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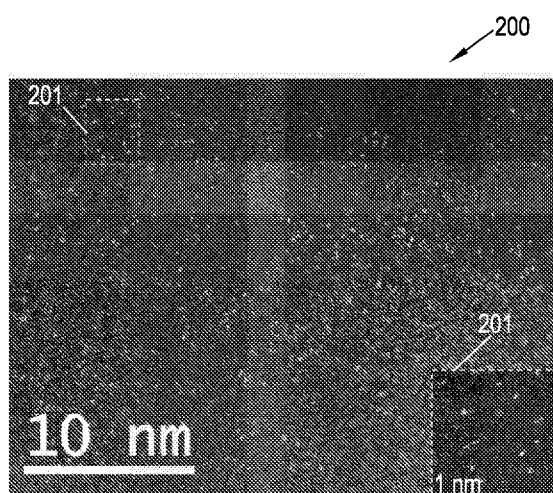


Figure 3

(57) Abstract: A method for preparing an atomically dispersed metal catalyst, comprising: depositing atomically dispersed metal onto a support by magnetron sputtering to directly form a catalyst comprising metal particles, with mean diameter up to 1 nm, dispersed on the surface of the support, wherein the support is water insoluble.



ATOMICALLY DISPERSED METAL CATALYST

FIELD

The present invention relates to a method of producing a catalyst.

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BACKGROUND

Atomically dispersed metal catalysts (ADMCs) on surfaces have demonstrated high activity and selectivity in many catalytic reactions. However, dispersing and stabilizing individual atoms onto support materials in an atom/energy-efficient scalable way still presents a significant challenge. Currently, their synthesis usually involves many steps and further purification/filtration procedures, creating a substantial hurdle to the production of ADCMs at industrial scale.

US2020/230589 discloses depositing atomically dispersed metal onto a water soluble support by physical vapour deposition (e.g. magnetron sputtering). The water soluble support is subsequently dispersed with a support (e.g. carbon particles) in water to obtain an aqueous dispersion containing a catalyst comprising support particles loaded with atomically dispersed metal. The catalyst (e.g. carbon supported atomically dispersed platinum) can be obtained by drying from the aqueous suspension.

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Although progress has been made in development of methods for producing atomically dispersed catalysts, there is room for improvement in improving the ease with which such catalysts can be prepared, and in reducing their cost in practical applications.

25 SUMMARY

According to an aspect of the invention, there is provided a method for preparing an atomically dispersed metal catalyst, comprising: depositing atomically dispersed metal onto a support by magnetron sputtering to directly form a catalyst consisting of metal particles, with mean diameter up to 1 nm, dispersed on the surface of the support, wherein the support is water insoluble.

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The mean diameter size may be determined by TEM (Transmission Electron Microscopy).

35 The metal particles may comprise single metal atoms.

The metal deposited onto the support may have a median particle size up to 1 nm.

The support may comprise or consist of graphitic carbon nitride.

- 5 The support may be selected from a carbon based material, a metal oxide, metal nitride, silica or combination thereof.

10 A carbon based material may comprise or consist essentially of a material with at least 90% carbon by mass, or at least 95% carbon by mass, such as carbon nanotubes, carbon black, graphite, graphene, activated carbon. The material may consist essentially of carbon. The surface of the carbon based material may consist essentially of carbon, or may consist essentially of a material with at least 90% carbon by mass. The support may comprise at least 90% carbon by mass, or at least 95% carbon by mass, or at least 99% carbon by mass.

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The support may be thermally stable at temperatures of 120 degrees C or more, or 150 degrees C or more, or 200 degrees C or more. The support may be photoactive, for example over a wavelength range above 320nm. The support may have electrical conductivity greater than: 0.1 S.cm^{-1} , 1 S.cm^{-1} or 10 S.cm^{-1} .

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The deposition of the metal atoms onto the support by magnetron sputtering may be at a working pressure of 0.1 Pa to 50 Pa, or 0.1 Pa to 30 Pa.

25 The deposition of the metal atoms onto the support by magnetron sputtering may be at a sputtering power of between 10W and 1000W, or between 20W and 120W, or between 10W and 50W.

The deposition of the metal atoms onto the support by magnetron sputtering may be at a sputtering power of less than 80W, or less than 50W.

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The magnetron sputtering may use argon (or another inert gas) as the sputtering gas.

The flow rate of the magnetron sputtering gas may be between 1sccm and 400sccm, or between 3sccm and 40sccm.

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The flow rate of the sputtering gas may be less than 20sccm.

Magnetron sputtering may comprise coating the support with metal sputtered from a target, and the working distance between the target and the support is between 1cm and 100cm, or between 20cm and 80cm, or between 20cm and 100cm.

The working distance between the target and the support may be less than 40cm.

The support may comprise a particulate support. The particulate support may be agitated during deposition of the metal atoms.

The particulate support may comprise a powder. The powder may comprise or consist essentially of nano-sheets, a powder comprising or consisting essentially of fibers or nanotubes.

Agitation may comprise at least one of: stirring, vibrating and/or tumbling of the particulate support. Gas nozzles may be coupled to the sample holder in order to provide agitation by impingement of gas flow on the particles/powder.

The metal may comprise a transition metal.

The metal may be, or comprise, a metal selected from: platinum, cobalt, nickel and other transition metals. Combinations of these metals may also be used.

The catalyst may be adsorbed on the surface of the support, and/or bonded to the surface of the support by a coordinate bond, and/or implanted in the support.

The interaction between metal catalyst and support may modify the electronic properties of the metal so as to change its catalytic activity and/or increase its catalytic activity.

The catalyst may be a thermal catalyst, an electrocatalyst, or a photocatalyst.

According to a second aspect, there is provided an atomically dispersed metal catalyst produced by the method according to the first aspect, including any optional features thereof.

BRIEF DESCRIPTION OF DRAWINGS

Embodiments will be described, by way of example only, with reference to the accompanying drawings, in which:

- 5 Figure 1 illustrates properties of different sized metal catalyst, ranging from bulk to single atom;

Figure 2 shows magnetron sputtering deposition of metal to form an atomically dispersed metal catalyst;

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Figure 3 is an aberration corrected scanning transmission electron microscopy (AC-STEM) image of dispersed Pt atoms in g-C₃N₄;

- 15 Figure 4 shows XANES spectra (X-ray absorption near edge structure) and Fourier transformed EXAFS (extended X-ray absorption fine structure) spectra of Pt/g-C₃N₄, Pt foil and PtO₂, respectively;

- 20 Figure 5 shows photocatalytic hydrogen production using 1mg/ml of photocatalyst produced according to an embodiment, 10vol% of TEOA, irradiation intensity of 300 mW.cm⁻², filter AM1.5G, at 30 °C;

Figure 6 shows photoluminescence spectra of g-C₃N₄ and Pt/g-C₃N₄ (excitation at 350 nm;

- 25 Figure 7 is an AC-STEM image showing that the high dispersion of Pt atoms on g-C₃N₄ was kept after the reaction of Figure 5;

Figure 8 illustrates the effect of increasing sputtering power on the production of metal atoms and metal atom clusters from the sputtering target;

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Figure 9 illustrates the effect of varying the working pressure of the magnetron sputtering chamber on deposition of metal atoms;

Figures 10, 11 and 12 are AC-STEM images showing Pt deposition under different process conditions, with different: sputtering power, argon flow rate and working pressure;

- 5 Figure 13 shows Fourier transformed EXAFS (extended X-ray absorption fine structure) spectra of Pt/g-C₃N₄ deposited under different working pressure;

Figure 14 is an AC-STEM image corresponding with a particular set of process conditions for deposition of atomically dispersed Pt on g-C₃N₄;

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Figure 15 shows AC-STEM images of (a, b) Ni/g-C₃N₄ and Co/g-C₃N₄, respectively, showing high dispersion of atomic nickel and cobalt;

- Figure 16 shows how to measure the mean diameter of metal cluster and nanoparticle from a TEM image of the metal clusters and nanoparticles on the support;
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- Figure 17 shows g-C₃N₄ measurements of: (a) IR and (b) PXRD, $2\theta \approx 27^\circ$, corresponding to the (002) reflection of the interlayer stacking of aromatic segments d-spacing of 0.32 nm, $2\theta \approx 13^\circ$, corresponding to the in-plane (100) reflection with a d-spacing of 0.64 nm;
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Figure 18 is an AC-STEM image of Pt atoms and Pt atom clusters deposited onto alumina (Al₂O₃) by magnetron sputtering;

- 25 Figure 19 shows an AC-STEM image of Pt atoms and Pt atom clusters, deposited on a carbon black support by magnetron sputtering;

Figure 20 shows an AC-STEM image of Pt atoms and Pt atom clusters, deposited on a boron nitride support (BN);

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Figure 21 shows a) an AC-STEM image of Pd atoms and Pd atom clusters, deposited on a boron nitride support (BN); and b) an AC-STEM image of Ru atoms and Ru atom clusters deposited on a boron nitride support.

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DETAILED DESCRIPTION

In this disclosure, a new pathway for producing atomically-dispersed metal catalysts (ADMCs) is developed where metal atoms are directly deposited onto a suitable support to form an ADMC using a scalable, one-pot magnetron sputtering deposition. In an example embodiment, platinum atoms are stabilised in the nitrogen-interstice of a graphitic carbon nitride (g-C₃N₄) support, but the methodology described herein is equally applicable to other supports and other metals.

