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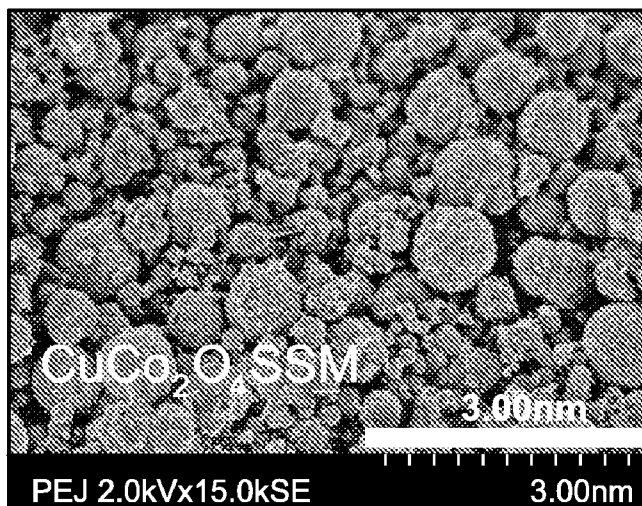
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(54) Title: BI-FUNCTIONAL CATALYSTS FOR OXYGEN REDUCTION AND OXYGEN EVOLUTION



(57) Abstract: A porous metal-oxide composite particle
suitable for use as a oxygen reduction reaction or oxy-
gen evolution reaction catalyst and sacrificial support
based methods for making the same.

FIG. 3

Bi-Functional Composite Catalysts for Oxygen Reduction and Oxygen Evolution

Cross-reference to Related Applications

[001] The following application claims benefit of U.S. Provisional Application No. 61/659152, filed June 13, 2012, which is hereby incorporated by reference in its entirety.

Background

[002] Fuel cells are receiving increasing attention as a viable energy-alternative. In general, fuel cells convert electrochemical energy into electrical energy in an environmentally clean and efficient manner, typically via an oxygen reduction reaction (ORR). Fuel cells are contemplated as potential energy sources for everything from small electronics to cars and homes. In order to meet different energy requirements, there are a number of different types of fuel cells in existence today, each with varying chemistries, requirements, and uses.

[003] As one example, Direct Methanol Fuel Cells (DMFCs) rely upon the oxidation of methanol on an electrocatalyst layer to form carbon dioxide. Water is consumed at the anode and produced at the cathode. Positive ions (H^+) are transported across a proton exchange membrane to the cathode where they react with oxygen to produce water. Electrons can then be transported via an external circuit from anode to cathode providing power to external sources.

[004] As another example, polymer electrolyte membrane (PEM) fuel cells (also called proton exchange membrane fuel cells) use pure hydrogen (typically supplied by a hydrogen tank) as a fuel. A stream of hydrogen is delivered to the anode side of a membrane-electrode assembly (MEA), where it is catalytically split into protons and electrons. As with the DMFC, the positive ions are transported across a proton exchange membrane to the cathode where they react with oxygen to produce water.

[005] Regenerative fuel cells run in reverse mode. For example, as described above, PEM fuel cells use hydrogen and oxygen to produce water and electricity using an ORR catalyst. Run in reverse mode, the fuel cell uses an Oxygen Evolution Reaction (OER) catalyst to use water and electricity to produce hydrogen and water. An external voltage is applied and water at the cathode side of the fuel cell undergoes electrolysis to form hydrogen and oxide ions which are transported through the electrolyte to the anode where they are oxidized to form oxygen. In OER mode, the polarity of the cell is the opposite of that for the ORR mode.

[006] Currently, one of the limiting factors in the wide scale commercialization of both ORR and OER is the cost associated with the precious metals that are used to produce effective catalysts. Both DMFC and PEM fuel cells commonly use platinum as an

electrocatalyst, while regenerative fuel cells often use iridium oxide or other rare platinum-family oxides in the coating of anode-electrodes for electrolysis.

[007] Transition metal-oxide systems are known catalysts for both ORR and OER. Previously described methods of forming transition metal-oxide catalysts typically involve pyrolyzing salts of the desirable metals to obtain solid particles of the desired metals, which are then milled to make a powder. It is of particular note that this method will only form solid particles and that porous particles cannot be formed using this methodology. However, previously described transition metal-oxide systems possess a number of disadvantages including low stability in alkaline media, low activity compared to conventional ORR/OER catalysts (i.e., platinum/iridium oxide), low surface area etc.

[008] Accordingly, novel, inexpensive methods of producing stable ORR and OER catalysts with sufficient activity suitable for commercial fuel cell use are desired.

