal alloys were used as cathode: $Pt_{90}Rh_{10}$, $Pt_{80}Rh_{20}$, $Pt_{70}Rh_{30}$, $Pt_{80}Ir_{20}$, $Pt_{50}Ni_{50}$, $Pt_{95.2}Ru_{4.8}$, wherein in the the subindexes in the alloys refer to the weight percentage. For all alloys the formation of nanoparticles was observed. The applicants have found that these nanoparticles exhibit an electrochemical behaviour in sulfuric acid solutions that clearly indicates that the nanoparticles are not a mixture of Pt nanoparticles and the other metal nanoparticles. Consequently, the chemical composition of the synthesized nanoparticles must be that of an alloy.

Example 12

Example 11 was repeated for all alloys using a 10 M NaOH electrolyte solution. For all alloys the formation of alloy nanoparticles was observed as in Example 11.

Examples 13

Example 2 was repeated at different frequencies of the alternating current: 10 Hz, 50 Hz, 100 Hz, 500 Hz, 1000 Hz and 10000 Hz. At all frequencies the formation of platinum nanoparticles was observed.

Example 14

The solution of platinum nanoparticles as obtained in Example 2 was subjected to a centrifuge at 3000 rpm to separate the majority of the electrolyte from the nanoparticles. The remaining concentrated nanoparticles solution was diluted with ultrapure water and redispersed by sonication in an ultrasonic bath at 40 kHz. The steps of centrifugation, dilution with water and sonication were repeated six times. At the end, the nanoparticle solution had pH=7 and the concentration was of 1 mgram of Pt in 1 ml of solution. 3 μl of said solution was deposited on a flat gold electrode having a diameter of 3 mm. The water content of the nanoparticle solution was dried under a flux of argon. The thus deposited platinum nanoparticles remain attached to the gold surface during the following electrochemical experiments. The platinum-nanoparticles-modified gold electrode was transferred to an electrochemical cell. The blank voltammogram was recorded in 0.5 M H_2SO_4 at a scan rate of 50 mV/s (Figure 7A, solid curve). Then, the electrooxidation of CO was measured after adsorption of CO at *E*=0.1 V vs. RHE (RHE=Reversible Hydrogen

Electrode)for 1 minute and consequent purging with of the CO dissolved in solution for 30 minutes. The CO electrooxidation was recorded with a scan rate of 20 mV/s. The results are shown in figure 7B, solid curve. Then, the catalysis for methanol oxidation was measured in a 0.5 M H_2SO_4 + 0.5 M CH_3OH solution at a scan rate of 50 mV/s (Figure 7C, solid curve). Current was normalized per gram of platinum.

Comparative experiment B

Example 5 is repeated using commercially obtained nanoparticles from the Tanaka Kikinzoku Inc company. The as-received nanoparticles were dispersed on Vulcan® carbon with 50%wt loading, and had an average size of 5nm diameter. A solution of of 1 mgram of Pt in 1 ml of solution was obtained by adding ultrapure water. Dispersion of the nanoparticles in solution was achieved by sonication for one hour. Afterwards, 3 μl of said solution was deposited on a glassy carbon electrode having a diameter of 3 mm as in Example 14. The water content of the nanoparticle solution was dried under a flux of argon. The thus deposited platinum nanoparticles remain attached to the glassy carbon surface during the following electrochemical experiments. The platinum-nanoparticles-modified glassy carbon electrode was transferred to an electrochemical cell. Further cleaning of the nanoparticles is achieved by cycling the electrode between 0.05 V and 1.1 V vs. RHE for 80 cycles in 0.5 M H_2SO_4 at 50 mV/s. Afterwards, the electrode was transferred to a new electrochemical cell, and the blank voltammogram was recorded in 0.5 M H_2SO_4 at a scan rate of 50 mV/s (Figure 7A, dashed curve). Then, CO and

methanol electrooxidation were recorded as described in example 5. The results are shown in figure 7B and 7C, dashed curves.

Figure 7B clearly shows that CO oxidation takes place at ca 0.1 V lower overpotential in Example 14 as compared to the results of Experiment B. Further the charge under the CO stripping peak is about two times lower for Example 14. The first observation shows that it is energetically more favourable to oxidize CO with the catalyst comprising the platinum nanoparticles as obtained by the present invention. The second observation indicates that our nanoparticles are ~1.5 times larger on average, which leads to a lower effective surface area per gram of platinum.

Figure 7C shows that the current towards methanol oxidation is markedly higher in Example 14 (solid line) than in the comparative experiment B (dashed line). Although the nanoparticles of Example 14 are ~1.5 times larger on average than the ones used in Experiment B (which leads to a lower effective surface area per gram of platinum) it is nevertheless observed that the intrinsic catalytic activity of the nanoparticles of Example 14 overcompensates for this effect in such a way that the maximum methanol oxidation current is double that of Experiment B using the commercial nanoparticles. Thus it is concluded that the platinum nanoparticles as prepared according to this invention are catalytically more active than the existing platinum nanoparticles of Experiment B.

CONCLUSIES

1. Werkwijze voor de bereiding van metalen nanodeeltjes of nanodeeltjes uit een metaaloxide, door middel van het uitoefenen van een kathodepotentiaal op een metalen startvoorwerp in vaste vorm, waarbij het metalen startvoorwerp in vaste vorm in contact staat met een vloeibaar elektrolyt dat een stabiliserend kation bevat.

2. Werkwijze volgens conclusie 1, waarbij het vloeibare elektrolyt water bevat.

3. Werkwijze volgens een der conclusies 1-2, waarbij het metaal of de metalen bij voorkeur gekozen worden uit de groepen van het Periodieke Systeem van Elementen volgens IUPAC, te beginnen bij 3 en met inbegrip van groep 15.

4. Werkwijze volgens conclusie 3, waarbij het metaal wordt gekozen uit de groep die bestaat uit Y, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Rh, Ag, Ta, W, Re, Os, Ir, Pt, Au, Al, Si, Ga, Ge, As, In, Sn, Sb, Te, Tl, Pb, en Bi.