ADMCs bridge the gap between homogenous and heterogeneous catalysis and can combine the best features of both: the high activity and selectivity of homogenous catalysts with the high stability and recyclability of heterogeneous catalysts. Current methods for the synthesis of ADMCs are based on either wet-chemistry (i.e. reduction of metal salts) or atomic layer deposition (ALD) approaches. However, industrial scale-up of these synthetic methods is difficult because they require multiple steps and/or high temperatures, generate large amounts of chemical waste, and are not readily generalizable across supports and metal catalysts. In contrast, top-down physical methods for ADMC synthesis do not need high-temperatures, and can be used for almost any type of solid support and transition metal, whilst generating no chemical waste. However, most physical methods are intrinsically limited to making small quantities of materials, and therefore not scalable to industrial levels.

Magnetron sputtering has recently emerged as a promising technique for the production of metal nanoparticles (MNPs) on a wide variety of supports (e.g. powder, liquids). It is one of the select few 'green' and scalable top-down methods, and has already been applied on a large scale in the glass-coating and semiconductor industry. This approach is carried out in ultraclean, high vacuum environments and can therefore generate extremely active metal species with clean surfaces not occluded by ligands or surfactants. In the magnetron sputtering process, accelerated argon ions collide elastically with a high purity metal target, which expels atoms from the target onto a support material. The sputtered metal atoms therefore can be adsorbed and/or implanted onto support material depending on their kinetic energy and the composition-structure of the support material.

Figure 2 shows a schematic of deposition according to an embodiment. Argon ions are accelerated towards a metal target by an electrical field. The collision of the

argon ions with the target 102 results in the ejection of atoms 103 of the metal target 102. The ejected metal atoms 103 land on the support 120 resulting in atomically dispersed metal atoms at the surface of the support 120. The support and atomically dispersed metal atoms deposited thereon together form a catalyst.

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The catalyst may comprise a particulate support, so that the catalyst is in particulate form, which increases surface to volume ratio and hence increases the activity of the catalyst. The support 120 may consequently be retained in a sample holder 106 in the magnetron sputtering chamber during deposition of the atomically dispersed metal atoms. In order to promote uniform deposition of metal atom on the particulate support 120, the support 120 may be agitated during deposition. Figure 2 illustrates one way of doing this, in which the sample holder 106 is rotated, as indicated by arrow 104, during deposition (e.g. by drive shaft 105). One or more agitators 111 are arranged to remain still while the sample holder 106 rotates, with the result that the one or more agitator rotates relative to the sample holder 106 and stirs the support 120.

In the embodiment of Figure 2 there are four agitators supported on a frame structure 110, but other arrangements may be used, including arrangements in which the sample holder does not rotate, but the agitator does. It may be advantageous to rotate the sample holder, since magnetron sputtering equipment typically comprises a sample holder configured for rotation, and rotation of the sample to be coated improves uniformity of coating (in addition to any effect from stirring).

Alternative methods for agitation of the support 120 may be used including vibration and tumbling. For example, the sample holder may: vibrate; vibrate and rotate; tumble; tumble and rotate; tumble and vibrate; and tumble, rotate and vibrate. Furthermore, gas nozzles can be coupled to the agitation system improving the uniformity of coating.

Figure 2 shows an example of a catalyst 125 produced according to an embodiment, and of a particulate support 120 before deposition of the atomically dispersed metal. The particulate support consists of g-C₃N₄, and was prepared via pyrolysis of melamine (10 g), heating under air at 300 °C for 2 hours and then 520 °C for 2 hours. The chemical composition and crystalline structure of the synthesized g-C₃N₄ support was confirmed by Fourier-transform infrared spectroscopy (FTIR) and powder X-ray diffraction (PXRD) measurements, as shown in Figure 17a and 17b, respectively.

The deposition of Pt atoms on g-C₃N₄ via magnetron sputtering was carried out using a bespoke magnetron sputtering system. The support (1g of g-C₃N₄) was placed into a stirring sample-holder 106, and then loaded in the magnetron sputtering pre-chamber, reaching 3x10⁻⁷ Torr background pressure in 40 min. The sample-holder was transferred to the main chamber where the background-pressure was 3x10⁻⁸ Torr, which took 10 min to stabilize its background-pressure. The Pt deposition was carried out with working-pressure of 3 mTorr Ar gas at room temperature. The applied power was 60 W (370 V and 16 mA) and deposition was carried out for 12 min yielding Pt/g-C₃N₄ 0.5 wt% of Pt onto 1 g of g-C₃N₄ measured by inductively coupled plasma optical emission spectrometry (ICP-OES). This gives an ADMC production-rate of 4.8 mg h⁻¹, with a Pt loading on g-C₃N₄ of 5 mg and a total 'feedstock-to-product' magnetron sputtering process time of 63 min. This represents a very high rate of production, and this approach does not generate chemical waste (i.e. solvents) which makes it a clean and sustainable route for production of supported ADMCs. To demonstrate the applicability of this method, Ni and Co atoms have been atomically dispersed onto g-C₃N₄ framework using similar parameters.

Figure 15 shows AC-STEM images of (a, b) Ni/g-C₃N₄ and Co/g-C₃N₄, respectively, showing the high dispersion of atomic nickel and cobalt. The magnetron sputtering deposition of Ni and Co atoms were carried out with work-pressure of 3mTorr using Ar gas, high purity Ni and Co targets (99.95%) under room temperature. The applied power utilized was 20W (283V and 72mA) for 60 min yielding Ni/g-C₃N₄ and Co/g-C₃N₄ 0.5 wt% of Ni or Co onto 1 g of g-C₃N₄ ICP-OES.

The AC-STEM shown in Figure 3 illustrates that the metal is atomically dispersed at the surface of the support. An inset image is shown at higher magnification – each bright dot is a single metal atom. The metal atoms are well dispersed at the surface, and are not formed into nanoparticles. Extensive AC-STEM measurements were performed on Pt/g-C₃N₄ and no Pt nanoparticles (comprising groups of atoms) were observed. Nanoparticles of atoms do not enable the greatly enhanced catalytic activity that is seen with supported atomic metal catalysts.

Figure 4 shows the XANES spectra 310 of Pt/g-C₃N₄ 313, and the standard spectra of Pt foil 312 and PtO₂ 311. The white line intensities of the spectra reveals the oxidation state of the Pt atoms, and are intermediate between the intensities of Pt foil and PtO₂.

This demonstrates that Pt atoms are slight positively charged due to is coordination onto g-C₃N₄ framework.

Figure 4 further shows K-edge EXAFS 320. The plot for Pt/g-C₃N₄ has only one peak at 1.5 Å (not phase-corrected) which is associated with Pt-N/C coordination. No peaks associated with Pt-Pt and/or Pt-O coordination can be seen in the plot 320 for Pt/g-C₃N₄, which is consistent with the AC-STEM analysis.

Photocatalytic hydrogen production reactions were performed to investigate the catalytic photoactivity of Pt/g-C₃N₄ and g-C₃N₄. Figure 5 shows the results 330, comparing hydrogen evolution using: pristine g-C₃N₄ 332; and using a Pt/g-C₃N₄ catalyst according to an embodiment 331 with 1 mg.ml⁻¹ of the catalyst, 10vol% of TEOA (Triethanolamine), irradiation intensity of 300 mW.cm⁻², filter AM1.5G, at 30°C. As expected, pristine g-C₃N₄ showed negligible hydrogen evolution and hydrogen was only detected in large enough quantities to be reliably measured after 3h. In contrast, Pt/g-C₃N₄ showed a much higher activity, improving the hydrogen production 3333 times after 5 h of reaction. Moreover, these results compare favorably to similar systems previously reported, demonstrating the high photocatalytic activity of catalyst produced according to an embodiment, such as the Pt/g-C₃N₄ example system.

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To gain further insights into the high photocatalytic activity of Pt/g-C₃N₄, photoluminescence (PL) measurements were carried out to investigate the efficiency of charge transfer and separation. Figure 6 shows PL spectra 340 for g-C₃N₄ 341 and Pt/g-C₃N₄ 342 produced according to an embodiment. The PL spectrum of g-C₃N₄ exhibits an intense peak at 460 nm, which is ascribed to excitation to electron-hole recombination of g-C₃N₄. The dispersion of Pt onto the g-C₃N₄ surface led to a decrease of the PL intensity, which is consistent with suppressed charge carrier recombination arising from the efficient dissociation of photogenerated electron-hole pairs of Pt/g-C₃N₄, in agreement with the photocatalytic results.

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Figure 7 shows an AC-STEM image 210 of the Pt/g-C₃N₄ after 5h of photocatalysis, showing no agglomeration, the major mechanism responsible for catalyst deactivation, which demonstrates the outstanding stability of Pt atoms in the g-C₃N₄ framework.

Figures 8 and 9 schematically illustrate the effect of magnetron sputtering conditions on the deposition process. Figure 8 shows sputtering at low power 150 and high power 151. At high power, the kinetic energy of the ions and the rate of sputtering are high enough that metal atoms 103 tend to form clusters 107 before they are deposited on the support. Sputtering at high power levels produces ADMCs, metal clusters of atoms and may produce metal nanoparticles.