Summary

[009] In the present disclosure, a method of preparing composite metal oxide catalytic materials utilizing a sacrificial support approach and using inexpensive and readily available nitrate and/or chloride precursors is described. The catalytic materials synthesized using this approach perform well in alkaline and neutral media, are highly durable, inexpensive to manufacture, and suitable for use in both traditional and regenerative fuel cells.

Brief Description of the Drawings

[010] Fig. 1 shows XRD data of a CuCo_2O_4 catalysts prepared by conventional methods (Pechinni - P), and the modified Pechinni Sacrificial Support Method (PSSM) illustrating that the PSSM method results in phase pure material – CuCo_2O_4 .

[011] Fig.2 is an SEM image of a CuCo_2O_4 catalyst prepared by a double heat treatment method.

[012] Fig. 3 is an SEM image of a CuCo_2O_4 catalyst prepared by a sacrificial support-based method illustrating that the method results in spherical, high surface area and porous structures.

[013] FIG. 4 is a Rotating Disc Electrode electro-voltamogram illustrating oxygen reduction for a CuCo_2O_4 catalysts prepared by different methods in 1M KOH saturated with O_2 (catalyst loading: $200 \mu\text{g cm}^{-2}$, 1200RPM, 5mV s^{-1}).

[014] FIG. 5 is a Rotating Disc Electrode electro-voltamogram illustrating oxygen evolution for a CuCo_2O_4 catalysts prepared by different methods in 1M KOH saturated with N_2 (catalyst loading: $200 \mu\text{g cm}^{-2}$, 1200RPM, 5mV s^{-1}).

Detailed Description

[015] The present disclosure provides novel materials and methods for making the same. According to various embodiments, the present disclosure provides a porous metal-oxide composite and methods for making the same. The porous metal-oxide composite is suitable for use in or as a catalyst in a fuel cell and is able to catalyze both ORR and OER reactions.

[016] For the sake of clarity, in the present application the term “catalyst” is used to refer to a final product, suitable for use, for example, in a fuel cell, which has catalytic activity. The catalyst may include multiple types of materials, some of which may not in themselves have catalytic activity (for example, supporting material.) The term “catalytic material” is any material which has catalytic activity either on its own or as part of a catalyst.

[017] According to the various embodiments described in greater detail below, a porous metal-oxide material is formed by depositing metal oxide precursors onto the surface of a sacrificial support, performing a chemical reaction to transform the precursors into their metal-oxide products, thereby forming a metal oxide coated sacrificial support, and then removing the sacrificial support to produce a porous metal oxide composite material. According to some embodiments, the precursors may be transition metal nitrite or chloride precursors.

[018] If the desired end-product is to be used as a catalyst, it may be desirable for the metal in the composite to be a transition metal. Accordingly, most of the following discussion is related to methods and materials using transition metals and their precursors. Examples of suitable transition metals include Ce, Cr, Cu, Fe, Mo, Ni, Ru, Ta, Ti, V, W, and Zr. Exemplary transition metal precursors include, but are not limited to, any soluble transition metal salts, for example: cerium nitrate, chromium nitrate, copper nitrate, ammonium molybdate, iron nitrate, iron chloride, nickel nitrate, ruthenium chloride, tantalum isopropoxide, titanium ethoxide, vanadium sulfate, ammonium tungstate and zirconium nitrate. However, it will be understood that the methods described herein may be suitable for use with non-transition metals and their precursors in order to form porous metal-oxide composites with other types of metals and thus, the methods and materials described herein are not intended to be limited solely to transition metals and their precursors.

[019] According to a first method, the porous metal-oxide composites are formed using a modified Pecchini synthesis method. (See U.S. Patent No. 3,330,697.) One or more transition metal precursors in the form of a metal nitrate or chloride are mixed with a salt that will melt without decomposition. Examples of suitable metal nitrates and metal chlorides include, but are not limited to, cobalt nitrate, zirconium oxynitrate hydrate, indium chloride

tetrahydrate, vanadyl sulfate hydrate, praseodymium nitrate hexahydrate, tin chloride pentahydrate, cerium nitrate hexahydrate, iron nitrate nonhydrate, yttrium nitrate hexahydrate, ammonium tungstate, niobium chloride, antimony chloride, neodymium nitrate hexahydrate, nickel nitrate hexahydrate and tantalum ethoxide. Suitable salts include, but are not limited to, sodium nitrate and potassium nitrate.

