



(51) International Patent Classification:

H01M 4/92 (2006.01)

B01J 23/46 (2006.01)

B01J 23/42 (2006.01)

(21) International Application Number:

PCT/IB2016/001946

(22) International Filing Date:

30 December 2016 (30.12.2016)

(25) Filing Language:

English

(26) Publication Language:

English

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,

SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: CORE-SHELL NANOPARTICLE CATALYSTS

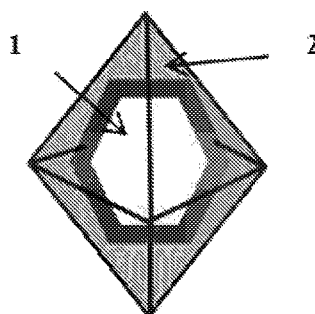


Figure 1

(57) Abstract: Core-shell nanoparticles and methods of fabricating core-shell nanoparticles are provided. A core-shell nanoparticle can include an inner core(1) surrounded by an outer shell(2). The core(1) can include one or more platinum group metal, noble metal, oxidized platinum group metal, and/or oxidized noble metal. The shell(2) can be platinum or platinum alloy. The platinum alloy can be a mixture of platinum and transition metals. The core(1) can be an oxidized ruthenium core, and the shell(2) can be a platinum-nickel alloy. A carbon source can also be included to act as a support for the core-shell nanoparticles.



DESCRIPTION

CORE-SHELL NANOPARTICLE CATALYSTS

BACKGROUND

The commercialization of Proton Exchange Membrane Fuel Cells (PEMFCs) has been hindered by sluggish reaction kinetics in the oxygen reduction reaction (ORR) at the cathode. In order for fuel cells to be cost-competitive, advanced ORR catalysts with much higher activity than current platinum (Pt)/C are required.

BRIEF SUMMARY

Embodiments of the present invention seek to improve on the related art by introducing novel oxygen reduction reaction catalysts, as well as methods of fabricating such oxygen reduction reaction catalysts.

Embodiments of the present invention include core-shell nanoparticles and methods of fabricating core-shell nanoparticles. More specifically, embodiments of the present invention relate to core-shell nanoparticles that can be used as catalysts in oxygen reduction reactions. Core-shell nanoparticles of some embodiments of the present invention can be used in the cathodic reaction of fuel cells.

In many embodiments, a core-shell nanoparticle can include an inner core surrounded by an outer shell. The shell can act as a catalyst in oxygen reduction reactions. The cores of core-shell nanoparticles can include one or more of platinum group metals, noble metals, oxidized platinum group metals, and oxidized noble metals. The shells can be, for example, platinum or a platinum alloy. The platinum alloys are preferably a mixture of platinum and transition metals. In a specific example, the core is an oxidized ruthenium core and the shell is a platinum-nickel alloy. A carbon source can also be included to act as a support for the core-shell nanoparticles.

A method of fabricating core-shell nanoparticles according to an embodiment of the present invention can include mixing one or more platinum group metals, noble metals, oxidized platinum group metals, and oxidized noble metals in one or more first solvents to form a first solution; oxygenating the first solution; heating the first solution; discarding a first supernatant and obtaining first product seeds; mixing a platinum source, an alloy

source, and the first product seeds with one or more second solvents to form a second solution; heating and mixing the second solution; cooling the second solution and adding one more third solvents to precipitate the core-shell nanoparticles; and separating a second supernatant from the core-shell nanoparticles.

5 The method can further include adding a carbon source to one or more fourth solvents to form a fourth solution, and sonicating the fourth solution; adding the core-shell nanoparticles to the fourth solution to form a fifth solution and sonicating the fifth solution to form carbon supported core-shell catalysts; and discarding a third supernatant and obtaining carbon supported core-shell nanoparticles. The solvents and additives that are
10 utilized can include, for example, oleylamine, benzyl ether, oleic acid, toluene, and alcohols (e.g., ethanol).