Figure 9 shows sputtering at low working pressure and high working pressure. High working pressures are associated with the formation of nanoparticles 107, whereas with lower pressures there is less potential for nanoparticles of atoms 103 to form before deposition. The inclusion of nanoparticles may decrease catalytic performance. The highest catalytic performance may be obtained when the deposited metal is fully atomically dispersed on the support (with no, or negligible clustering).

Figures 10 to 13 illustrate the effects of varying magnetron sputtering deposition parameters on the quality of the ADMC produced according to an embodiment. Figures 10 to 12 are AC-STEM images obtained with different magnetron sputtering parameters, and Figure 13 shows EXAFS analysis of samples prepared with different sputtering working pressures along with a Pt Foil and PtO₂ standard.

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Figure 10 shows AC-STEM images of Pt deposition onto graphitic carbon nitride by magnetron sputtering using 60 W (370 V and 16 mA) and 150 W (411 V and 36 mA) yielding 0.29 wt% and 0.38 wt% of Pt onto graphitic carbon nitride, respectively. Magnetron sputtering parameters used for both depositions: argon working pressure of 3mTorr, argon flow rate of 6sccm, working distance of 30cm, angle between target-sample of 10°, and powder sample holder stirring rotation of 20rpm. The 60W deposition results in atomically dispersed metal, whereas the 150W power results in both atomically dispersed metal and Pt nanoparticles on the support.

Figure 11 also shows AC-STEM images of Pt deposition onto graphitic carbon nitride by magnetron sputtering using argon flow rates of 6sccm and 40sccm yielding 0.29 wt% and 0.31 wt% of Pt onto graphitic carbon nitride, respectively. Magnetron sputtering parameters used for both depositions: argon working pressure of 3mTorr, sputtering power 60W, working distance of 30cm, angle between target-sample of 10°, and powder sample holder stirring rotation of 20rpm. Both the flow rates result in atomically

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dispersed metal, and the rate of deposition is relatively insensitive to the argon flow rate.

Figure 12 shows AC-STEM images of Pt deposition onto graphitic carbon nitride by magnetron sputtering using argon work pressure of 3mTorr and 30mTorr yielding 0.31 wt% and 0.25 w% of Pt onto graphitic carbon nitride, respectively. Magnetron sputtering parameters used for both depositions: argon flow rate of 40sccm, power applied of 60W (3mTorr: 369V and 16mA and 30mTorr 338V and 18mA), work distance of 30cm, angle between target-sample of 10°, and powder sample holder stirring rotation of 20rpm. The 3mTorr deposition results in atomically dispersed metal, whereas the 30mTorr deposition results in both atomically dispersed metal and nanoparticles of Pt on the support. The EXAFS analysis in Figure 13 shows that, while for deposition using work-pressure 3mTorr only ADMCs were produced for the deposition using 30mTorr there is considerable atomically dispersed metal and there are also nanoparticles.

Figure 14 shows an AC-STEM image of atomically dispersed Pt on a g-C₃N₄ support, with deposition conditions: argon work pressure of 3mTorr, argon flow rate of 6sccm, power applied of 60W (370V and 16 mA), work distance of 30cm, angle between target-sample of 10°, and powder sample holder stirring rotation of 20rpm; yielding 0.29 w% of Pt onto graphitic carbon nitride. This set of process conditions provides an ADMC with well dispersed metal atoms, at a good production rate.

This disclosure provides for deposition of ADMC into bulk powder using magnetron sputtering approach. In an example, Pt atoms are stabilized into the nitrogen-interstices of graphitic carbon nitride (g-C₃N₄). The approach disclosed herein has a very high rate of ADMC catalyst production (4.8 mg h⁻¹), and does so without generating chemical waste. The dispersion of Pt atoms onto a g-C₃N₄ support was confirmed by aberration corrected scanning transmission electron microscopy (AC-STEM) imaging and extended x-ray absorption fine structure (EXAFS) measurements. Furthermore, the photocatalytic performance of Pt/g-C₃N₄ was tested for hydrogen evolution. AC-STEM analysis before and after hydrogen evolution reaction confirmed the high stability of dispersed Pt atoms on g-C₃N₄ framework. Pt/g-C₃N₄ shows outstanding photocatalytic activity when compared with similar reported systems. The scalable magnetron sputtering approach disclosed herein can generate effective ADMC catalysts for

hydrogen production using only one clean synthetic step. Embodiments therefore provide a transformative method for the synthesis of ADMCs.

The g-C₃N₄ framework absorbs visible light leading to electron-hole pair generation that injects electrons on Pt-centers enhancing the hydrogen evolution. Deposition of only 0.5 weight percent of Pt onto g-C₃N₄ led to improved hydrogen production by factor of *ca.* 3333 when compared to bare g-C₃N₄. Scanning transmission electron microscopy imaging before and after the hydrogen evolution reaction revealed that the Pt atoms dispersed in g-C₃N₄ have a high stability, with no agglomeration observed. Herein, it is shown that this scalable and clean approach can produce effective ADMC for hydrogen production with no further synthetic steps required and that it can be readily use for catalytic reactions.

Figure 16 illustrates that the size of metal catalyst particles may be measured by AC-STEM or TEM. An AC-STEM image is shown in Figure 16 comprising atom clusters/nanoparticles 51, and dispersed atoms 50. The atoms 50 can be identified a single points of contrast in the AC-STEM that are not in close proximity with any other atoms. The clusters 51 comprise groups of closely packed atoms, and the diameter of a cluster can be determined with reference to the longest dimension visible in the AC-STEM image. In this example, there are clusters of atoms with diameter 2.1nm and 1.6nm, alongside some atomically dispersed metal atoms 50.

Figure 18 shows an AC-STEM image of Pt atoms 302 and Pt atom clusters 301, deposited on an alumina support (Al₂O₃). The Pt clusters have a mean average diameter of 0.41 ± 0.12nm. Pt deposition on carbon black (0.5g) conditions: deposition time of 30min, argon work pressure of 3mTorr, argon flow rate of 10sccm, power applied of 20W (320V and 62 mA), work distance of 90cm, angle between target-sample of 10°, and powder sample holder stirring rotation of 50rpm; yielding 0.14 w% of Pt onto carbon black. This set of process conditions provides an ADMC with well dispersed metal atoms. Pt deposition on Al₂O₃ (3g) conditions: deposition time of 30min, argon work pressure of 3mTorr, argon flow rate of 10sccm, power applied of 20W (322V and 62 mA), work distance of 90cm, angle between target-sample of 10°, and powder sample holder stirring rotation of 50rpm; yielding 0.15 w% of Pt onto Al₂O₃. This set of process conditions provides an ADMC with well dispersed metal atoms.

Figure 19 shows an AC-STEM image of Pt atoms 302 and Pt atom clusters 301, deposited on a carbon black support. The Pt clusters have a mean average diameter of $0.53 \pm 0.12\text{nm}$. Pt deposition on carbon black (0.5g) conditions: deposition time of 30min, argon work pressure of 3mTorr, argon flow rate of 10sccm, power applied of 20W (320V and 62 mA), work distance of 90cm, angle between target-sample of 10° , and powder sample holder stirring rotation of 50rpm; yielding 0.14 w% of Pt onto carbon black. This set of process conditions provides an ADMC with well dispersed metal atoms.

Figure 20 shows an AC-STEM image of Pt atoms 302 and Pt atom clusters 301, deposited on a boron nitride support (BN). The Pt clusters have a mean average diameter of $0.68 \pm 0.13\text{nm}$. Pt deposition on boron nitride (1.5g) conditions: deposition time of 30min, argon work pressure of 3mTorr, argon flow rate of 10sccm, power applied of 20W (320V and 62mA), work distance of 90cm, angle between target-sample of 10° , and powder sample holder stirring rotation of 50rpm; yielding 0.11 w% of Pt onto boron nitride. This set of process conditions provides an ADMC with well dispersed metal atoms.

Figure 21 shows a) an AC-STEM image of Pd atoms and Pd atom clusters 301, deposited on a boron nitride support (BN). The Pt clusters have a mean average diameter of $0.68 \pm 0.13\text{nm}$; and b) an AC-STEM image of Ru atoms and Ru atom clusters 301, deposited on a boron nitride support (BN). The Pd clusters have a mean average diameter of $0.79 \pm 0.18\text{nm}$ and the Ru clusters have a mean average diameter of $0.61 \pm 0.14\text{nm}$. The magnetron sputtering settings used were similar to those reported for the deposition of Figure 14.

From reading the present disclosure, other variations and modifications will be apparent to the skilled person. Such variations and modifications may involve equivalent and other features which are already known in the art of time to digital converters and phase locked loops, and which may be used instead of, or in addition to, features already described herein.

Although the appended claims are directed to particular combinations of features, it should be understood that the scope of the disclosure also includes any novel feature or any novel combination of features disclosed herein either explicitly or implicitly or any

generalisation thereof, whether or not it relates to the same subject matter as presently claimed in any claim and whether or not it mitigates any or all of the same technical problems.

- 5 Features which are described in the context of separate embodiments may also be provided in combination in a single embodiment. Conversely, various features which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable sub-combination. The applicant hereby gives notice that new claims may be formulated to such features and/or combinations of such features
- 10 during the prosecution of the present application or of any further application derived therefrom.

- For the sake of completeness it is also stated that the term "comprising" does not exclude other elements or steps, the term "a" or "an" does not exclude a plurality and reference
- 15 signs in the claims shall not be construed as limiting the scope of the claims.