[020] A colloidal suspension of a sacrificial support such as silica is then added to the mixture. According to an embodiment, the colloidal suspension may be formed by dispersing silica (or another sacrificial material) in an aqueous solution such as deionized water using a high power ultrasound probe. The sacrificial support-containing solution is dried to allow the resulting solution to evaporate, thereby producing a dry resin comprising metal-oxide coated sacrificial particles. The resin is then ground and heat treated at a sufficient temperature. According to various embodiments the resin may be ground by ball milling or mortar and pestle, or any other suitable method. Heat treatment is typically performed by calcination, which may be performed, for example, isothermally in a box furnace. Specific temperatures for various end-products are provided in the Examples section below, but in general calcination may be performed between 150 and 1000°C. According to some embodiments, the resin may be heated at a specific rate and annealed at this temperature. The furnace may then be cooled to room temperature and the calcined sample removed and ground again. The sacrificial support is then removed, typically by chemical etching. It is important that the removal method used not harm the oxide materials. Accordingly KOH or NaOH, as opposed to HF or other very aggressive acids, are recommended for use as etchants. The final composite material is achieved by washing the etched material until a neutral pH is reached, drying the material (for example at 55-85°C for 24-48 hours) and then grinding to the desired particle size.

[021] According to yet another method, referred to herein as the “double heat-treatment method,” a colloidal suspension is formed from a solution of sucrose, urea (or another pore forming agent), and a sacrificial support. An aqueous solution containing dissolved transition metal precursors is then added to the colloidal suspension, which is dried at a temperature of between 45 and 85°C to evaporate the resulting solution and produce a dry resin. The resin is then ground and pyrolyzed (first heat treatment) at a suitable temperature (typically between 150 and 1000°C.) Pyrolyzation typically takes place in an inert atmosphere such as N₂, Ar, or He. The sample is then cooled to room temperature and then ground and calcined (second heat treatment) in an oxygen environment at a suitable temperature (typically between 150 and 1000°C.) The sacrificial support is then removed, typically by chemical etching. Again, KOH or NaOH, as opposed to HF or other very aggressive acids, are recommended for use as

etchants, so as not to harm the oxide material. The final composite material is achieved by washing the etched material until a neutral pH is reached, drying the material (for example at 55-85°C for 24-48 hours) and then grinding to the desired particle size.

[022] Both methods described above utilize a sacrificial support to achieve the final porous material. It will be appreciated that the sacrificial support may be synthesized and infused in a single synthesis step or the sacrificial support may be synthesized first (or otherwise obtained) and then infused with the appropriate precursors. Suitable sacrificial supports include, but are not limited to silicas, zeolites, aluminas, and the like.

[023] It should be appreciated that the size and shape of the sacrificial particles may be selected according to the desired shape(s) and size(s) of the voids within the resulting material. Accordingly, by selecting the particular size and shape of sacrificial particles, one can produce catalytic material having voids of a predictable size and shape. For example, if the sacrificial particles are spheres, the resulting material will contain a plurality of spherical voids. Those of skill in the art will be familiar with the electrocatalyst Pt-Ru black, which consists of a plurality of platinum-ruthenium alloy spheres. An electrocatalyst formed from using sacrificial spheres with the above-described method looks like a negative image of the Pt-Ru black; the space that existed as a void in the Pt-Ru black is filled with metal electrocatalyst, and the space that existed as metal electrocatalyst in the Pt-Ru black is void.

[024] Accordingly, the support may take the form of spheres, particles, or other two or three dimensional regular, irregular, or amorphous shapes. The spheres, particles, or other shapes may be monodisperse, or irregularly sized. As described below, the spheres, particles, or other shapes may or may not have pores and such pores may be of the same or different sizes and shapes.

[025] According to a further embodiment, mesoporous sacrificial supports, such as mesoporous silica, can be used. In this case the templating involves intercalating the mesopores of the sacrificial material and results in a self-supported electrocatalysts with porosity in the 2-20 nm range. In one particular embodiment, the sacrificial template is Cabosil amorphous fumed silica (325 m²/g). As stated above, because the spheres serve as the template for the formation of the electrocatalyst, in an embodiment where silica particles having an average diameter of 20 nm is used, the spherical voids in the electrocatalyst will typically have a diameter of approximately 20 nm. Those of skill in the art will be familiar with a variety of silica particles that are commercially available, and such particles may be used. Alternatively, known methods of forming silica particles may be employed in order to obtain particles of the desired shape and/or size.

[026] As stated above, according to some embodiments, particles of any diameter may be used. In some preferred embodiments, particles having a characteristic length of between 1 nm and 100 nm, in more preferred embodiments, particles having characteristic lengths of between 100 nm and 1000 nm may be used and in other preferred embodiments, particles having an characteristic lengths of between 1 mm and 10 mm may be used.