BRIEF DESCRITPION OF THE DRAWINGS

15 **Figure 1** is a schematic diagram of a core-shell nanoparticle according to an embodiment of the present invention.

DETAILED DESCRIPTION

Embodiments of the present invention relate to core-shell nanoparticles and methods of fabricating core-shell nanoparticles. The core-shell nanoparticles can be used
20 as a catalyst in oxygen reduction reactions. Specifically, the core-shell nanoparticles can be used in the cathodic reaction of fuel cells.

It has been found that the oxygen reduction reaction (ORR) activity of platinum can be enhanced by alloying with transition metals (Fe, Co, Ni, Cu, etc.). Furthermore, the activity of platinum alloys are also highly dependent on the crystallite orientations (or
25 facets), with {111} being preferable. The reaction catalysis occurs on the outer surface of the platinum nanoparticles; therefore, most of the platinum atoms not on the surface do not participate in catalytic reaction. This is seen as economic waste, as platinum is an expensive material.

Embodiments of the present invention combine three strategies for improving the
30 mass activity of platinum. First, a platinum alloy surface including a transition metal, such as nickel, can be included. Second, a way to optimize the surface structure of the core-shell nanoparticles through shape-controlled synthesis can be provided. Third, platinum

can be replaced inside of the nanocatalysts (or nanoparticles) with cheaper materials, such as ruthenium-based materials. These three strategies allow for high platinum utilization efficiency as well as high ORR reactivity. In practice, core-shell nanoparticles of embodiments of the present invention have been shown to achieve a platinum mass activity that is six to eight or more times that of platinum catalysts of the related art. Furthermore, the cost of the catalysts can be reduced significantly as substituting other metals besides platinum in the core (e.g., ruthenium) and alloying the shell (e.g., with nickel) can dramatically reduce material costs.

Figure 1 is a schematic diagram of a core-shell nanoparticle according to an embodiment of the present invention. Referring to Figure 1, a core-shell nanoparticle can include an inner core **1** surrounded by an outer shell **2** that covers the core **1**. The core **1** can be made of platinum group metals (i.e., Ru, Rh, Pd, Os, Ir, Pt), noble metals (i.e., Ru, Rh, Pd, Os, Ir, Pt, Cu, Ag, Re, Au), oxidized platinum group metals, and oxidized noble metals. The shell **2** can include platinum and one or more platinum alloys. The platinum alloys can include one or more transition metals (e.g., Ni, Co, Fe, Cr, V, Mn, Cu, Zn, Ti, Zr, Y, W, or Ta). In a particular embodiment, the core **1** can be ruthenium, or oxidized ruthenium, and the shell **2** can be a nickel-platinum alloy. Using oxidized metals as the core (e.g., oxidized ruthenium) has been shown to decrease the difficulty of depositing platinum and platinum alloys on the core to form the shell **2**. In addition, oxidized metal cores have been shown to be highly stable during catalysis and fuel cell operation

The core-shell nanoparticles can have {111} facets and, using fabrication methods described herein, a majority of the facets on the core-shell nanoparticles can be {111} facets. In an embodiment, as a final product, the core-shell nanoparticles can be placed on a carbon or other type of support structure.

In an embodiment, a method of fabricating core-shell nanoparticles can include mixing one or more platinum group metals (i.e., Ru, Rh, Pd, Os, Ir, and Pt), noble metals (i.e., Ru, Rh, Pd, Os, Ir, Pt, Cu, Ag, Re, and Au), oxidized platinum group metals, and oxidized noble metals in one or more first solvents to form a first solution. The first solution can then be oxygenated and heated, and the supernatant can be discarded and first product seeds can be obtained.

A platinum source, an alloy source, and the first product seeds can be mixed with one or more second solvents to form a second solution. The second solution can then be

heated and mixed, then cooled, and one or more third solvents and additives can be used to precipitate the core-shell nanoparticles. Then, the second supernatant can be separated from the core-shell nanoparticles.