5. Werkwijze volgens een der conclusies 1-4, waarbij het startmetaal in vaste vorm een legering is van twee of meerdere metalen.

6. Werkwijze volgens conclusie 5, waarbij de legering wordt gekozen uit de groep die bestaat uit PtNi, PtIr, PtRh, PtRu, PtCo, PtMo, PtAu, PtAg, PtRuMo, PtFe, AuCu, PtCu, PtOs, PtSn, PtBi, CuNi, CoNi, AgCu, AgAu, en NiSn.

7. Werkwijze volgens een der conclusies 1-6, waarbij het startmetaal in vaste vorm nagenoeg uit een metaal bestaat.

8. Werkwijze volgens een der conclusies 1-7, waarbij het stabiliserende kation een alkali-, aardalkali-, ammonium-, of een alkylammoniumkation is.

9. Werkwijze volgens een der conclusies 1-8, waarbij de kathodepotentiaal wordt uitgeoefend in de vorm van een gelijkspanning (DC).

10. Werkwijze voor de bereiding van metalen voorwerpen die gecoat zijn met nanodeeltjes door de werkwijze uit te voeren volgens conclusie 9, en door vervolgens de vloeibare elektrolytoplossing te verwijderen van het voorwerp door het voorwerp te wassen met water.

11. Gebruik van het gecoate metalen voorwerp zoals bekomen aan de hand van de werkwijze volgens conclusie 10, als katalysator, condensator, opslag van chemische stoffen, of als SERS-substraat.

12. Werkwijze volgens een der conclusies 1-8, waarbij de kathodepotentiaal wordt uitgeoefend in de vorm van een wisselspanning (AC), teneinde een suspensie te bekomen van nanodeeltjes in het vloeibare elektrolyt.

13. Werkwijze volgens conclusie 12, waarbij de nanodeeltjes worden gescheiden van het vloeibare elektrolyt.

14. Werkwijze volgens conclusie 13, waarbij de scheiding wordt uitgevoerd door gebruik te maken van centrifugaalkrachten, teneinde een fase te bekomen die rijk is aan nanodeeltjes en een elektrolytfase, door opnieuw gebruik te maken van het elektrolyt in de werkwijze volgens conclusies 1-9, de fase die rijk is aan nanodeeltjes, te verdunnen met water, en het opnieuw in dispersie brengen door middel van een geluidsbehandeling.

15. Gebruik van nanodeeltjes, zoals die bekomen worden aan de hand van de werkwijze volgens een der conclusies 12-14, als katalysator.

16. Gebruik volgens conclusie 15, als katalysator in brandstofcelreacties.

17. Gebruik volgens conclusie 15, als katalysator in de oxidatie van waterstof, ethanol, mierezuur, ammoniak, boorhydride, en andere organische verbindingen, alsook de reductie van zuurstof, nitraten, en nitrieten.

18. Gebruik volgens conclusie 15, als katalysator voor de neutralisatie van uitlaatgassen.

19. Gebruik volgens conclusie 15, als katalysator voor de behandeling van afvalwater.

20. Gebruik van nanodeeltjes, zoals die bekomen worden aan de hand van de werkwijze volgens een der conclusies 12-14, als elektrochemische sensoren.

21. Gebruik van nanodeeltjes, zoals die bekomen worden aan de hand van de werkwijze volgens een der conclusies 12-14, in fotovoltaïsche toepassingen.

22. Gebruik van nanodeeltjes, zoals die bekomen worden aan de hand van de werkwijze volgens een der conclusies 12-14, als onderdeel van een geleidende nanoverbinding.

23. Gebruik van zilveren nanodeeltjes, zoals die bekomen worden aan de hand van de werkwijze volgens een der conclusies 12-14, als onderdeel van een antimicrobiële inrichting of samenstelling.