CLAIMS

1. A method for preparing an atomically dispersed metal catalyst, comprising:
depositing atomically dispersed metal onto a support by magnetron sputtering to directly
5 form a catalyst consisting of metal particles, with mean diameter up to 1 nm, dispersed
on the surface of the support, wherein the support is water insoluble.
2. The method of claim 1, wherein the support comprises a particulate material
with a surface consisting essentially of carbon.
- 10 3. The method of claim 1, wherein the support comprises or consists of a material
selected from a carbon based material, a metal oxide, a metal nitride, silica or a
combination thereof.
- 15 4. The method of claim 1 or 2, wherein the support comprises or consists of a
material with at least 90% carbon by mass, such as carbon nanotubes, carbon black,
graphite, graphene, activated carbon.
5. The method of claim 1 or 3, wherein the support comprises or consists of
20 graphitic carbon nitride.
6. The method of any preceding claim, wherein the deposition of the metal atoms
onto the support by magnetron sputtering is at a working pressure of 0.1 Pa to 50 Pa.
- 25 7. The method of claim 6, wherein the deposition of the metal atoms onto the
support by magnetron sputtering is at a working pressure of 0.1 Pa to 30 Pa.
8. The method of any preceding claim, wherein the deposition of the metal atoms
onto the support by magnetron sputtering is at a sputtering power of between 10W and
30 1000W.
9. The method of claim 8, wherein the deposition of the metal atoms onto the
support by magnetron sputtering is at a sputtering power of between 20W and 120W.

10. The method of any preceding claim, wherein the deposition of the metal atoms onto the support by magnetron sputtering is at a sputtering power of less than 80W.

11. The method of any preceding claim, wherein the flow rate of the sputtering gas is between 1sccm and 400sccm.

12. The method of claim 11, wherein the flow rate of the sputtering gas is between 3sccm and 40sccm.

13. The method of claim 11 or 12, wherein the flow rate of the sputtering gas is less than 20sccm.

14. The method of any preceding claim, wherein magnetron sputtering comprises coating the support with metal atoms sputtered from a target, and the working distance between the target and the support is between 1cm and 100cm.

15. The method of any preceding claim, wherein magnetron sputtering comprises coating the support with metal atoms sputtered from a target, and the working distance between the target and the support is between 20cm and 80cm.

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16. The method of any preceding claim, wherein magnetron sputtering comprises coating the support with metal atoms sputtered from a target, and the working distance between the target and the support is less than 40cm.

17. The method of any preceding claim, wherein the support comprises a particulate support, and the particulate support is stirred and/or vibrated and/or tumbled.

18. The method of claim 17, wherein gas nozzles are coupled to a sample-holder to provide agitation by impingement of gas flow on the particulate support during deposition of the metal catalyst.

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19. The method of any preceding claim, wherein the metal is or comprises a metal selected from: platinum, cobalt, nickel and others transition metals, or a combination thereof.

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20. The method of any preceding claim, wherein the metal catalyst is adsorbed and/or coordinated and/or implanted in the support.

21. The method of claim 20, wherein the interaction between the catalyst and the support modifies the electronic properties of the catalyst so as to modify and/or increase its catalytic activity.

22. The method of any preceding claim, wherein the catalyst is a thermal catalyst, electrocatalyst or photocatalyst.

23. The method of any preceding claim, wherein the catalyst is at least one of: thermally stable at temperatures of over 120 degrees C; photoactive, and electrically conductive.