[027] The specific methods and compositions described herein are representative of preferred embodiments and are exemplary and not intended as limitations on the scope of the invention. Other objects, aspects, and embodiments will occur to those skilled in the art upon consideration of this specification, and are encompassed within the spirit of the invention as defined by the scope of the claims. It will be readily apparent to one skilled in the art that varying substitutions and modifications may be made to the invention disclosed herein without departing from the scope and spirit of the invention. The invention illustratively described herein suitably may be practiced in the absence of any element or elements, or limitation or limitations, which is not specifically disclosed herein as essential. The methods and processes illustratively described herein suitably may be practiced in differing orders of steps, and that they are not necessarily restricted to the orders of steps indicated herein or in the claims.

[028] All patents and publications referenced below and/or mentioned herein are indicative of the levels of skill of those skilled in the art to which the invention pertains, and each such referenced patent or publication is hereby incorporated by reference to the same extent as if it had been incorporated by reference in its entirety individually or set forth herein in its entirety. Applicants reserve the right to physically incorporate into this specification any and all materials and information from any such cited patents or publications.

[029] References:

[030] [1] M. H. Robson, A. Serov, K. Artyushkova, P. Atanassov "A Mechanistic Study of 4-Aminoantipyrine and Iron Derived Non-Platinum Group Metal Catalyst on the Oxygen Reduction Reaction" *Electrochim. Acta*, 90 (2013) Pages 656-665

[031] [2] S. Brocato, A. Serov, P. Atanassov "pH Dependence of Catalytic Activity for ORR of the non-PGM Catalyst Derived from Heat-Treated Fe-Phenanthroline" *Electrochim. Acta*, 87 (2013) 361-365

[032] [3] A. Serov, M. H. Robson, K. Artyushkova, P. Atanassov "Templated non-PGM cathode catalysts derived from iron and poly(ethyleneimine) precursors" *Appl. Catal. B* 127 (2012) 300-306.

[033] [4] A. Serov, M. H. Robson, M. Smolnik, P. Atanassov "Templated bi-metallic non-PGM catalysts for oxygen reduction" *Electrochim. Acta* 80 (2012) 213-218.

[034] [5] A. Serov, U. Martinez, A. Falase, P. Atanassov "Highly Active Pd-Cu Catalysts for Electrooxidation of 2-Propanol" *Electrochem. Comm.* 22 (2012) 193-196.

[035] [6] A. Serov, M. H. Robson, B. Halevi, K. Artyushkova, P. Atanassov "Highly Active and Durable Templated Non-PGM Cathode Catalysts Derived from Iron and Aminoantipyrine" *Electrochem. Comm.* 22 (2012) 53-56.

[036] Additional information may be gathered from the Examples section below.

Examples:

Synthesis of Co-Cu-O material

[037] 16.4g of cobalt nitrate and 21.4g of copper nitrate dissolve in 345ml of water. 18.5g of silica is added to solution and dispersed using ultrasound bath. Mixture allows to dry at T=85C for 48 hours. As prepared dry composite materials is ground and heat treated at air at T=525C. The silica is removed by 7M KOH for 24 hours. As results high surface area mixed-oxide washed by DI water until neutral reaction and dried at T=85C for 24 hours.

[038] FIG. 1 illustrates XRD data for selected porous copper-cobalt catalyst prepared by the above-described methods compared to the conventional Pechinni method. It will be appreciated that the mixed oxide catalysts disclosed herein possess high activity in ORR/OER in alkaline and neutral as well as stability and durability and can be used in fuel cell, electrolyzers and batteries systems. Furthermore, the disclosed catalysts possess high electroconductivity due to their optimal composition.

[039] Figs.2 and 3 illustrate the morphological advantages of the SSM method. The utility of these materials is illustrated in oxygen reduction/evolution tests, illustrated in Figs. 4 and 5.

[040] These reaction tests demonstrate that mixed oxides catalysts prepared from copper and cobalt precursors using the method described possess high activity in alkaline and neutral medias. Thus, Cu-Co-O catalysts formed using this method are effective catalysts for oxygen reduction and evolution.

Synthesis of Co_3O_4

[041] 26.8g of cobalt nitrate dissolves in 145ml of water. 8.5g of silica is added to solution and dispersed using ultrasound bath. Mixture allows to dry at T=85C for 48 hours. As prepared dry composite materials is ground and heat treated at air at T=525C. The silica is

removed by 7M KOH for 24 hours. As results high surface area oxide washed by DI water until neutral reaction and dried at T=85C for 24 hours.

Synthesis of ZrO₂

[042] 52.8g of zirconium oxynitrate hydrate dissolves in 450ml of water. 34.7g of silica is added to solution and dispersed using ultrasound bath. Mixture allows to dry at T=50C for 4 hours, then T=85 for 24 hours. As prepared dry composite materials is ground and heat treated at air at T=895C. The silica is removed by 4M KOH for 48 hours. As results high surface area oxide washed by DI water until neutral reaction and dried at T=85C for 48 hours.