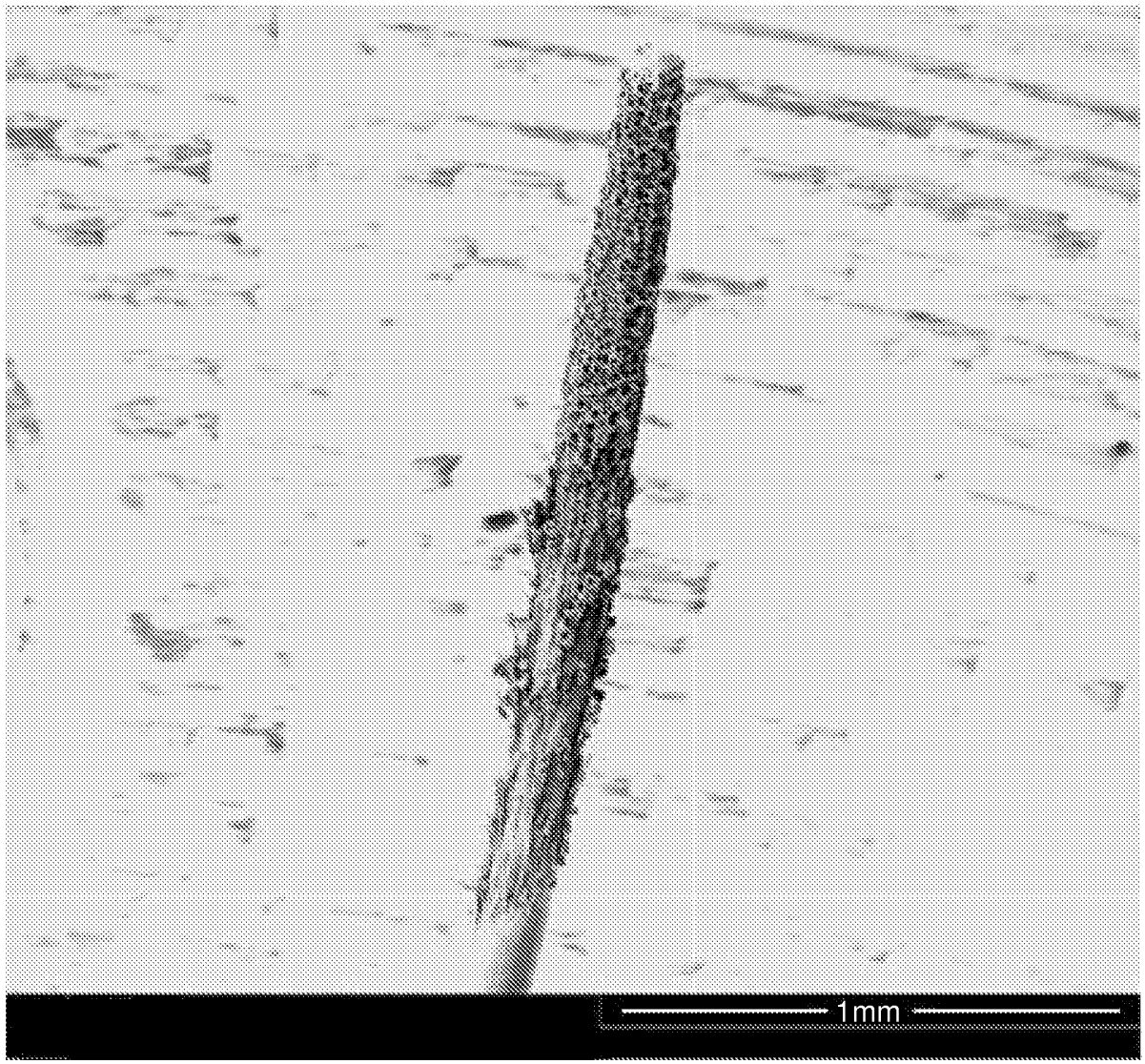

Fig.1

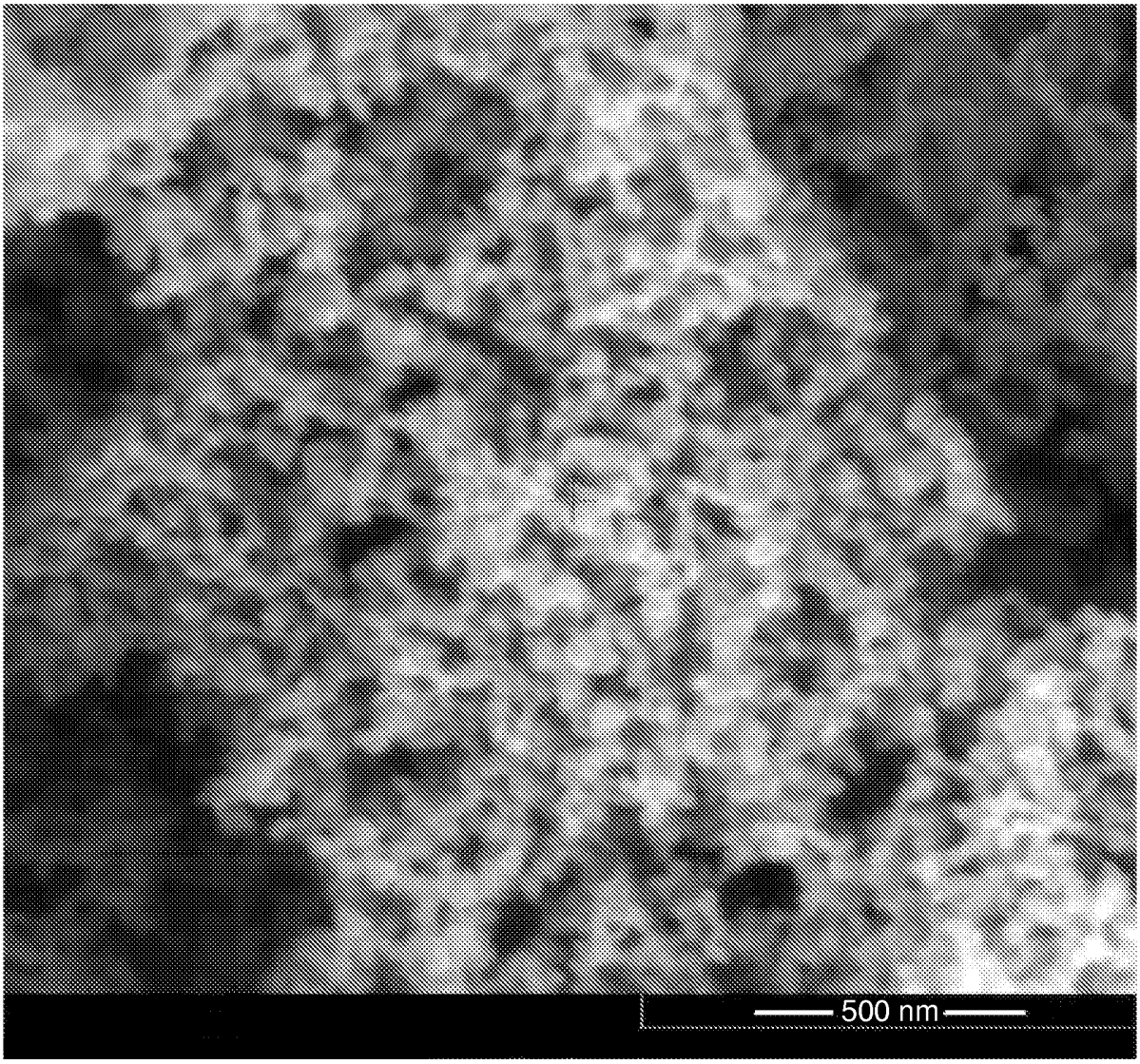

Fig.2

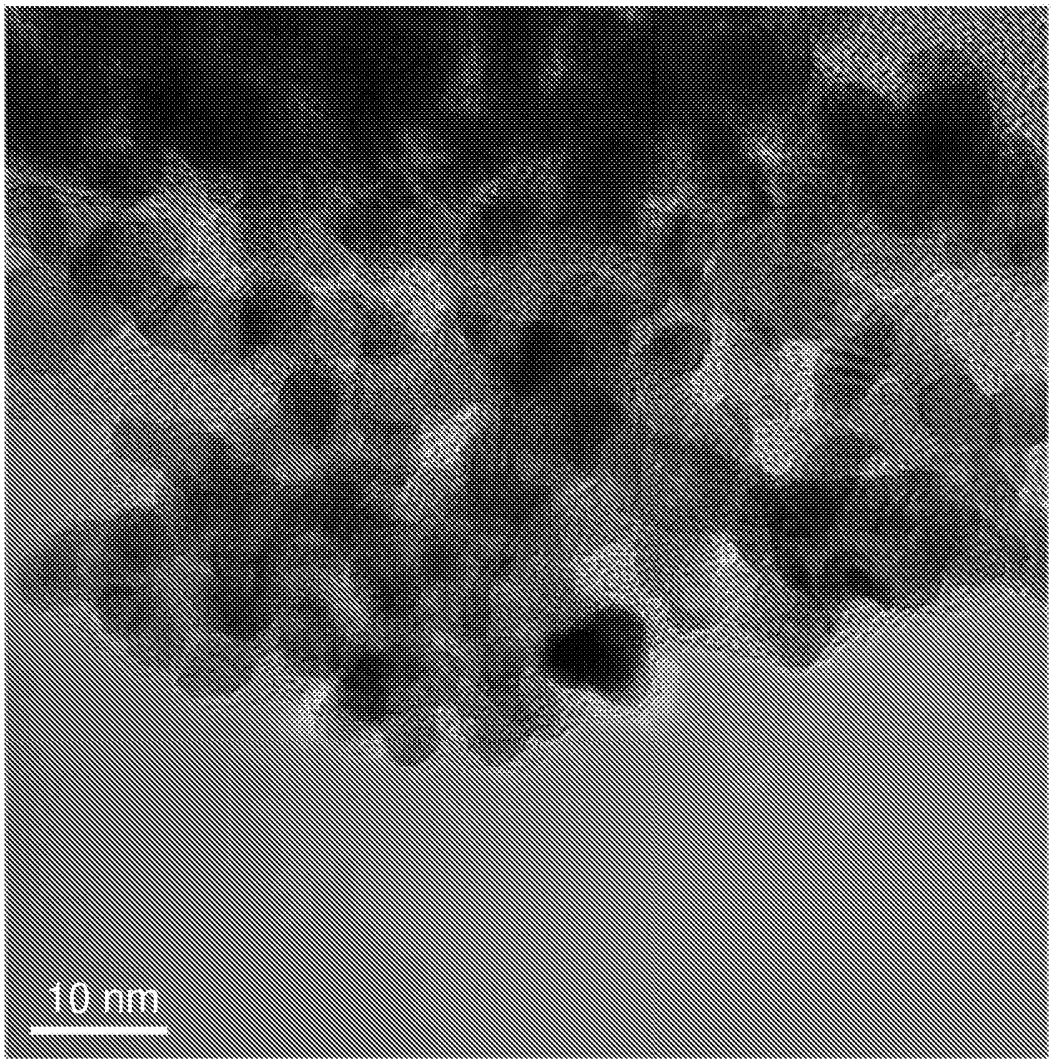