24. An atomically dispersed metal catalyst produced by the method according to any preceding claim.

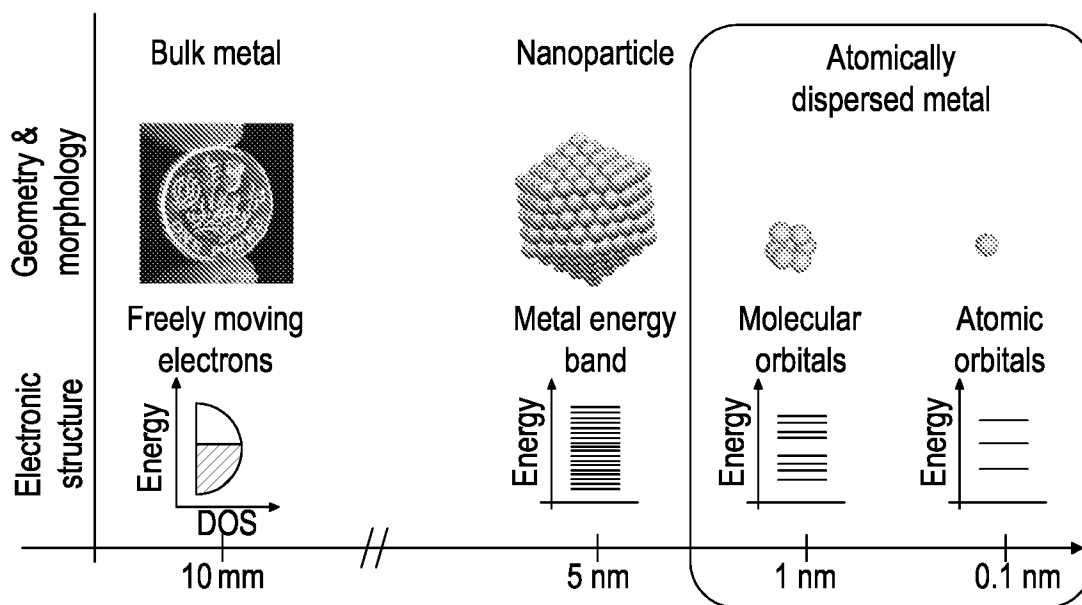


Figure 1

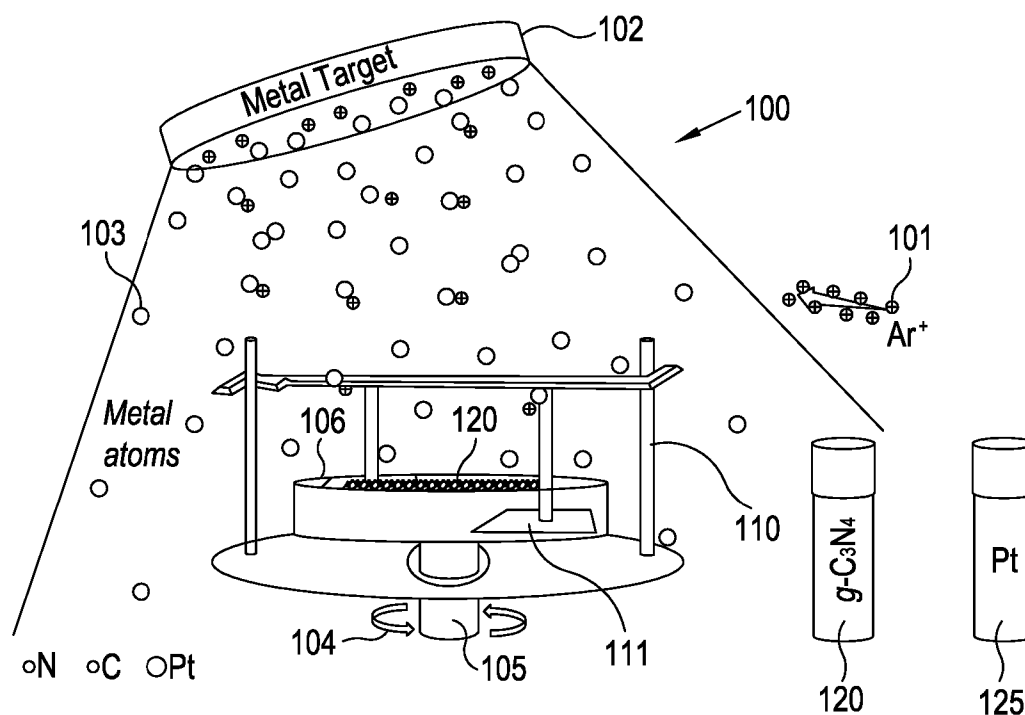


Figure 2

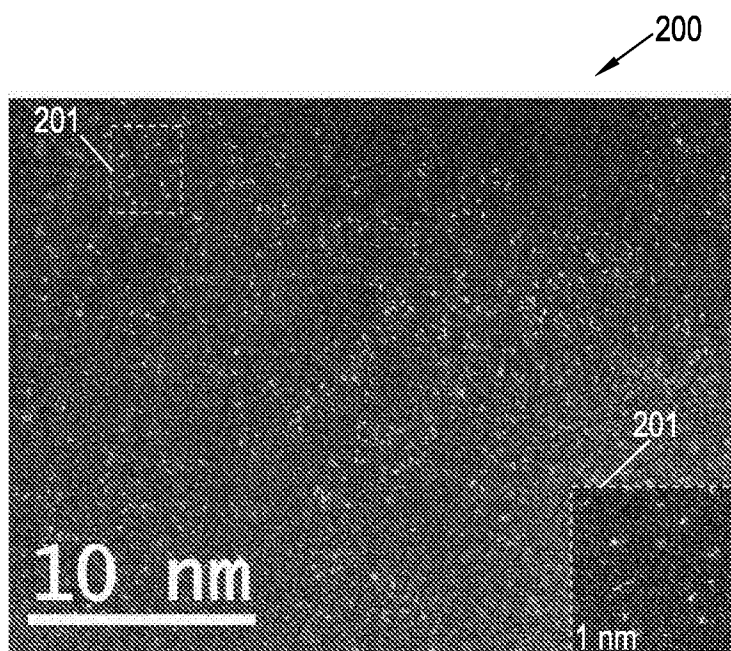


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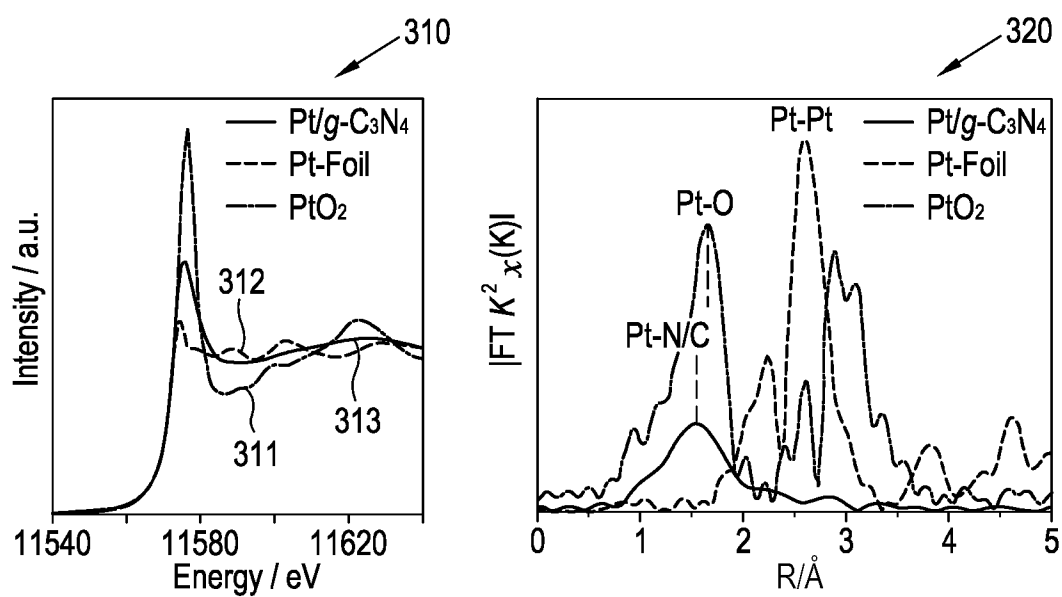


Figure 4

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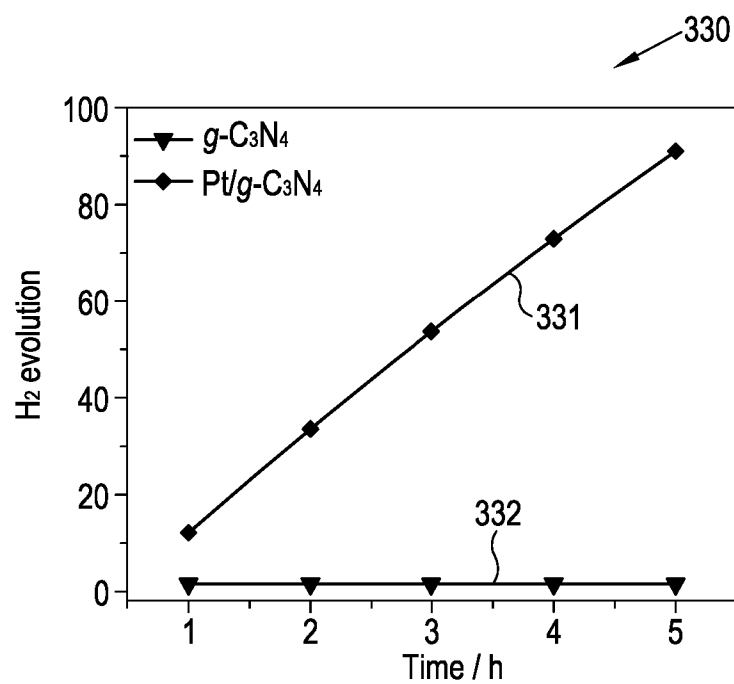


Figure 5

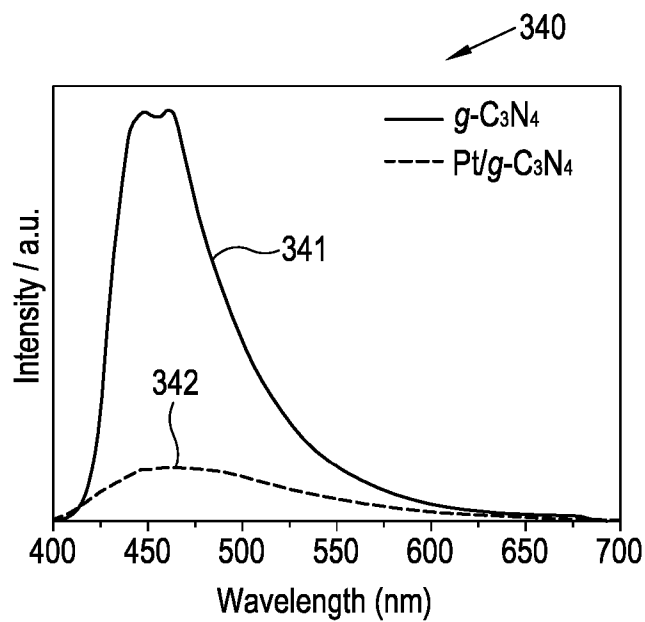


Figure 6

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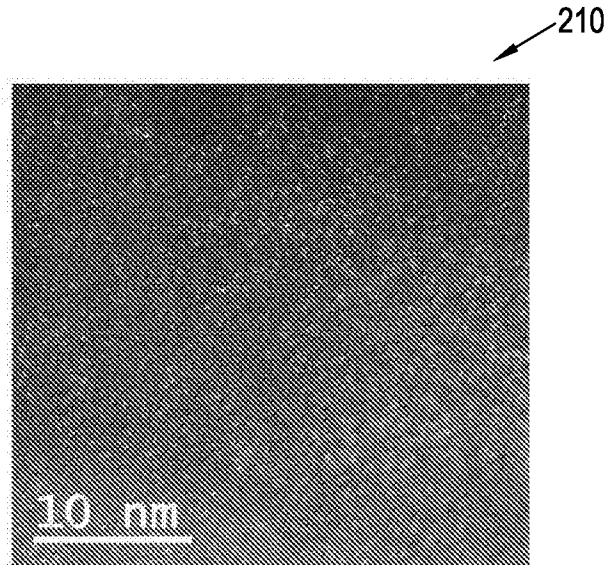