A carbon source can be added to one more fourth solvents to form a fourth solution. The fourth solution can then be sonicated. The core-shell nanoparticles can then be added to the fourth solution to form a fifth solution, and the fifth solution can then be sonicated again to form carbon supported core-shell nanoparticles. The carbon-supported core-shell nanoparticles can then be collected, and the supernatant can be discarded.

Throughout the process, different solvents and/or additives can be used. The solvents and additives that can be utilized include one or more of oleylamine, benzyl ether, oleic acid, toluene, and alcohols (e.g., ethanol).

The subject invention includes, but is not limited to, the following exemplified embodiments.

Embodiment 1. A plurality of core-shell nanoparticles, each core-shell nanoparticle comprising:

a core; and
a shell.

Embodiment 2. The core-shell nanoparticles of Embodiment 1, wherein the core is a ruthenium core and the shell is a platinum shell or a platinum alloy shell.

Embodiment 3. The core-shell nanoparticles of any of Embodiments 1-2, wherein the core is an oxidized ruthenium core and the shell is a platinum shell or a platinum alloy shell (e.g., a nickel platinum alloy shell).

Embodiment 4. The core-shell nanoparticles of any of Embodiments 1-3, wherein the shell includes an alloy having one more transition metals (e.g., Ni, Co, Fe, Cr, V, Mn, Cu, Zn, Ti, Zr, Y, W or Ta).

Embodiment 5. The core-shell nanoparticles of any of Embodiments 1-4, wherein the core includes one or more of platinum group metals (i.e., Ru, Rh, Pd, Os, Ir, Pt), noble metals (i.e., Ru, Rh, Pd, Os, Ir, Pt, Cu, Ag, Re, Au), oxidized platinum group metals, and oxidized noble metals.

5

Embodiment 6. The core-shell nanoparticles of any of Embodiments 1-5, wherein the core-shell nanoparticles are on a carbon support.

Embodiment 7. The core-shell nanoparticles of any of Embodiments 1-6, wherein the core-shell nanoparticles have a plurality of {111} facets.

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Embodiment 8. The core-shell nanoparticles of Embodiment 7, wherein the majority of facets on the core-shell nanoparticles are {111} facets.

Embodiment 9. The core-shell nanoparticles of Embodiment 7, wherein all of the facets on the core-shell nanoparticles are {111} facets.

15

Embodiment 10. The method of any of Embodiments 1-9, wherein the core-shell nanoparticles include a platinum alloy shell of platinum-cobalt, or platinum-iron, or platinum-nickel-cobalt, or platinum-nickel-chrome, or platinum-cobalt-chrome, or a combination of the previous alloys.

20

Embodiment 101. A method of fabricating core-shell nanoparticles, the method comprising:

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mixing one or more metals (e.g., platinum group metals, noble metals, oxidized platinum group metals, and/or oxidized noble metals) in one or more first solvents to form a first solution;

oxygenating the first solution;

heating the first solution and discarding a first supernatant and obtaining first product seeds;

30

mixing a platinum source, an alloy source, and the first product seeds with one or more second solvents to form a second solution;

heating and mixing the second solution;

cooling the second solution and adding one more third solvents to precipitate the core-shell nanoparticles; and

separating a second supernatant from the core-shell nanoparticles.

Embodiment 102. The method of Embodiment 101, further comprising:

adding a carbon source to one or more fourth solvents to form a fourth solution and sonicating the fourth solution;

adding the core-shell nanoparticles to the fourth solution to form a fifth solution and sonicating the fifth solution to form carbon-supported core-shell catalysts; and

discarding a third supernatant and obtaining carbon-supported core-shell nanoparticles.

Embodiment 103. The method of any of Embodiments 101-102, wherein the first solvents include oleylamine.

Embodiment 104. The method of any of Embodiments 101-103, wherein the second solvents include one or more of benzyl ether, oleylamine, and oleic acid.

Embodiment 105. The method of any of Embodiments 101-104, wherein the third solvents include one or more of toluene and an alcohol (e.g., ethanol).