Fig.3

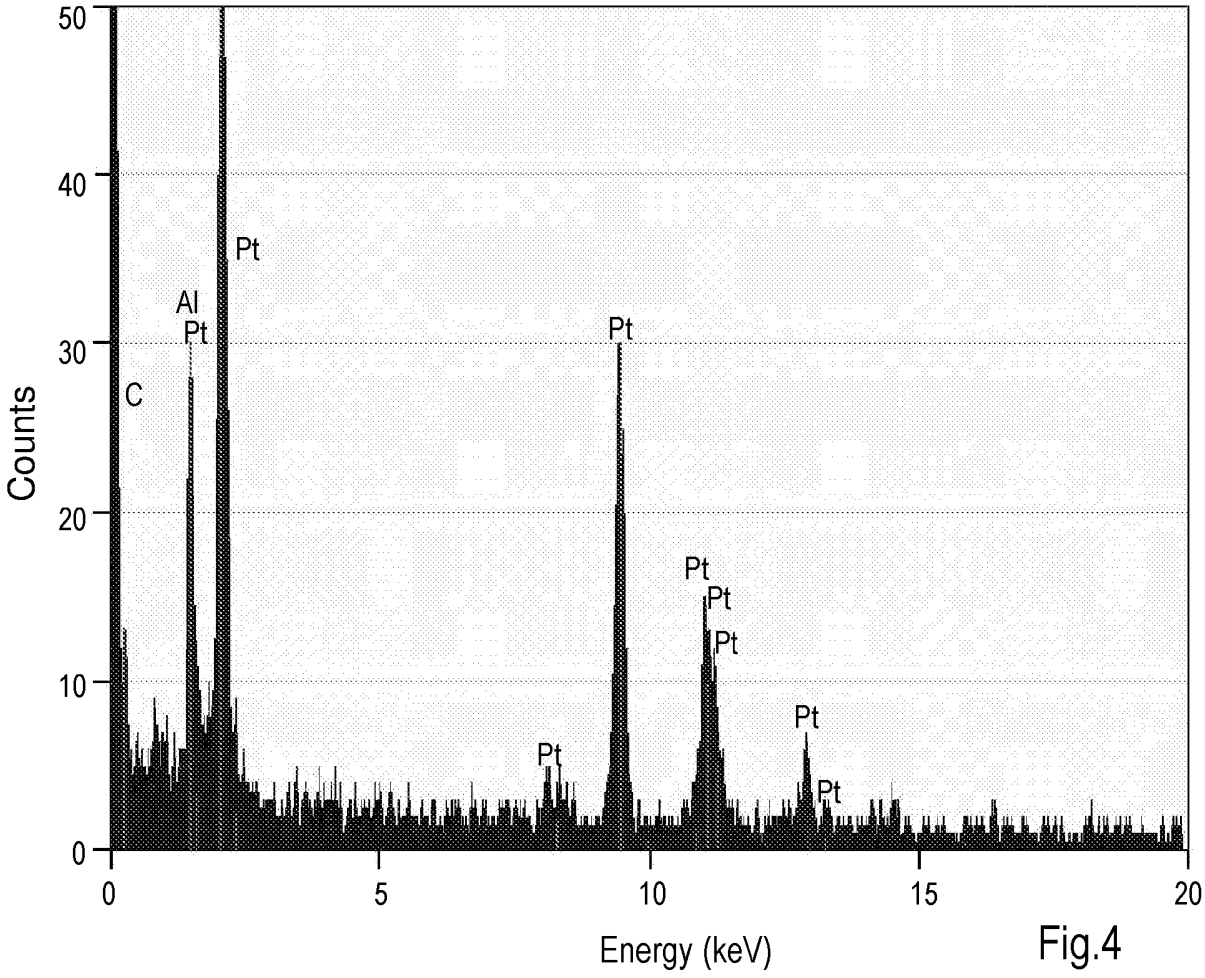
Counts
Energy (keV)
C
Al
Pt
Pt
Pt
Pt
Pt
Pt
Pt
Pt
Pt
0
10
20
30
40
50
0
5
10
15
20