Figure 7

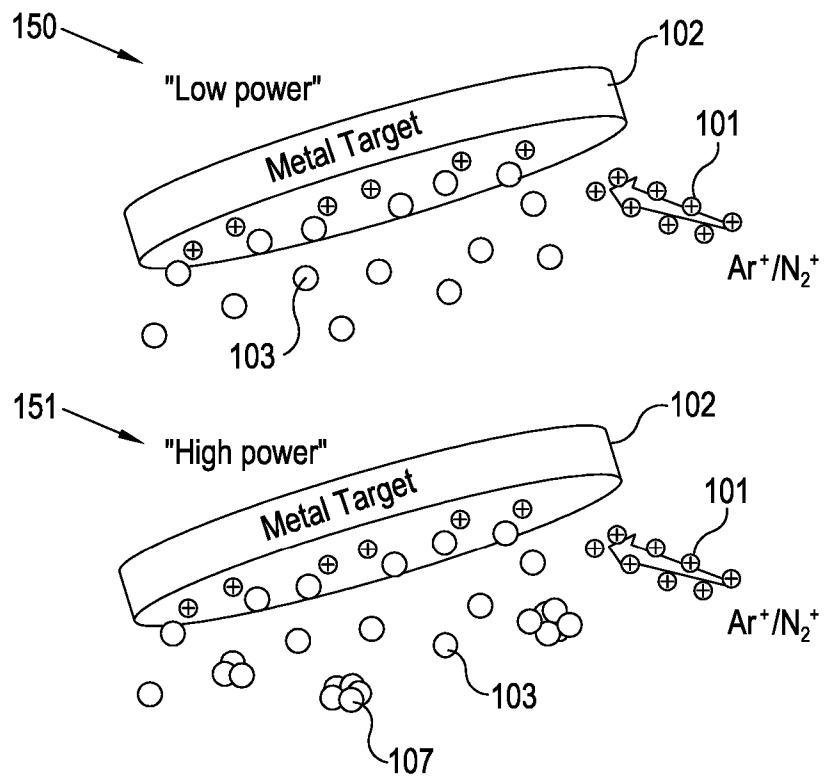


Figure 8

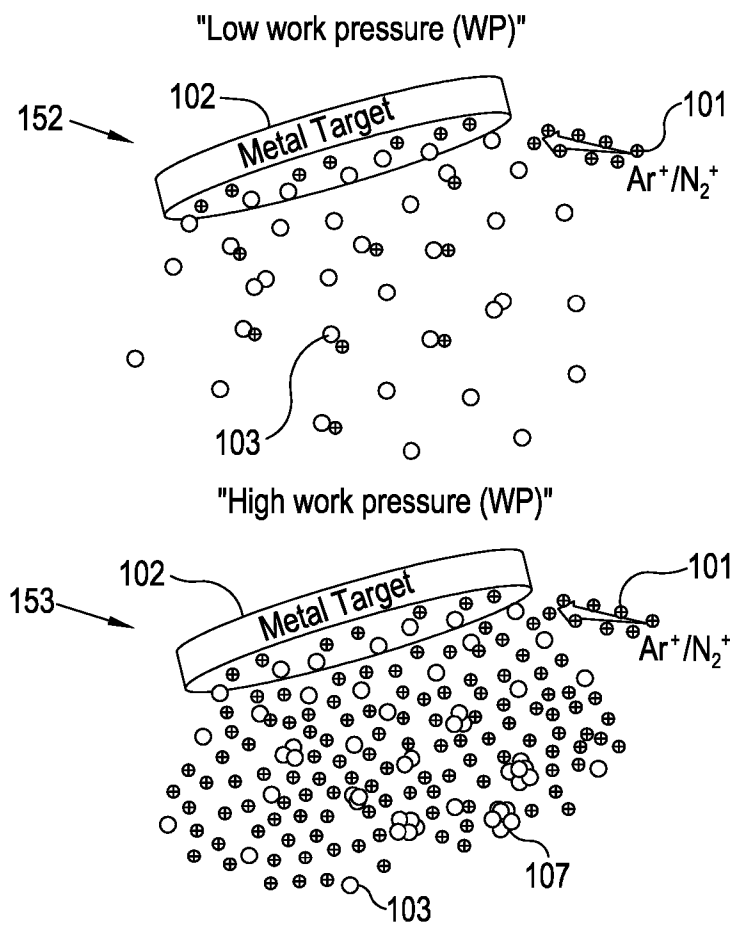


Figure 9

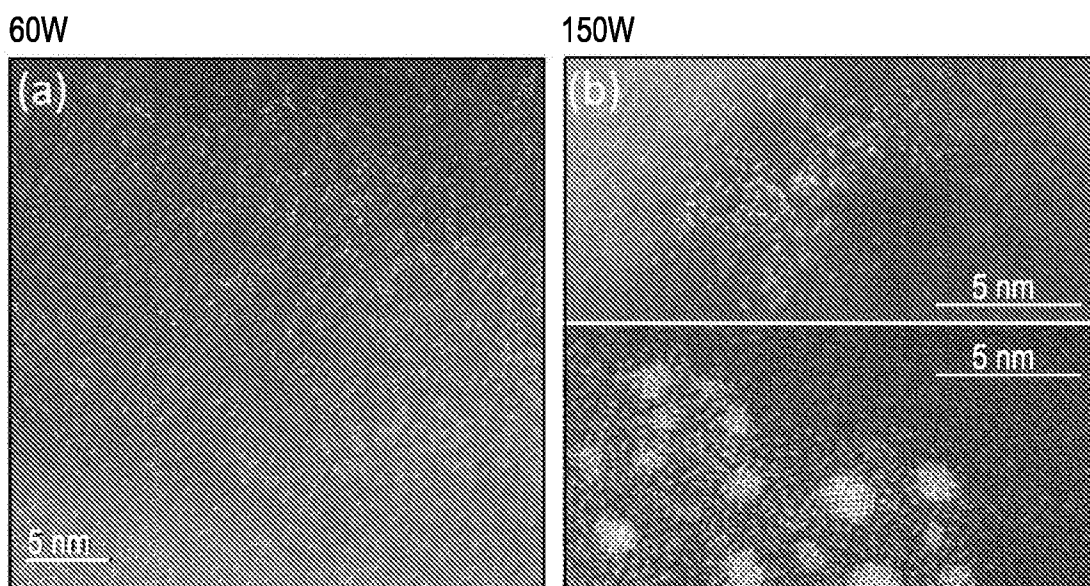


Figure 10

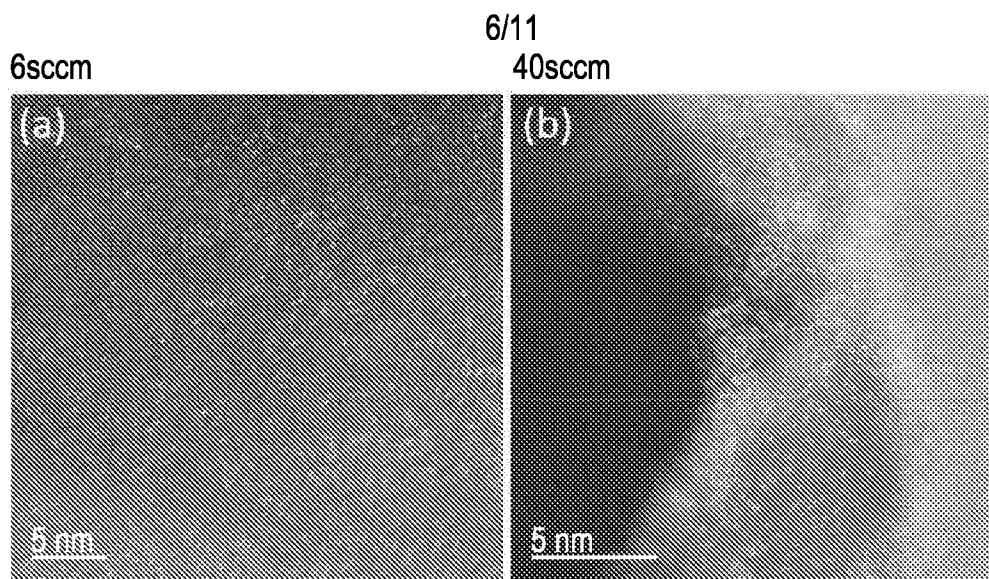


Figure 11

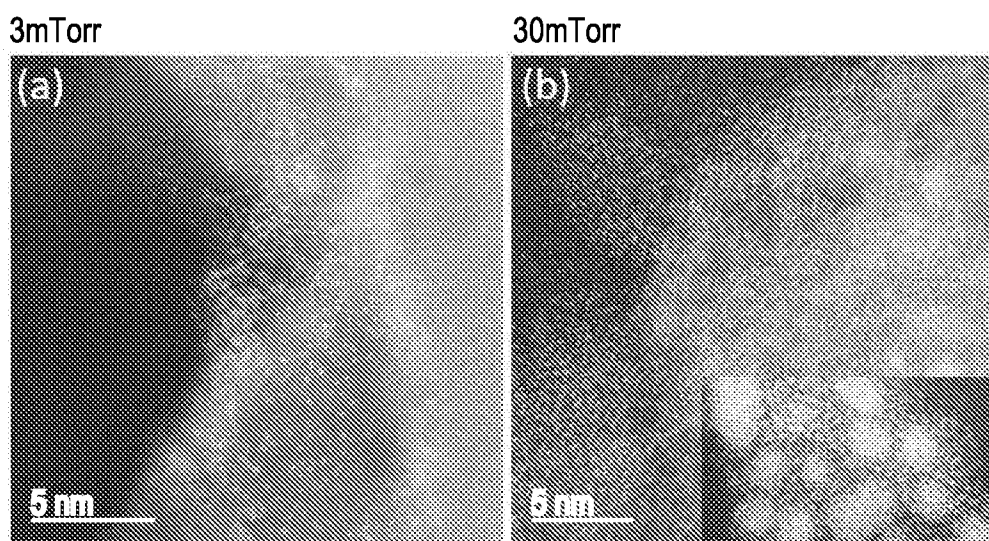


Figure 12

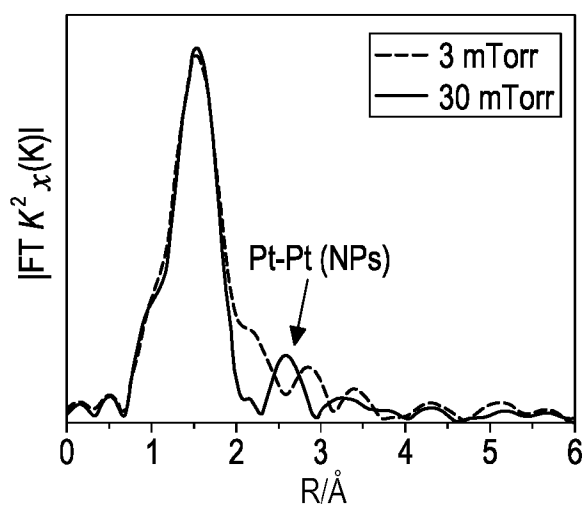


Figure 13

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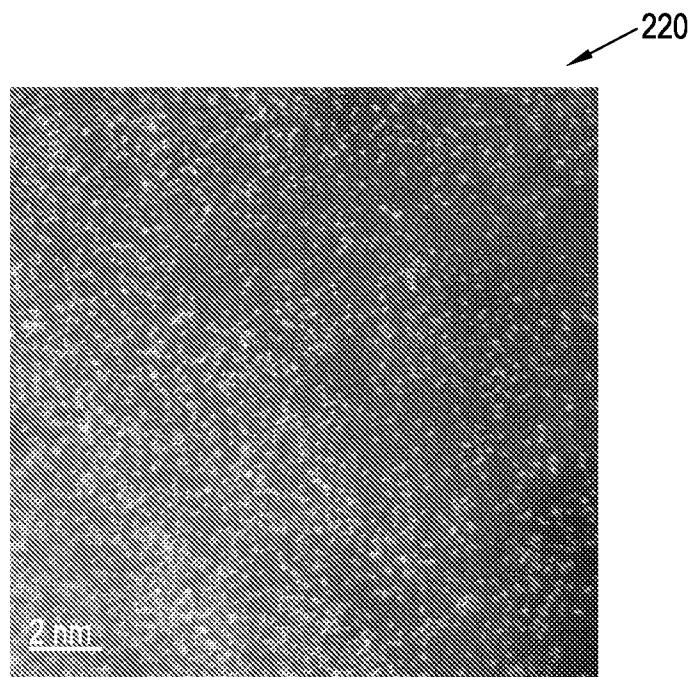