Synthesis of In₂O₃

[043] 47.56g of indium chloride tetrahydrate dissolves in 126ml of water. 8.2g of silica is added to solution and dispersed using ultrasound bath. Mixture allows to dry at T=85 for 24 hours. As prepared dry composite materials is ground and heat treated at air at T=375C. The silica is removed by 6M KOH for 24 hours. As results high surface area oxide washed by DI water until neutral reaction and dried at T=65C for 48 hours.

Synthesis of V₂O₅

[044] 88.2g of vanadyl sulfate hydrate dissolves in 1140ml of water. 240.5g of silica is added to solution and dispersed using ultrasound bath. Mixture allows to dry at T=85 for 48 hours. As prepared dry composite materials is ground and heat treated at air at T=5950C. The silica is removed by 10M KOH for 12 hours. As results high surface area oxide washed by DI water until neutral reaction and dried at T=85C for 24 hours.

Synthesis of Pr₂O₃-SnO₂

[045] 16.8g of praseodymium nitrate hexahydrate and 11.54g tin chloride pentahydrate dissolves in 56.3ml of water. 5.28g of silica is added to solution and dispersed using ultrasound bath. Mixture allows to dry at T=75 for 24 hours. As prepared dry composite materials is ground and heat treated at air at T=975C. The silica is removed by 2M KOH for 96 hours. As results high surface area oxide washed by DI water until neutral reaction and dried at T=65C for 48 hours.

Synthesis of CeO₂-Fe₂O₃-Y₂O₃

[046] 54.3g of cerium nitrate hexahydrate, 17.8g iron nitrate nonahydrate, and 2.2g yttrium nitrate hexahydrate dissolves in 1023.5ml of water. 14.8g of silica is added to solution and dispersed using ultrasound bath. Mixture allows to dry at T=75 for 28 hours. As prepared dry

composite materials is ground and heat treated at air at $T=1000^{\circ}\text{C}$. The silica is removed by 6M KOH for 24 hours. As results high surface area oxide washed by DI water until neutral reaction and dried at $T=85^{\circ}\text{C}$ for 24 hours.

Synthesis of WO_3

[047] 34.3g of ammonium tungstate dissolves in 54.9ml of water. 13.9g of silica is added to solution and dispersed using ultrasound bath. Mixture allows to dry at $T=65^{\circ}\text{C}$ for 24 hours. As prepared dry composite materials is ground and heat treated at air at $T=670^{\circ}\text{C}$. The silica is removed by 7M KOH for 24 hours. As results high surface area oxide washed by DI water until neutral reaction and dried at $T=45^{\circ}\text{C}$ for 48 hours.

Synthesis of Nb_2O_5

[048] 33.7g of niobium chloride dissolves in 39.7ml of water. 16.5g of silica is added to solution and dispersed using ultrasound bath. Mixture allows to dry at $T=80^{\circ}\text{C}$ for 24 hours. As prepared dry composite materials is ground and heat treated at air at $T=800^{\circ}\text{C}$. The silica is removed by 3M KOH for 96 hours. As results high surface area oxide washed by DI water until neutral reaction and dried at $T=65^{\circ}\text{C}$ for 24 hours.

Synthesis of Sb_2O_3

[049] 12.9g of antimony chloride dissolves in 460.6ml of water. 3.8g of silica is added to solution and dispersed using ultrasound bath. Mixture allows to dry at $T=85^{\circ}\text{C}$ for 24 hours. As prepared dry composite materials is ground and heat treated at air at $T=825^{\circ}\text{C}$. The silica is removed by 9M KOH for 15 hours. As results high surface area oxide washed by DI water until neutral reaction and dried at $T=50^{\circ}\text{C}$ for 24 hours.

Synthesis of Nd_2O_3

[050] 1.34g of neodymium nitrate hexahydrate dissolves in 23.2ml of water. 0.5g of silica is added to solution and dispersed using ultrasound bath. Mixture allows to dry at $T=85^{\circ}\text{C}$ for 24 hours. As prepared dry composite materials is ground and heat treated at air at $T=750^{\circ}\text{C}$. The silica is removed by 7M KOH for 24 hours. As results high surface area oxide washed by DI water until neutral reaction and dried at $T=55^{\circ}\text{C}$ for 48 hours.

Synthesis of $\text{NiO-Ta}_2\text{O}_5$

[051] 18.2g of nickel nitrate hexahydrate and 29.3g tantalum ethoxide dissolves in 188.9ml of water. 18.5g of silica is added to solution and dispersed using ultrasound bath. Mixture

allows to dry at $T=70$ for 24 hours. As prepared dry composite materials is ground and heat treated at air at $T=825^{\circ}\text{C}$. The silica is removed by 10M KOH for 17 hours. As results high surface area oxide washed by DI water until neutral reaction and dried at $T=45^{\circ}\text{C}$ for 48 hours.