Embodiment 106. The method of any of Embodiments 101-105, wherein the fourth solvent includes toluene.

Embodiment 107. The method of any of Embodiments 101-106, wherein the platinum group metals include Ru, Rh, Pd, Os, Ir, and Pt, and the noble metals include Ru, Rh, Pd, Os, Ir, Pt, Cu, Ag, Re, and Au.

Embodiment 108. The method of any of Embodiments 101-107, wherein the alloy source includes one or more of Ni, Co, Fe, Cr, V, Mn, Cu, Zn, Ti, Zr, Y, W and Ta.

Embodiment 109. The method of any of Embodiments 101-108, wherein the core-shell nanoparticles include an oxidized ruthenium core and a platinum alloy shell.

Embodiment 110. The method of any of Embodiments 101-109, wherein the core-shell nanoparticles are fabricated to have facets.

Embodiment 111. The method of Embodiment 110, wherein a plurality of the facets are {111}.

Embodiment 112. The method of Embodiment 110, wherein a majority of the facets are {111}.

Embodiment 113. The method of Embodiment 110, wherein all of the facets are {111}.

Embodiment 114. The method of any of Embodiments 101-113, wherein the core-shell nanoparticles include a platinum alloy shell of platinum-cobalt, or platinum-iron, or platinum-nickel-cobalt, or platinum-nickel-chrome, or platinum-cobalt-chrome, or a combination of the previous alloys.

Embodiment 201. A method of fabricating core-shell nanoparticles, the method comprising:

forming a core made of one or more metals (e.g., platinum group metals, noble metals, oxidized platinum group metals, and/or oxidized noble metals); and

forming a shell around the core, wherein the shell comprises a platinum alloy including platinum and one or more transition metals.

Embodiment 202. The method of Embodiment 201, wherein the core is oxidized ruthenium.

Embodiment 203. The method of any of Embodiments 201-202, wherein the shell is a platinum-nickel alloy.

5 Embodiment 204. The method of any of Embodiments 201-203, wherein the core-shell nanoparticles are fabricated to have facets.

Embodiment 205. The method of Embodiment 204, wherein a plurality of the facets are {111}.

10 Embodiment 206. The method of Embodiment 204, wherein a majority of the facets are {111}.

15 Embodiment 207. The method of Embodiment 204, wherein all of the facets are {111}.

20 A greater understanding of the present invention and of its many advantages may be had from the following example, given by way of illustration. The following example is only illustrative of some of the methods, applications, embodiments and variants of the present invention. It is, of course, not to be considered as limiting the invention. Numerous changes and modifications can be made with respect to the invention.

EXAMPLE 1

25 Core-shell nanoparticles with an oxidized ruthenium core, a platinum alloy shell, and {111} facets were fabricated. The procedure was as follows.

30 One-hundred and four (104) mg of ruthenium-chloride (RuCl_3) and twenty (20) ml of oleylamine were mixed in a beaker and heated to 350 °C and kept at this temperature for one (1) hour in argon. After the synthesis of the ruthenium nanoparticles, oxygen (O_2) was added into the beaker for 3 h. The mixture was allowed to settle overnight, the supernatant was discarded, and the oxidized ruthenium nanoparticles (or seeds) were recovered.

Twenty (20) mg of Platinum(II) acetylacetonate ($\text{Pt}(\text{acac})_2$), ten (10) mg of Nickel(II) acetylacetonate ($\text{Ni}(\text{acac})_2$), one (1) mg of the oxidized ruthenium seeds, seven (7) ml of benzyl ether, two (2.0) ml of oleylamine, and one (1.0) ml of oleic acid were mixed in a flask. The flask was placed on a heating mantle, connected to a condenser, and the flask was gently stirred using a magnetic stirrer while the temperature was measured using a thermocouple and argon gas was added to the system.