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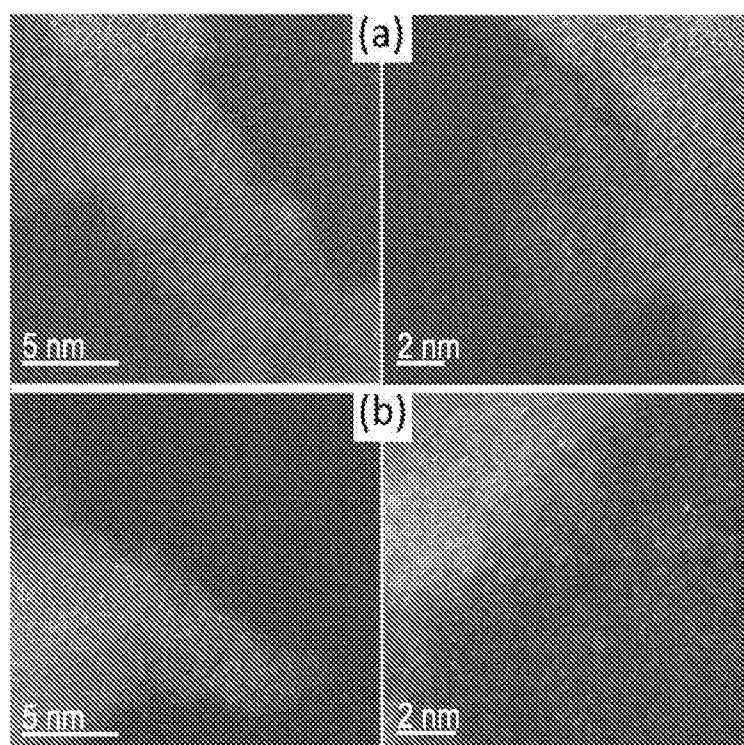