What is claimed is:

1. A method for forming a porous metal oxide material comprising:
providing sacrificial template particles;
reacting one or more metal precursors and an oxide precursor onto the sacrificial template particles to produce coated template particles;
heat treating the coated template particles; and
removing the sacrificial template particles to produce a highly dispersed, self-supported, high surface area electrocatalytic material.
2. The method of claim 1 wherein the metal is a transition metal.
3. The method of claim 1 wherein at least one of the metal precursors is a metal citrate or metal nitrate.
4. The method of claim 1 wherein the step of reacting one or more metal precursors and an oxide precursor onto the sacrificial template particles comprises mixing a colloidal suspension of template particles with a solution containing a transition metal citrate or nitrate and sodium nitrate.
5. The method of claim 4 wherein the step of heat treating the coated template particles comprises calcination.
6. The method of claim 1 wherein the step of reacting one or more metal precursors and an oxide precursor onto the sacrificial template particles comprises mixing a colloidal suspension of template particles, sucrose and urea with a solution containing transition metal precursors.
7. The method of claim 1 wherein the step of heat treating the coated template particles comprises pyrolyzation, followed by calcination.
8. The method of claim 1 wherein the step of removing the sacrificial template particles comprises chemical etching.
9. The method of claim 1 wherein the chemical etchant is HF.

10. The method of claim 1 wherein the metal precursor is selected from the group consisting of cobalt nitrate, zirconium oxynitrate hydrate, indium chloride tetrahydrate, vanadyl sulfate hydrate, praseodymium nitrate hexahydrate, tin chloride pentahydrate, cerium nitrate hexahydrate, iron nitrate nonhydrate, yttrium nitrate hexahydrate, ammonium tungstate, niobium chloride, antimony chloride, neodymium nitrate hexahydrate, nickel nitrate hexahydrate and tantalum ethoxide.
11. The method of claim 2 wherein the transition metal is selected from the group consisting of Ce, Cr, Cu, Fe, Mo, Ni, Ru, Ta, Ti, V, W, and Zr.
12. A porous metal-oxide particle formed by the method of claim 1.
13. The porous metal oxide particle of claim 11 wherein the metal is a transition metal.
14. The porous metal oxide of claim 12 wherein the transition metal is selected from the group consisting of Ce, Cr, Cu, Fe, Mo, Ni, Ru, Ta, Ti, V, W, and Zr.

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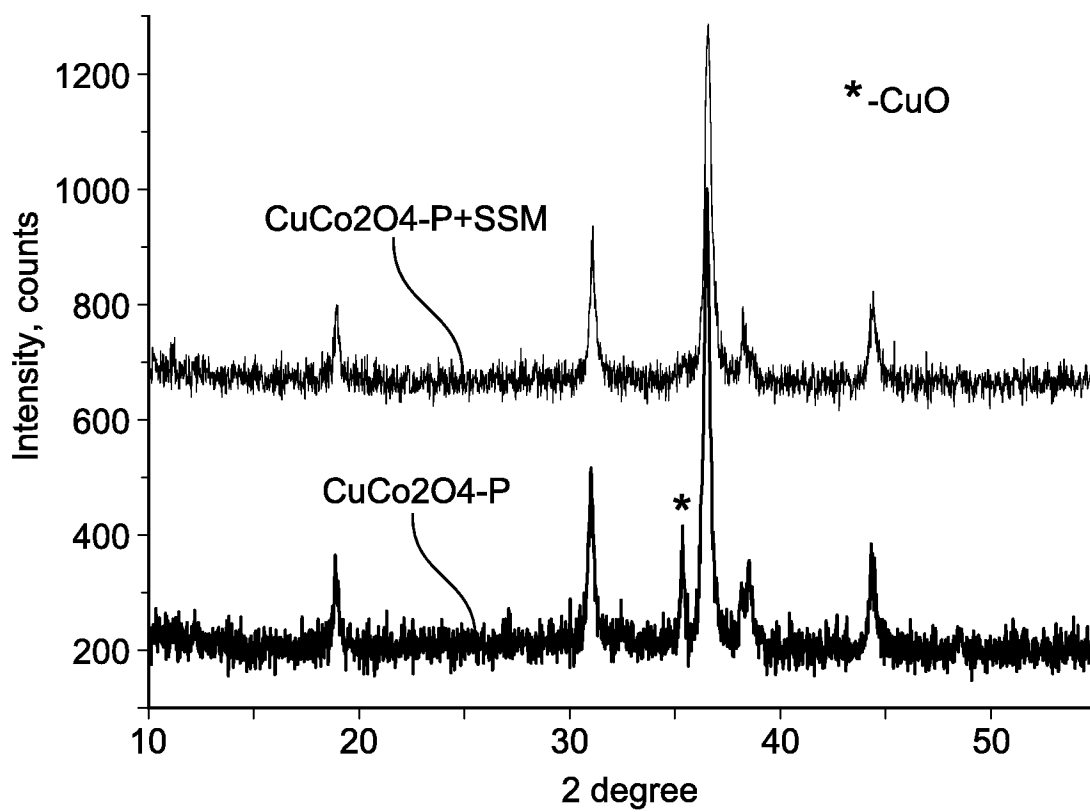