The mixture was heated to 130 °C, and sixty (60) mg of tungsten hexacarbonyl $\text{W}(\text{CO})_6$ was added. The temperature inside the flask was heated to 200 °C for forty (40) minutes. The mixture was then cooled to approximately room temperature, and five (5) ml of toluene and fifteen (15) ml of ethanol were added to the mixture, causing the core-shell nanoparticles to precipitate out of the solution.

The mixture was placed into a fifty (50) ml centrifuge tube and centrifuged for ten (10) minutes at 3,000 rpm, causing the nanoparticles to settle. The supernatant was then separated from the nanoparticle product and discarded.

Twelve (12) mg of carbon black was mixed with 10-15 ml of toluene in a 50 ml glass vial. The glass vial and the solution within were sonicated for ten (10) minutes. The nanoparticle product that was previously synthesized was then added to the carbon/toluene solution and sonicated for approximately (3) hours. This mixture was then placed in a clean fifty (50) ml centrifuge tube and centrifuged for fifteen (15) minutes. The supernatant was then discarded, and the ruthenium-cored nanoparticles were dried in an oven for three hours to obtain the final product.

It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application.

All patents, patent applications, provisional applications, and publications referred to or cited herein (including those in the "References" section) are incorporated by reference in their entirety, including all figures and tables, to the extent they are not inconsistent with the explicit teachings of this specification.

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CLAIMS

What is claimed is:

5 1. A core-shell nanoparticle comprising:
a core that includes an oxidized metal; and
a shell that surrounds the core and includes platinum or a platinum alloy, wherein
the core-shell nanoparticle includes {111} facets.

10 2. The core-shell nanoparticle according to claim 1, wherein the core is oxidized
ruthenium.

 3. The core-shell nanoparticle according to any of claims 1-2, wherein the shell is a
platinum-nickel alloy.

15 4. The core-shell nanoparticle according to any of claims 1-2, wherein the shell is a
platinum alloy including platinum and one or more of Ni, Co, Fe, Cr, V, Mn, Cu, Zn, Ti,
Zr, Y, W, and Ta.

20 5. The core-shell nanoparticle according to any of claims 1-4, wherein a majority
of the facets of the core-shell nanoparticle are {111} facets.

 6. The core-shell nanoparticle according to any of claims 1-4, wherein all of the
facets of the core-shell nanoparticle are {111} facets.

25 7. The core-shell nanoparticle according to any of claims 1-6, wherein the core-
shell nanoparticle is carbon-supported.

 8. A method of fabricating core-shell nanoparticles, the method comprising:
forming a core including one or more oxidized noble metals; and
30 forming a shell around the core, wherein the shell comprises a platinum alloy
including platinum and one or more transition metals.

9. The method according to claim 8, wherein the core includes oxidized ruthenium and the shell includes a nickel-platinum alloy.

10. The method according to any of claims 8-9, wherein the core-shell nanoparticles are fabricated to have facets, and wherein a majority of the facets are {111}.

11. The method according to any of claims 8-9, wherein all of the facets of the core-shell nanoparticles are {111} facets.

12. A method of fabricating core-shell nanoparticles, the method comprising:
mixing one or more metals in one or more first solvents to form a first solution;
oxygenating the first solution;
heating the first solution and discarding a first supernatant and obtaining first product seeds;
mixing a platinum source, an alloy source, and the first product seeds with one or more second solvents to form a second solution;
heating and mixing the second solution;
cooling the second solution and adding one more third solvents to precipitate the core-shell nanoparticles; and
separating a second supernatant from the core-shell nanoparticles.

13. The method according to claim 12, wherein the one or more metals comprises at least one of a platinum group metal, a noble metal, an oxidized platinum group metal, and an oxidized noble metal.

14. The method according to any of claims 12-13, further comprising:
adding a carbon source to one or more fourth solvents to form a fourth solution and sonicating the fourth solution;
adding the core-shell nanoparticles to the fourth solution to form a fifth solution and sonicating the fifth solution to form carbon-supported core-shell catalysts; and
discarding a third supernatant and obtaining carbon-supported core-shell nanoparticles.