Figure 15

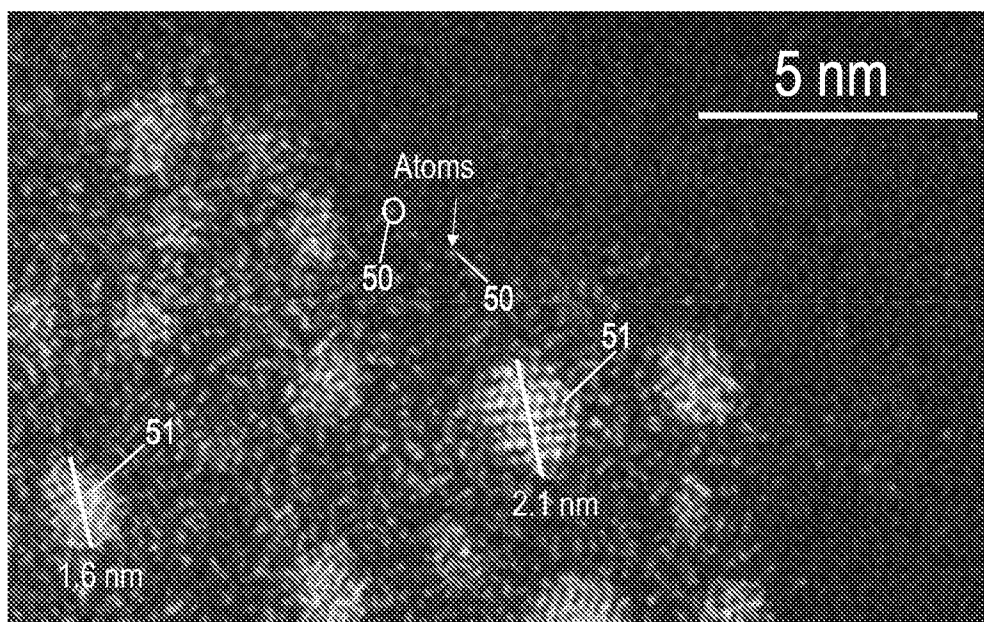


Figure 16

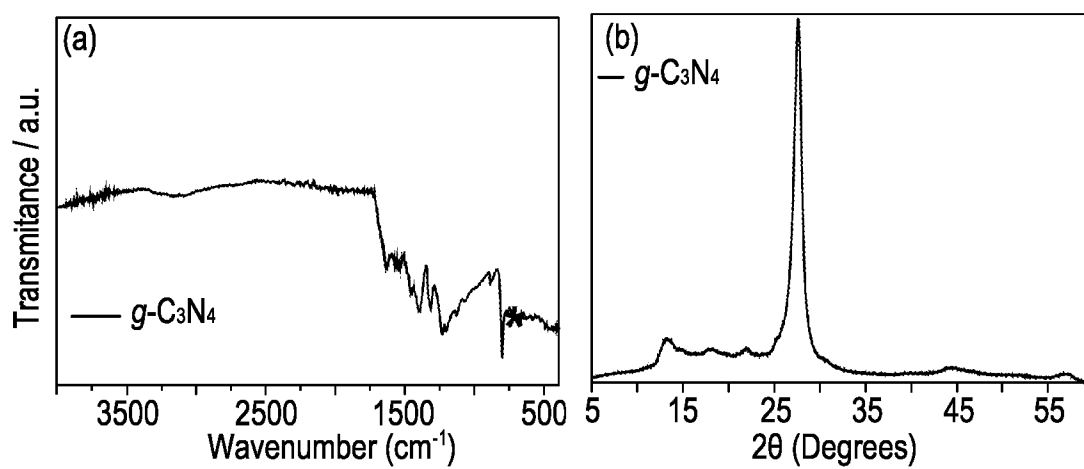


Figure 17

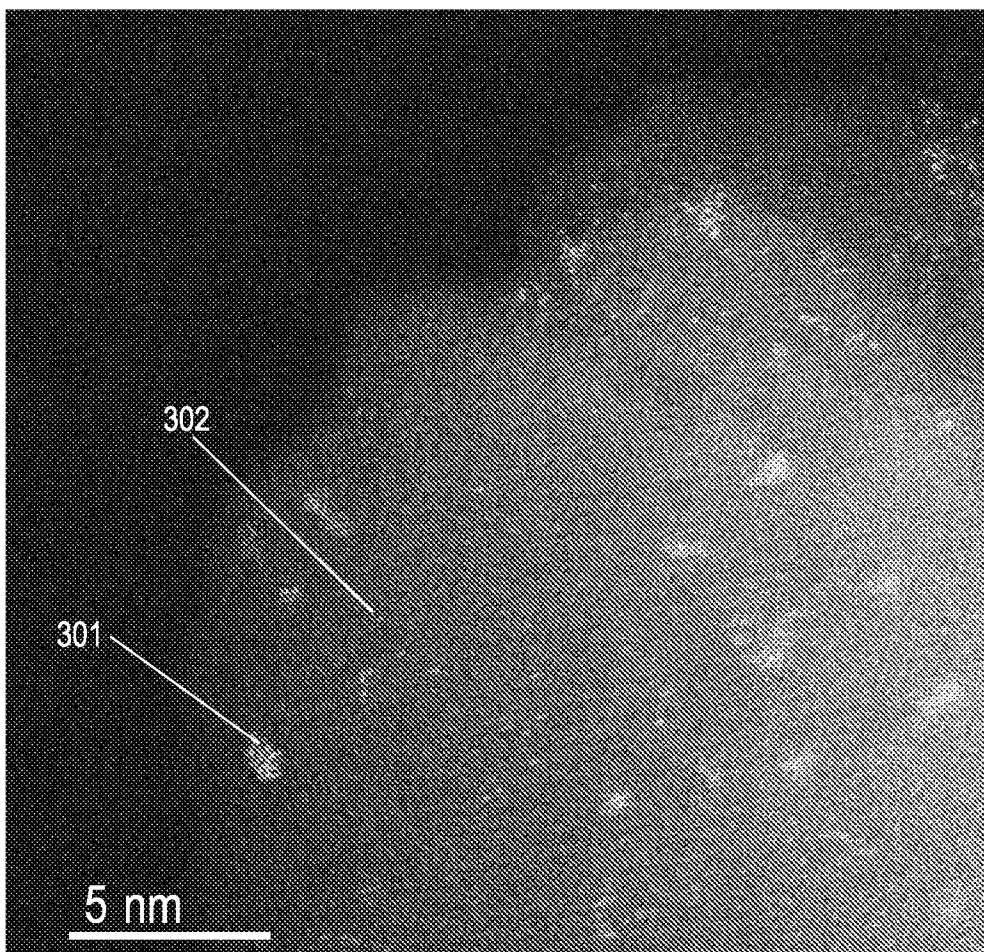


Figure 18

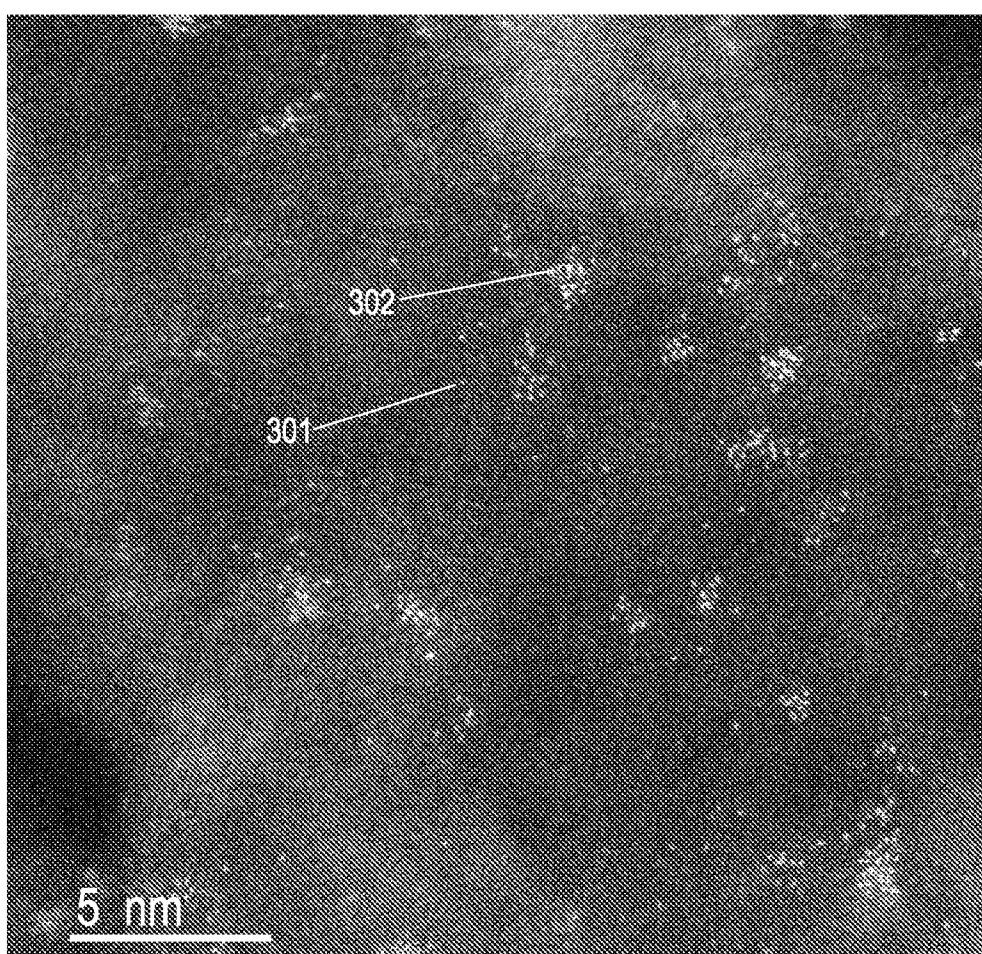


Figure 19

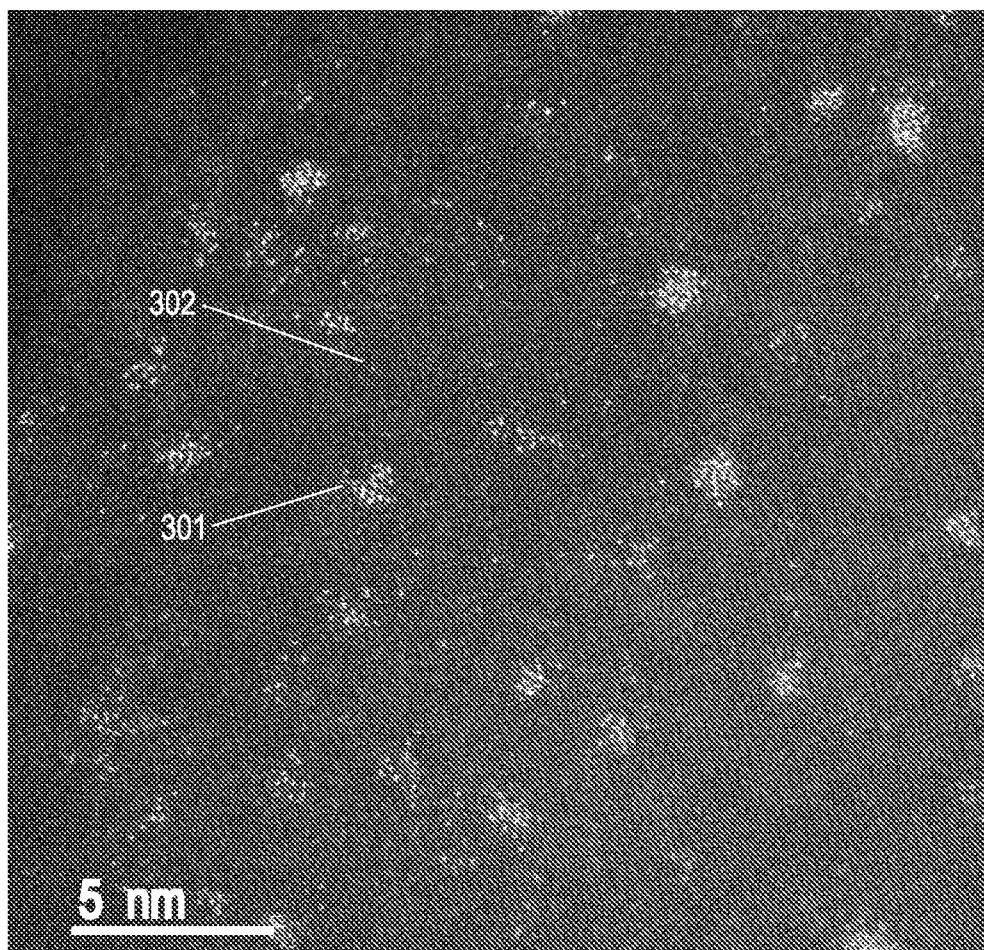


Figure 20

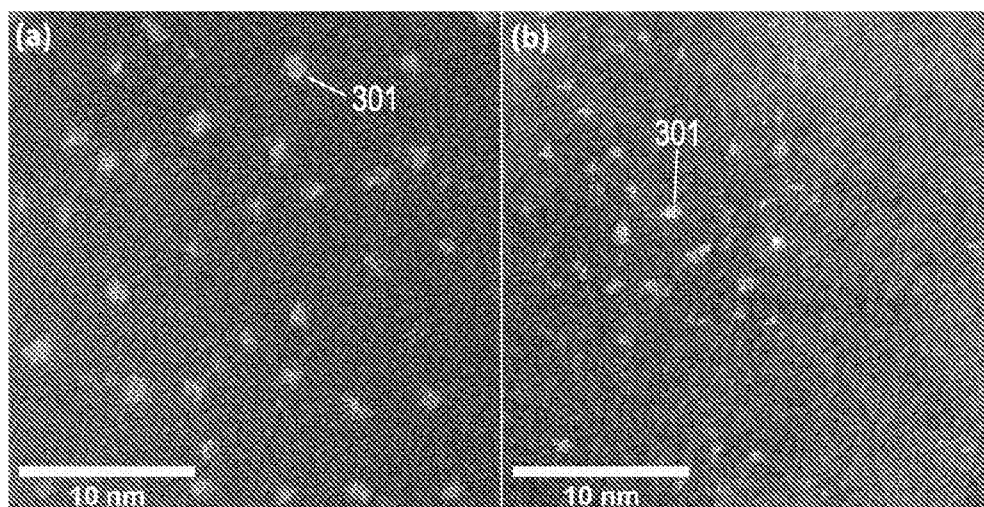


Figure 21

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2022/052018

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	B01J21/18	B01J23/42
	B01J35/02	B01J35/00
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
B01J		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2017/135136 A1 (NAT UNIV CORP HOKKAIDO UNIV [JP]) 10 August 2017 (2017-08-10) claims 1-6 -----	1-4, 19-24
X	US 7 691 772 B2 (TANAKA PRECIOUS METAL IND [JP]) 6 April 2010 (2010-04-06) comparative examples 1 and 2 -----	24
X	WO 2020/141936 A1 (SEOUL NAT UNIV R&DB FOUNDATION [KR]; INST BASIC SCIENCE [KR]) 9 July 2020 (2020-07-09) claims -----	24
X	US 2019/099742 A1 (SCHLÖGL ROBERT [DE] ET AL) 4 April 2019 (2019-04-04) paragraph [0110] -----	24
	-/--	
☒ 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 "E" earlier application or patent but published on or after the international filing date "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) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "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 "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 "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 "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
9 November 2022		16/11/2022
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Zieba, Roman

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2022/052018

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	CN 113 058 635 A (UNIV NANCHANG HANGKONG) 2 July 2021 (2021-07-02) claims -----	24
A	YOO S J ET AL: "Particle size effects of PtRu nanoparticles embedded in TiO ₂ on methanol electrooxidation", ELECTROCHIMICA ACTA, ELSEVIER, AMSTERDAM, NL, vol. 55, no. 27, 30 November 2010 (2010-11-30), pages 7939-7944, XP027428406, ISSN: 0013-4686, DOI: 10.1016/J.ELECTACTA.2010.03.049 [retrieved on 2010-10-19] the whole document -----	1-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2022/052018

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