Fig.4

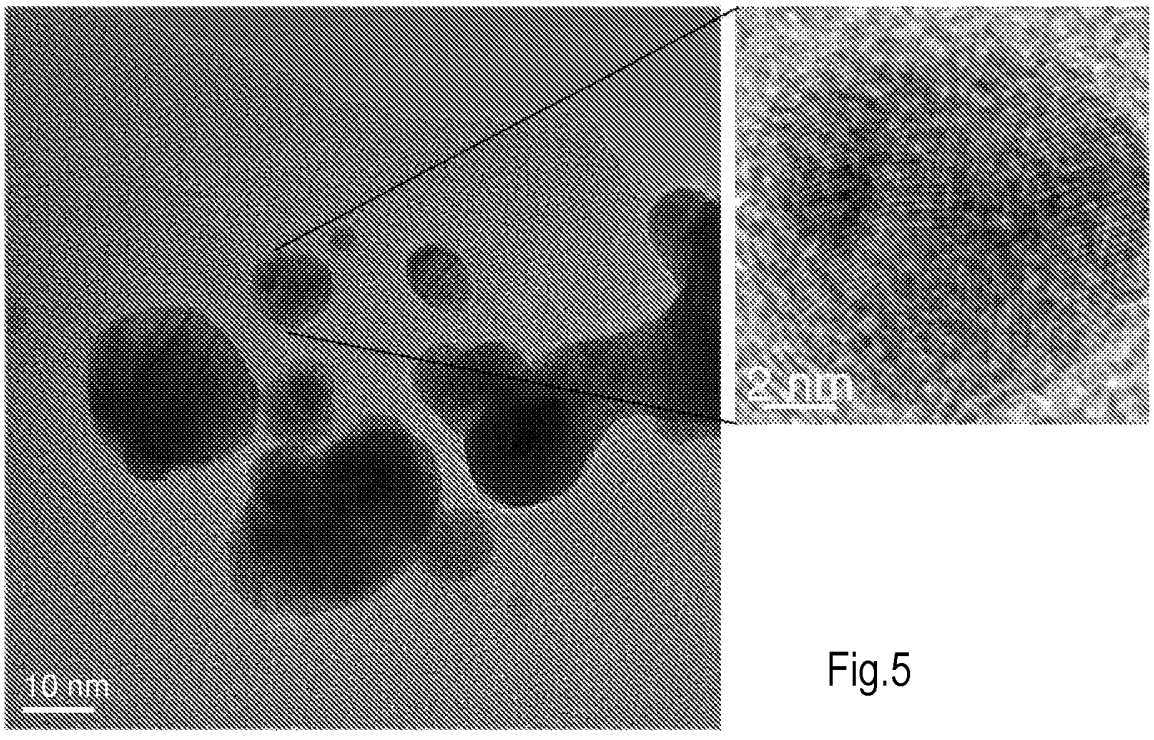
10 nm
2 nm

Fig.5

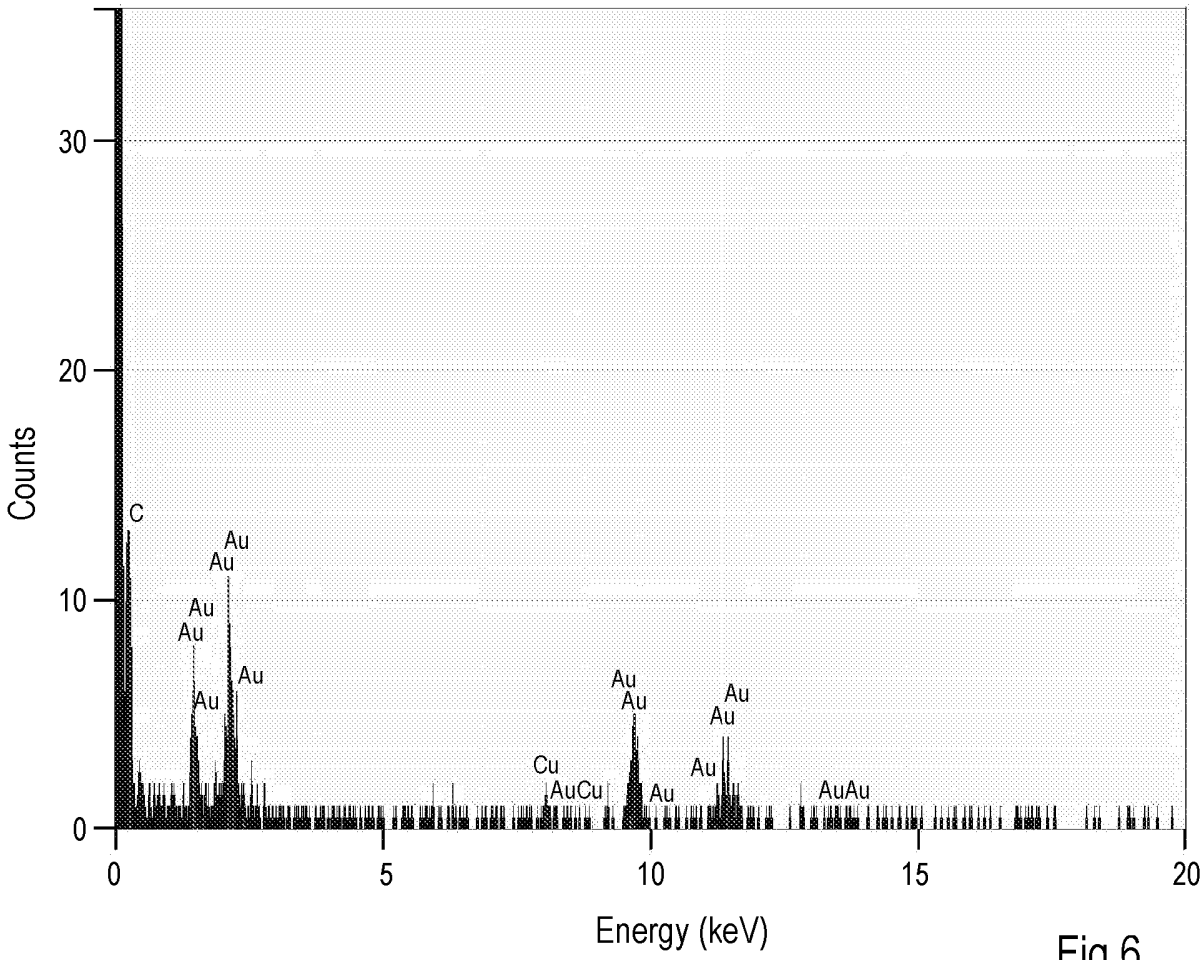
Counts
30
20
10
0
0
5
10
15
20
Energy (keV)
C
Au
Au
Au
Au
Au
Au
Au
Au
Au
Au
Au
Au
Cu
AuCu
Au
Au
AuAu