15. The method according to any of claims 12-14, wherein the first solvents include oleylamine.

5 16. The method according to any of claims 12-15, wherein the second solvents include one or more of benzyl ether, oleylamine, and oleic acid.

17. The method according to any of claims 12-16, wherein the third solvents include one or more of toluene and an alcohol.

10 18. The method according to any of claims 12-17, wherein the fourth solvent includes toluene.

15 19. The method according to any of claims 12-18, wherein the one or more metals includes at least one of Ru, Rh, Pd, Os, Ir, Cu, Ag, Re, and Au.

20 20. The method according to any of claims 12-19, wherein the one or more metals includes at least one of Ni, Co, Fe, Cr, V, Mn, Cu, Zn, Ti, Zr, Y, W, and Ta.

25 21. The method according to any of claims 12-20, wherein the core-shell nanoparticles include an oxidized ruthenium core and a platinum alloy shell.

22. The method according to any of claims 12-21, wherein the core-shell nanoparticles are fabricated to have facets, and wherein a plurality of the facets are {111}.

23. The method according to claim 22, wherein a majority of the facets are {111}.

24. The method according to claim 22, wherein all of the facets are {111}.

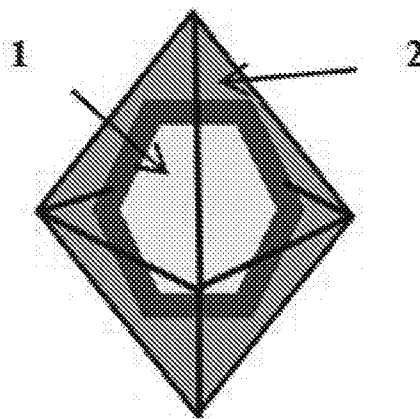


Figure 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2016/001946

A. CLASSIFICATION OF SUBJECT MATTER

H01M 4/92(2006.01)i; B01J 23/42(2006.01)i; B01J 23/46(2006.01)i

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)

H01M; 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)

CNABS,CNTXT,DWPL,SIPOABS,SCIENCE DIRECT: Core, shell, Pt, Ru, RuO₂, RuO, nano+, particle?, platinum, The Hong Kong University of Science, shao minhua, ruthenium, oxid+, heat+, cool+, discard+, supernatant, separat+, catalyst**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015/0255798 A1 (UNITED TECHNOLOGIES CORPORATION ET AL.) 10 September 2015 (2015-09-10) see paragraphs 0006-0007, 0017-0020 of the description	1, 3-6
Y	US 2015/0255798 A1 (UNITED TECHNOLOGIES CORPORATION ET AL.) 10 September 2015 (2015-09-10) see paragraphs 0006-0007, 0017-0020 of the description	2-11, 13-24
X	US 2008/0220296 A1 (UNIVERSITY OF MARYLAND OFFICE OF TECHNOLOGY COMMERCIALIZATION) 11 September 2008 (2008-09-11) see claim 20 and paragraph 0036 of the description	1-2, 5-7
Y	US 2008/0220296 A1 (UNIVERSITY OF MARYLAND OFFICE OF TECHNOLOGY COMMERCIALIZATION) 11 September 2008 (2008-09-11) see claim 20 and paragraph 0036 of the description	2-11, 13-24
Y	US 2011/0086295 A1 (UMICORE AG & CO. KG) 14 April 2011 (2011-04-14) see paragraphs 0031-0036, 0056, 0059-0060, 0064-0066, 0070-0071 of the description	7, 12-24
A	US 2008/0138693 A1 (MIN MYOUNG-KI ET AL.) 12 June 2008 (2008-06-12) the whole document	1-24



Further documents are listed in the continuation of Box C.



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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 101038969 A (FUDAN UNIVERSITY) 19 September 2007 (2007-09-19) the whole document	1-24

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Information on patent family members

International application No.

PCT/IB2016/001946

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