FIG. 1

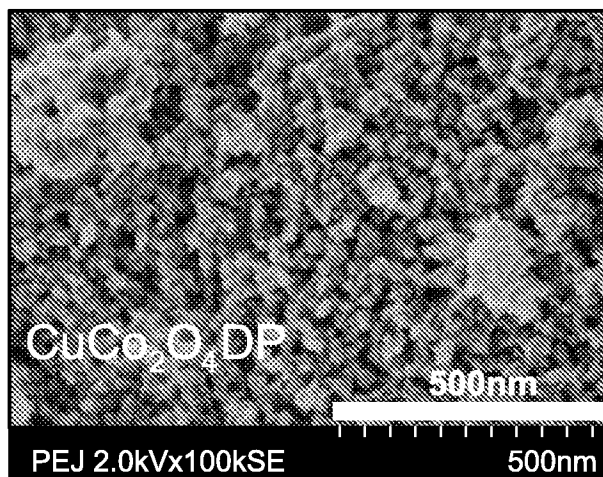


FIG. 2

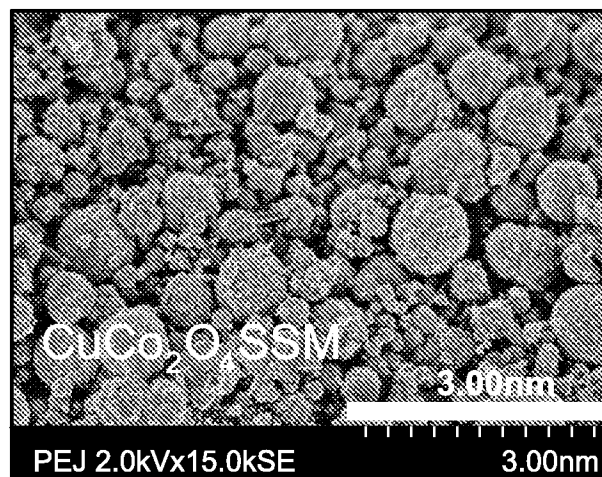
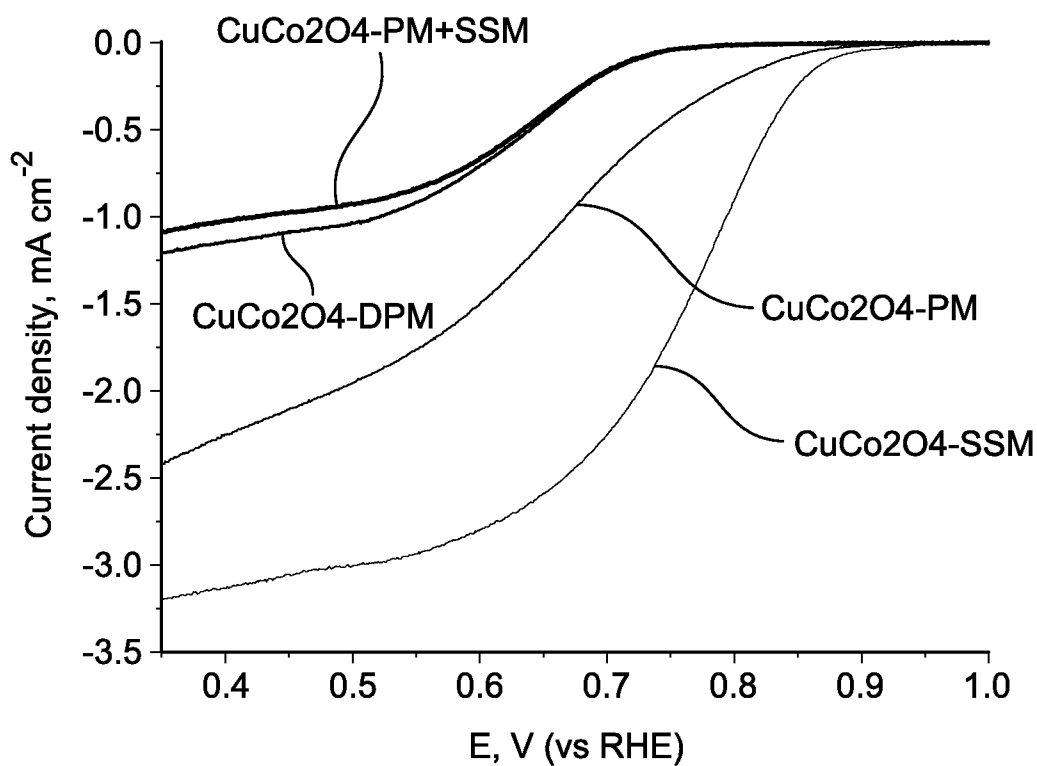
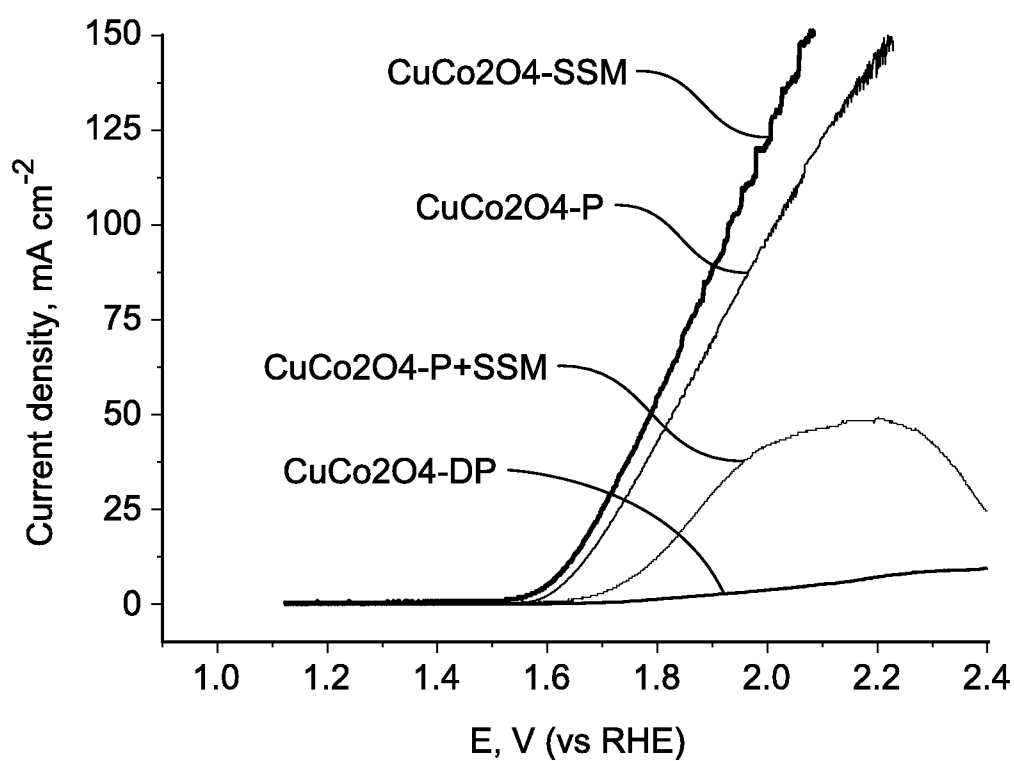


FIG. 3

**FIG. 4****FIG. 5**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/031917**A. CLASSIFICATION OF SUBJECT MATTER****B01J 37/08(2006.01)i, B01J 35/10(2006.01)i, B01J 23/86(2006.01)i, B01J 6/00(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)

B01J 37/08; A61K 9/14; C25B 9/00; B01J 21/18; H01M 4/96; C03B 19/00; C01B 31/02; B01J 31/00; C07D 487/22; C01B 13/00; H01M 4/88; B01J 35/10; B01J 23/86; B01J 6/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: porous, metal oxide, sacrificial template, self-supported, electrocatalytic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011-0311635 A1 (STUCKY, GALEN D. et al.) 22 December 2011 See claims 1, 2, 4, 13, 26, 31, 34; paragraphs [0036], [0043].	1-5, 7-14
A		6
A	US 7678728 B2 (OLSON, TIM et al.) 16 March 2010 See claims 1-5.	1-14
A	US 2009-0166214 A1 (TAO, TAO T. et al.) 02 July 2009 See claims 1, 18.	1-14
A	US 2006-0166811 A1 (HUANG, CHUN-CHIEH et al.) 27 July 2006 See claims 1, 5.	1-14
A	US 2010-0167106 A1 (PAK, CHAN-HO et al.) 01 July 2010 See claims 9, 12.	1-14
A	US 2011-0082024 A1 (LIU, HANSAN et al.) 07 April 2011 See claims 1, 9.	1-14



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/031917

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