Fig.6

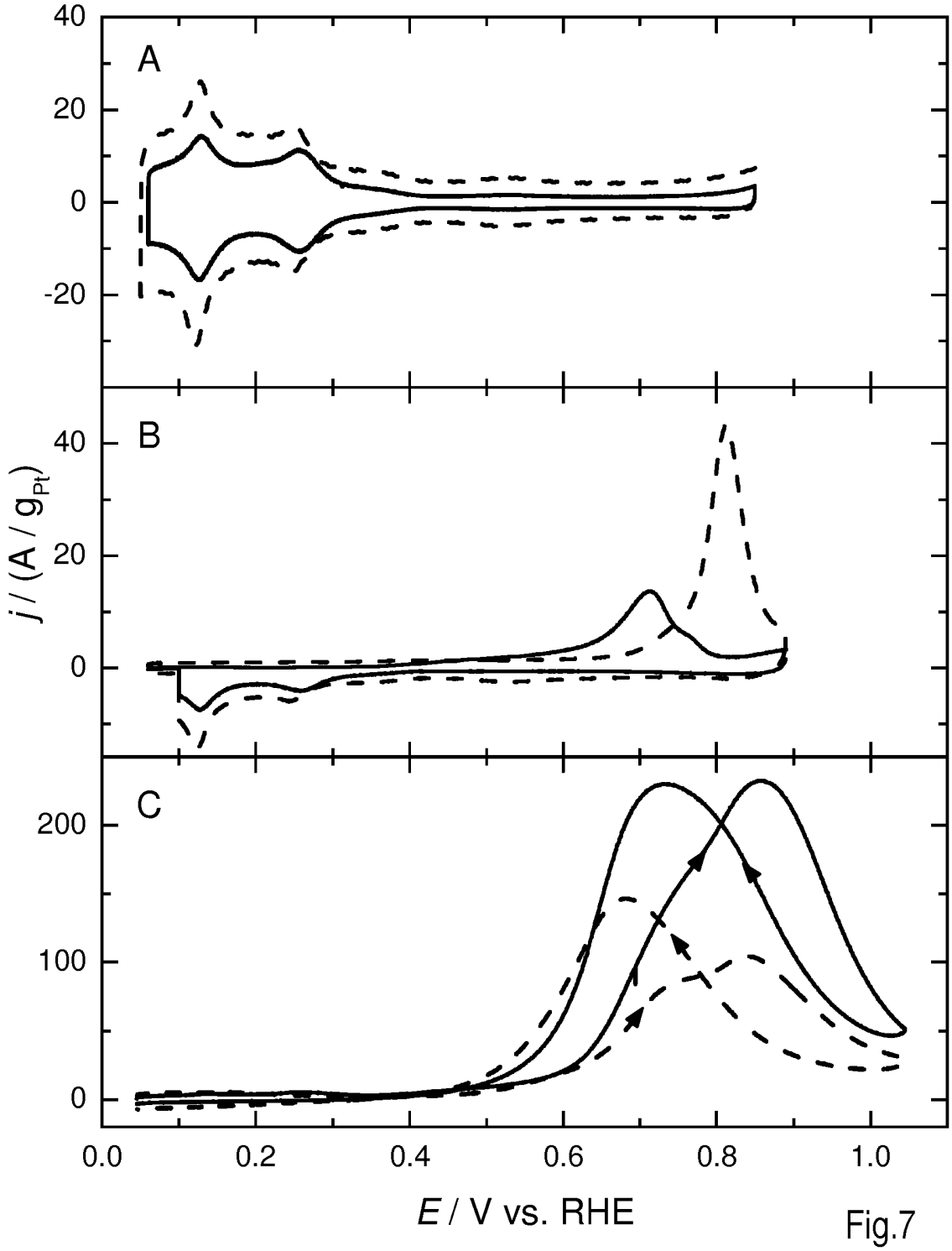

Fig.7

Agentschap NL
Ministerie van Economische Zaken, Landbouw en Innovatie

RAPPORT BETREFFENDE HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK

Octrooiaanvrage 2005112

Classificatie van het onderwerp[1]: C25C1/00, B22F1/00, B01J37/00, C25B1/00	Onderzochte gebieden van de techniek[1]: C25C, B22F, B01D, C25B
Computerbestanden: EPODOC, WPI	Omvang van het onderzoek: Volledig
Indien gewijzigde conclusies; indieningsdatum van deze conclusies:	Niet onderzochte conclusies[2]:

Van belang zijnde literatuur

Categorie[3]	Vermelding van literatuur met aanduiding, voor zover nodig, van speciaal van belang zijnde tekstgedeelten of figuren.	Van belang voor conclusie(s) nr.:
X Y	US 2009/0218234 A (JAYARAMAN SHRISUDERSAN) 3 september 2009 * figuren; paragrafen [0006], [0033],[0060] *	1-4, 7-11 5, 6
	- - -	
Y	DE 102005044873 A (LEIBNIZ INST NEUE MATERIALIEN) 29 maart 2007 * gehele document, in het bijzonder de figuren; paragrafen [0016], [0020], [0021], [0023], [0059]; de voorbeelden * & samenvatting DE 102005044873 A (WPI)	5, 6
	- - -	
Y	DE 10245509 B (SUSTECH GMBH & CO KG) 3 juni 2004 * gehele document, in het bijzonder paragrafen [0014]-[0017], [0032], [0044], [0045], * & samenvatting DE 10245509 B (WPI)	5, 6
	- - -	
A	US 2002/0037320 A (WISCONSIN ALUMNI RES FOUND) 28 maart 2002 * gehele document *	1-23
	- - -	
A	US 2005/0072679 A (NAYFEH MUNIR H et al.) 7 april 2005 * gehele document*	1-23

>> Als het gaat om octrooien

[1] Gedefinieerd volgens International Patent Classification (IPC).
[2] Voor motivering zie toelichting in de schriftelijke opinie.
[3] Verklaring van de categorie-aanduiding: zie apart blad.

A	--- US 2008/0251390 A (TSAI MING-CHI et al.) 16 oktober 2008 * gehele document * -----	1-23

Datum waarop het onderzoek werd voltooid: 2 februari 2011	De bevoegde ambtenaar: Mw. dr. ing. L. Bechger **NL Octrooicentrum**

Categorie van de vermelde literatuur:

X: op zichzelf van bijzonder belang zijnde stand van de techniek
Y: in samenhang met andere geciteerde literatuur van bijzonder belang zijnde stand van de techniek
A: niet tot de categorie X of Y behorende van belang zijnde stand van de techniek
O: verwijzend naar niet op schrift gestelde stand van de techniek
P: literatuur gepubliceerd tussen voorrangs- en indieningsdatum
T: niet tijdig gepubliceerde literatuur over theorie of principe ten grondslag liggend aan de uitvinding
E: octrooiliteratuur gepubliceerd op of na de indieningsdatum van de onderhavige aanvrage en waarvan de indieningsdatum of de voorrangsdatum ligt voor de indieningsdatum van de onderhavige aanvrage.
D: in de aanvrage genoemd
L: om andere redenen vermelde literatuur
&: lid van dezelfde octrooifamilie; corresponderende literatuur

AANHANGSEL BEHORENDE BIJ HET RAPPORT BETREFFENDE HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK, UITGEVOERD IN OCTROOIAANVRAGE NR. 2005112

Het aanhangsel bevat een opgave van elders gepubliceerde octrooiaanvragen of octrooien (zogenaamde leden van dezelfde octrooifamilie), die overeenkomen met octrooigeschriften genoemd in het rapport. De opgave is samengesteld aan de hand van gegevens uit het computerbestand van het Europees Octrooibureau per 8 maart 2011.

De juistheid en volledigheid van deze opgave wordt noch door het Europees Octrooibureau, noch door NL Octrooicentrum gegarandeerd; de gegevens worden verstrekt voor informatiedoeleinden.

In het rapport genoemd octrooi-geschrift		datum van publicatie	overeenkomend(e) geschrift(en)		datum van publicatie
US2009218234	A	2009-09-03			
DE102005044873	A	2007-03-29			
			WO2007033815	A	2007-03-29
DE10245509	B	2004-06-03			
			WO2004031449	A	2004-04-15
			AU2003262513	A	2004-04-23
US2002037320	A	2002-03-28			
			US2007013317	A	2007-01-18
US2005072679	A	2005-04-07			
			EP1756335	A	2007-02-28
			JP2008504448T	T	2008-02-14
			CN101379222	A	2009-03-04
US2008251390	A	2008-10-16			

SCHRIFTELIJKE OPINIE

Octrooiaanvrage 2005112

Indieningsdatum: 19 juli 2010	Voorrangsdatum:
Classificatie van het onderwerp[1]: C25C1/00, B22F1/00, B01J37/00, C25B1/00	Aanvrager: Universiteit Leiden

Deze schriftelijke opinie bevat een toelichting op de volgende onderdelen:

☑ Onderdeel I	Basis van de schriftelijke opinie
☐ Onderdeel II	Voorrang
☐ Onderdeel III	Vaststelling nieuwheid, inventiviteit en industriële toepasbaarheid niet mogelijk
☐ Onderdeel IV	De aanvraag heeft betrekking op meer dan één uitvinding
☑ Onderdeel V	Gemotiveerde verklaring ten aanzien van nieuwheid, inventiviteit en industriële toepasbaarheid
☐ Onderdeel VI	Andere geciteerde documenten
☐ Onderdeel VII	Overige gebreken
☑ Onderdeel VIII	Overige opmerkingen

De bevoegde ambtenaar:

Mw. dr. ing. L. Bechger

NL Octrooicentrum

[1] Gedefinieerd volgens International Patent Classification (IPC).

Schriftelijke Opinie

Octrooiaanvrage **2005112**

Onderdeel I Basis van de schriftelijke opinie

Deze schriftelijke opinie is opgesteld op basis van de meest recente conclusies ingediend voor aanvang van het onderzoek.

Onderdeel V Gemotiveerde verklaring ten aanzien van nieuwheid, inventiviteit en industriële toepasbaarheid

1. Verklaring

Nieuwheid	Ja:	Conclusies	5, 6, 12-23
	Nee:	Conclusies	1-4, 7-11
Inventiviteit	Ja:	Conclusies	12-23
	Nee:	Conclusies	5, 6
Industriële toepasbaarheid	Ja:	Conclusies	1-23
	Nee:	Conclusies	

2. Literatuur en toelichting

D1: US 2009/0218234 A
D2: DE 102005044873 A
D3: DE 10245509 B
D4: US 2005/0072679 A
D5: US 2002/0037320 A
D6: US 2008/0251390 A

Interpretatie van conclusie 1

De term "metalen startvoorwerp" in conclusie 1 is niet duidelijk. Uit de beschrijving blijkt dat met deze term een metalen startvoorwerp in vaste vorm wordt bedoeld welke de *bron* is van de te bereiden nanodeeltjes. Niet bedoeld is dat de materiaalbron van de nanodeeltjes zich als ion/zout/precursor in een elektrolyt oplossing bevindt en zich op een metalen (start)voorwerp afzet. Derhalve is conclusie 1 geïnterpreteerd als "Werkwijze voor de bereiding van metalen nanodeeltjes of nanodeeltjes uit een metaaloxide,
- door middel van het uitoefenen van een kathodepotentiaal op een metalen startvoorwerp in vaste vorm,
- waarbij het metalen startvoorwerp in vaste vorm de materiaalbron is van de nanodeeltjes,
- en het metalen startvoorwerp in contact staat met een vloeibaar elektrolyt dat een stabiliserend kation bevat".

Nieuwheid

D1 wordt gezien als de meest nabije stand der techniek. D1 openbaart een werkwijze voor de bereiding van nanodeeltjes uit een metaaloxide ("nanowires" van titaniumdioxide (TiO_2), zie samenvatting, figuren en paragraaf [0060]),

- door middel van het uitoefenen van een kathodepotentiaal (paragraaf [0033], "direct current (DC) power supply" 18 in figuur 1) op een metalen startvoorwerp in vaste vorm (kathode voorzien van titanium, zie figuur 1 en paragraaf [0033]),
- waarbij het metalen startvoorwerp in vaste vorm de materiaalbron is van de nanodeeltjes,
- en het metalen startvoorwerp in contact staat met een vloeibaar elektrolyt dat een stabiliserend kation bevat (het alkali kation Na^+ in de vorm van een waterige natriumhydroxide oplossing, zie paragrafen [0033] en [0046]).

De materie van conclusies 1 t/m 4 en 7 t/m 9 is derhalve bekend uit D1. Deze conclusies zijn dan ook niet nieuw.

De op deze wijze met nanostructuur gecoate metalen voorwerpen (elektrodes) worden gescheiden van de elektrolytoplossing en gewassen met o.a. water (zie paragrafen [0037], [0038]). De gecoate metalen voorwerpen kunnen gebruikt worden in fotovoltaïsche toepassingen zoals in (foto)katalyse. Ook conclusies 10 en 11 zijn niet nieuw in het licht van D1.

De werkwijze volgens conclusie 5 (en 6) verschilt van de werkwijze bekend uit D1 daarin, dat het startmetaal in vaste vorm een legering is van twee of meer metalen. Conclusies 5 en 6 zijn daarmee nieuw.

Conclusies 12 t/m 23 betreffen een werkwijze volgens conclusies 1 t/m 8, waarbij de kathodepotentiaal als wisselspanning (AC) wordt uitgeoefend, teneinde een suspensie van nanodeeltjes in het elektrolyt te verkrijgen. Deze maatregel is niet bekend uit D1 en derhalve zijn ook de conclusies 12 t/m 23 nieuw ten opzichte van D1.

De documenten D2 t/m D6 staan verder van het onderhavige onderwerp af dan D1. Deze documenten zijn derhalve niet nieuwheidsbezwarend voor de conclusies van de aanvrage.

Inventiviteit

De maatregel van conclusie 5 (en 6), namelijk dat het startvoorwerp in vaste vorm in een metaallegering is uitgevoerd, is op zichzelf bekend uit D2 (zie de paragrafen [0016], [0059], en de voorbeelden) en D3 (zie paragraaf [0045]). Voor een vakman uitgaande van de werkwijzen van D1 ligt de toepassing van deze maatregel uit D2 of D3 voor de hand om zo nanodeeltjes van een metaallegering te verkrijgen. Conclusies 5 en 6 zijn daarmee niet inventief.

De maatregel van conclusie 12 betreft het toepassen van de kathodepotentiaal als wisselspanning. Op deze manier wordt bewerkstelligd dat de nanodeeltjes niet als coating op het metalen startvoorwerp worden verkregen maar als een suspensie in het elektrolyt. Hoewel deze maatregel op zichzelf bekend is uit D3 (zie paragraaf [0032]), wordt in D3 de kathodepotentiaal niet op het metalen startvoorwerp toegepast maar op de tegenelektrode. Op het metalen startvoorwerp wordt in D3 een anodepotentiaal uitgeoefend. Voorts worden de in D3 geproduceerde metaaloxide nanodeeltjes reeds bij het toepassen van een gelijkspanning als suspensie in het elektrolyt verkregen. Een vakman op het gebied van electrochemische productie van metaal(oxide) nanodeeltjes leert uit D3 dus niet dat juist het toepassen

van een wisselspanning resulteert in een suspensie van metaal(oxide) nanodeeltjes. Er is dan ook geen aanleiding om deze maatregel toe te passen in de werkwijze van D1. Daarmee wordt de materie van conclusie 12, en de daarvan afhankelijke conclusies 13 t/m 23 inventief bevonden.

Onderdeel VIII Overige opmerkingen

De volgende opmerkingen met betrekking tot de duidelijkheid van de conclusies, beschrijving, en figuren, of met betrekking tot de vraag of de conclusies nawerkbaar zijn, worden gemaakt:

De woorden "bij voorkeur" in conclusie 3 zijn niet beperkend en de zinsneden achter deze woorden kunnen daarom worden weggedacht.